

# RENDICONTI *Online* della *Società Geologica Italiana*

*Volume 31, Supplemento n. 1 - Settembre 2014*

## **The Future of the Italian Geosciences - The Italian Geosciences of the Future**

87° Congresso della Società Geologica Italiana e  
90° Congresso della Società Italiana di Mineralogia e Petrologia



Abstract Book

Milan, Italy, September 10-12, 2014

edited by: B. Cesare, E. Erba, B. Carmina,  
L. Fascio, F.M. Petti, A. Zuccari.



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**Milan, Italy. September 10-12, 2014**

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# **PLENARY LECTURES**

## Back to Exploration with geological drivers: New frontiers of the last decade

Bertelli L.\*, Giammetti S., Lottaroli F.

eni E&P, Via Emilia 1, 20097, San Donato Milanese (MI).

Corresponding email: [luca.bertelli@eni.com](mailto:luca.bertelli@eni.com)

Keywords: Deep water exploration, Frontier Basins, Play Openers, Pre-salt, Abrupt Margins, East Africa, Levantine Basin, Play based exploration, Conjugate Margins.

Exploration trends have always been linked to the oil price. The last decade has been dominated by two main phenomena: the exploration and exploitation of Unconventional reservoirs and the deep water conventional exploration.

The oil Industry put priority on investing in new Plays Concept and new basins pushing conventional exploration spend to grow 4 times since early 2000. Limits have been pushed forward towards Ultra Deep waters, pre/sub salt Plays, subtle traps, harsh environments. Besides technology, sound geology and the capability to innovatively describe the subsurface and associates Petroleum Systems proven to be key to success in exploration and new venture activities.

Reserves discovered in the period 2004 – 2013 are almost three times the amount of reserves exploration brought to replacement during previous decades (Biteau et al., 2014). Most of these reserves comes from new Plays and frontier basins in deep waters that gained a primary role in reserve replacement eclipsing the golden exploration targets of the 80's and 90's. The last decade exploration arena has been characterized by fast movers International Independents and NOC's (National Oil Companies) opening Plays and Majors fast reloading their Portfolios on these new exploration frontiers while the Supermajors partially loose their grip on exploration arena. Few majors Integrated have been successful, among these eni, especially in the last few years. Moreover eni results have been achieved only based on conventional exploration, thus re-enforcing the central role of geology, geophysics and exploration technology in our organization. Being Play Openers (e.g. Anadarko/eni in east Africa) has been the key to be successful: coming first on under-explored areas, with new ideas to exploit new play concepts has proven the right attitude to access the best assets at the best contractual conditions. The barycentre of eni activity rapidly shifted towards new basins and countries (e.g. Mozambique, Ghana, Cyprus, Myanmar, Greenland) with new geological challenges.

Breakthrough events of the last 10 years exploration are: the emergency of the pre-salt play in south Atlantic deep waters; Cretaceous turbidites Play on Abrupt Margins (e.g. Equatorial Transform Margin); Rovuma and Tanzania Tertiary and Cretaceous clastic Play and Levantine Basin pre-salt clastic Play.

The Atlantic Margins have increasingly established their role of global "sweet spot" for the oil search, while east Africa and Levantine have delivered gas.

The opening of *Pre-Salt Carbonates oil Play* of Santos Basin has added over 30 billion barrels of oil since 2006 accounting almost 60% of the total volumes discovered in the decade. Spectacular interest rose for trying to export on the West African margin the Santos Play (Lottaroli et al., 2013). In this perspective, the Kwanza Basin (South Angola) gained most of the attention promising to be the focus of future pre-salt exploration.

In 2007 the discovery of the Jubilee Field unlocked the exploration potential of the *Cretaceous deep water Play* in offshore Ghana. The Zaedyus discovery in French Guyana, extending the successful play to the South American, have contributed to increasing the focus on exploration along the entire margin. Recent drilling activity turned out in light and shadows and so far the oil sweet spot of the margin seems restricted to the Ghana/Ivory Coast Tano Basin but the evolution of abrupt margins is still poorly known and the deposition of organic facies (source rocks) still away to be understood.

The entire Deep water tract of *East Africa* was hardly considered an area holding some exploration potential since the drilling of the first Anadarko well in Mozambique in 2010. Enormous volumes of Gas have been discovered in Mozambique/Tanzania (Rovuma Basin) in the last 2 years. Eni, alone, proven in excess of 15 bbnoc with 12 wells in Area 4 in Mozambique. Exceptional quality reservoirs have been encountered increasingly fitting the innovative and poorly documented model of a prevalent interaction of turbidite turbulent flow and bottom-current motion, with winnowing and redistribution of the finer materials deflected within sediment drifts (Fonnesu & Orsi, 2013).

In the past two years, the *eastern Mediterranean* has been transformed from an industry backwater, to one of the world's most exciting exploration plays. The catalyst for the transformation was the discovery of the giant Tamar gas field, in offshore northern Israel in 2009, followed by other significant discoveries in the surroundings made by Noble Energy. Since then the whole Levant Basin has witnessed a proliferation of bid rounds, well beyond the Israeli sector, in offshore Cyprus, Lebanon and Syria with increasing expectations and different Companies exposures.

Exploration drivers have radically changed in the last decade and results have been far better than the previous. The recent successes overturned most of the geological and exploration paradigms we brought from previous activity.

Non marine carbonates were almost completely disregarded under the reservoir perspective before the Santos pre-salt successes.

Being located down-dip from productive Tertiary Delta System and the presence of a mobile substratum (Salt/Shale) was considered a key driver for exploring deep-water Plays based on 1980/2000 historical record (Pettingill & Weimer 2003). None of these elements is present in the emerging deep-water provinces of the last decade (e.g Mozambique, Ghana).

Pure stratigraphic traps are having an increasing role in this new exploration phase while has been long disregarded, mainly when not DHI (Direct Hydrocarbon Indicators) supported.

Turbiditic reservoirs have been proven far away from main traditionally envisaged entry points in some basins (e.g Levantine). As well interaction between down-current evolution and bottom currents overprint gain new insights (e.g. Rovuma Basin).

Large accumulations of biogenic gas seem an overcome contradiction after the Levantine results.

Plate tectonics and geodynamic have been brought back to the base of exploration workflow. The conjugate margin perspective has been exported from the pre-salt of South Atlantic to the entire Atlantic and also to different Plays. Large scale paleogeographic and geodynamic reconstruction and the basic importance of a regional, Play based, approach are today largely agreed as basics in exploration.

Apparently there is still wide space to “invent” in exploration and probably, more than economical and commercial drivers, the geological “thinking” will be, also in the next future, the more powerful tool for success.

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## Insights into the Geological Carbon Cycle from subduction to erosion

Beysnac O.\*

Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie, Sorbonne Universités, CNRS-UPMC, Paris, France.

Corresponding email: [Olivier.Beyssac@upmc.fr](mailto:Olivier.Beyssac@upmc.fr)

Keywords: carbon, subduction, erosion, graphitic carbons, carbonates.

Carbon is ubiquitous on Earth from the deepest levels to the atmosphere, and is recycled between the different terrestrial envelopes on various timescales and lengthscales. There is considerable ongoing research effort dedicated to the long-term carbon cycle, for instance regarding the Deep Earth to assess the carbon content in the Earth's mantle and core, but also to identify and quantify the contribution of various carbon carriers (diamond, carbonates, fluids, minerals...). Interaction between the solid Earth and the exosphere (atmosphere, hydrosphere and biosphere) is also matter of active research. Recent advances include mapping of non-volcanic CO<sub>2</sub> degassing at different scales in active orogenic belts, or the characterization of synthesis pathways for organic molecules during alteration of the oceanic crust. Altogether, we do have a broad view of the geological carbon cycle, which is the basis for complex models of the global carbon cycle (e.g. Berner 2003). However, if the major carbon terrestrial reservoirs are identified, their respective contributions are not well quantified, and the detailed picture for the fluxes between these reservoirs remains barely known.

This lecture will be focused on the carbon cycle in the Earth's lithosphere. This is a key segment of the geological carbon cycle at the interface between the exosphere and the solid Earth (Hayes and Waldbauer 2006), and where carbon is exchanged between the biomass and the mineral world. Also, there are two carbon subcycles in the Lithosphere, organic versus inorganic cycles, which broadly corresponds to the distinction between reduced versus oxidized carbon. Interactions between the two subcycles are largely unknown, although they may have profound implications for buffering redox conditions, or controlling the speciation of deep fluids. This means that an in-depth characterization of the carbon carriers by means of petrological and mineralogical investigations is required to complement and interpret geochemical data. Main lithospheric fluxes are identified: on one side, carbon is incorporated into the Lithosphere through burial of organic carbon as well as formation of carbonates in sediments or during weathering of the oceanic lithosphere. On the other side, carbon is released from the Lithosphere through degassing, erosion of continental surfaces or subduction to the deep Earth. The broad picture seems relatively simple (Gaillardet & Galy 2008), but field and experimental studies reveal that the reality is indeed much more complex, and that it depends on many local parameters.

A first example of this natural complexity will be discussed and regards the fate of carbonates during subduction based on field studies in high-pressure metamorphism settings. It has been recently proposed that carbonates can be dissolved due to intense fluid-rock interactions during subduction, and that the carbon-bearing fluids can migrate into the mantle wedge and ultimately could feed CO<sub>2</sub> degassing in Arc volcanism (Frezzotti et al. 2011; Ague & Nicolescu 2014). On the other hand, based on a similar approach, calcite reduction in metasediments at the contact with serpentinites has been evidenced and yielded wollastonite and graphite which can be highly refractory and could transfer carbon to the deep Earth instead of feeding the mantle wedge (Galvez et al. 2013). There might be other processes yet to be found, and the global respective contributions of devolatilization, dissolution or reduction of carbonates during subduction have now to be established. Another example regards the carbon budget during erosion of continental surfaces. A major point is then the fate of modern carbon deriving from the biomass (e.g. Galy et al. 2007): burial in sediments, or oxidation and release as CO<sub>2</sub> to the atmosphere? Also, the fate of carbonates and rock-derived organic carbon during continental erosion as well as the CO<sub>2</sub> consumption for silicates weathering have to be considered for a complete budget on various timescales. This is a complex factory that depends highly on the scale and dynamics of the erosion system, and that will be discussed in light of recent studies in active small-scale (Taiwan) and large-scale (Himalayas, Andes) systems.

The geological carbon cycle is a global issue that have implications for the geological cycle of many other elements like water, trace elements, sulfur or nitrogen. As such, it must be considered with a global approach involving geochemistry (isotopic, organic, bulk chemistry...) but also petrology, mineralogy, biology and thermodynamics among others. Tracking carbon reservoirs and fluxes in the solid Earth also requires investigations down to the finest observation scale (e.g. Wu & Buseck, 2013), as carbon may be present even when non expected, and therefore carbon may be widespread in deep geological settings as it is at the Earth's surface.

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## **Paleomagnetism in Italy: contributions to tectonics, stratigraphy, and timescale**

Channell J.E.T.\*

Dept. Geological Sciences, POB 112120, University of Florida, Gainesville, FL 32611

Corresponding email: [jetc@ufl.edu](mailto:jetc@ufl.edu)

Keywords: Adria, apparent polar wander, palinspastic reconstructions, magnetic stratigraphy, timescales

Fifty years since the first paleomagnetic work in Italy, it's apparent that paleomagnetism in Italy has been transformational in three aspects of geologic research.

(1) In the 1960s, it was first realized that the Southern Alps of northern Italy possess Early Permian paleomagnetic declinations deviating from coeval directions from non-Alpine Europe by  $\sim 50^\circ$  (Van Hilten, 1962). It was then realized that Southern Alpine data agree with coeval directions from Africa (Zijderveld et al., 1970), a coherence that was later proven valid also for the Mesozoic (e.g., Channell, 1996). Recent analyses of paleomagnetic data from Italy (Muttoni et al., 2013) support the concept of "Adria as a promontory of the Africa plate" (Channell et al., 1979), a concept that can be traced back to the classic work of Argand (1924). The corollary from this work is a "Pangea B" configuration for Atlantic-bordering continents in Early Permian, a conclusion that remains unpopular particularly amongst field geologists.

(2) Palinspastic reconstruction of the Sicilian and Apenninic fold-and-thrust belts has helped to reveal the paleogeography of these "African" Mesozoic continental margins prior to deformation, and has emphasized thrust-sheet rotation and oroclinal bending associated with the Tyrrhenian extension and its propagation northward into Tuscany, driving thrusting that largely postdates the initial collision of the Sardinia/Corsica island arc with the Sicilian/Apenninic "African" continental margin. The origin of the subducting slab beneath the Tyrrhenian Sea remains enigmatic because of the external/internal polarity of the "African" margin in this region (ocean to the west), uncertainties concerning the crustal basement in the Ionian Sea, and the necessity for continuity of the Sicilian Mesozoic continental margin into the Southern Apennines until deposition of the Oligocene to Early Miocene Numidian Flysch.

(3) The Upper Cretaceous magnetic polarity stratigraphy from the Gubbio section (Lowrie and Alvarez, 1977) was matched to marine magnetic anomalies (MMAs) and combined with the foraminiferal biostratigraphies (Premoli-Silva, 1977) to provide correlation of geologic stage boundaries to the emerging MMA-based geomagnetic polarity timescale (GPTS). This work spawned the correlation of the Cretaceous and Cenozoic GPTS to foraminiferal and nannofossil zones and hence to stage boundaries, both from marine cores recovered through ocean drilling for late Cenozoic time, and in land sections (largely from Italy) for the early Cenozoic and Cretaceous. The strong legacy of both micropaleontological and magnetostratigraphic research in Italy has resulted in the GPTS becoming central to geologic timescales for the last 160 Myr. The GPTS now provides linkage among biostratigraphies, chemostratigraphies, radiometric ages and astrochronologies; and has resulted in radical improvement in the resolution of time in Earth history.

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## Deep drilling in the ocean crust : where are we, and what's next ?

Ildefonse B.\*

Géosciences Montpellier, CNRS/Université Montpellier 2, France.

Corresponding email: [ildefonse@um2.fr](mailto:ildefonse@um2.fr)

Keywords: Ocean drilling, International Ocean Discovery Program, IODP, ocean crust, mid-ocean ridges, Mohole to the mantle.

This lecture will draw from the latest results from Integrated Ocean Drilling Program (IODP) drilling expeditions in both fast-spread and slow-spread ocean crust, highlighting scientific questions related to accretion processes at mid-ocean ridges. In 2004-2005, IODP Expeditions 304 and 305 (Ildefonse et al., 2007; Blackman et al., 2011) illustrated the role of detachment faulting and associated hydrothermal alteration, together with localized and protracted magmatic construction recorded in the footwall of these faults, possibly involving recycling of mantle rocks (Drouin et al., 2010), in building crust in volcanic-poor regions of slow-spreading ridges. In fast-spread crust, observations from the lower crust gabbros are essential to test models on crustal accretion and cooling. IODP Expedition 345 at Hess Deep (Dec 2012 – Feb 2013) drilled and sampled for the first time the layered primitive gabbros of fast-spread crust (Gillis et al., 2014). The preliminary results will be summarized. At site 1256, in intact East Pacific superfast spread crust, operations during IODP Expedition 335 in 2011 (Teagle et al., 2012) proved challenging throughout, and the lower crustal gabbros are yet to be recovered. The material recovered from the complex dike-gabbro transition zone document evolving geological conditions and the coupling between temporally and spatially intercalated intrusive, hydrothermal, contact-metamorphic, partial melting, and retrogressive processes at the interface between the magma chamber and the hydrothermal system. I will also shed light on some of the next challenges for scientific drilling in the ocean lithosphere, exemplified by the shallow coring project on the Atlantis Massif oceanic core complex on the Mid-Atlantic Ridge ([http://www.iodp.org/doc\\_download/3299-758-full2cover](http://www.iodp.org/doc_download/3299-758-full2cover)), the “SloMo” project at the Southwest Indian Ridge ([http://www.iodp.org/doc\\_download/3557-800-mdp](http://www.iodp.org/doc_download/3557-800-mdp)), and the “MoHole to the Mantle” project (<http://mohole.org>), which aims to reach and sample the uppermost mantle beneath the Pacific fast-spread crust.

Blackman D.K., Ildefonse B., John B.E., Ohara Y., Miller D.J., et al. 2011. Drilling constraints on lithospheric accretion and evolution at Atlantis Massif, Mid-Atlantic Ridge 30° N. *Journal of Geophysical Research*, 116, B07103. doi:10.1029/2010JB007931

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## One hundred years of mineral crystal chemistry

Merlino S.\*

Past-Professor of Crystallography at University of Pisa.

Corresponding email: [stefano.merlino38@gmail.com](mailto:stefano.merlino38@gmail.com)

Keywords: X-ray diffraction, Laue and Bragg interpretation, Crystal structures, Barlow contribution, Ionic radii, Goldschmidt rules, Pauling stability rules, Classification schemes, Polymorphic relationships and polymorphic transformations, Modular crystal chemistry, Crystal structure prediction, Automated electron diffraction tomography.

After the experience of Friedrich and Knipping suggested and interpreted by Laue, the young Bragg correctly explained the results of the Munich discovery and showed how to use X-rays to determine the arrangement of atoms in crystals and, in few years, actually derived the structures of several inorganic compounds. From then on it was possible to do something which had been conjectured about in the past several hundred years (Kepler, Huygens, Dalton, Barlow) without conclusive proof: namely to study the relationships between the chemical compositions of crystals and their atomic arrangements in space and their physical properties.

The comparison of the structural data permitted to Bragg to assert that crystals are composed of ‘inelastic spheres in contact’ and that ‘it is possible to assign to the sphere representing an atom... a constant diameter.’ This assertion marks the beginning of the modern crystal chemistry. The development of these concepts by Goldschmidt led to the first reliable list of ionic radii, to the rules relating ionic size and atomic structure and to the relationship between radius ratio and coordination number. Shortly thereafter, Pauling, using a different approach through wave mechanics, produced a similar list of radii, the well known table of ionic radii of Pauling, who – at the same time - proposed the rules for the stability of ionic compounds, based on the concept of coordination polyhedrons as building elementary modules of inorganic compounds.

The stability rules of Pauling, as well as the conception, formulated by Bragg, of the structures of complex oxides as characterized by ‘close packing’ of oxygen anions, were the main guiding lines in the ‘trial and error’ procedures to determine the atomic arrangements in minerals and in inorganic compounds in general.

The increasing number of known structures raised the need for proper classification schemes, largely based on elementary structural units and the various ways of their connection. Machatschki, an outstanding coworker of Goldschmidt and Bragg, applied the Goldschmidt’s ideas on crystal chemistry to the problem of silicate structures, demolishing current theories of silicate structures based on hypothetical silicic acids and established the concept of the silicon tetrahedral coordination by oxygen anions as the basic structural unit in silicates. The brilliant idea of Machatschki was then developed by L. Bragg, who sketched a reliable classification of the structures of silicate minerals, a classification which was subsequently updated and completed by F. Liebau.

At the same time the wide basis of structural data and the increased precision and accuracy of those data stimulated the revision of the old compilations of ionic radii (new compilation by Shannon and Prewitt), as well as a re-formulation of the Pauling’s rule of valence bond balance (Baur; Donnay and Allmann; Brown and Shannon).

Examples are presented of the application of the crystal chemical tools to some important mineralogical, geochemical and geophysical problems: patterns of element distribution and partition; polymorphism in serpentine minerals; polymorphic transformations in the transition zone; spin pairing in the lower mantle.

An explosive growth of structural knowledge in the last decades of the twentieth century was stimulated by the new techniques of data collection, the high speed of computing and the advent of direct methods of structure solution, which resulted not only in an enormous increase in the number of known structures, but also in unraveling very complex arrangements. This increasing structural knowledge accompanied and stimulated the development of a new way to look at the arrangements of inorganic compounds, based on their modular aspects, from OD (order-disorder) theory (Dornberger-Schiff), particularly useful in dealing with polytypic families, to polysomatism and polysomatic series (Thompson), to the other types of approach to modularity.

The concept of assembling different, geometrically compatible modules, mainly structural layers, to build up complex structures has been very productive; in fact it not only consented a deep knowledge of the structural relationships inside wide families of natural and synthetic compounds, but also favored the solution of complex structural problems and permitted careful previsions of new possible structural arrangements.

Few lines of future developments of the crystal chemical study of minerals are briefly presented and discussed: ‘synergy’ between mineralogists and material chemists; computational simulations of structural arrangements; new possibility of automated electron diffraction tomography; ultra-intense pulses of radiation obtained with the new source, the x-ray free-electron laser (FEL).

## **SESSIONE S1**

### **Holes in the Bottom of the Sea: discoveries and challenges in marine geology**

*CONVENORS*

*A. Camerlenghi (OGS Trieste)*

*M. Ligi (CNR-ISMAR, Bologna)*

*I. Raffi (UdA Chieti-Pescara)*

## **Paleogene Newfoundland Sediment Drifts (Iodp Expedition 342): preliminary results**

Agnini C.\*<sup>1-2</sup> & Expedition 342 Scientists<sup>3</sup>

1. Dipartimento di Geoscienze, Università degli Studi di Padova. 2. Department of Geological Sciences, Stockholm University, Sweden. 3. Expedition 342 Scientists – See [http://publications.iodp.org/preliminary\\_report/342/342pr\\_3.htm](http://publications.iodp.org/preliminary_report/342/342pr_3.htm) for full list.

Corresponding email: [claudia.agnini@unipd.it](mailto:claudia.agnini@unipd.it)

Keywords: IODP Exp. 342, Paleogene, Newfoundland.

In summer 2012, IODP Expedition 342 drilled the seafloor off Newfoundland (NW Atlantic) with two primary drilling target: (1) the southern toe and eastern flank of J-Anomaly Ridge and (2) the north-facing slopes of seamounts on Southeast Newfoundland Ridge. This cruise successfully recovered high quality cores from ten sites (U1402 to U1411) that mainly consists of carbonate clay to oozes. One of the benefits of the Newfoundland sediment drift complex is the near-absence of Neogene sedimentary cover. Since late Cenozoic, most areas were affected by strong currents that inhibit the deposition of younger strata. Before these currents become active, the presence of units characterized by outstanding thickness, absence of internal reflections, and peculiar drift morphology suggest high sedimentation rates (SRs), higher than in typical deep-sea sediments (0.5–1 cm/kyr). The scientific objectives of the Paleogene Newfoundland Sediment Drifts Expedition included the study of: 1) the onset and development of Cenozoic glaciation; 2) the history of North Atlantic DWBC deep waters in the Paleogene and Cretaceous; 3) changes in the CCD of the Deep North Atlantic during latest Cretaceous and Paleogene “Extreme Climate” Events; 4) the calibration of the Astronomical Time scale into the Early Cenozoic (Expedition 342 Scientists, 2012). The sediments recovered during Exp.342 effectively document the main climatic events occurring from Cretaceous to the Miocene. Among these the K/Pg boundary, the Paleocene/Eocene thermal maximum (PETM), the middle Eocene climatic optimum (MECO), and the Eocene–Oligocene glaciation are the most prominent. The shipboard bio-magnetostratigraphic framework provides high-quality age models of the sediments that reveal high SRs in middle Eocene (47–40 Ma; > 3 cm/kyr) and in the Oligo–Miocene sediments (26–22 Ma; >10 cm/kyr; Norris et al., 2014). Hence, preliminary results show the high potential of cores drilled during Exp. 342, which will likely provide high-quality data to improve our understanding of the Paleogene paleoceanographic evolution as well as the calibration of the Time Scale of the Eocene.

Expedition 342 Scientists 2012. Paleogene Newfoundland sediment drifts. IODP Prel. Rept., 342. doi:10.2204/iodp.pr.342.2012.

Norris R.D., Wilson P.A., Blum P., Fehr A., Agnini C., Bornemann A., Boulila S., Bown P.R., Cournede C., Friedrich O., Ghosh A.K., Hollis C.J., Hull P.M., Jo K., Junium C.K., Kaneko M., Liebrand D., Lippert P.C., Liu Z., Matsui H., Moriya K., Nishi H., Opdyke B.N., Penman D., Romans B., Scher H.D., Sexton P.F., Takagi H., Turner S.K., Whiteside J.H., Yamaguchi T. & Yamamoto Y. 2014. Proc. IODP, 342: College Station, TX (Integrated Ocean Drilling Program). doi:10.2204/iodp.proc.342.2014.

## **Acquisition, processing and geologic interpretation of Multibeam bathymetric datasets and correlations with multichannel seismic profiles: applications to the Naples and Salerno Gulfs (Southern Tyrrhenian sea)**

Aiello G.\*<sup>1</sup>, Marsella E.<sup>1</sup> & D'Isanto C.<sup>2</sup>

1. IAMC-CNR, Napoli. 2. Collaboratore esterno, Dottore di Ricerca in Scienze ed Ingegneria del Mare,  
Università degli Studi di Napoli "Federico II".

Corresponding email: [gemma.aiello@iamc.cnr.it](mailto:gemma.aiello@iamc.cnr.it)

Keywords: Multibeam bathymetry, multichannel seismic profiles, Naples and Salerno Gulfs, Campania continent.

The research project is based on the processing and the interpretation of bathymetric data recorded by the IAMC-CNR of Naples, Italy through different types of Multibeam lateral echosoundings. An analytic comparison between one of the automatic methods most efficient for the data processing, i.e. the CUBE and the manual processing of swath packages has been attempted. The efficiency of the algorithm has been tested on complex morphologies, such as the Capri continental slope and the related geological structures occurring in the Salerno Gulf. Multibeam data processing and interpretation has been carried out for the following research projects: 1) CNR-SGN Convention for the redaction of marine geological maps at the 1:25.000 scale of Naples and Salerno Gulfs (maps n. 465 "Procida", n. 466 "Sorrento", n. 467 "Salerno"); 2) CARG Project at the scale 1:10.000 of the Campania region at the 1:10.000 scale (maps n. 464 "Ischia", n. 465 "Procida", n. 466 "Sorrento", n. 446-447 "Napoli", n. 484 "Capri", n. 468 "Foce del Sele", n. 502 "Agropoli", n. 519 "Capo Palinuro", n. 520 "Sapri"); 3) GEOSSED project for the acquisition of morphological data for the geomorphological and sedimentological study of selected areas of Campania continental shelf (Capri and Ischia islands); 4) SISTER II oceanographic cruise of morpho-bathymetric acquisition in intermediate and deep sea bottoms through the RESON 8160 Multibeam and finalized to the geological knowledge of the Sorrento continental slope, Salerno Valley, northern and southern Sele highs; 5) morpho-bathymetric surveys committed to the CNR by the Authority of the Naples harbour for monitoring the marine pollution of sediments. Dedicated software as the PDS2000 (Thales), the NEPTUNE (Merlin) and the ISIS (Triton Elics) have been used for the cartographic restitution of bathymetric and Sidescan Sonar data. The bathymetric maps, both contour isobaths maps and shaded-relief maps have been interpreted with the aim of reconstructing the main morphological lineaments occurring at the sea bottom, in particular for the Naples Bay canyons, the continental slope off the Sorrento Peninsula, the sedimentary basin of the Salerno Valley and the related depocenters. Bathymetric profiles have been also produced, allowing to distinguish erosional and depositional areas. The correlation of Multibeam data with some significant seismic profiles recorded in Naples and Salerno Gulfs has completed the geological interpretation.

## **Status of the Italian participation in ECORD and perspective of “IODP-Italia” for the next decade**

Argnani A.\*<sup>1</sup>, Camerlenghi A.<sup>2</sup>, Sacchi M.<sup>3</sup>, Erba E.<sup>4</sup> & Sagnotti L.<sup>5</sup>

1. ISMAR-CNR, Bologna. 2. OGS, Trieste. 3. IAMC-CNR, Napoli. 4. Dipartimento di Scienze della Terra, Università di Milano. 5. INGV, Roma

Corresponding email: [andrea.argnani@ismar.cnr.it](mailto:andrea.argnani@ismar.cnr.it)

Keywords: IODP, ECORD, ESSAC, ICDP, Italy.

The decade spanning from 2003 to 2013 of the Integrated Ocean Drilling Program (IODP) has seen the debut of three new drilling platforms, and the establishment of the European Consortium for Ocean Research Drilling (ECORD) as the operator of the Mission Specific Platforms (MSP). Italy participated in ECORD through a bottom-up assembled consortium constituted by Public Research Institutions (CNR, INGV, and OGS) together with the University-based “CONSORZIO NAZIONALE INTERUNIVERSITARIO PER LE SCIENZE DEL MARE” (CONISMA). These institutions agreed to contribute by paying a membership fee required to join ECORD, and to establish a “IODP Italia” informal structure to manage the relationships with ECORD and IODP. Because of the progressive reduction of Italian funds for research, only the CNR's contribution was maintained in the last three years of the IODP decade, seriously limiting the Italian participation in ECORD. In 2013, when the International Ocean Discovery Program (IODP, 2013-2023) debuted, the above mentioned institutions submitted a funding request to the MIUR, as applicable to the large infrastructures for Environment, in support of the Italian participation in ECORD. The request was accepted and the managing of the Italian participation in ECORD has been assigned to CNR, who is about to create a specific IODP-Italia Commission, composed by members representing the participating institutions (CNR, INGV, OGS e CONISMA). This welcome turn in policy can hopefully bring the Italian community back to a position that is more appropriate to its scientific level of contribution to IODP, both in terms of quality and number of IODP-related research projects and initiatives. Besides managing the ECORD activities, the MIUR-funded infrastructure will also coordinate and support the Italian participation in ICDP (International Continental Drilling Program). At present, the Italian contribution is still one order of magnitude less than that of France, Germany and the UK, though comparable to that of countries like The Netherlands and Sweden. It is of paramount importance that this contribution is maintained in the next years, in order to ensure the continuity of the Italian presence on the scene of the international ocean discovery program.

## **The Pacific (DSDP Site 463) and Tethys Ocean record of OAE1a: a taxonomic and quantitative analyses of planktonic foraminifera**

Barchetta A. \*, Petrizzo M.R., Bottini C. & Erba E.

Dipartimento di Scienze della Terra "A. Desio", Università degli Studi di Milano.

Corresponding email: [alessia.barchetta@unimi.it](mailto:alessia.barchetta@unimi.it)

Keywords: Early Aptian, Selli Level, Foraminifera.

The Selli Level (Early Aptian) is a regional marker-bed identified in the Umbria-Marche area (central Italy) consisting of laminated black shales rich in organic matter, alternated with radiolarian beds. The Selli Level is regarded as the sedimentary expression of the OAE1a (Oceanic Anoxic Event 1a) and is marked by a  $\delta^{13}C$  anomaly, comprising of a pronounced negative shift followed by a positive excursion.

A detailed and quantitative documentation in terms of species identification and distribution, variation of shell size, diversity and abundance of planktonic foraminifera across Selli Level equivalents is presented for a 24 m-thick stratigraphic section of the Cismon core (southern Alps, Italy) and a 60 m-thick stratigraphic interval from DSDP Site 463 (Mid-Pacific Mountains).

Foraminiferal quantitative (species richness and abundance) and morphometric analyses (shell size measurements) were conducted on washed residues and thin sections.

Results from the Cismon Core allow identification of three intervals (below, within and above the Selli Level equivalent) characterized by minor to major changes in species richness and abundance. Planktonic foraminifera are common and diversified below the Selli Level, being the assemblage composed by hedbergellids, few leupoldinids and globigerinelloidids. A similar composition in terms of species richness is recorded within the Selli Level, whereas abundance shows a marked decline. The planktonic foraminiferal assemblage above the Selli is characterised by the occurrence of common hedbergellids, clavate hedbergellids, leupoldinids and both globular and elongate globigerinelloidids. An increase in shell size of the planispiral taxa is also observed. Planktonic foraminifera at Site 463 are generally poorly preserved and rare or absent, especially below and within the Selli Level equivalent. An increase in abundance is observed in the interval above the Selli Level.

Comparison with calcareous nannoplankton abundance data highlights significant similarities and differences: 1) the onset of OAE1a is characterized by a marked decline of both planktonic foraminifera and calcareous nannoplankton. This distinctive decrease does not correspond to extinctions but to a period of virtual absence; 2) after the decline, planktonic foraminifera are rare within the Selli Level while calcareous nannoplankton shows a first increase in abundance; 3) both planktonic foraminifera and calcareous nannoplankton present a full recovery above the Selli Level.

The different trend within the Selli Level could be the effect of preservation and may be related to the higher susceptibility to dissolution of foraminifera than nannofossils.

## **Cold-water carbonate mounds and beyond: the Italian activity within COCARDE-ERN**

Basso D.\*<sup>1</sup>, Vertino A.<sup>1</sup>, Anzalone E.<sup>2</sup>, Barbieri R.<sup>3</sup>, Montagna P.<sup>4</sup>, Rosso A.<sup>5</sup>, Taviani M.<sup>4</sup>  
& the COCARDE-ERN Steering Committee

1. Università di Milano-Bicocca, Dept. of Earth and Environmental Sciences. 2. IAMC-CNR, Istituto per l'Ambiente Marino Costiero, Napoli. 3. Università di Bologna, Dept. of Earth and Environmental Sciences. 4. ISMAR-CNR, Istituto di Scienze Marine, Bologna. 5. Dipartimento di Scienze Biologiche, Geologiche, Ambientali, Università di Catania.

Corresponding email: [daniela.basso@unimb.it](mailto:daniela.basso@unimb.it)

Keywords: Cold-water carbonate mounds, COCARDE-ERN.

COCARDE-ERN ([www.cocarde.eu](http://www.cocarde.eu); [www.esf.org/cocarde](http://www.esf.org/cocarde)) is an international research network programme supported by the European Science Foundation, aimed at bringing together Earth scientists working on modern and ancient carbonate systems. Although originally focussed on cold-water coral mounds, COCARDE-ERN is expanded at present to include a wider suite of carbonate expertises on marine and fresh-water environments from "shallow to deep time". The main goal of this network is to cross inter-sectorial boundaries within the academic community and build bridges towards industrial research in order to perform advanced multidisciplinary studies and train young scientists. A range of integrated workshops and field seminars, consisting of a combination of indoor and outdoor (field seminar) initiatives, forms the core activity of the network. The participation of young scientists in COCARDE activities such as workshops/conferences attendance and training periods abroad, is fostered by the online publication of calls for grants. The Italian COCARDE-ERN community is coordinated by the University of Milano-Bicocca and includes the Universities of Bologna and Catania, the ISMAR- and IAMC- CNR Institutes. The Italian community has been contributing to the network since 2011 (i) as a member of the Steering Committee, (ii) through the coordination of networking activities and (iii) by multidisciplinary research within new international collaborations. More in detail, our major activities to date resulted in the organization in 2013 of the workshop and field seminar held in Sicily, that served as a start-up for the COCARDE database project on Pleistocene to modern marine and terrestrial "unconventional" carbonate buildups. The marine research has been mainly devoted to the coordination and/or participation in several oceanographic cruises in the NE Atlantic and Mediterranean, aimed at coring cold-water coral (CWC) mounds. In addition, other topics tackled by the Italian group are the comparison between carbonate platforms and travertines as depositional systems recording paleoenvironmental changes and paleoclimatic cycles; the paleoecology and geochemistry of biogenic archives in shallow and deep waters; the geobiology of seep carbonates and associated chemosynthetic communities.

## Uncovering a Salt Giant. Deep-Sea Record of Mediterranean Messinian Events (DREAM) multi-phase drilling project

Camerlenghi A.\*<sup>1</sup>, Aloisi G.<sup>2</sup>, Lofi J.<sup>3</sup>, Hübscher C.<sup>4</sup>, deLange G.<sup>5</sup>, Flecker R.<sup>6</sup>, Garcia-Castellanos D.<sup>7</sup>, Gorini C.<sup>2</sup>, Gvirtzman Z.<sup>8</sup>, Krijgsman W.<sup>5</sup>, Lugli S.<sup>9</sup>, Makowsky Y.<sup>10</sup>, Manzi V.<sup>11</sup>, McGenity T.<sup>12</sup>, Panieri G.<sup>13</sup>, Rabineau M.<sup>14</sup>, Roveri M.<sup>11</sup>, Sierro F.-J.<sup>15</sup> & Waldmann N.<sup>10</sup>

1. OGS, Trieste. 2. Université Pierre et Marie Curie, Paris. 3. Université de Montpellier 2. 4. University of Hamburg  
5. Utrecht University. 6. University of Bristol. 7. ICTJA-CSIC, Barcelona. 8. Geological Survey of Israel, Jerusalem  
9. University of Modena and Reggio Emilia. 10. University of Haifa. 11. University of Parma. 12. University of Essex  
13. University of Tromsø. 14. CNRS Plouzané Brest. 15. University of Salamanca.

Corresponding email: [acamerlenghi@ogs.trieste.it](mailto:acamerlenghi@ogs.trieste.it)

Keywords: Salt, Messinian, Scientific drilling.

In May 2013, the DREAM MagellanPlus Workshop was held in Brisighella (Italy). The initiative builds from recent activities by various research groups to identify potential sites to perform deep-sea scientific drilling in the Mediterranean Sea across the deep Messinian Salinity Crisis (MSC) sedimentary record.

In this workshop three generations of scientists were gathered: those who participated in formulation of the deep desiccated model, through DSDP Leg 13 drilling in 1973; those who are actively involved in present-day MSC research; and the next generation (PhD students and young post-docs). The purpose of the workshop was to identify locations for multiple-site drilling (including riser-drilling) in the Mediterranean Sea that would contribute to solve the several open questions still existing about the causes, processes, timing and consequences at local and planetary scale of an outstanding case of natural environmental change in the recent Earth history: the Messinian Salinity Crisis in the Mediterranean Sea.

The product of the workshop is the identification of the structure of an experimental design of site characterization, riser-less and riser drilling, sampling, measurements, and down-hole analyses that will be the core for at least one compelling and feasible multiple phase drilling proposal. Particular focus has been given to reviewing seismic site survey data available from different research groups at pan-Mediterranean basin scale, to the assessment of additional site survey activity including 3D seismics, and to ways of establishing firm links with oil and gas industry.

The scientific community behind the DREAM initiative is willing to proceed with the submission to IODP of a Multi-phase Drilling Project including several drilling proposals addressing specific drilling objectives, all linked to the driving objectives of the MSC drilling and understanding. A series of critical drilling targets were identified to address the still open questions related to the MSC event. Several proposal ideas also emerged to support the Multi-phase drilling project concept: Salt tectonics and fluids, Deep stratigraphic and crustal drilling in the Gulf of Lion (deriving from the GOLD drilling project), Deep stratigraphic and crustal drilling in the Ionian Sea, Deep Biosphere, Sapropels, and the Red Sea.

A second MagellanPlus workshop, held in January 2014 in Paris, (France), has proceeded a step further towards the drafting of the Multi-phase Drilling Project and a set of pre-proposals for submission to IODP on April 1st 2014. This presentation is taken from a talk given at the Euroforum Session held in Vienna during the EGU General Assembly in April 2014 (Camerlenghi et al., 2014). It will be complemented in Milano with the results of the IODP Evaluation of the Multi-phase Drilling Project proposal expected in July 2014, beyond the deadline for abstract submission.

Camerlenghi A., Aloisi G., Lofi J., Hübscher C., deLange G., Flecker R., Garcia-Castellanos D., Gorini C., Gvirtzman Z., Krijgsman W., Lugli S., Makowsky Y., Manzi V., McGenity T., Panieri G., Rabineau M., Roveri M., Sierro F.-J. & Waldmann N. 2014. Uncovering a Salt Giant. Deep-Sea Record of Mediterranean Messinian Events (DREAM) multi-phase drilling project. *Geophysical Research Abstracts*, Vol. 16, EGU2014-7443, 2014, EGU General Assembly 2014.

## **Marine geology challenges: integration and harmonization of data**

D'Angelo S. & Fiorentino A.\*

Geological Survey of Italy – ISPRA.

Corresponding email: [andrea.fiorentino@isprambiente.it](mailto:andrea.fiorentino@isprambiente.it)

Keywords: Geological map, European Framework Directive, multidisciplinary.

Studies on marine geology have evidenced the need of a multidisciplinary approach to achieve a level of integrated knowledge useful for a comprehensive characterization of the submerged areas.

The Geological Survey of Italy (SGI) has produced national cartography of submerged areas for over 30 years. Geological surveying has allowed to collect a large amount of data from remote sensing (multibeam, sidescan sonar and seismics) as well as from sampling and scuba diving. Maps have been realized within the CARG Project, which covers at present about 40% of the Italian territory. Guide lines for submerged areas have been harmonised with those for the terrestrial sectors in order to have consistent representation throughout the maps. The SGI, as a member of EuroGeoSurveys, has also participated in numerous European Projects on Marine Geology. The major aims of such projects are to collect into a single database information regarding submerged areas and harmonize data on a European scale. EMODnet-Geology 2 is the ongoing Project in which the SGI is Work Package leader for the subject Geological events and probabilities. Within this Project other work packages foresee the production of GIS maps regarding seafloor sediments, pre-Quaternary substrate, coastal behaviour, accumulation rates and mineral resources. Data from the DSDP-ODP Legs in the Mediterranean are being used to complement the information requested. Regarding the integration with biological data, the SGI has contributed to the Marine Strategy Framework Directive, providing detailed descriptions of the physiography of Italian Seas and the geology of the continental shelf. This issue was the subject of studies addressed at the production of the Geological map of the Cilento, Vallo di Diano and Alburni Geopark which includes submarine landscapes. The aim of this map is to disseminate the geological knowledge for the fruition and management of the territory, also considering submerged areas. In the last few years, the SGI has contributed to GeoHab, a marine scientists community of geologists, biologists, acousticians, statisticians, spatial analysts and environmental managers. The GeoHab 2013 conference was hosted by the SGI in Rome; a selection of papers presented at the conference is currently under review for a volume of the Italian Journal of Geosciences.

## **New Geological, seismological and geodetic evidence of active thrusting and folding south of Mt. Etna (eastern Sicily): revaluation of “seismic efficiency” of the Sicilian Basal Thrust**

De Guidi G.\*<sup>1</sup>, Barberi G.<sup>2</sup>, Barreca G.<sup>1</sup>, Bruno V.<sup>2</sup>, Cultrera F.<sup>1</sup>, Grassi S.<sup>1</sup>, Imposa S.<sup>1</sup>, Mattia M.<sup>2</sup>, Monaco C.<sup>1</sup>, Scarfi L.<sup>2</sup> & Scudero S.<sup>1</sup>

1. Dept. of Biological, Geological and Environmental Sciences, University of Catania. 2. Istituto Nazionale di Geofisica e Vulcanologia, Osservatorio Etneo - Sezione di Catania.

Corresponding email: [giorgio.deguidi@alice.it](mailto:giorgio.deguidi@alice.it)

Keywords: Active thrusting and folding, seismotectonic, Etna volcano.

New geological, seismological and geodetic data indicate that a NNW-SSE compressive regime occurs in the southern and western sector of Mt. Etna, accommodated by aseismic folding at the front of the chain. In particular, a large WSW-ENE trending anticline (the Catania anticline) is growing west and north of Catania within a middle-late Pleistocene fold system. For its location, geometry and growth rate, it is consistent with detachment fold models. We exclude that this structure have developed in response to volcanic spreading, as proposed by previous authors. Looking at the earthquakes distribution, an interesting finding is a clear trend of the seismic events deepening from very shallow hypocenters, in the area south of Etna, down to a depth of about 35 km, towards the NNW. Moreover, most of the events are clustered. We computed the focal mechanisms for the major and best recorded earthquakes occurring in the area. One cluster located at few kilometers north-west of the summit craters shows fault mechanisms of the deeper events with nearly horizontal P-axes striking NNW-SSE. A segment of the Sicilian Basal Thrust, located at crustal depth under the northwestern sector of the volcano, could be the seismic source. We propose the occurrence of detachment folding at the chain front, as response of a surface frontal propagation of this regional structure, migrating within the clayish middle-late Pleistocene foredeep deposits or at the top of the buried Hyblean foreland sequence. Geological and morphometric analyses suggest a maximum up warp deformation along the anticline axis of 40 m in the last 6000-7000 yrs, with a vertical slip-rate of 5 - 7 mm/yr. These values are consistent with the growth rate of 9 - 10 mm/yr estimated by interferometric data and the horizontal shortening of 5 mm/yr obtained by GPS measurements.

Our analysis confirms that, besides the activity related to the volcanic feeding system, the seismic pattern under Mt. Etna edifice can be certainly related to the regional dynamics. The compressive stress is converted into elastic accumulation and then in earthquakes along the ramps to the rear of the chain, whereas along the frontal detachment it is accommodated by aseismic ductile deformation. In fact, despite the high rates of convergence, the seismicity is moderate at the front of the chain and the “seismic efficiency” of the Sicilian Basal Thrust is greater in correspondence of ramps at the rear, where strong earthquakes can occur.

## **Sulfide deposits from south-eastern Tyrrhenian Sea: new geochemical, isotopic and fluid inclusion data**

Dini A.\*<sup>1</sup>, Boschi C.<sup>1</sup>, Gamberi F.<sup>2</sup>, Laurenzi MA.<sup>1</sup>, Marani M.<sup>2</sup>, Rovere M.<sup>2</sup>, Ruggieri G.<sup>3</sup> & Trua T.<sup>4</sup>

1. IGG - CNR, Pisa. 2. ISMAR - CNR, Bologna. 3. IGG - CNR, Firenze. 4. Dipartimento di Fisica e Scienze della Terra, Università di Parma

Corresponding email: [a.dini@igg.cnr.it](mailto:a.dini@igg.cnr.it)

Keywords: Sulfide deposits, Tyrrhenian Sea, isotope geochemistry.

The aim of this contribution is to present new mineralogical, geochemical, isotopic and fluid inclusion data on volcanogenic-hydrothermal sulfides occurring in the southeast Tyrrhenian Sea. Subduction-related volcanic activity in the southeast Tyrrhenian back-arc basin has resulted in a large variety of calcalkaline rocks (ranging from arc tholeiitic to shoshonitic and rhyolitic composition), which were emplaced in both oceanic and continental crust (Trua et al., 2007). Hydrothermal systems in the SE Tyrrhenian Sea generated a wide range of oxyhydroxide and sulfide deposits (Dekov and Savelli, 2004). Samples of sulfides from Palinuro and Marsili Seamounts have been selected for a detailed isotopic (Pb, Sr) and fluid inclusion study coupled with geochemical and petrographic characterization. Large variation in base metals (Pb, Zn and Cu) and trace metals (Bi, Au, Ag, As, Sb, Tl etc.) have been compared with the isotopic compositions (hydrothermal and magmatic products) and the geological setting of the studied seamounts.

This research is part of the “Progetto Bandiera RITMARE”, coordinated by CNR (Italy).

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Dekov V.M. & Savelli C. 2004. Hydrothermal activity in the SE Tyrrhenian Sea: an overview of 30 years of research. *Mar. Geol.*, 204, 161-185.

## **A new Late Cretaceous record of oxygen and carbon trends from the southern mid latitudes (ODP Leg 122) and insights on planktonic foraminiferal evolution.**

Falzone F.\*<sup>1</sup>, Petrizzo M.R.<sup>1</sup> & MacLeod K.G.<sup>2</sup>

1. Dipartimento di Scienze della Terra "A. Desio", Università degli Studi di Milano. 2. Department of Geological Sciences, University of Missouri, Columbia.

Corresponding email: [francesca.falzone1@gmail.com](mailto:francesca.falzone1@gmail.com)

Keywords: Late Cretaceous, planktonic foraminifera, Exmouth Plateau.

Patterns and timing of Late Cretaceous climatic evolution and biotic responses have been object of a number of studies for the similarities between this ancient greenhouse period and some of the predictions for the Earth's next future. However, while Cenomanian–Turonian and late Campanian–Maastrichtian intervals have been widely studied and climatic trends are relatively well established, little information is available for the ~20 m.y. long Turonian–early Campanian, despite it represents a key-period to examine the decline of the maximum greenhouse phase and the associated biotic response. In detail, the Turonian–Campanian cooling phase was likely associated with changing intermediate and deep-water circulation including enhanced deep-water formation in southern high latitudes. Keeled Cretaceous planktonic foraminifera underwent a major turnover across a ~5 m.y. long Coniacian–early Campanian interval, but the main controlling factors and how they might relate to changing greenhouse climate dynamics have never been established. This lack of understanding is related to the limited recovery of stratigraphically complete Turonian–early Campanian sediments from DSDP, ODP and IODP cruises and to poor preservation of microfossils that compromises stable isotope approaches for reconstructing paleoceanographic conditions and species paleoecological preferences. Further uncertainty is introduced by several recent studies that found a traditional morphologically-based scheme for the interpretation of Cretaceous planktonic foraminiferal paleoecology likely incorrect. For instance, several keeled species always interpreted as deep-dwellers yield an isotopic signature that suggests a near-to-surface habitat, whereas several small biserial, planispiral and low trochospiral taxa may have inhabited deep layers of the water column.

We present new  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  isotopic measurements of well-preserved benthic and planktonic foraminifera from Exmouth Plateau (eastern Indian Ocean, ODP Leg 122, Hole 762C) to provide (a) a continuous, highly-resolved and stratigraphically constrained sea-surface and bottom water record of Cenomanian to Maastrichtian oxygen and carbon trends in the southern mid latitudes, and (b) new information on the paleoecological preferences of planktonic foraminiferal taxa. Results suggest persisting warmth up to the mid Santonian and prevailing short-term climatic oscillations in the late Campanian–Maastrichtian. Our conclusions imply re-thinking of Cretaceous planktonic foraminiferal depth-organization and suggest cooling sea-surface temperatures associated to competition as controlling factors on species turnover.

## **Tectonic analysis and paleostress determination of the upper lava section at ODP/IODP Site 1256 (east Pacific Ocean)**

Fontana E.\*

Dipartimento di Scienze della Terra, Università degli Studi di Milano, Milano, Italy.

Corresponding email: [emanuele.fontana@unimi.it](mailto:emanuele.fontana@unimi.it)

Keywords: Paleostress, IODP, inversion method.

Research on deep-sea is of great importance to better understand the mechanism of magma emplacement and tectonic evolution of the oceanic crust. However, details of internal structure in the upper levels of the oceanic crust are much less complete than that of the better studied subaerial areas because of the inaccessibility under deep water and of paucity of direct observations.

After Carey and Brunier (1974) kinematic indicators (e.g. slickenslides) have been considered as the main key for the reconstruction of the geological paleostress tensor in the analysis of failure population. Such approaches are commonly referred as “inversion method”.

Nevertheless, difficulties in operating at deep seafloor make similar studies on cores achieved from the deep-sea basement of the oceanic crust hardly usable.

Since Bell and Gough (1979) the crustal stress in drilled holes is generally studied using borehole breakouts and drilling-induced fractures due to either compressive or tensile stress concentrations exceeding the *in situ* rock strength.

In both subaerial and subaqueous environments, natural earthquake focal mechanism is also used to define present-day stress field. However, inversion methods represent a more complete source of information, since neither borehole breakouts nor earthquake focal mechanism can be used for the paleostress evaluation.

This study proposes, for the first time, a kinematic analysis using the inversion method on core data deriving from the drilled basement of the present day intact oceanic crust at ODP/IODP Site 1256 in the Cocos plate.

The research is based on a innovative core reorientation process and combines different stress hypothesis approaches for the analysis of heterogeneous fault-slip data, by exploiting two distinct techniques (gauss method and multiple inverse method), which use both mechanical and geometrical constraints.

From the analysis of the failure-slip data, both techniques produce 5 distinct subsystem datasets. All calculated subsystems are mechanically acceptable and show low misfit angles. Interpretation of the results, even if concerning an extremely localized investigation, allows to point out a complex local and regional tectonic evolution deriving from the interplay of (1) the ridge push and the rotation of both East Pacific Rise, and Cocos-Nazca Spreading Center; (2) the effect of the slab pull of the Middle America Trench; and (3) the influence of the cooling subsidence and intraplate deformation.

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## **The opening of the Arctic-Atlantic Gateway: tectonic, oceanographic and climatic dynamics (“AAG-Drill” – Arctic-Atlantic Gateway Drilling Campaign”)**

Geissler W.<sup>1</sup>, Lucchi R.\*<sup>2</sup> & Rebesco M.<sup>2</sup>

1. Alfred-Wegener-Institut. 2. OGS.

Corresponding email: [rglucchi@inogs.it](mailto:rglucchi@inogs.it)

Keywords: IODP, Fram Strait, paleoclimate.

The modern polar cryosphere reflects an extreme climate state with profound temperature gradients towards high-latitudes. It developed in association with stepwise Cenozoic cooling, beginning with ephemeral glaciations and the appearance of sea ice in the late middle Eocene. The polar ocean gateways played a pivotal role in changing the polar and global climate, along with declining greenhouse gas levels. The opening of the Drake Passage finalized the oceanographic isolation of Antarctica, some 40 Ma ago. The Arctic Ocean was an isolated basin until the early Miocene when rifting and subsequent sea-floor spreading started between Greenland and Svalbard, initiating the opening of the Fram Strait / Arctic-Atlantic Gateway (AAG). Although this gateway is known to be important in Earth's past and modern climate, little is known about its Cenozoic development. However, the opening history and AAG's consecutive widening and deepening must have had a strong impact on circulation and water mass exchange between the Arctic Ocean and the North Atlantic.

To study the AAG's complete history, ocean drilling at two primary sites and one alternate site located between 73°N and 78°N are proposed. These sites will provide unprecedented sedimentary records that will unveil (1) the history of shallow-water exchange between the Arctic Ocean and the North Atlantic, and (2) the development of the AAG to a deep-water connection and its influence on the global climate system.

The specific overarching goals of this proposal are to study:

- the influence of distinct tectonic events in the development of the AAG and the formation of deep water passage on the North Atlantic and Arctic paleoceanography, and
- the role of the AAG in the climate transition from the Paleogene greenhouse to the Neogene icehouse for the long-term (~50 Ma) climate history of the northern North Atlantic.

The proposed drilling addresses a number of key questions raised in the IODP Science Plan 2013-2023. It is specifically linked to the Research Theme "Climate and Ocean Change: Reading the Past, Informing the Future".

## Deep submarine explosive eruptions at the Marsili Seamount (Tyrrhenian Sea, Italy)

Iezzi G.<sup>1-2</sup>, Ventura G.<sup>2</sup>, Caso C.<sup>1-3</sup>, Vallefucio M.\*<sup>4</sup>, Cavallo A.<sup>2</sup>, Behrens H.<sup>5</sup>, Mollo S.<sup>2</sup>, Paltrinieri D.<sup>6</sup>,  
Signanini P.<sup>1</sup> & Vetere F.<sup>5</sup>

1. Dipartimento di Ingegneria & Geologia, Università G. d'Annunzio, Chieti. 2. Istituto Nazionale di Geofisica e Vulcanologia, Roma.  
3. Schlumberger Information Solutions, Madrid, Spain. 4. Istituto Ambiente Marino Costiero IAMC, CNR, Napoli. 5. Institute for Mineralogy,  
Leibniz University, Hannover, Germany. 6. Eurobuilding, Servigliano (AP).

Corresponding email: [mattia.vallefucio@iamc.cnr.it](mailto:mattia.vallefucio@iamc.cnr.it)

Keywords: tephra, submarine, explosive eruption, simulation.

The Marsili Seamount (MS) is a huge volcanic complex measuring 70 × 30 km, with height of about 3200 m and the top at ~500 m b.s.l.. MS is interpreted as the ridge of the 2 Ma old Marsili back-arc basin belonging to the Calabrian Arc–Ionian Sea subduction system (Southern Tyrrhenian Sea, Italy). Previous studies indicate that MS activity developed between 1 and 0.1 Ma through effusions of lava flows.

Here, new stratigraphic, textural, geochemical, and <sup>14</sup>C geochronological data from a 95 cm long gravity core (COR02) recovered at 839 m b.s.l. in the MS central sector are presented (Iezzi et al., 2014). COR02 contains mud and two tephra consisting of 98 to 100 area% of volcanic ash. The thickness of the upper tephra (TEPH01) is 15 cm, and that of the lower tephra (TEPH02) is 60 cm. The tephra have poor to moderate sorting, loose to partly welded levels, and erosive contacts, which imply a short distance source of the pyroclastics (Iezzi et al., 2014).

<sup>14</sup>C dating on fossils above and below TEPH01 gives an age of 3 ka BP; sedimentation rates of mud sediments above and between the tephra suggest that TEPH02 was emplaced 5 ka BP. These MS ashes have a high-K calcalkaline affinity with 53 wt.% < SiO<sub>2</sub> < 68 wt.%, and their composition overlaps that of the MS lava flows (Iezzi et al., 2014). The trace element pattern is consistent with fractional crystallization from a common, OIB-like basalt. The source area of ashes is thus the central sector of MS rather than a subaerial volcano of the Campanian and/or Aeolian Quaternary volcanic districts (Iezzi et al., 2014).

Submarine, explosive eruptions occurred at MS in historical times are the first evidence of explosive volcanic activity at a significant (700–800 m b.s.l.) water depth in the Mediterranean Sea. Therefore, MS can be considered still active and it should be monitored in order to evaluate the different types of hazard (Iezzi et al., 2014).

Finally, the isotopic signature of these two tephra are cogenetic with those of MS lavas and represent end-members of the Aeolian volcanic geochemical trend; textures (bubble and crystal contents) and compositions (minerals and matrix glasses) of these two tephra allowed to better understand the peculiar eruptive conditions of these two recent submarine volcanic products.

Iezzi G., Caso C., Ventura G., Vallefucio M., Cavallo A., Behrens H., Mollo S., Paltrinieri D., Signanini P. & Vetere F. 2014. Deep submarine explosive eruptions at the Marsili Seamount (Tyrrhenian Sea, Italy). *Gondwana Research*, 25, 764-774.

## **Gas hydrates, methanogenesis, and carbon cycling at continental margins**

Malinverno A.\*

Lamont-Doherty Earth Observatory of Columbia University, Palisades, New York, USA.

Corresponding email: [alberto@ldeo.columbia.edu](mailto:alberto@ldeo.columbia.edu)

Keywords: Methane gas hydrates, microbial methanogenesis, organic matter remineralization.

In the last few decades vast natural deposits of gas hydrate, a solid ice-like compound of water and methane, have been discovered in the sediments of the world continental margins. These deposits accumulate where methane is abundant, pressure is high, and temperature is low. Gas hydrates can dissociate when temperatures rise, releasing large amounts of greenhouse gases to the ocean-atmosphere system, and can amplify a warming trend. Gas hydrate dissociation may have played a key role in past climate perturbations, could be relevant for future climate change, and has the potential to trigger large submarine landslides. Finally, gas hydrates are being actively investigated as a possible energy resource. Scientific ocean drilling has provided crucial information on the distribution of gas hydrates in sediments. This talk will review studies on the quantification of organic matter remineralization and methane generation (Martinez & Malinverno, 2013) and on the migration of microbial methane to form concentrated gas hydrate deposits in coarse-grained layers (Malinverno, 2010). Future research will concentrate on microbial methanogenesis and gas hydrate formation in the context of the organic carbon cycle in marine sediments. These interdisciplinary studies will integrate data from geophysics, sedimentology, microbiology, and geochemistry in a quantitative model.

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## **IODP751-full2 prop. Ocean-ice sheet interactions and West Antarctic Ice Sheet vulnerability: clues from the Neogene and Quaternary record of the outer Ross Sea continental margin**

McKay R.<sup>1</sup>, De Santis L.\*<sup>2</sup>, Bart P.<sup>3</sup>, Shevenell A.<sup>4</sup>, Williams T.<sup>5</sup>, Levy R.<sup>6</sup>, Bartek L.<sup>7</sup>, Sjunneskog C.<sup>8</sup>, Orsi A.<sup>9</sup>, Warny S.<sup>3</sup>, DeConto R.<sup>10</sup>, Pollard D.<sup>11</sup>, Suganuma Y.<sup>12</sup> & Hong J.<sup>13</sup>

1. Antarctic Research Centre, Victoria University of Wellington (NZ). 2. Istituto Nazionale di Oceanografia e di Geofisica Sperimentale, Trieste. 3. Department of Geology and Geography, Louisiana State University, Baton Rouge, La., USA. 4. College of Marine Science, University of South Florida, St Petersburg, FL, USA. 5. Lamont-Doherty Earth Observatory of Columbia University, New York, USA. 6. GNS Science, Lower Hutt, New Zealand. 7. University of North Carolina, Chapel Hill, NC, USA. 8. Florida State University, Tallahassee, Florida, USA. 9. Texas A&M University, College Station, Texas, USA. 10. Department of Geosciences, University of Massachusetts, Amherst, Massachusetts, USA. 11. Earth and Environmental Systems Institute, Pennsylvania State University, University Park, Pennsylvania, USA. 12. National Institute of Polar Research, Midorimachi, Tachikawa, Tokyo, Japan. 13. Division of Polar Earth-System Sciences, Korean Polar Research Institute, Incheon, Korea.

Corresponding email: [ldesantis@ogs.trieste.it](mailto:ldesantis@ogs.trieste.it)

Keywords: Neogene, ice sheet, seismic stratigraphy.

Southern Ocean is warming significantly (Gille, 2008), while westerly winds migrated southward and strengthened due to increasing atmospheric CO<sub>2</sub> concentrations. These changes are linked to thinning of Antarctic ice shelves and marine terminating glaciers (Pritchard et al., 2012). Results of geologic drilling on Antarctic continental margins document late Neogene marine-based ice sheet large variability (Naish et al., 2009; Cook et al., 2013), but sedimentologic sequences from the outer continental shelf are still required to evaluate the extent of past ice sheet variability and the role of oceanic heat flux in controlling ice sheet mass balance. IODP 751-Full2 proposes a latitudinal and depth transect from the outer continental shelf and rise in the Ross Sea to resolve the relationship between climatic/oceanic change and marine based ice sheets evolution through the Neogene and Quaternary. Ice sheet models suggest that this location is highly sensitive to changes in ocean heat flux and sea level (Pollard and DeConto, 2009; Golledge et al., 2012) and links ice proximal records from the inner Ross Sea continental shelf (ANDRILL sites) to deep Southwest Pacific drilling sites/targets to obtain an ice proximal to far-field view of Neogene climate and Antarctic cryosphere evolution. The proposed drilling is designed on the basis of a large geophysical data set integrated with DSDP leg 28 data (De Santis et al., 1995). The data-model integration will enable an improved understanding of the sensitivity of Antarctic Ice Sheet mass balance during warmer-than present climates. Additionally, the proposed transect The proposed scientific objectives directly address Ocean and Climate Challenges 1 and 2 of the 2013-2023 IODP Science Plan.

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## A geochemical record of the magmatic activity at Bouvet Island

Meyzen C.M.\*<sup>1</sup>, Marzoli A.<sup>1</sup>, Bizimis M.<sup>2</sup> & Bellieni G.<sup>1</sup>

1. Dipartimento di Geoscienze - Università di Padova. 2. Department of Earth and Ocean Sciences – University of South Carolina.

Corresponding email: [christine.meyzen@unipd.it](mailto:christine.meyzen@unipd.it)

Keywords: Bouvet, hotspot, magmatism, trace and major elements, isotopes.

Sitting atop old oceanic crust of 7 Ma, Bouvet (Lat. 54°26'S, long. 3°24'E) is a solitary, ice-capped and pint sized (55 km<sup>2</sup>) volcanic island in the Southernmost Atlantic Ocean. It is located off-axis the Southwest Indian Ridge in the vicinity of the triple point joining the African, South American, and Antarctic plates. As early as the seventies, this island has been regarded as being the surface expression of a mantle plume, which triggered the break-up of the Gondwanaland supercontinent. However, the detailed lower mantle structure of the Bouvet hotspot is largely unknown, because seismic ray coverage of the lowermost mantle under the southwestern Indian Ocean is weak. Surface wave tomography lacks the lateral resolution to image small-scale structures such as hotspots, expected to generate anomalies only a few hundred kilometers wide. The geology of the island is also poorly known because of the presence of a permanent ice cap. Previous studies (e.g. Verwoerd et al., 1990) have established the presence of solely two geological formations: a lower hydrothermally altered sequence of mainly pyroclastic rocks and an upper formation of predominantly subaerial lava flows. This latter unit consists of mainly mildly alkaline basalts, and carries minor amounts of intermediate and acid lavas, ranging in age from 1.39 Ma to < 0.1 Ma. The early magmatic evolution of the island is virtually unknown.

The geochemical data presented here are based on a suite of about 25 samples collected from the coastlines of Bouvet Island. The serie extends from basic (mildly alkaline basalts) to intermediate (benmoreites) and acid rocks (rhyolites). None of our samples (MgO < 4.84 wt. %) can be regarded as a primary product of mantle melting. The alkali basalt lavas are chemically homogeneous in spanning a narrow range of major and trace element variability. These lavas all show strong light Rare Earth Element (REE) enrichment typical of ocean island basalts and the overall parallel REE trends show increasing enrichment in all the REE from hawaiiite through to rhyolite. The similarity of their trace element ratios and parallelism of their rare earth element patterns indicate: (1) a mantle source homogeneity; (2) an uniformity of the melting conditions (i.e. degree of melting and residual mineralogy) during most of the sub-aerial eruptive history. Their trace element systematics are not typical of a HIMU-like mantle source. Their homogeneous Sr-Nd-Pb isotopic composition occupy an intermediate position among the isotopic variability spectrum defined by Earth's oceanic island basalts, encompassing the isotopic variability range of the common component "C" representing the intersection point of the isotopic arrays of ocean island and mid-ocean ridge suites in two or in three dimensional isotopic spaces.

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## A possible evolutionary model of “aligned pockmarks”

Pennino V.\* & Sulli A.

Dipartimento di Scienze della Terra e del Mare - Università degli Studi di Palermo.

Corresponding email: [valentina.pennino@unipa.it](mailto:valentina.pennino@unipa.it)

Keywords: Pockmarks, Fluid Escape, Submarine Gullies.

Pockmarks are circular or nearly circular morphological submarine structures linked with escaping fluids, 10-700 m in diameter, and from a few meters to 45 m in depth (Judd and Hovland, 2007). They occur singly or randomly, in cluster, and can be aligned along the strike of faults and incisions (Pilcher et al., 2007), especially in areas subject to submarine landslides and tectonic activity (Judd and Hovland, 2007).

In the northern Sicily continental margin we recognized different morphological classes of pockmarks associated with escaping fluids (Pennino et al., 2014). In this paper we will suggest a possible evolutionary model of pockmarks, particularly those that occur aligned along straight direction, which could also have a key role in understanding the genetic mechanism of some furrowed structures.

The study area is located in a transitional area between the Sicilian-Maghrebian Chain to the south and the southern Tyrrhenian Sea to the north, and in particular in the offshore sector spanning between Castellammare del Golfo and Termini Imerese.

We used a dataset of seismic reflection profiles, both high and very high resolution single-channel and multi-channel profiles, acquired respectively with sparker, CHIRP and airgun sources, and morphobathymetric data collected during several oceanographic cruises between 2001 and 2013, in the context of the MaGIC and CARG projects.

The data allowed us to subdivide the pockmarks into three different morphological classes, that are 1) singly, 2) in cluster, 3) aligned, by means of the peculiar morphological features and seismic attributes. In the investigated area pockmarks occur exclusively on the continental slope at a depth between 250 and 900 m. In particular the class with the highest frequency and the highest percentage (75%) has been attributed to aligned pockmarks. They are arranged along a preferential direction, which generally coincides with that of the neotectonic lineaments and submarine gullies. Moreover, within some of the latter structures, pockmarks have been observed with eroded edges, and, in the neighbor, arranged in a parallel strike, with the shape still well-preserved. This evidence makes it possible to hypothesize their genetic mechanism. The aligned circular structures, formed in correspondence of tectonic features, coalesce creating the grooves. The latter could initially evolve into channels and later possibly into greater structures.

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## Internal structure of the shallow plate boundary slip zone for the 2011 Tohoku-Oki Earthquake sampled during the Japan Trench Fast Drilling Project (JFAST)

Remitti F.\*<sup>1</sup>, Kirkpatrick J.<sup>2</sup>, Ujiie K.<sup>3</sup>, Mishima T.<sup>4</sup>, Chester F.<sup>5</sup>, Rowe C.<sup>6</sup>, Regalla C.<sup>7</sup>, Moore C.<sup>8</sup>, Toy V.<sup>9</sup>,  
Kameda J.<sup>10</sup>, Bose S.<sup>11</sup> & Wolfson-Schwehr M.<sup>12</sup>

1. Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia. 2. Department of Geosciences, Colorado State University, Fort Collins, CO, USA. 3. Graduate School of Life and Environmental Sciences, University of Tsukuba, Japan. 4. Graduate School of Science, Osaka City University, Japan. 5. Center for Tectonophysics, Department of Geology and Geophysics, Texas A&M University, USA. 6. Earth and Planetary Sciences Department, McGill University, Montreal, Canada. 7. Department of Geosciences, The Pennsylvania State University, University Park, USA. 8. Department of Earth and Planetary Sciences, University of California Santa Cruz, USA. 9. Department of Geology, University of Otago, Dunedin, New Zealand. 10. The University of Tokyo, Department of Earth and Planetary Science, Japan. 11. University of Calcutta, Department of Geology, Kolkata, India. 12. Center for Coastal and Ocean Mapping/Joint Hydrographic Center, University of New Hampshire, Durham, NH, USA.

Corresponding email: [francesca.remitti@unimore.it](mailto:francesca.remitti@unimore.it)

Keywords: megathrust, 2011 Tohoku-Oki earthquake, IODP exp. 343.

The Mw=9 2011 Tohoku-oki earthquake ruptured to the Japan Trench, with largest coseismic slip (c. 50 m) unexpectedly occurring on the shallow part of the décollement. The JFAST Project, Integrated Ocean Drilling Program (IODP) Expedition 343/343T, successfully located and sampled the shallow part of the subduction thrust shear zone (Chester et al. 2013a,b). Temperature data from a downhole observatory confirm that a thin and weak clay rich layer, identified in logging-while-drilling data and core-sample observations, is the plate boundary fault that accommodated the large slip of the earthquake rupture, as well as most of the kilometres interplate motion at the drill site (Chester et al. 2013b; Fulton et al. 2013; Lin et al. 2013; Ujiie et al. 2013). The décollement separates folded and faulted frontal prism sediments in the overriding plate from incoming flat-lying sediments along the top of the subducting plate (Chester et al., 2013b). Observed stratigraphic discontinuities at the boundary and inside the recovered fault material (Chester et al. 2013a) suggest that it contains multiple slip surfaces, many of them probably not recovered. Core analysis shows that the décollement is localized upon a strongly deformed 5≤ m thick layer of smectite-rich clay, likely derived from the Paleogene to middle Miocene Pacific Plate pelagic sediments. A pervasive scaly fabric, defined by polished lustrous surfaces, commonly striated, enclosing lenses of less fissile material (phacoids), which are self-similar at scales ranging from a few micrometers to centimeters, is distributed throughout the clay. The spacing of the surfaces increase from millimeter scale near the top of the recovered core to centimetre scale, toward the lower tectonic contact, reflecting a decrease in the magnitude of shear strain. In the upper highly sheared section, one extremely narrow discontinuity, crosscuts this fabric, truncating without deflection the foliations that are not parallel across the contact. While the scaly fabric is indicative of distributed shear across the recovered interval (~1 m) the sharp discontinuity, resulted from localized deformation and similar to those observed at coseismic slip rates in friction experiments, could record seismic slip although not necessarily that of the Tohoku-Oki earthquake.

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## Space-time aspects of the oceanic opening of Tyrrhenian Sea: 1 - The Bathyal Plain of Vavilov

Savelli C.\*

CNR, ISMAR, Geologia Marina.

Corresponding email: [carlo.savelli@bo.ismar.cnr.it](mailto:carlo.savelli@bo.ismar.cnr.it)

Keywords: oceanic opening, hyperextension and extension, volcanism and spreading axes.

DSDP and ODP drilling results unveil fundamental aspects of the oceanic lithosphere emplacement in the geological medley of Tyrrhenian seafloor. Above the subducting Adria and Ionian micro-plates, four distinct episodes of extension tectonics and volcanism formed bathyal zone within a disrupted submerged Orogen of Alpine Age (OAA). The episodes 1 and 3 exhibit strong extensional deformation (Savelli, 1988; Tectonophysics, 146). In the late Tortonian-early Messinian (LT-EM), hyperextension and volcanism induce the opening of the Vavilov bathyal plain. The low-standing basalts drilled at DSDP373 (eastern edge of the plain) show MOR-type nature and a range of six whole-rock K/Ar datings between 7.5 and 6.3 $\pm$ 0.8 Ma (LT-EM). As long as refining Ar/Ar data is not available, the K/Ar range may be taken as sufficient approximation of eruption time. The LT-EM age indicates that ocean opening precedes the salinity crisis (late Messinian; 5.96 - 5.33 Ma). The absence of evaporite deposits in the Vavilov deep-plain ought to reflect a shallow waterdepth. In fact, a high-stand of seafloor probably impeded inflow of Atlantic water in sufficient amount to form evaporites at the time of desiccation. LT-EM hyperextension and low-angle detachment faulting are associated to localized, non axial MORB volcanism. Concomitantly, simple-shear deformation strongly stretches and thins the wide submerged area of the Hercynian Sardinia margin (former foreland of local OAA) in the absence of volcanism. Strong extension produced probable denudation of the low-standing peridotite of ODP651, too. Always during episode 1, weak extension of the north Tyrrhenian goes with acidic intrusive activity showing age of 8-6 Ma. Moving from S to N, the submerged granitoids of Vercelli seamount and Etruschi ridge precede the intrusions of the islands of Montecristo and Elba. In the Pliocene (5.33 – 1.87 Ma), weak extension linked to high-angle normal faults forms spreading ridges. Uprise of 4.3 Ma old, MORB-type lavas (ODP655) produces the modest elevation of Gortani ridge, NW of DSDP373. Afterwards, MORB volcanism migrates from the Gortani to ESE towards the hinge zone. In the axial zone of Vavilov basin, a major magnetic lineation shows N-S trending positive and negative anomalies. The N positive is likely associated with the ODP651 peridotite and the negative magnetic field with the Vavilov spreading axis to the S. If this anomaly belongs to Matuyama chron the axial volcano is < 2.4 Ma old. 3.0 and 2.6 Ma basalt flows showing MOR and calc-alkaline nature occur above the ODP651 peridotite, and below Plio-Quaternary sediment. Crest elevation and magma input of Vavilov volcano are larger than at the Gortani spreading ridge to NNW. Episodes 3 and 4 are described in the next abstract. In the episode 4 (<1 Ma), weak horizontal deformation and high-angle normal faulting are linked to ascent and emplacement of alkaline basalt melts in the crest of Vavilov volcano.

## **Space-time aspects of the oceanic opening of Tyrrhenian Sea: 2 - The Bathyal Plain of Marsili**

Savelli C.\*

CNR-Ismar, Geologia Marina Bologna.

Corresponding email: [carlo.savelli@bo.ismar.cnr.it](mailto:carlo.savelli@bo.ismar.cnr.it)

Keywords: oceanic spreading, hyperextension and MORB volcanism, rift/spreading transition.

A previous abstract describes the episodes 1 (late Tortonian-early Messinian; LT-EM) and 2 (Pliocene) of the Tyrrhenian oceanic spreading above subducting lithosphere. During the episode 3 (late Pliocene), hyperextension and low-standing volcanism force the opening of the bathyal plain of Marsili. In a round-shaped magnetic anomaly of the plain western edge, ODP650 drilled deep seated basalts which show age of 1.87-1.67 Ma and MOR-like or transitional nature. In the fourth episode (<1 Ma), voluminous volcanism and weak extension form the high-standing axial seamount Marsili. This is the last of the “sui generis” magma-rich spreading ridges of the Tyrrhenian. With time, in the bathyal plains of Vavilov and Marsili the MORB volcanism of the spreading axes migrates ESE, from Gortani (4.3 Ma) to Vavilov (<2.4 Ma) and Marsili (<1Ma to Recent). In the course of the migration towards hinge zone magma uprise increased beneath the spreading axis and finally formed the young super-inflated Marsili seamount. Above WNW-directed subduction, the strong extensional episodes 3 and 1 (late Pliocene and LT-EM) saw emplacement of low-lying basalts of MORB composition linked to round-shaped magnetic anomaly. Concomitantly, volcanism is absent in the peri-bathyal passive and active margins. In the West Mediterranean, on the contrary, peri-oceanic volcanism of calc-alkaline (CA) nature accompanies the opening of the Provence-Sardinia and north-Algeria oceanic basins (Burdigalian; 20-16 Ma). Such clearly diverse space-time aspects may indicate that, unlike the Tyrrhenian, the oceanic opening of the W Mediterranean did not occur above subduction. It is here considered that WNW subduction beneath the Tyrrhenian Orogen of Alpine Age (OAA) was commenced at 16/15 Ma (late Burdigalian-Langhian). In the absence of subduction, extension, oceanic spreading, and CA volcanism of Oligo-Burdigalian age took place in Hercynian lithosphere (Provence-Sardinia foreland of the Tyrrhenian OAA), and in the OAA bordering north Algeria basin, too. The CA volcanics distributed around the Provence-Sardinia and north Algeria oceanic basins reflect source area metasomatic modifications likely linked to ancient, Hercynian, and early-Alpine episodes of orogenic accretion. If the lost emission centres of allochthonous volcanoclastics of the Apennines of Oligo-Burdigalian age were sited in the Tyrrhenian OAA, also this area was affected by CA volcanism and extension in the absence of subduction. In conclusion, these space-time aspects indicate that the CA volcanism is not linked only to subduction

## **SESSIONE S2**

### **Geological timescales**

*CONVENORS*

*M. Balini (Univ. Milano)*

*M. Sprovieri (IAMC-CNR, Torretta Granitola)*

*I. Villa (Univ. Milano Bicocca)*

## The Italian contribution to the definition of the ICS timescale: ongoing research

Balini M.<sup>1</sup>, Monechi S.<sup>2</sup> & Raffi I.\*<sup>3</sup>

1. Dipartimento di Scienze della Terra "Ardito Desio", Università di Milano. 2. Dipartimento di Scienze della Terra, Università di Firenze.  
3. Dipartimento di Ingegneria e Geologia, Università di Chieti.

Corresponding email: [raffi@unich.it](mailto:raffi@unich.it)

Keywords: geological timescales, GSSP, Italy.

Italian stratigraphers actively participate in many working groups (WG) of the International Commission on Stratigraphy, from the Cambrian to the Quaternary. They are members of international research groups working abroad but also in Italy, a country that for some geologic time intervals is rich in well-exposed, continuous, fossil-rich successions that fulfill the basic requirements for the GSSP sections. This outstanding geological heritage of our country is documented by the selection in Italy of 9 GSSPs of the Triassic, Paleogene, Neogene and Quaternary systems and it is even more confirmed by the number of sections in Italy candidate for GSSPs not yet formalized.

### Triassic GSSPs

Three stages out of seven of the Triassic are defined by GSSP, and two of them (Ladinian and Carnian) are formalized in Italy. Of the remaining four stages, two of them are well documented in Italy.

Two sections are under examination for the Norian stage, namely the Black Bear Ridge section (British Columbia) and the Pizzo Mondello section (Sicily). Some years ago the Rhaetian WG focused on the Steinbergkogel section in the Northern Alps, but in this session a second option for this GSSP will be proposed, based on the Pignola section in Lagonegro.

### Paleogene GSSPs

At present most of the Paleogene GSSPs have been formalized and only Bartonian, Priabonian and Chattian lack of formal definition. The three possible candidates are all in Italy.

The Contessa Highway section (Gubbio) was proposed in 2010 as possible GSSP for the Bartonian. Afterwards some other sections in the Umbria-Marche Basin have been investigated in order to test the reproducibility of the suggested criterion. The Alano section (NE Italy) is the only candidate for defining the GSSP of the Priabonian and the Monte Cagnero section (central Italy) has been recently presented as a potential candidate for the Chattian.

### Neogene GSSPs

The Langhian and Burdigalian are the not yet resolved Miocene GSSPs. There are good possibilities to have the Langhian defined in Italy, because La Vedova section (central Italy) is candidate for this boundary together with St. Peter's Pool section (Malta Is.). The solution for the Burdigalian is still open and the WG is searching for suitable candidates.

### Quaternary GSSPs

The Gelasian and the Calabrian are already defined in Italy, but there are some possibilities to define in Italy also the other two boundaries of the Pleistocene.

Lower/Middle Pleistocene. Two sections in Southern Italy document at best this boundary and are appropriate candidates as GSSP: the Montalbano Jonico section, unfortunately remagnetized, and the Valle di Manche section, with the documentation of the Matuyama-Brunhes magnetic reversal.

Middle/Upper Pleistocene. The best sections in the world for this time interval are Il Fronte (Taranto) and Chiba (Japan). Il Fronte is a rather thin section studied in detail, while the Chiba succession is expanded and probably needs some more investigations.

## **Integrated bio-chronostratigraphic calibration of the Carnian/Norian boundary in the Sicano basin (western Sicily) and its significance for long distance correlations**

Balini M.\*<sup>1</sup>, Di Stefano P.<sup>2</sup>, Levera M.<sup>1</sup>, Mazza M.<sup>1</sup>, Muttoni G.<sup>1</sup>, Nicora A.<sup>1</sup>, Preto N.<sup>3</sup>, Rigo M.<sup>3</sup> & Tripodo A.<sup>2</sup>

<sup>1</sup> Dipartimento di Scienze della Terra "Ardito Desio", Università di Milano. <sup>2</sup> Dipartimento di Scienze della Terra e del Mare, Università di Palermo. <sup>3</sup> Dipartimento di Geoscienze, Università di Padova.

Corresponding email: [marco.balini@unimi.it](mailto:marco.balini@unimi.it)

Keywords: Triassic, integrated chronostratigraphy, GSSP.

The Scillato Formation of western Sicily provides one of the best record in the world for the Late Carnian and Norian, in term of continuous pelagic sedimentation, rather high sedimentation rate, primary magnetization and stable isotope record. The succession is also quite rich in fossils, specially halobiids, conodonts, ammonoids and radiolarians. In the last decade the Pizzo Mondello section has been studied in details and proposed as candidate section for the definition of the Norian GSSP. This section is thus far the best in the Tethys Realm, and has been compared with the other GSSP candidate Black Bear Ridge in northeastern British Columbia (Canada).

In order to test the quality of the record of the proposed Pizzo Mondello section, we have recently investigated a new section in the Sicano Basin, located in a quarry at Pizzo Lupo (Castronovo di Sicilia), about 20 km from Pizzo Mondello. The new section, perfectly exposed, has been sampled for ammonoids, conodonts and halobiids. The sedimentary succession is totally equal to that of Pizzo Mondello and thicker calcareous beds and marly intervals are identifiable in both the sections. The new bio-chronostratigraphic data are also totally consistent with those of Pizzo Mondello. The ammonoids document the Upper Carnian *Spinosus* Zone and the Lower Norian Jandianus Zone allowing the high resolution calibration of the two sections. Ammonoid collections from the *Spinosus* Zone at Pizzo Lupo are richer than at Pizzo Mondello and prove a better characterization of this zone.

The bivalve record at Pizzo Lupo consists of *Halobia lenticularis* and *H. radiata* in the *Spinosus* Zone, and by *H. austriaca* and *H. styriaca*, in the Jandianus Zone. The conodont faunas are fully comparable with the conodont record of Pizzo Mondello. A very important bioevent, characteristic of the boundary interval recognized at Pizzo Mondello and present also at Pizzo Lupo, is the mass occurrence of metapolygnathids belonging to the *communisti* group (*Metapolygnathus communisti*, "*M. echinatus*", *M. linguiformis*, *M. parvus* and *M. mazzai*).

The new data from Pizzo Lupo replicate the fossil record of Pizzo Mondello and demonstrate the quality and significance of Pizzo Mondello within the Sicano Basin. Furthermore, the significance of the Sicano Basin in the Western Tethys is supported by conodont correlations between Pizzo Mondello and other Tethyan key sections [Silická Brezová (Slovakia), Bölücektasi Tepe and Erenkolu Mezarlik (Turkey)] (Mazza & Krystyn, 2013). As regard the Tethyan-Panthalassan correlations, Pizzo Mondello can be easier correlated with Nevada than with British Columbia.

Mazza M. & Krystyn L. 2013. Revision of the conodonts of key Upper Triassic Tethyan sections: A step forward in definition of the Carnian/Norian boundary and new correlation options. Conodonts from the Andes. Publicación Especial N° 13, Asociación Paleontológica Argentina. 146.

## The significance of the Lower/Upper Carnian faunal turnover for the definition of the Late Triassic time scale

Brenna A., Caronni V., Grilli D., Landini E., Marchesi R., Schettino A., Vitiello A., Mazza M., Nicora A. & Balini M.\*

Dipartimento di Scienze della Terra "Ardito Desio", Università degli Studi di Milano

Corresponding email: [marco.balini@unimi.it](mailto:marco.balini@unimi.it)

Keywords: Upper Triassic, Carnian Pluvial Event, chronostratigraphy.

The Carnian stage of the Upper Triassic series, was characterized by one of the most impressive climatic changes in the Triassic. This change consisted in short-lived event of increased precipitation (Carnian Pluvial Event) which occurred over large parts of central Pangea, slightly before the Lower/Upper Carnian boundary. This event was coeval with marked sea-level fall and resulted in a significant faunal turnover in the marine biota. In the last 15 years the CPE has become a matter of study and discussion as one example of fast change from arid to humid climate. Several contributions focused on the reconstruction of the climatic change through the study of stable isotopes, but very few papers investigated in depth the biotic response. Aim of this work is to compare the faunal turnover in ammonoids, conodonts and pelagic bivalves and to discuss its possible significance for improving the Upper Triassic chronostratigraphic scale.

The ammonoids faunas show the most impressive turnover across the Lower/Upper Carnian boundary, consisting in extinctions followed by extremely fast radiations. Evolutionary changes occurred not only at genus level, but also subfamily/family or even to superfamily rank. Three groups are identified: a) groups that got extinct at the end of the Early Carnian, b) groups apparently not affected by significant changes, c) newcomers with high rate of differentiations.

The pelagic bivalves underwent a much reduced turnover. *Halobia* Bronn, 1830 is the genus dominating the Carnian pelagic environments, with a faunal turnover across the Lower/Upper boundary that is limited to species level.

The conodonts show an important faunal change, whose importance, however is strongly influenced by different taxonomic approach of the specialists. Emphasis (? overemphasis) on interspecific variation might result in increasing the number of genera and then in the amplifying the crisis. As matter of fact, the Early Carnian conodont faunas are much more similar to the Ladinian ones, than those of the Late Carnian.

The full understanding of the chronostratigraphic significance of the faunal turnover across the CPE would require at least the study of the shallow water biota, but on the available data the recent proposal of subdivision of the Carnian into two independent stages (Lucas 2013) on the basis of the mid-Carnian crisis does not seem to be justified.

Lucas S.G. 2013. A new Triassic timescale. In: Tanner, L.H., Spielmann, J.A. and Lucas, S.G., Eds., The Triassic System. New Mexico Museum of Natural History and Science, Bulletin 61, 366-374.

## Quaternary magnetic stratigraphy: more than polarity reversals

Channell J.E.T.\*

Dept. Geological Sciences, University of Florida, USA.

Corresponding email: [jetc@ufl.edu](mailto:jetc@ufl.edu)

Keywords: paleomagnetism, relative paleointensity, magnetic excursions, magnetic stratigraphy, timescales.

Improving stratigraphic resolution is one of the great challenges in paleoceanography. The unprecedented stratigraphic resolution of Greenland and Antarctic ice cores has led to major advances in climate science, however, ice cores are restricted in time-span and geographic distribution. In Quaternary marine sediments, oxygen isotopes ( $\delta^{18}\text{O}$ ) provide the traditional stratigraphy although, even for benthic data,  $\delta^{18}\text{O}$  is not usually a synchronous global signal due to variations in water temperature and chemistry. Magnetic polarity stratigraphy is the now an indispensable element of geologic timescales for the last 160 Myrs, mainly because reversals are globally recorded and synchronous on millennial timescales, although polarity reversals are only useful for high-resolution correlation in their immediate stratigraphic vicinity. Two other facets of the paleomagnetic record can, however, be used for correlation within polarity chrons. The intensity of the Earth's dipole field, which has decreased by  $\sim 5\%$ /century in the last few hundred years, is a parameter that varies on short timescales, and is manifest globally. Relative paleointensity (RPI) can be recorded by sediments in which (titano)magnetite, in a restricted submicron to few-micron grain-size range, is the sole magnetic mineral. Laboratory-produced magnetizations are used to normalize the intensity of natural remanent magnetization (NRM) for changes in concentration of remanence-carrying grains. "Tandem" correlation of  $\delta^{18}\text{O}$  and RPI, facilitated through the *Match* protocol, has been utilized to generate optimal matches of these two ostensibly global signals in sediment sequences recovered by ocean drilling. The purpose has been to ratify the use of RPI as a global correlation tool, and generate reference stacks of RPI and  $\delta^{18}\text{O}$  based on these tandem correlations. Superimposed on this  $\delta^{18}\text{O}$ /RPI variability are geomagnetic excursions, defined here as brief directional aberrations of the main dipole field outside the range of expected secular variation. Although records of magnetic excursions date from the 1960s, the record has become better resolved in recent years. The number of Brunhes Chron excursions in recent reviews of the subject have reached the 12-17 range, of which only about  $\sim 7$  are adequately and/or consistently recorded. For the Matuyama Chron, the current inventory of excursions stands at about 10. Magnetic excursions occupy RPI minima, and excursion records with good age control imply millennial-scale or even centennial-scale excursion durations. The higher-fidelity excursion records indicate that excursions are essentially paired polarity-reversals flanking virtual geomagnetic poles (VGPs) that reach high latitudes in the opposite hemisphere. Based on these observations, excursions can be considered a feature of the axial dipole field, are therefore manifest globally, and provide a high-resolution stratigraphic tool in addition to  $\delta^{18}\text{O}$  and RPI.

## Revised Upper Albian–Maastrichtian planktonic foraminiferal biostratigraphy and magnetostratigraphy of the classical Tethyan Gubbio section (Italy)

Coccioni R.<sup>1</sup> & Premoli Silva I.\*<sup>2</sup>

1. Dipartimento di Scienze della Terra, della Vita e dell'Ambiente, Università degli Studi di Urbino "Carlo Bo". 2. Dipartimento di Scienze della Terra "Ardito Desio", Università degli Studi di Milano

Corresponding email: [isabella.premoli@unimi.it](mailto:isabella.premoli@unimi.it)

Keywords: Calcareous plankton, integrated bio-magnetostratigraphy, Late Cretaceous, Gubbio.

The Tethyan pelagic sections at Bottaccione and Contessa Highway (Gubbio, Italy) are internationally recognized to be the standard reference sections for the Late Cretaceous to Eocene geomagnetic polarity time scale calibrated to the integrated planktonic foraminiferal and calcareous nannofossil biostratigraphy. Due to the presence of a gap within Chron C31n in the Bottaccione section, we use two distinct portions of these sections to construct a complete and well-preserved composite stratigraphic record, named "Gubbio section", 333.1 m in thickness and ~36 myr in duration, that begins in the upper part of the Marne a Fucoidi and extends through the Scaglia Bianca and Scaglia Rossa to the Cretaceous/Paleogene boundary. A refined magnetostratigraphy and planktonic foraminiferal biostratigraphy integrated with calcareous nannofossil data, is here presented for this stratigraphic succession. In particular, the recovery of planktonic foraminifera successfully disaggregated from the Scaglia hard lithologies allows more precise placement of several bioevents that include the lowest occurrence (LO) of *Thalmanninella globotruncanoides* defining the Albian/Cenomanian boundary, the LOs of *Globotruncana linneiana* and *Pseudoguembelina palpebra* that approximate respectively the base of the Santonian and of the Maastrichtian, the LO of *Globotruncana aegyptiaca* occurring earlier than previously recognized, and, in addition, the well-constrained, complete pattern of the evolutionary origin of *Racemiguembelina fructicosa* from *Pseudotextularia elegans* through *Pseudotextularia intermedia* and *Racemiguembelina powelli* previously undetected. Moreover, the LO of *Pseudoguembelina hariaensis*, the highest occurrence of *Gansserina gansseri* and the LO of *Plummerita hantkeninoides* allow subdivision of the latest Maastrichtian, previously included in the *Abathomphalus mayaroensis* Zone, into the *Pseudoguembelina hariaensis*, *Pseudotextularia elegans* and *Plummerita hantkeninoides* planktonic foraminiferal Zones. Moreover, planktonic foraminiferal, calcareous nannofossil, inoceramid and paleomagnetic datums have been integrated to construct a reliable age-depth model for the Campanian–Maastrichtian time interval that allows age assignments of each biohorizon and to estimate the variations of sedimentation rates. Finally, an almost complete, high-resolution carbon isotope curve, which was recently presented for the upper Albian through the Maastrichtian interval from the Bottaccione-Contessa Highway succession, is here integrated with the updated bio-, magneto-stratigraphies, providing an invaluable tool for improving global correlation.

## The Burdigalian GSSP: the missing tile to complete the Neogene interval of the Geological Time Scale

Di Stefano A.\*<sup>1</sup>, Foresi L.M.<sup>2</sup>, Sagnotti L.<sup>3</sup>, Baldassini N.<sup>1</sup>, Bonomo S.<sup>4</sup>, Cascella A.<sup>5</sup>, Dinarès-Turell J.<sup>3</sup>,  
Di Stefano E.<sup>6</sup>, Ferraro L.<sup>4</sup>, Incarbona A.<sup>6</sup>, Lirer F.<sup>4</sup>, Russo B.<sup>7</sup> & Winkler A.<sup>3</sup>

1. Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Sezione di Scienze della Terra, Università di Catania. 2. Dipartimento di Scienze Fisiche, della Terra e dell'Ambiente, Sezione di Scienze della Terra, Università di Siena. 3. Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Roma2. 4. Istituto per l'Ambiente Marino Costiero, CNR, Napoli. 5. Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Pisa. 6. Dipartimento di Scienze della Terra e del Mare, Università di Palermo. 7. Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università Federico II di Napoli

Corresponding email: [distefan@unict.it](mailto:distefan@unict.it)

Keywords: Burdigalian GSSP, Mediterranean, Atlantic Ocean, integrated stratigraphy.

The Italian Ministry of the University of Research has recently founded a project (PRIN2012) entitled “The Burdigalian GSSP (Global Stratotype Section and Point): the missing tile to complete the Neogene interval of the Geological Time Scale”, whose goal is to identify a section suitable to host the Burdigalian GSSP.

At the present time, all the Neogene stages are presently formally ratified with the exception of the Burdigalian and Langhian ones. If on the one hand for the latter stage a working group is completing studies that will shortly result in presenting a proposal for a section containing the GSSP (Iaccarino et al. 2011), on the other hand the Burdigalian question still remains unsolved.

The project is organized into three units, each specialized in one of the three main disciplines that characterize the research: biostratigraphy, based on calcareous nannofossils (University of Catania with the collaboration of the University of Palermo and the INGV of Pisa) and Foraminifers (University of Siena with the collaboration of the IAMC-CNR and the University of Naples), and paleomagnetism (INGV of Rome).

The project will benefit of the modern methodologies that, in the recent past, led to the formalization of most of the Neogene GSSPs; in particular:

- High resolution sampling.
- Calcareous plankton quantitative biostratigraphy.
- Magnetostatigraphy.
- Analysis of the Oxygen and Carbon stable isotopes.
- Cyclostratigraphy and astrochronology.

Preliminary investigations and literature data allowed the identification of two well-exposed and easy to be reached sections that, based on their litho-micropaleontological and magnetic properties, are potentially suitable for the definition of the Burdigalian GSSP: the St. Thomas section (SE coast of Malta Island), and the S. Croce di Arcevia section (Marche Region, Central Italy), investigated in the past but with traditional methodologies and in low resolution. There is also the possibility to investigate a succession outcropping in the Cyprus Island, which according to very recent data seems to fit the purpose. The large-scale correlation with extra Mediterranean areas will be guaranteed by the investigation of oceanic successions, the DSDP Site 608 (NE Atlantic), and the IODP U1405 and U1406 cores (NW Atlantic).

The starting point is to study in detail the stratigraphic intervals yielding the events traditionally used to approximate the Aquitanian/Burdigalian boundary to test their reliability or eventually to propose new criteria.

The achievement of the aim of this project will allow the completion of the Neogene interval of the Geological Time Scale, an essential means to all who investigate questions connected to the Earth Sciences.

## Revised calcareous nannofossil biostratigraphy of the Cenomanian/Turonian boundary: implications for global correlations and timescales

Erba E.\*, Russo F., Bottini C. & Giulia F.

Dipartimento di Scienze della Terra, Università degli Studi di Milano.

Corresponding email: [elisabetta.erba@unimi.it](mailto:elisabetta.erba@unimi.it)

Keywords: nannofossil biostratigraphy, Cenomanian/Turonian Boundary, timescale.

Calcareous nannofossil biostratigraphy is proven to be a reliable tool for dating and correlating Upper Cretaceous sequences at regional and global scale. Although high-resolution biozonations are available for the Cenomanian/Turonian boundary interval, assessment of nannofossil event reproducibility still demands detail investigations of different oceanic basins, paleolatitudes and settings.

The Cenomanian/Turonian stage boundary is characterized by an ample C isotopic excursion marking the Oceanic Anoxic Event (OAE) 2. Thus nannofossil biozonation is often used to constrain the latest Cenomanian C isotopic anomaly and the anoxic interval of enhanced burial of organic matter.

We selected pelagic and hemipelagic sections from the Tethys, Pacific, Indian, Atlantic Oceans and the Western Interior Basin. Section selection was based on availability of stratigraphic data (e.g. isotopic stratigraphy and planktonic foraminifera biostratigraphy).

The correlation among the studied sections shows that only five nannofossil bioevents occur, relative to the  $\delta^{13}\text{C}$  curve, at the same stratigraphic position. They are: the LOs of *C. kennedyi*, *A. albianus*, *L. acutus*, *H. chiastia* and the FO of *Q. gartneri*, the same five events reported in the GSSP section. Additional zonal and subzonal markers and a secondary bioevent reported in the three Cretaceous zonations were recognized. However, *R. biarcus* and *C. striatus* are too rare to be suitable as global biostratigraphic markers, whilst the FOs of *Q. intermedium-5*, *E. octopetalus* and *E. eptapetalus* have been found at different stratigraphic levels in the studied sections and in previous studies.

Our results prove that nannofossil biostratigraphy is extremely useful for identification of the Cenomanian/Turonian boundary and constraining OAE2 at global scale.

## The St. Peter's Pool section (Malta Island): progress towards the Langhian GSSP

Foresi L.M.<sup>1</sup>, Baldassini N.\*<sup>2</sup>, Lirer F.<sup>3</sup>, Verducci M.<sup>1</sup>, Mazzei R.<sup>1</sup>, Salvatorini G.<sup>1</sup>, Ferraro L.<sup>3</sup>,  
Da Prato S.<sup>4</sup> & Di Stefano A.<sup>2</sup>

1. Dipartimento di Scienze Fisiche, della Terra e dell'Ambiente - Sezione di Scienze della Terra, Università di Siena. 2. Dipartimento di Scienze Biologiche, Geologiche e Ambientali - Sezione di Scienze della Terra, Università di Catania. 3. Istituto per l'Ambiente Marino Costiero - CNR, Napoli. 4. Istituto di Geoscienze e Georisorse - CNR, Pisa.

Corresponding email: [luca.foresi@unisi.it](mailto:luca.foresi@unisi.it)

Keywords: Langhian GSSP, Malta Island, calcareous plankton biostratigraphy, magnetostratigraphy.

The main goal of the project "In search of the Global Stratotype Section and Point of the Langhian Stage and paleoceanographic implication" granted by the Italian Ministry of University and Research and supported by the Subcommission on Neogene Stratigraphy, was to find a potential candidate for hosting the Langhian GSSP.

In the framework of the project several sections were investigated and among the others the St. Peter's Pool one (Foresi et al., 2011), spectacularly outcropping in the Delimara Peninsula, SE of the Malta Island.

This section was studied through high-resolution bio-magnetostratigraphy, which resulted in a remarkable improvement of the Mediterranean Langhian knowledge. Calcareous plankton quantitative analyses allowed the definition of several bioevents with a great potential for biostratigraphic correlations. To the well-known bio-horizons, such as the *Helicosphera ampliaperta* Last Common Occurrence (LCO), the *Sphenolithus heteromorphus* Paracme and the *Paragloborotalia siakensis* Acme, many others were added, such as the *Paragloborotalia bella* LCO and a new *P. siakensis* Acme, documented for the first time in the Mediterranean area.

The following aspects play in favor of the St. Peter's Pool section as a candidate for hosting the Langhian GSSP:

- the excellent exposure and the easy accessibility;
- the well-preserved and abundant content of calcareous plankton and the high number of significant bioevents. Two of these can be selected for approximating the Langhian GSSP, namely the LCOs of the nannofossil *H. ampliaperta* and of the planktonic foraminifer *Paragloborotalia bella*, both falling in the Chron C5Cn.1n. Particularly the LCO of *H. ampliaperta* represents a well-defined horizon, also recognizable in extra Mediterranean areas, and its choice could represent a good compromise between the two recommended events for the definition of the Langhian GSSP (the *Praeorbulina* datum and the C5Cn/C5Br reversal);
- the stratigraphic continuity with the section yielding the Serravallian GSSP (Ras il-Pellegrin in Malta Island);
- the cyclic pattern of the succession.

On the other hand the magnetostratigraphic data show some uncertainties. Yet, the cyclostratigraphic reconstruction, which is the subject of ongoing studies, has a high potential for establishing a reliable astronomical tuning of the section, providing a further positive element for proposing it as a candidate for the Langhian GSSP. The study will be completed by Oxygen and Carbon isotopes analyses to individuate global paleoclimatic changes.

Foresi L.M., Verducci M., Baldassini N., Lirer F., Mazzei R., Salvatorini G., Ferraro L. & Da Prato S. 2011. Integrated stratigraphy of St. Peter's Pool section (Malta): new age for the Upper Globigerina Limestone Member and progress towards the Langhian GSSP. *Stratigraphy*, 8, 125-143.

## **Integrated stratigraphy of the lower Paleocene from the Bottaccione section (Gubbio, Central Italy)**

Galeotti S.\*<sup>1</sup>, Moretti M.<sup>1</sup>, Cappelli C.<sup>2</sup>, Phillips J.<sup>3</sup>, Lanci L.<sup>4</sup>, Littler K.<sup>3-5</sup>, Monechi S.<sup>2</sup>, Petrizzo M.R.<sup>6</sup>,  
Premoli Silva I.<sup>6</sup> & Zachos J.C.<sup>3</sup>

1. Dipartimento di Scienze della Terra, della Vita e dell'Ambiente, Università di Urbino, Campus Scientifico 'E. Mattei'. 2. Dipartimento di Scienze della Terra, Università di Firenze. 3. Earth Sciences Department, University of California, Santa Cruz, USA. 4. Dipartimento di Scienze di Base e Fondamenti, Università di Urbino. 5. Camborne School of Mines, University of Exeter, U.K. 6. Dipartimento di Scienze della Terra "A. Desio", Università degli Studi di Milano

Corresponding email: [simone.galeotti@uniurb.it](mailto:simone.galeotti@uniurb.it)

Keywords: Paleocene, Integrated Stratigraphy, Bottaccione.

The upper Cretaceous to Paleocene Bottaccione section (Gubbio, central Italy) represents a classical Tethyan setting that served as a standard for the construction of the geomagnetic polarity time scale. Existing biomagnetostratigraphy suggests that the Paleocene interval of the Bottaccione section is condensed relative to other outcrops in the area or that it might contain a non-identified stratigraphic gap. A new high-resolution integrated stratigraphic record, including bio-, magneto-, chemo-, and cyclostratigraphy, however, provides evidence that the Bottaccione record is complete and comparable to other successions outcropping in the Umbria-Marche area as well as records from the South Atlantic and North Pacific. Unfortunately, the paleomagnetic signal of this classical section is partially corrupted in the stratigraphic interval spanning the top of magnetochron C28n to the lower part of C26r, possibly due to diagenetic alteration of clay minerals. The recognition of orbitally-forced sedimentary cycles, corresponding to long eccentricity (405 kyr) and possibly other higher frequency cycles, together with a well preserved carbon isotope profile, makes the Bottaccione outcrop a potential reference section for comparison with existing carbon isotope records of Early–Middle Paleocene age and an auxiliary setting for the development of an astrochronological time scale in the Paleocene.

## Orbital tuning of the late Albian to early Turonian C isotopic record (Umbria-Marche Basin, central Italy)

Gambacorta G.\*<sup>1</sup>, Malinverno A.<sup>2</sup> & Erba E.<sup>1</sup>

1. Dipartimento di Scienze della Terra ‘‘A. Desio’’, Università di Milano. 2. Lamont-Doherty Earth Observatory, Columbia University, Palisades, New York, USA.

Corresponding email: [gabriele.gambacorta@unimi.it](mailto:gabriele.gambacorta@unimi.it)

Keywords: Bonarelli, Cenomanian, cyclostratigraphy, orbital time scale, Scaglia Bianca.

We applied a cyclostratigraphic analysis to the late Albian – early Turonian time interval in four Tethyan sections from the Umbria-Marche Basin (Furlo, Contessa, Le Brece and Monte Petrano) (see Schwarzacher, 1994; Mitchell et al., 2008; Lanci et al., 2010). Starting from high-resolution (cm- to mm-scale) lithological logs (Gambacorta, 2013), simulated calcium carbonate contents were used as input data for a probabilistic cyclostratigraphic analysis (slightly modified from Malinverno et al., 2010). The estimated distribution of sedimentation rates allowed us to date the  $\delta^{13}\text{C}$  record from the four studied sections (Gambacorta, 2013). The results, obtained by orbital tuning according to short eccentricity and obliquity components, show that there is an influence of astronomical cyclicities on the geological record, resulting in coeval sedimentation rate patterns throughout all the studied sections. An increase in the average sedimentation rates right after the Mid-Cenomanian Event (MCE) is interpreted as the result of an increase in weathering and/or carbonate productivity.

The OAE2 is preceded by an overall decrease in sedimentation rates, culminating in minimum rates in the Bonarelli Level. Orbital eccentricity and obliquity might have played an important role in controlling the latitudinal thermal gradients and indirectly the hydrological cycle. Cyclic variations in precipitation rates and runoff coupled with possible variations in the circulation patterns might have led to fluctuations in the availability of nutrients, leading to the cyclic deposition of carbonate-dominated versus siliceous-dominated sediments.

Gambacorta G. 2013. Paleooceanographic and paleoclimatic reconstruction of the Albian - Cenomanian interval: from an unstable to a stable ocean. PhD Thesis, University of Milan, Milan, Italy.

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Schwarzacher W. 1994. Cyclostratigraphy of the Cenomanian in the Gubbio District, Italy; a field study. In: de Boer P.L. & Smith D.G. Eds., *Orbital forcing and cyclic sequences*. Spec. Publ. Int. Ass. Sedimentologists, 19, 87-97.

## Magnetostratigraphic investigation of the Pignola-Abriola section (Southern Apennines, Italy): new constraints for the Rhaetian chronology

Maron M.\*<sup>1</sup>, Muttoni G.<sup>2</sup>, Rigo M.<sup>1</sup>, Bertinelli A.<sup>3</sup>, Godfrey L.<sup>4</sup>, Katz M.E.<sup>5</sup> & Zaffani M.<sup>1</sup>

1. Dipartimento di Geoscienze-Università di Padova. 2. Dipartimento di Scienze della Terra-Università di Milano. 3. Dipartimento di Fisica e Geologia-Università di Perugia. 4. Department Earth and Planetary Sciences-Rutgers University. 5. Department of Earth and Environmental Sciences-Rensselaer Polytechnic Institute.

Corresponding email: [matteo.maron.1@studenti.unipd.it](mailto:matteo.maron.1@studenti.unipd.it)

Keywords: Norian/Rhaetian boundary, Chronology, Magnetostratigraphy.

The Norian/Rhaetian section of Pignola-Abriola (Southern Apennines, Italy), consisting in ca. 60 m of pelagic sediments (cherty limestones and shales), provided new magnetostratigraphic data for the upper Norian (Sevastian) and the lower Rhaetian. The magnetostratigraphic sequence, subdivided in 10 magnetozones, is calibrated with conodont and radiolarian biostratigraphy. The Norian/Rhaetian boundary in Pignola-Abriola is defined by the first appearance of conodont *Misikella posthernsteini*, within the *Proparvicingula moniliformis* radiolarian Zone 1. Other Norian and Rhaetian magneto-biostratigraphic sections from the Tethys realm such as Brumano-Italcementi Quarry, Oyuklu, Pizzo Mondello and Steinbergkogel have been successfully correlated with the Pignola-Abriola section. According to our correlations, the oldest occurrences of *M. posthernsteini* at Steinbergkogel and Oyuklu, used to place the Norian/Rhaetian boundary in these sections (e.g. Krystyn et al., 2007), correspond at Pignola-Abriola to *M. hernsteini/posthernsteini* transitional morphotypes (Giordano et al., 2010).

In order to obtain an age for the Norian/Rhaetian boundary, the Pignola-Abriola section has been correlated with the Newark APTS 2010 using a statistical method, assuming the stratigraphic depth as a proxy of time. This yielded 19 correlations in which the thicknesses of the Pignola-Abriola magnetozones were compared with the durations of the Newark magnetozones. Every single option was then processed using linear regression and their coefficients R have been subjected to a student t-test to identify the most reliable correlation. The best correlation option places the magnetostratigraphy of the Pignola-Abriola section from magnetozones E13r (ca. 217 Ma) to E20r (ca. 205 Ma) in the Newark APTS. The age model derived from this option provides an age of 205.4 Ma for the Norian/Rhaetian boundary, within Newark magnetozones E20r; assuming a Triassic/Jurassic boundary age of 201.3 Ma, the Rhaetian was 4.1 My long.

Noteworthy is the marked negative shift of the  $\delta^{13}\text{C}_{\text{org}}$  curve occurring at ca. 42 m (0.5 meters below the FAD of *M. posthernsteini*). Once its global extension is verified, it could be proposed as a physical marker for the Norian/Rhaetian boundary, alternative to the biostratigraphic definition.

Giordano N., Rigo M., Ciarapica G. & Bertinelli A. 2010. New biostratigraphical constraints for the Norian/Rhaetian boundary: data from Lagonegro Basin, Southern Apennines, Italy. *Lethaia*, 43, 573-586.

Krystyn L., Bouquerel H., Kuerschner W., Richo S. & Gallet Y. 2007. Proposal for a candidate GSSP for the base of the Rhaetian stage. In: Lucas S. G. & Spielman J. A. Eds., *The Global Triassic*. New Mexico Museum of Natural History and Science Bulletin, 41, 189-199.

## **Magnetostratigraphy from the Pignola 2 section (Southern Apennines, Italy) and the Dibona section (Dolomites, Italy): chronology of the main Carnian events**

Maron M.\*<sup>1</sup>, Muttoni G.<sup>2</sup>, Rigo M.<sup>1</sup>, Roghi G.<sup>1</sup> & Solazzi L.<sup>1</sup>

1. Dipartimento di Geoscienze-Università di Padova. 2. Dipartimento di Scienze della Terra-Università di Milano.

Corresponding email: [matteo.maron.1@studenti.unipd.it](mailto:matteo.maron.1@studenti.unipd.it)

Keywords: Carnian, Magnetostratigraphy, Carnian Pluvial Event.

In order to improve the magnetostratigraphy of the Carnian, we studied the sections of Pignola 2 (Southern Apennines, Italy) and Dibona (Dolomites, Italy), both covering the Julian/Tuvalian boundary (lower/upper Carnian). This boundary is characterized by an important climate change to more humid conditions called Carnian Pluvial Event (Simms & Ruffell, 1989), affecting the sedimentary record. In a pelagic context, i.e. the Pignola 2 section, the CPE appears as a condensed sequence of shales and radiolarites called the “green clay-radiolaritic horizon” (Rigo et al., 2007). In a shallow-water environment, i.e. the Dibona section, the CPE manifests with the deposition of a thick, expanded sequence of various-grained sandstone and silty-clayey levels within the Heiligkreuz Fm. By comparison of palynomorphs record, the magnetostratigraphy of the Dibona section can be considered coeval to the shaley level of the “green clay-radiolaritic horizon” in Pignola 2, filling the lack in magnetostratigraphy of the Pignola 2 section. To provide ages and durations of the events in the uppermost Carnian, the Pignola 2/Dibona composite was correlated with the Newark APTS 2010 using a statistical method and considering the U/Pb age of  $230.91 \pm 0.33$  Ma for the upper “green clay-radiolaritic horizon” (the “Aglanico ash-bed” by Furin et al., 2006) in the Pignola 2 section as a constraint. Furthermore, a composite magnetostratigraphy of the Carnian could be obtained by the association of the Pignola 2 and Dibona sections with other Ladinian/Carnian to Carnian/Norian sections, as Prati di Stuares, Mayerling, Bolücektasi Tepe, Guri Zi, Pizzo Mondello and Silická Brezová (summarized in Hounslow & Muttoni, 2010).

Furin S., Preto N., Rigo M., Roghi G., Gianolla P., Crowley J.L. & Bowring S.A. 2006. A high-precision U/Pb zircon age from the Triassic of Italy – implication for the Carnian origin of calcareous nannoplankton and dinosaurs. *Geology*, 34, 1009-1012.

Hounslow M.W. & Muttoni G. 2010. The geomagnetic polarity timescale for the Triassic: linkage to stage boundary definitions. In: Lucas S.G. Ed., *The Triassic Timescale*. Geological Society, London, Special Publications, 334, 61-102.

Rigo M., Preto N., Roghi G., Tateo F. & Mietto P. 2007. A rise in the Carbonate Compensation Depth of western Tethys in the Carnian (Late Triassic): Deep-water evidence for the Carnian Pluvial Event. *Palaeogeogr., Palaeoclimat., Palaeoecol.*, 246, 188-205.

Simms M.J. & Ruffell A.H. 1989. Synchronicity of climatic change and extinction in the Late Triassic. *Geology*, 17, 265-268.

## **Recent advances in the accuracy and resolution of planktonic foraminifera biostratigraphy for improving Late Cretaceous chronostratigraphy**

Petrizzo M.R.\*

Dipartimento di Scienze della Terra "A. Desio", Università degli Studi di Milano.

Corresponding email: [mrose.petrizzo@unimi.it](mailto:mrose.petrizzo@unimi.it)

Keywords: Planktonic foraminifera, Integrated stratigraphy, Global Boundary Stratotype Section, Point.

Planktonic foraminifera have been widely used in biostratigraphy and strongly contributed to the multi-disciplinary efforts to improve Cretaceous chronostratigraphy in pelagic settings. A critical time is the Albian to Santonian interval for which a high-resolution integrated geochemical, physical and biostratigraphic framework exportable worldwide is still needed. This is partially because a consistent correlation of biostratigraphic events and calibration against other stratigraphic tools often lacks in accuracy, resolution and reproducibility of the data. At present, the Global Boundary Stratotype Section and Point for the base of the Cenomanian (Mt Risou, SE France), the base of the Turonian (Pueblo, Colorado) and the base of the Santonian (Olazagutia, N Spain) stages have been established and ratified by IUGS. Planktonic foraminifera bioevents are primary and/or secondary defining criteria for those boundaries and are correlated with other fossil groups (i.e., nannofossils, ammonites, inoceramids) and with physico-chemical markers. In addition, a major turnover in planktonic foraminifera coupled with the appearance of a distinctive species and with a negative 1‰  $\delta^{13}\text{C}$  excursion (Petrizzo et al., 2012) have been recently proposed as boundary criteria for identifying the base of the Albian Stage at the Col de Pré-Guittard section (SE France). To date, the identification of the foraminiferal index species across those boundary intervals have been reported to be sometimes difficult and unreliable from a number of localities worldwide either because of their rarity or uncertainty in the taxonomic identifications. Reasons could rely on many factors, such as poor sampling resolution, facies differences and fossil preservation quality. However, discrepancies mostly pertain to taxonomic inconsistencies, species misidentifications and different species concepts that accumulate over time in the literature. Biostratigraphic discrepancies across the Aptian/Albian, Albian/Cenomanian, Cenomanian/Turonian and Coniacian/Santonian boundaries are unraveled through a detailed and high-resolution analysis of the stratigraphic distribution of planktonic foraminifera from sections located in NW Atlantic, SE France and Tanzania. Each section is compared with the equivalent stratotype or with the proposed GSSP section. Results provide insights into the correct taxonomic identification of foraminiferal species and allow refining of the planktonic foraminifera biozonation. Finally, the reproducibility of the bioevents is highlighted in an integrated bio- and chemostratigraphic framework.

Petrizzo M.R., Huber B.T., Gale A.S., Barchetta A. & Jenkyns H.C. 2012. Abrupt planktic foraminiferal turnover across the Niveau Kilian at Col de Pré-Guittard (Vocontian Basin, southeast France): new criteria for defining the Aptian/Albian boundary. *Newsletters on Stratigraphy*, 45, 55-74.

## New GSSP candidate for the base of the Rhaetian: the Pignola-Abriola section

Rigo M.<sup>\*1-7</sup>, Agnini C.<sup>1-7</sup>, Bertinelli A.<sup>2</sup>, Casacci M.<sup>2</sup>, Concheri G.<sup>3</sup>, Gattolin G.<sup>1,9</sup>, Giordano N.<sup>2</sup>, Godfrey L.<sup>4</sup>, Katz M.E.<sup>5</sup>, Maron M.<sup>1</sup>, Muttoni G.<sup>6</sup>, Tateo F.<sup>7</sup>, Sprovieri M.<sup>8</sup>, Stellan F.<sup>3</sup> & Zaffani M.<sup>1</sup>

1. Department of Geosciences - University of Padova. 2. Department of Physics and Geology - University of Perugia. 3. Department of Agronomy Food Natural Resources Animals and Environment, University of Padova. 4. Department Earth and Planetary Sciences, Rutgers University, Piscataway, USA. 5. Department of Earth and Environmental Sciences, Rensselaer Polytechnic Institute, Troy, USA. 6. Department of Earth Sciences, University of Milano. 7. IGG-CNR, Padova. 8. IAMC-CNR, Trapani. 9. ENI, E&P division, San Donato Milanese, Milano.

Corresponding email: [manuel.rigo@unipd.it](mailto:manuel.rigo@unipd.it)

Keywords: GSSP, Rhaetian, Late Triassic.

The Global boundary Stratotype Section and Point (GSSP) for the base of the Rhaetian Stage (Late Triassic) is not yet defined and only the Steinbergkogel section (Austria) has been suggested as a candidate (Krystyn et al., 2007). We present the Pignola-Abriola section as a prime candidate for the Rhaetian GSSP, which fulfills the requirements for the selection of boundary-stratotypes of chronostratigraphic units. The Pignola-Abriola section:

- represents a continuous 60 m long basinal succession, consisting of thin-bedded cherty limestones, shales and rare layers of calcarenites (Calcari con Selce Fm), deposited in the Lagonegro Basin (Southern Apennines);
- is a fossiliferous section, with abundant, distinctive, and well-preserved conodont and radiolarian cosmopolitan fauna; the FAD of the conodont *Misikella posthernsteini* and the base of the radiolarian *Proparvicingula moniliformis* Zone, the two bioevents suggested to mark the base of the Rhaetian, are well documented and intercalibrated;
- shows a negative  $\delta^{13}\text{C}_{\text{carb}}$  excursion close to the Norian/Rhaetian boundary that is mirrored by a marked negative shift of  $\text{d}^{13}\text{C}_{\text{org}}$  curve (ca. 6‰) occurring ca. 0.5 meters below the FAD of *M. posthernsteini*, within the Assemblage 1 of the radiolarian *P. moniliformis* Zone. This negative carbon isotope shift is here interpreted as a physical marker for the Norian/Rhaetian boundary, as an alternative to the biostratigraphic definition;
- is subdivided into 10 magnetozones, integrated with conodont and radiolarian biostratigraphy, and statistically correlated with the Newark APTS;
- is well exposed in an area of minimal structural deformation with easy access along the SS 5 road “la Sellata” and located in the protected area of the Parco Appennino Lucano Val d'Agri Lagonegrese. All of these features assure free long-range preservation and access.

Krystyn L., Bouquerel H., Kuerschner W., Richoz S. & Gallet Y. 2007. Proposal for a candidate GSSP for the base of the Rhaetian stage. In: Lucas S. G. & Spielman J. A. Eds., The Global Triassic. New Mexico Museum of Natural History and Science Bulletin, 41, 189-199.

## Astrochronology of the Late Cretaceous

Sabatino N.\*<sup>1</sup>, Sprovieri M.<sup>1</sup>, Pelosi N.<sup>2</sup>, Batenburg S.<sup>3</sup> & Coccioni R.<sup>4</sup>

1. IAMC-CNR, Capo Granitola (TP). 2. IAMC-CNR, Napoli. 3. SEES, University of Portsmouth, United Kingdom.  
4. DiSTeVA, Università di Urbino.

Corresponding email: [nadia.sabatino@iamc.cnr.it](mailto:nadia.sabatino@iamc.cnr.it)

Keywords: Carbon isotopes stratigraphy, Long-term cycles, Astronomical tuning.

During the Cretaceous, the carbon cycle was affected by major perturbations related to intense volcanic outgassing and possibly to sudden methane release. Also, some recent studies suggest that orbital forcing may have played an important role in carbon cycling. The Bottaccione section, with a detailed and integrated bio-magnetostratigraphy combined with  $\delta^{13}\text{C}$  stratigraphy for the upper Albian–lower Campanian stratigraphic interval, offers an unprecedented opportunity to explore very long-term cyclicity in the  $\delta^{13}\text{C}$  signal. Application of integrated methodologies of non-stationary/non-linear signal analysis, specifically Intrinsic Mode Functions, the WWZ Wavelet, the “REDFIT” periodogram, filtering-reconstruction techniques and direct tuning with the new solution of the astronomical curve (La2010<sub>a</sub>), give us the opportunity to achieve a new orbital tuning for a Late Cretaceous ~23 Myr long record. Long-term eccentricity cycles filtered from a high-resolution  $\delta^{13}\text{C}$  record were tuned to the highly stable 405 kyr cycles of the La2010 astronomical solution for the Earth’s orbital elements. The achieved orbital tuning provides a new precise, and accurate age model for dating biostratigraphic, magnetostratigraphic and carbon isotope events through a ~23 Myr long record.

Cycles of ~8.0, 4.7, 3.4 and ~2.4 Myr modulate the entire  $\delta^{13}\text{C}$  record, thus extending their detection from the Cenozoic to ~100 Ma and represent primary and stable long-term oscillation modes of Earth’s climate-ocean system. Noteworthy, the long-term periodicities potentially reflect an unexplored expression of the low-frequency response of the carbon cycle to global biogeochemical dynamics of major nutrients, particularly phosphorus, associated with modulation of inputs to the ocean in turn triggered by high-order marine transgressions and formation of highly productive shelf seas. This very long-term eccentricity control, modulated by periodic low-energy cycles, is suggested to play a crucial role in carbon cycling, controlling a chain of climate sensitive global biogeochemical processes on the Earth. Finally, these grand-cycles provide a potential tool for geological correlation and provide a robust constraint for accurate calculation of the orbital evolution of the Solar System.

## Early Cretaceous magnetostratigraphy of the Salto del Cieco section (Northern Apennines, Italy)

Satolli S.\*<sup>1-2</sup> & Turtù A.<sup>1-2</sup>

1. Dipartimento di Ingegneria e Geologia, Università "G. D'Annunzio" di Chieti-Pescara  
2. ALP – Alpine Laboratory of Paleomagnetism, Peveragno (CN).

Corresponding email: [s.satolli@unich.it](mailto:s.satolli@unich.it)

Keywords: Early Cretaceous, magnetostratigraphy, chrons.

The 290-m thick Early Cretaceous Salto del Cieco section (Valnerina, Northern Apennines, Italy) was sampled from the Maiolica Fm. to the lowermost part of the Marne a Fucoidi Fm, spanning the Berriasian - Lower Aptian interval. A total number of 281 cylindrical samples were gathered with a sampling spacing of approximately 1 m in order to gather a complete and detailed magnetic polarity record. Moreover, thin sections were obtained from 75 samples spread over the section in order to acquire age constraints through calpionellids biostratigraphy. The cores were analyzed at the Alpine Laboratory of Paleomagnetism (ALP) of Peveragno (Cuneo, Italy) using a 2G DC-SQUID cryogenic magnetometer. A Characteristic Remanent Magnetization was isolated between 300°C and 580°C in 70% of the samples. Its primary nature is strongly supported by the positive reversal tests (McFadden and McElhinny, 1990).

The comparison of our polarity zones to the geomagnetic polarity timescale (Ogg et al., 2008) permitted to infer the sedimentation rate of the Salto del Cieco section. It is 11.9 m/Myr, thus slightly higher than expected in pelagic carbonates deposited far from continents and reaches a peak of 20.83 m/Myr during chron M17r. The detected magnetozones provided a detailed record of polarity chrons from M19 to M15 and M10 to M0, encompassing the Early Cretaceous time from Berriasian to Early Aptian. The high resolution sampling allowed detecting subchron M19n.1r, that is documented for the seventh time in a land section. Furthermore, a geomagnetic excursion is documented in M17r (sdc42r.2n) with respect to the sequence of M polarity chrons inferred from oceanic magnetic anomaly profiles, corresponding to events previously interpreted as remagnetization or VGP departures in other sections (Speranza et al., 2005; Grabowski et al., 2010). More than half of samples characterized by a weak intensity belong to the central part of the section, from chrons M14 to M11. This evidence confirms the magnetostratigraphic "recording gap" gathered in other sections and attributed to diagenetic magnetite dissolution related to the Late Valanginian carbon isotope event (e.g., Speranza et al., 2005).

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## **Integrated stratigraphy and orbital tuning of the Mid-Cretaceous Piedicammoro section, Northern Apennines, Italy**

Turtù A.\*<sup>1-2</sup>, Abels H. A.<sup>3</sup>, Lourens L.J.<sup>3</sup> & Satolli S.<sup>1-2</sup>

1. Dipartimento di Ingegneria e Geologia - Università degli Studi "G. d'Annunzio" di Chieti-Pescara. 2. Alpine Laboratory of Paleomagnetism (ALP) - Peveragno (CN). 3. Department of Earth Sciences - Utrecht University (Netherlands).

Corresponding email: [a.turtu@unich.it](mailto:a.turtu@unich.it)

Keywords: Cyclostratigraphy, magnetostratigraphy, mid-Cretaceous.

The Mesozoic Italian Umbria–Marche sections of the Apennines have shown to be suitable for integrated stratigraphy, among which magneto-, carbon-isotope- and cyclostratigraphy, allowing regional-to-global correlations and environmental reconstructions across this time interval. Together with many well-known sections, the 170-m thick Piedicammoro section (Northern Apennines, Italy) offers a complete sedimentary record spanning the Late Barremian - Earliest Turonian (top of Maiolica Fm. to top of Scaglia Bianca Fm.) and can provide new insights in the relationships between carbon cycling and orbital forcing as well as constraints for Mid-Cretaceous chronostratigraphy. Here we present a new high-resolution isotope carbon record, magnetostratigraphy, and cyclostratigraphic analysis on the cyclically bedded Piedicammoro section. Comparison of the magnetostratigraphy with the Geomagnetic Polarity Timescale reveals that Barremian M1n polarity chron and the lowermost Albian M0r chron are present in the lower part of the section. The middle and upper parts are entirely characterized by the “Long Normal Cretaceous Superchron” (C34n); evidence for short-lived reversed episodes in this interval lacks. The obtained carbon isotope signal displays transient episodes of positive and negative excursions, which can be correlated to coeval published records according to very similar trends and absolute values. Furthermore, the carbon isotope record reveals the presence of a dominant 405-kyr eccentricity-driven cyclicity, matching the stacking pattern of the lithologies in the succession. In addition, a long-term variation of the carbon record has been identified at a 4.5 Myr-scale, seemingly an amplitude modulation of eccentricity. The expression of the 405-kyr-eccentricity cycle is subsequently used for astronomical tuning, which allows providing age constraints and new evidence about the role of orbital forcing on Mid-Cretaceous climate.

## Geochronology from the producer to the consumer

Villa I.M.\*

CUDAM, Università di Milano Bicocca.

Corresponding email: [igor.villa@unimib.it](mailto:igor.villa@unimib.it)

Keywords: Geochronology, Thermochronology, Hygrochronology.

Tectonic modelling requires large amounts of age data. Automated hardware appears capable to deliver numbers at an unprecedented rate. From the consumer's point of view, this may look like paradise.

The problem is, automation has not been the only advance. Improvements in sensitivity and precision have initiated a wave of innovative experiments on age patterns within and between mineral grains. Today we know more than was thought possible two decades ago. More knowledge means that the interpretive paradigm is no longer the simple "closure temperature" scheme fashionable in the early 1960s, yet consumers sometimes struggle to keep up-to-date in an exponentially rising amount of literature. As a consequence, a comment very frequently made by consumers is "I am not interested in your discussions, I want data quickly".

The producers of age data have reached a consensus on the paired geochronology+petrology advances. Pseudosections in P-T-A-X space, developed by petrologists, have taken the place of the "thermal isograds" of yore. Most minerals record internally discordant ages, diffusion being usually overrun by recrystallization. Petrographic relics coincide with isotopic inheritance. Zircon is the most obvious example, but similar observations are being increasingly documented for every single mineral chronometer (Villa & Williams, 2013). This requires to no longer view minerals as "thermochronometers", but as *hygrochronometers* instead, and demands that each analysis be provided its complete context at the intercrystalline (retrogression, petrologic disequilibria, etc) and intracrystalline (microchemical gradients, age patches, etc) level. The modelling of exhumation rates by dating context-free detrital minerals, which forgoes the necessary petrologic equilibrium information, is not founded on solid bases. As context-finding is a typically human task, no automated protocol is predicted to reliably provide correct interpretations. One must never forget that accuracy must be laboriously sought and is not a guaranteed by-product of better precision. Today we know more: there are many more factors to be taken into account nowadays than our forefathers thought of half a century ago, and the complexity of the petrology-geochronology dependence is not going to make data production faster. The good news is that taking into account this complexity makes accurate geological reconstructions possible.

Villa I.M. & Williams M.L. 2013. Geochronology of metasomatic events. In: Harlov D.E. & Austrheim H. Eds., *Metasomatism and the Chemical Transformation of Rock*, 171-202. Springer, Heidelberg, ISBN 978-3-642-28393-2

## Preliminary $\delta^{13}\text{C}_{\text{org}}$ and TOC data from the Lagonegro Basin (Southern Italy) across the Norian-Rhaetian boundary

Zaffani M.\*<sup>1</sup>, Agnini C.<sup>1</sup>, Bertinelli A.<sup>2</sup>, Concheri G.<sup>3</sup>, Galatà F.<sup>2</sup>, Godfrey L.<sup>4</sup>, Katz M.E.<sup>5</sup>, Rigo M.<sup>1</sup> & Stellan F.<sup>3</sup>

1. Department of Geosciences, University of Padova. 2. Department of Physics and Geology, University of Perugia. 3. Department of Agronomy Food Natural Resources Animals and Environment, University of Padova. 4. Department Earth and Planetary Sciences, Rutgers University. 5. Department of Earth and Environmental Sciences, Rensselaer Polytechnic Institute.

Corresponding email: [mariachiara.zaffani@studenti.unipd.it](mailto:mariachiara.zaffani@studenti.unipd.it)

Keywords:  $\delta^{13}\text{C}_{\text{org}}$ , Lagonegro Basin, Norian-Rhaetian boundary.

Four sections belonging to the Lagonegro Basin (Southern Apennines) have been investigated for geochemical purposes ( $\delta^{13}\text{C}_{\text{org}}$ ; Total Organic Carbon %). These successions crop out at Pignola-Abriola, Mt Volturino, Mt S. Enoc and Mt Sirino and consists of continuous and well-exposed basinal series belonging to the Calcari con Selce Formation (marls, shales, cherty limestones) and the Scisti Silicei Formation (cherts and radiolarites). These strata are Upper Norian (Sevatian 1) to Hettangian in age.

The organic carbon isotope curve ( $\delta^{13}\text{C}_{\text{org}}$ ) depicts three negative shifts: the first in the lower Sevatian 1, the second during the middle Sevatian 2 and the third just predating the Norian-Rhaetian boundary (NRB). The excursion found close to the NRB is virtually coincident with the FAD of the conodont *Misikella posthernsteini*, here suggested as marker for the base of the Rhaetian. Overall, these excursions show amplitudes ranging between 3 and 6‰, likely resulting from a  $^{12}\text{C}$ -enriched input into the ocean-atmosphere reservoir. The possible sources of  $^{12}\text{C}$  are: i) occurrence of Large Igneous Provinces (LIPs); ii) dissociation of gas hydrates; iii) coal thermal metamorphism; iv) massive oxidation of soil organic matter. Instead, the positive fluctuations might be interpreted as an increase in the primary productivity, as confirmed by the increase in Total Organic Carbon (TOC%) associated with the negative fluctuations of the  $\delta^{13}\text{C}_{\text{org}}$  curve.

The comparison between the  $\delta^{13}\text{C}_{\text{org}}$  values and the TOC content also suggests that anoxic/dysoxic conditions likely occurred in the Lagonegro Basin around the Norian-Rhaetian boundary (e.g., Jenkyns, 2010).

Once it is verified globally, the  $\delta^{13}\text{C}_{\text{org}}$  negative excursion occurring close to the FAD of *M. Posthernsteini* can be suggested as a possible physical proxy for the definition of the Norian-Rhaetian boundary.

Jenkyns H.C. 2010. Geochemistry of oceanic anoxic events. *Geochemistry Geophysics Geosystems*, 11, 1-30

## **SESSIONE S3**

### **Geological causes and consequences of Life evolution on Earth: the paleontological record of igneous/tectonic events**

#### *CONVENORS*

*L. Angiolini (Univ. Milano)*

*S. Cirilli (Univ. Perugia)*

## The Permian-Triassic extinction and biotic recovery in the terrestrial ecosystems of the Southern Alps: ichnological and paleobotanical evidence

Bernardi M.<sup>1-2</sup>, Petti F.M.\*<sup>1</sup>, Kustatscher E.<sup>3</sup> & Avanzini M.<sup>1</sup>

1. Museo delle Scienze di Trento, Trento. 2. School of Earth Sciences, University of Bristol, UK. 3. Naturmuseum Südtirol, Bolzano.

Corresponding email: [fabio.petti@socgeol.it](mailto:fabio.petti@socgeol.it)

Keywords: Permian-Triassic, mass extinction, biotic recovery.

During the Late Permian terrestrial life was subjected to the most severe extinction event that wiped out up to 63% of the terrestrial families. The causes are still unclear even if many killing agents have hitherto been proposed. The Permian-Triassic sedimentary successions of the Southern Alps are exceptionally exposed and several track- and plant-bearing horizons have been recognized within these sequences.

The Permian ichnoassemblage is represented by at least thirteen ichnotaxa belonging to various groups such as pareiasaurs (indicated by the presence of *Pachypes*), therapsids (indet.), captorhinids (*Hyloidichnus*), neodiapsids as younginiformes (*Rhynchosauroides*, *Ganasauripus*), and archosauriformes (chirotheriids). The Permian flora is dominated by ginkgophytes (*Baiera*, *Sphenobaiera*), closely followed by the conifers (e.g., *Ortiseia*, *Pseudovoltzia*, *Quadrocladus*), while seed ferns (*Sphenopteris*, *Germanopteris*), taeniopterids and sphenophytes are rare elements in the association.

On the other hand, the Early Triassic (Olenekian) ichnoassemblage is characterized by monotypic lepidosauromorph tracks. The paucity of vertebrate tracks and the complete absence of skeletal remains and plants may be due to the lack of extensive emergent land but are probably biased by the unfavourable conditions of preservation for the terrestrial record. During the early Middle Triassic (Bithynian-Pelsonian) the ichnoassemblages document a again a diversified tetrapod fauna composed of lepidosauromorphs (*Rhynchosauroides*), basal amniotes (*Procolophonichnium*), amphibians (*Capitosauroides*) archosauriformes (*Brachychirotherium*, *Chirotherium*, *Isochirotherium*, *Parasynaptichnium*) and possible dinosauromorphs (*Rotodactylus*). The middle Anisian (Pelsonian) flora of the Southern Alps is one of the best example of the biotic recovery after the P-T crisis. It consists of typical Middle Triassic elements such as the osmundaceous ferns *Neuropteridium*, *Anomopteris* and *Gordonopteris*, the lycophyte *Lepacyclotes* and the conifers *Albertia* and *Aethophyllum*. However, the flora also contains “modern” Mesozoic taxa, such as the fern *Chiropteris*, the cycadophytes *Bjuvia* and *Nilssonia*, the conifer *Voltzia*, the Caytoniales (*Sagenopteris*) and possibly the seed fern *Ptilozamites*.

These findings provide a noticeable example of well diversified terrestrial ecosystems during the Late Permian (Lopingian) and the Middle Triassic (Bithynian-Pelsonian). The time interval between the last Permian terrestrial assemblages and those of the Bithynian-Pelsonian makes still difficult to understand how much of this genera/families turnover was due to an increased macro-evolutionary process triggered by the environmental changes or to the extinction process related to the biological crisis of end-Permian.

## Calcareous nannofossil absolute abundances across the Toarcian Oceanic Anoxic Event (T-OAE): implications for paleoceanographic changes

Casellato C.E.\* & Erba E.

Università degli Studi di Milano, Dipartimento di Scienze della Terra "Ardito Desio".

Corresponding email: [cristina.casellato@unimi.it](mailto:cristina.casellato@unimi.it)

Keywords: Calcareous nannofossils; Toarcian Oceanic Anoxic Event.

The T-OAE (~183 Ma, Early Jurassic) is a global climatic-oceanographic perturbation, marked by a C-isotopic anomaly, coeval with the emplacement of the Karoo-Ferrar igneous province. Climate change, accelerated hydrological cycle and weathering, enhanced nutrient availability and productivity resulted in the widespread Corg-rich sediment deposition in O-depleted oceans.

The selected Colle di Sogno section is one of the best exposures of the T-OAE in the Southern Alps: here, upper Pliensbachian limestones (Domaro lmst.) are followed by lower Toarcian marly limestones and marlstones (Sogno Fm.). Calcareous nannofossil assemblages were quantitatively investigated in ultrathin sections through the Pliensbachian/Toarcian boundary (Pl/T) and across the T-OAE.

The total nannofloral abundance shows highest values in the uppermost Pliensbachian through lowermost Toarcian interval (~ 1000 specimens/mm<sup>2</sup>). At the onset of T-OAE total abundance is halved (50%) and remains at similar values after the end of black shale deposition. As far as single taxon abundances are concerned, there is a general relationship between *Schizosphaerella* abundances and carbonate content. A significant decrease in *Schizosphaerella* abundance marks the Pl/T boundary and the “*Schizosphaerella* crisis” marks the T-OAE inception. *M. jansae* only partly shows similar abundance patterns.

A major shift in nannofossil assemblages corresponds to the T-OAE interval, with a dramatic drop of *Schizosphaerella* and *M. jansae* and an increase in abundance of *Lotharingius*, *Carinolithus* and *Biscutum*. The interval following the T-OAE sees the slight recover of *Schizosphaerella*, while *Lotharingius*, *Biscutum*, *Carinolithus* and *Calyculus* display a decrease in abundance. *M. jansae* does not recover the anoxic episode and after a short interval of suppressed abundances, disappears.

Our results are consistent with previous data: the “*Schizosphaerella* decline and crisis” are reliable events at least at regional scale. The decrease of total abundances and of largest, most calcified taxa, paralleled by an increase of small species across the T-OAE suggests paleoenvironmental perturbations governing calcareous nannoplankton composition. Signals of ecosystem modifications anticipate the T-OAE and considerable variations are evident since the Pl/T boundary interval. This was the time of a spectacular diversification, the most important evolutionary event in the history of calcareous nannoplankton.

Although absolute abundances are not a good measure of calcite production, we infer that the observed nannofossil variations are due to a combination of higher fertility and lower calcification under high CO<sub>2</sub> levels. Such a scenario is compatible with a major tectonic-igneous event profoundly affecting the ocean/atmosphere system. Variations in atmospheric CO<sub>2</sub> triggered by the emplacement of Karoo-Ferrar province started to stress the climate, ocean chemistry and nutrient cycling at least 1 My before the T-OAE.

## Global and regional factors responsible for the drowning of the Central Apennine Chattian carbonate platforms

Cornacchia I.\*<sup>1</sup>, Brandano M.<sup>1-2</sup>, Lustrino M.<sup>1-2</sup> & Sprovieri M.<sup>3</sup>

1. Dipartimento di Scienze della Terra, Università La Sapienza Roma. 2. Istituto di Geologia Ambientale e Geoingegneria (IGAG) CNR, Area della Ricerca di Roma 1. 3. Istituto per l'Ambiente Marino Costiero (IAMC), CNR, Campobello di Mazara (TP).

Corresponding email: [irene89@alice.it](mailto:irene89@alice.it)

Keywords: Carbonate platforms, trophism, volcanism, carbon isotope, Mediterranean, Chattian, Apennine.

Two stratigraphic sections of Central Apennine have been analyzed to interpret the factors responsible for the Oligocene-Miocene drowning of the carbonate platforms. The Mt. La Serra section, representing the Northern sector of the Latium-Abruzzi carbonate platform and the Opi section, representing the Eastern sector of the same domain have been investigated for facies and stable isotope characteristics (Brandano et al., in press).

Important positive  $\delta^{13}\text{C}$  shifts have been recorded at the Oligocene-Miocene boundary in both sections. These shifts range from  $-0.34\text{‰}$  1 m below the top of the Chattian to  $+0.85\text{‰}$  in the Aquitanian spongolitic marls in the Mt. La Serra section, and from  $+0.05\text{‰}$  to  $+0.60\text{‰}$  in the Aquitanian spongolitic interval of the Opi section. These facies and C-isotope variations reflect an increased productivity of surface seawater and correspond to changes from a middle carbonate ramp to outer ramp depositional environment. This drowning event is recorded not only in Apennine platforms, but also in other Mediterranean platforms such as in southern Apulia, Sicily and Malta, and outside the Mediterranean Basin, (e.g., the Caribbean area).

We propose two possible major factors responsible for this drowning event: the Mi-1 event, and the volcanic activity peak developed in the Central-Western Mediterranean during the Chattian-Burdigalian interval. The Mi-1 glacial maximum ( $\sim 24\text{--}23.5$  Ma) may have had a strong influence on the drowning event on a global scale, as it triggered a weathering and continental runoff increase, which sustained eutrophic conditions and water turbidity. The development of a widespread subduction-related igneous activity in the Western Mediterranean during the Latest Oligocene-Early Miocene may have had even a stronger effect on the carbonate production of the Apennine platforms. Arrival of volcanic material such as airborne ash can have increased water turbidity, reducing light penetration and, above all, producing a huge fertilization effect of the euphotic marine environments, bringing micro- and macronutrients to the surface waters. A second consequence is an increase of the  $\text{SiO}_2$  seawater content, thus favouring siliceous organisms. Last not least, it has to be mentioned that the propellants for explosive volcanism are  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and sulphur. A raise of both atmospheric and marine  $\text{CO}_2$  concentration could have led to a greenhouse effect and, thus, to an additional increase of weathering and runoff, and also to a decrease of seawater pH and a reduction of carbonate ions concentration, favouring calcite-dominated skeletal assemblages (heterozoans) and, above all, siliceous production.

Brandano M., Lustrino M., Cornacchia I. & Sprovieri M. (in press). Global and regional factors responsible for the drowning of the Central Apennine Chattian carbonate platforms. *Geological Journal*, DOI: 10.1002/gj.2575.

## The role of CAMP volcanism in the end Triassic carbon isotope perturbation and mass extinction

Dal Corso J.\*<sup>1</sup>, Marzoli A.<sup>1-2</sup>, Tateo F.<sup>2</sup>, Jenkyns H.C.<sup>3</sup>, Cirilli S.<sup>4</sup> & Youbi N.<sup>5-6</sup>

1. Dipartimento di Geoscienze, Università degli Studi di Padova. 2. Istituto di Geoscienze e Georisorse, CNR. 3. Department of Earth Sciences, University of Oxford, UK. 4. Dipartimento di Scienze della Terra, Università di Perugia. 5. Geology Department, Faculty of Sciences-Semlalia, Cadi Ayyad University, Morocco. 6. Universidade de Lisboa, Faculdade de Ciências, Departamento de Geologia, Centro de Geologia, Portugal.

Corresponding email: [jacopo.dalcorso@unipd.it](mailto:jacopo.dalcorso@unipd.it)

Keywords: CAMP, Late Triassic, carbon isotope.

The end Triassic biological crisis is one of the “Big Five” mass extinctions in Earth history, marked by a major terrestrial turnover and the loss of ca. 50% of marine genera, and coincident with an abrupt negative global carbon-isotope excursion (CIE). The most likely “smoking gun” for the carbon-cycle perturbation and extinction is the eruption of the continental flood basalts of the Central Atlantic Magmatic Province (CAMP), the largest known Large Igneous Province, and associated release of huge amounts of volcanic gases (mainly CO<sub>2</sub> and SO<sub>2</sub>) into the atmosphere. Existing carbon-isotope records, palaeontological data and radioisotopic ages suggest that extinction, negative CIE and CAMP eruption have been coeval but the precise temporal relationships between the phenomena remain uncertain due to the difficulty in correlating events mainly recorded in marine successions (CIE and mass extinction) with the continental CAMP volcanism. Hence, the role of the LIP eruption in triggering the end-Triassic carbon cycle perturbation and extinction remains questionable. Here, we present mineralogical, geochemical and palynological data from two stratigraphic successions underlying CAMP basalts in the Central High Atlas (Morocco). Sporomorph assemblages of the studied sediments give a Late Triassic age. X-ray diffraction analysis of claystones and siltstones highlights a marked mafic signature with high contents of MgO (10–32 wt%) and mafic clay minerals (11–84%). Given the regional geological setting, this mafic signature can only be linked to the deposition of clay minerals derived from early-erupted basalts of the CAMP. Organic-carbon isotope analysis of bulk organic matter shows ~6‰ negative CIEs that are coincident with the highest MgO content. This carbon-isotope perturbation can be correlated, via magneto- and chemostratigraphy, with the initial negative CIE that just pre-dates the Triassic–Jurassic boundary. These data show that the end-Triassic CIE is unequivocally synchronous with an already active CAMP volcanism and could coincide with peaks of volcanic activity. Moreover, this finding suggests that the cause of the mass extinction was relatively long-term pollution of atmosphere and seawater by CAMP-derived volcanic gases.

## Carbon isotope perturbation and intensification of Pangea mega-monsoon in the Carnian (early Late Triassic)

Dal Corso J.\*<sup>1</sup>, Gianolla P.<sup>2</sup>, Newton R.J.<sup>3</sup>, Franceschi M.<sup>4</sup>, Caggiati M.<sup>2</sup>, Roghi G.<sup>5</sup>, Raucsik B.<sup>6</sup>, Budai T.<sup>7</sup>, Haas J.<sup>8</sup> & Preto N.<sup>1</sup>

1. Dipartimento di Geoscienze, Università degli Studi di Padova. 2. Dipartimento di Fisica e Scienze della Terra, Università degli Studi di Ferrara. 3. School of Earth and Environment, University of Leeds, UK. 4. MuSe - Museo Delle Scienze, Trento, Italy. 5. Istituto di Geoscienze e Georisorse (IGG-CNR), Padova. 6. Department of Mineralogy, Geochemistry and Petrology, University of Szeged, Hungary. 7. Geological and Geophysical Institute of Hungary, Hungary. 8. MTA-ELTE Geological, Geophysical and Space Science Research Group Hungarian Academy of Sciences, Hungary.

Corresponding email: [jacopo.dalcorso@unipd.it](mailto:jacopo.dalcorso@unipd.it)

Keywords: Carnian Pluvial Event, carbon-isotope, Large Igneous Province.

In the Late Triassic a period of increased rainfall, called the Carnian Pluvial Event (CPE), was marked by the sudden input of siliciclastic material, anoxia and a crisis of carbonate production into sedimentary basins (Preto et al., 2010). In continental environments, palaeosols typical of tropical humid environments developed, and the floral associations shifted towards more hygrophytic elements (Preto et al., 2010). The CPE is also closely associated with biological turnover among some marine groups and could be linked to major evolutionary innovations (Simms et al., 1995; Dal Corso et al., 2012).

Here, we present organic-carbon isotope data from two Carnian deep-water stratigraphic successions in the Northern Calcareous Alps (Austria) and the Transdanubian Range (Hungary) that highlight a sharp negative carbon-isotope excursion (CIE) at the onset of the CPE. A negative 2‰–3‰ CIE slightly precedes warming and terrigenous input into the studied basins and is correlated with carbon-isotope records from higher plant and marine algal biomarkers of the Dolomites, Northern Italy (Dal Corso et al., 2012), thus testifying for a global perturbation of the carbon cycle. The CIE seems to have been articulated in two distinct negative  $\delta^{13}\text{C}_{\text{org}}$  excursions. The source of depleted  $\text{CO}_2$  could be the roughly coeval eruption of Wrangellia Large Igneous Province (LIP).

Our results show that the injection of  $\text{CO}_2$  into the Carnian atmosphere–ocean system slightly preceded the increase of continental weathering and nutrients flux into the basins of the northwestern Tethys that may have caused the local development of anoxia and the crisis of the microbial carbonate factory (Keim et al., 2006). Intensification of the monsoon activity triggered by volcanic  $\text{CO}_2$ -induced global warming and consequent increase of the precipitable water (total column water vapour) can explain the increase in rainfall and continental weathering at the CPE. This event could be an important analogue that may help to understand the long-term consequences of today's increase in heavy rainfall, especially in monsoonal regions due to anthropogenic  $p\text{CO}_2$  rise (Trenberth et al., 2011).

Dal Corso J., Mietto P., Newton R., Pancost R., Preto N., Roghi G. & Wignall P. 2012. Discovery of a major negative  $\delta^{13}\text{C}$  spike in the Carnian (Late Triassic) linked to the eruption of Wrangellia flood basalts. *Geology*, 40, 7982.

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Simms M.J., Ruffel A.H. & Johnson L.A. 1995. Biotic and climatic changes in the Carnian (Triassic) of Europe and adjacent areas. In: Fraser N.C. & Sues H.D. Eds, *In the shadow of the dinosaurs. Early Mesozoic tetrapods*. Cambridge University Press, 352–365.

Trenberth K.A. 2011. Changes in precipitation with climate change. *Climate Research*, 47, 123–138.

## Living in a crazy ocean: calcareous nannoplankton response to Oceanic Anoxic Event 2 and comparison with living coccolithophores algae

Faucher G.\* & Erba E.

Dipartimento di Scienze della Terra "Ardito Desio" - Università degli Studi di Milano.

Corresponding email: [giulia.fraucher@unimi.it](mailto:giulia.fraucher@unimi.it)

Keywords: nannofossil, dwarfism, OAE2.

Coccolithophores are phytoplanktonic organisms that play a fundamental role in the ocean food web and in the global carbon cycle. They produce tiny calcium carbonate plates, named coccoliths, and therefore actively contribute to the marine carbonate cycling. Nowadays the ocean is facing a profound alteration of the carbonate system due to anthropogenic release of carbon dioxide, absorbed by surface waters becoming progressively more acidic.

Laboratory experiments suggest that coccolithophores are very sensitive to seawater pH, dissolved CO<sub>2</sub>, temperature and nutrient concentration all of which are impacted by human CO<sub>2</sub> emissions. Furthermore, studies on large volcanic eruptions, demonstrate that metals contained in volcanic ashes, such as Cd, Cu, Pb and Zn, can have both fertilizing and toxic effects on marine phytoplankton species (diatoms and coccolithophores) which will ultimately lead to changes in species composition with implications for community productivity. Some species might have the ability to adapt to perturbed conditions, but coccolithophore responses to environmental stress in culture experiments are not straightforward.

The geological record is imprinted with numerous examples of natural perturbations of the global carbon cycle and climate changes, usually associated to large-scale release of volcanogenic CO<sub>2</sub> and ocean acidification.

We analyzed the latest Cenomanian Oceanic Anoxic Event (OAE2), during which the formation of the Caribbean Plateau Large Igneous Province (LIP) induced the degassing of large amounts of CO<sub>2</sub> and triggered environmental consequences including warming, oceanic anoxia, fertilization and acidification. Here we present biometric data of 4 coccolith species dominant in Cenomanian–Turonian assemblages. The morphometric analyses showed a species-specific response across the OAE2 perturbation. *W. barnesiae*, the most cosmopolitan species, doesn't show any significant variation in size, on the contrary the r-strategist taxa, namely *B. constans*, *D. rotatorius* and *Z. erectus*, display a strong reduction in size. Dwarfism mimics the pCO<sub>2</sub> fluctuations as reconstructed via geochemical proxies: a progressive increase in size take place when pCO<sub>2</sub> start to decrease while dwarf coccolith are coeval with a strong increase in CO<sub>2</sub>. Notably, the maximum reduction in size occurs with the highest CO<sub>2</sub> estimates, very high sea surface temperature and a remarkable biolimiting metal peak.

It's extremely difficult to disentangle the complex interplay of paleoecological parameters and pinpoint the most relevant cause of dwarfism.

To constrain the role of individual parameters on coccolith production (number of coccoliths, their size and degree of calcification), we performed several culture experiments on four species of living coccolithophores taking in account toxic metal content, carbonate chemistry, nutrient content and light intensities. Preliminary results will be presented and compared to the geological record.

## **New Early Pliensbachian high-resolution C-isotope record from the Trento Platform (Early Jurassic) and insights on the diffusion of the *Lithiotis* Fauna**

Franceschi M.\*<sup>1</sup>, Dal Corso J.<sup>2</sup>, Posenato R.<sup>3</sup>, Roghi G.<sup>4</sup>, Masetti D.<sup>3</sup> & Jenkyns H.C.<sup>5</sup>

1. MuSe, Museo Delle Scienze, Trento. 2. Dipartimento di Geoscienze, Università degli Studi di Padova. 3. Dipartimento di Fisica e Scienze della Terra, Università di Ferrara. 4. Istituto di Geoscienze e Georisorse (IGG-CNR), Padova. 5. Department of Earth Sciences, University of Oxford.

Corresponding email: [marco.franceschi79@gmail.com](mailto:marco.franceschi79@gmail.com)

Keywords: Early Jurassic, Pliensbachian, C-isotope, *Lithiotis* Fauna, Paleoclimate.

In this contribution a new high-resolution carbonate carbon-isotope record and the distribution of the *Lithiotis* Fauna in the Lower Jurassic marine shallow-water carbonates of the Trento Platform (Southern Alps, Italy) are compared. The *Lithiotis* Fauna represents a unique and short-lived event in which mound-building bivalves experienced global diffusion in the Early Jurassic. The integration of isotope data with the fossil distribution allowed to explore the possible cause-effect relationships between the climate and environmental changes marked by features in the isotope record and the diffusion of the peculiar *Lithiotis* Fauna.

A set of carbonate carbon-isotope excursions of 2–3‰, articulate in three distinct negative shifts followed by positive rebounds, are recorded in the isotope stratigraphy carried out on three stratigraphic sections and can be correlated to the global negative  $\delta^{13}\text{C}$  shift of the Sinemurian–Pliensbachian boundary event (S–P Event) and to the subsequent phase of C-isotope perturbation that characterized the lower Pliensbachian.

The S–P Event triggered eutrophic conditions as illustrated by the presence of organic-rich facies and by fossil associations characteristic of poorly oxygenated waters. After the eutrophic phase, an amelioration of environmental conditions is marked by a positive  $\sim 3\%$  rebound of the  $\delta^{13}\text{C}_{\text{carb}}$  values, and by the occurrence of marine stenotypic faunas. On the Trento Platform, the stabilization of the  $\delta^{13}\text{C}_{\text{carb}}$  values is coincident with the appearance of the *Lithiotis* Fauna that subsequently becomes widely distributed in the entire range of platform environments showing maximum abundance in the late Pliensbachian when metric-scale mounds were generated. During the same time, the maximum proliferation of the *Lithiotis* Fauna is recorded both in the Tethyan and Panthalassa regions together with a continent reorganization that may have led to the opening of the Hispanic Corridor, a seaway cutting through Pangea at tropical latitudes. The processes behind the opening of the Hispanic Corridor may have been responsible of the injection of  $\text{CO}_2$  into the atmosphere-ocean system that triggered the S–P Event. Hence, the reported relationships between the  $\delta^{13}\text{C}_{\text{carb}}$  data and the distribution and ecological characteristics of the genera contained in the *Lithiotis* Fauna suggest that the S–P Event and its aftermath, possibly coupled with the opening of the Hispanic Corridor, could have set the stage for the rapid diffusion of these unusual bivalves across many parts of the globe.

## **Can we use brachiopod shell fabric as tracer for the end Permian environmental changes caused by the Siberian Traps?**

Garbelli C.\* & Angiolini L.

Dipartimento di Scienze della Terra "A. Desio", Università degli Studi di Milano.

Corresponding email: [claudio.garbelli@unimi.it](mailto:claudio.garbelli@unimi.it)

Keywords: Biofabric, acidification, P/T extinction.

Flood basalts, global warming and ocean acidification are grabbing the attention of the scientific community for their devastating effects on life; studies suggest that taxa secreting a carbonate skeleton could be particularly subjected to negative effects such as decreasing growth rates and calcification, that cause fitness reduction and eventually extinction. Ocean warming and acidification resulting from volcanisms are too protracted in time to be reproduced in laboratory, and their effects are strongly dependent on both the rate of change in the ocean carbonate chemistry and the adaptation potential of a given species. The fossil record provides a high resolution archive to study the long term effects of environmental changes on marine organisms. Among these, brachiopods, rulers of the Palaeozoic benthic communities, are an important group of calcifier organisms, which were sensitive to global geochemical changes in the oceans through extreme events. Some recent advancements have shown that their inorganic shell content is affected by seawater temperature and by its carbonate saturation state. Shell change in organic and inorganic content may have long term effects, producing permanent variations in brachiopods shell fabric and/or selectively causing extinction. The end of the Permian is one of the best time interval where to study the long term interplay between change in the ocean temperature and brachiopod biomineralization processes and its chemistry. Global warming and ocean acidification, related to the Siberian Traps volcanism culminated at the P/T boundary with the largest mass extinction of the Phanerozoic. Since brachiopods are low-metabolism, and physiologically unbuffered organisms, which are forced to change in response to extreme environmental variations, we are searching for evidences to track any possible modifications in their shell fabric. Detecting very fine and progressive biotic modifications related to global warming and acidification in the fossil record could be a powerful tool to unravel past climate changes and to predict their future consequences on the biotic systems.

## **Tempo and mode of Pleistocene paleoenvironmental dynamics in the Eritrean Rift: insights from the Homo-bearing Aalat succession (Dandiero Basin, East Africa)**

Ghinassi M.\*<sup>1</sup>, Carnevale G.<sup>2</sup>, Delfino M.<sup>2-3</sup>, Oms O.<sup>4</sup>, Papini M.<sup>5</sup>, Pavia M.<sup>2</sup>, Rook, L.<sup>5</sup> & Scarciglia F.<sup>6</sup>

1. Dipartimento di Geoscienze, Università di Padova. 2. Dipartimento di Scienze della Terra, Università di Torino  
3. Institut Català de Paleontologia Miquel Crusafont, Universitat Autònoma de Barcelona, Spain. 4. Dpt. de Geologia, Universitat Autònoma de Barcelona, 08193, Bellaterra, Spain. 5. Dipartimento di Scienze della Terra, Università di Firenze. 6. Dipartimento di Biologia, Ecologia e Scienze della Terra, Università della Calabria, Arcavacata di Rende (CS)

Corresponding email: [massimiliano.ghinassi@unipd.it](mailto:massimiliano.ghinassi@unipd.it)

Keywords: East Africa, Buia, Homo, Paleoenvironments.

Pleistocene environmental instability of East Africa has been linked with the main steps of faunal dispersal and human evolution (deMenocal, 2004). These environmental changes are largely documented by deep marine or lacustrine proxies, which are usually correlated with landward-located, Homo-bearing successions through high-resolution chronological datasets. Notwithstanding, only few studies were aimed at inferring these paleoecological changes from continental sedimentary successions, given the common paucity of continuous and expanded records of the latter. The present work focuses on Pleistocene deposits of the Dandiero Basin (Eritrean rift margin). The Dandiero Basin (110 km south of Massawa) is filled by about 500-600 m thick fluvio-lacustrine deposits bearing Homo erectus remains (Ghinassi et al., 2009). This study aims at providing a paleoenvironmental and chronological frame for the 285 m thick Aalat section, located in the northern part of the Dandiero Basin (Papini et al., 2014). Along this section fluvial, deltaic and lacustrine deposits are vertically stacked, displaying early-stage weathering and pedogenetic features, and two main fossiliferous horizons have been detected at about 70 m from the base. Especially because of the ecological preference of some significant taxa (e.g. bovids, suids, herpetofauna etc.), fossil vertebrate assemblages provide significant insight into the paleoenvironment in the Dandiero Basin area. High-quality paleomagnetic data, integrated with radiometric dating and vertebrate paleontology, allow to ascribe the the Aalat section to C1r.1n (Jaramillo), C1r.1r and C1n (Brunhes) magnetic events. The Aalat section accumulated under significantly high aggradation rate (e.g. about 160 m during C1r.1r) confirmed by an overall poor soil development, and represents an outstanding archive for the main environmental changes occurred during the Lower-Middle Pleistocene transition in East Africa.

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## **Geological causes and consequences of Life evolution at the end of the Triassic: the igneous record of paleontologic events**

Marzoli A.\*, Callegaro S., Dal Corso J. & Bellieni G.

Dipartimento di Geoscienze, Università di Padova.

Corresponding email: [andrea.marzoli@unipd.it](mailto:andrea.marzoli@unipd.it)

Keywords: Central Atlantic magmatic province (CAMP), end Triassic, LIP magmatism.

In this presentation we will review the hypothesis that volcanic gas emissions from the Central Atlantic magmatic province (CAMP) basalts triggered the end-Triassic mass extinction. Therefore, we will first constrain the relative and absolute age of the volcanism and of the environmental-biotic crisis. Multidisciplinary evidences will be discussed, including mineralogical, geochemical, biostratigraphic data. These clearly show that the onset of CAMP volcanism shortly preceded the end-Triassic extinction, as is now agreed by most researchers after some decades of lively debate. The second part of the presentation will deal with the actual mechanisms by which widespread magmatism can have a severe environmental impact. First, it will be shown that eruption of CAMP basalts occurred as short-lived volcanic events with extremely high eruption rate. Then, we will discuss the emission of green- or ice-house gases related to the volcanic activity. We have now a relatively good understanding of the (large) amounts of volcanogenic SO<sub>2</sub> emissions, through direct measurements of S in volcanic materials. CAMP SO<sub>2</sub> emissions were as large as those of other large igneous provinces (LIPs) such as the end-Permian Siberian Traps and the end-Cretaceous Deccan Traps and likely triggered repeated events of short-lived yet severe global cooling. On the other hand, the quantification of CO<sub>2</sub> emissions of CAMP (and of all other LIP) basalts could not be constrained, so far, by direct chemical analyses of C in the magmatic rocks. We will therefore propose an alternative approach, which is based on C isotopic analyses of basaltic rocks combined with a study of fluid inclusions. Based on these new (and preliminary) data, we can demonstrate that the end-Triassic carbon budget was modified by CAMP magmatism, mainly.

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## Palynological associations across the T-J boundary and their changes with the climate variations and the CAMP onset: a case study from subsurface of SE Sicily (Italy)

Panfili G.<sup>1</sup>, Buratti N.<sup>1</sup>, Cirilli S.\*<sup>1</sup> & Frixia A.<sup>2</sup>

1. Dipartimento di Fisica e Geologia, Università di Perugia. 2. Eni e&p.

Corresponding email: [simonetta.cirilli@unipg.it](mailto:simonetta.cirilli@unipg.it)

Keywords: Palynology, Hyblean Plateau, Late Triassic-Early Jurassic.

A palynological and palynofacies analysis of two wells (Streppenosa 1 and Bimmisca 1) drilled in the Hyblean Plateau Petroleum System (SE Sicily) was carried out with the aim to better constrain the age and the depositional environment across the Triassic – Jurassic boundary. The study was focused on the Late Triassic–Early Jurassic Streppenosa and Noto Fms., deposited respectively in an intraplatform basin and lagoon environment. The Streppenosa Fm. is characterized by alternation of organic rich shales, marly limestones and limestones containing calciturbidic intervals. The Noto Fm. is mostly composed of organic matter bearing marls and marly limestones. The investigated intervals in Streppenosa 1 and Bimmisca 1 wells were comprised between the base of the the Noto Fm. and the top of the Streppenosa Fm.. By palynological data, the age attribution of the Noto Fm. results slightly diachronous in the two wells: in the Streppenosa 1, results as late Norian, up to lowermost Rhaetian for the presence of the index species *Limbosporites lundbladii* and *Acanthotriletes varius*, whereas in the Bimmisca 1 is referable to the Rhaetian for the presence of *Krauselisporites reissingeri* and *Leptolepidites major*. The Streppenosa Fm. yielded, in both the wells, palynological assemblages assigned to the Rhaetian probably up to the Rhaetian–Hettangian boundary, for the presence of some index species as *Triancoresporites ancorae*, *Ischyosporites variegatus*, *Leptolepidites bossus*, *Ischyosporites variegatus* and *Callialasporites sp.*

The vertical palynofacies variations across the Triassic-Jurassic sedimentary succession, penetrated in the two boreholes, suggest a strong control by the relative sea level changes. During the relative sea level fall the amount of terrestrial organic matter increased, whereas during the relative sea level rise the amount and preservation of the total organic matter content increased. The relative sea level changes were linked both to the intense Triassic-Jurassic tectonic activity and paleoclimate fluctuations, related to the Pangea opening and to the Central Atlantic Magmatic Province (CAMP) onset. This latter should be the cause of a climate deterioration towards more humid conditions.

Moreover, the palynological associations from both wells are characterized by the abundant presence of trilete spores referable to plants living in a humid climate environment as: *Anapiculatisporites*, *Baculatisporites*, *Conbaculatisporites*, *Densosporites*, *Krauselisporites* etc.. The abundance of this taxa can be considered linked to the climate variation across the T-J boundary. The increase of humidity in this time interval is proved by the deposition of organic matter rich shales in restricted circulation basins of western Tethys. According to several authors, the causes of this climatic deterioration are linked properly to the CAMP onset and to the consequent immission of green-house gases in the atmosphere and in the ocean waters.

## Latest Miocene palaeogeography of northern Tyrrhenian area: evidences from terrestrial vertebrate faunas

Rook L.\*

Dipartimento di Scienze della Terra, Università di Firenze.

Corresponding email: [lorenzo.rook@unifi.it](mailto:lorenzo.rook@unifi.it)

Keywords: Palaeobiogeography, Tusco-Sardinian vertebrate faunas, latest Miocene.

The Late Miocene continental successions of the so-called Tusco-Sardinian palaeobioprovince (several sites in Grosseto Province, Tuscany, and Fiume Santo in NW Sardinia) record at least four superimposed vertebrate-bearing horizons. The Baccinello-Cinigiano basin (Grosseto) sedimentary succession, bracketed in the time span 8.2 - 6.4 Ma (Rook et al., 2011), is one of the longest continuous vertebrate bearing continental succession in the Neogene Italian record. The recentmost (Messinian) vertebrate faunal assemblage includes the colobine monkey *Mesopithecus*, and testifies a dramatic faunal turnover in respect to older ones, well known for recording endemic vertebrate assemblages including the youngest European Miocene hominoid, *Oreopithecus bambolii* (OZF assemblages in Bernor et al., 2001).

A similar turnover pattern (Late Miocene ape/latest Miocene Cercopithecidae) is generally observed in Late Miocene continental successions across Eurasia and an abundant literature reports that Late Miocene Eurasian hominoids distribution closely tracks climatic/environmental changes during the 12–9 Ma interval, until their extinction in western Europe (Andrews et al., 1996). In the primate record the dispersion of Cercopithecidae and contraction of hominoids is interpreted as an event depicting a pattern of “continentalization” in the Old World.

Recent data provide no evidence for an ecologically significant difference in palaeoecology and vegetation between the ecosystems inhabited by *Oreopithecus* and those from after its extinction. Different lines of evidence support that environmental change was not an important factor in the disappearance of the endemic OZF assemblages, and substantiates the interpretation by previous workers (cfr. Chesi et al., 2009) that the extinction was driven largely by changes linked to the latest Miocene palaeogeographic evolution of the northern Tyrrhenian area, and associated interaction with species from mainland Europe.

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## The response of the plant kingdom to the Late Ordovician climatic changing and related mass extinction; an example from the Zagros Basin (Southern Iran)

Spina A.\*<sup>1</sup>, Cirilli S.<sup>1</sup>, Rettori R.<sup>1</sup>, Aria Nasab M.R.<sup>2</sup>, Hamdi B.<sup>3</sup> & Kani A.<sup>4</sup>

1. Dipartimento di Fisica e Geologia-Università di Perugia. 2. Geology Department, Earth Sciences Faculty, Kharazmi University, Tehran, Iran. 3. Geological Survey of Iran 4. Geology Department, Shahid Beheshti University, Tehran, Iran.

Corresponding email: [amalia.spina@unipg.it](mailto:amalia.spina@unipg.it)

Keywords: Late Ordovician, glaciation, terrestrialization.

During the Late Ordovician, many Gondwana regions were affected by a major glaciation that resulted in global palaeoenvironmental perturbations and was associated with one of the largest extinction events in biosphere's history. Sporomorph assemblages from the Late Ordovician sediments, including the Hirnantian glacial-related deposits of Gondwana, consist of the occurrence of terrestrially-derived palynomorphs (mainly cryptospores and, more rarely, trilete spores), which testifies a key phase of the evolution of the plant terrestrialization. The cryptospore-producing embryophytic vegetation was not significantly affected by the Late Ordovician glaciation: this should indicate a large tolerance to climatic changing of the earliest land plants. In the present study, rich palynological assemblages have been recovered from Gondwanan deposits of Late Ordovician age in the Zagros Basin (Southern Iran). The marine and terrestrial palynological associations include acritarchs, chitinozoans and cryptospores. The age of the deposits is well constrained by means of palynomorphs (acritarchs). Sporomorph assemblages mainly include permanent tetrads as *Tetraedraletes medinensis*, *Cheilotetras caladonica* and *Velatitetras* spp., permanent dyads as *Dyadospora murusattenuata* and *D. murusdensa*, pseudodyads as *Segestrespora* spp. and *Pseudodyadospora laevigata*. Monads are less abundantly present and are characterized by *Gneudnaspora divellomedia*. These findings provide new data which contribute to the understanding of the evolution of the early vegetation cover in Gondwana during a time of climatic change and biospheric perturbations.

## **SESSIONE S4**

### **Geoscience frontiers: the role of Polar Regions in Global change**

#### *CONVENORS*

*G. Villa (Univ.Parma)*

*M. Frezzotti (ENEA, Roma)*

*M. Rebesco (OGS, Trieste)*

*F. Talarico (Univ. Siena)*

## A multiproxy approach to reconstruct late Quaternary climate and environments in the Ross Sea (Antarctica)

Bergami C.\*<sup>1</sup>, Capotondi L.<sup>1</sup>, Langone L.<sup>1</sup>, Sangiorgi F.<sup>1-2</sup>, Giglio F.<sup>1</sup> & Ravaioli M.<sup>1</sup>

1. CNR - National Research Council of Italy, ISMAR - Institute of Marine Sciences, Bologna. 2. Marine Palynology and Paleoceanography, Dept. Earth Sciences, Faculty of Geosciences, Utrecht University, The Netherlands.

Corresponding email: [caterina.bergami@ismar.cnr.it](mailto:caterina.bergami@ismar.cnr.it)

Keywords: Antarctic paleoceanography, microfossils, geochemistry.

Traditionally, paleoclimatic and paleoenvironmental studies of the Southern Ocean are primarily based on analyses of remains of diatoms, since these algae are, quantitatively, the most important eukaryotic phytoplankton class in the region with respect to export production. However, this approach may have led to the potential loss of information, which could be derived by other biological proxies.

This study aims at investigating palaeoenvironmental changes occurred in the late Quaternary in the South-western Ross Sea by employing less exploited micropaleontological proxies (foraminifera and dinoflagellate cysts), integrated with geochemical data (TOC, BioSi, and TEX<sub>86</sub>). Our combined multiproxy approach allows us to identify some climatic events with sudden changes in SST and sea-ice extent. The data derive from a box core (BC22) collected at 790 m water depth in the Lewis basin (SW Ross Sea). The chronology of the core was defined by means of three AMS <sup>14</sup>C ages determined on the bulk organic fraction. The sedimentary sequence consists of three lithologies: massive diamicton at the base (basal till, 37-35 cm), overlain by grey sandy sediments (deposition beneath an ice-shelf, 35-25.5 cm), and topped by olive biosiliceous mud (seasonally open sea, 25.5-0 cm). Focusing on the biosiliceous mud unit, radiocarbon chronology together with other geochemical proxies suggest that the present-day seasonal open-sea conditions were established about 6.5 cal ka BP in agreement with other studies in the same area.

Foraminiferal assemblage is dominated by agglutinated benthic foraminifera such as *Miliammina arenacea*, *Reophax* sp., *Trochammina* sp. and *Hyperhammina* sp. The association is abundant and diversified in the uppermost portion of the core (0-1.75 cm), which represents a climatic phase younger than ~200 a, and is characterized by the presence of some calcareous specimens, too. This would indicate a deeper Carbonate Compensation Depth, probably due to relatively stable and warmer environmental conditions, as also confirmed by SST reconstruction based on TEX<sub>86</sub>.

The dinocyst assemblage is dominated by *Selenopemphix antarctica*, with *Cryodinium meridianum*, *Brigantedinium* spp., and *Islandinium* sp. also commonly present. A striking feature is the massive occurrence, between 2.5 and 5.5 cm of *Polarella glacialis*, a small photosynthetic dinoflagellate, which blooms in sea-ice brine channels, originally described from the Ross Sea and never previously observed in a sedimentary sequence. The timing of this interval suggests that it may correspond to a colder period, probably imputable to the Little Ice Age (LIA) in this area, characterized by a prolonged sea-ice season and stronger katabatic winds, causing enhancing activity of the Ross Sea polynya.

## Research and School for the Polar Sciences: a teacher training experience told by participants

Cicconi A.\*<sup>1</sup>, Beltrami M.L.<sup>2</sup>, Cattadori M.<sup>3</sup>, Ciceri P.<sup>4</sup>, Macario M.<sup>1</sup> & Miserere L.<sup>5</sup>

1. School of Science and Technology, University of Camerino, Camerino. 2. Ufficio Scolastico Regionale, Direzione Lombardia, Cremona. 3. Trento Science Museum, Trento. 4. I.C. Alighieri, Scuola secondaria di primo grado "Ottolini", Rescaldina, Milano.  
5. I.I.S. "J.C. Maxwell" Nichelino, Torino.

Corresponding email: [profic@libero.it](mailto:profic@libero.it)

Keywords: Outreach, Education, Polar Sciences.

This work aims to show how outreach meetings between researchers and teachers become a the starting point for a variety of educational activities that are able to involve a number of students , teachers and stakeholders at greater extent than other methods of dissemination.

The Polar Summer School for Teachers (SPEs) was a teachers professional development initiative organized in the years 2011, 2012 and 2013 by the National Antarctic Museum (MNA), with the support of the Italian Ministry of Education in cooperation with the National Program for Antarctic Research (PNRA). SPEs school was carried out with the collaboration of international research and outreach organizations such as the International Polar Foundation (IPF) and Polar Educator International (PEI).

The SPEs was the very first entirely educational project ever funded by the PNRA. The aim was to raise awareness of public opinion and, in particular schools, of the role and importance of polar regions for the Earth system.

A total of 40 teachers of secondary schools took part to the Spes and coming from all over Italy (including the authors of this work) attending a week long course lasting, for over 40 hours of lessons.

The main aims of the Spes school were:

- Highlight the crucial role in the school of the Polar Sciences related to the Integrated Sciences
- Creation of a network of Italian Science teachers aiming at bringing Polar Science topics in Italian science curricula
- Create a link between the polar researchers and teachers of the Italian schools

The program of the Spes include the following different activities:

- Lectures given by polar researchers.
- Workshop activities, experiments and exhibits to be used by participants in their classroom.
- Field activities to the sea to show monitoring activities that could be made in the classroom..
- Participation of a selected teacher, one per year, to an Antarctic scientific expedition in the framework of the Italian Antarctic Program

In addition to the course, the SPEs organization provided support to participants teachers all along the subsequent school year with the purpose of helping them to effectively include polar topics in their lessons.

This innovative approach of SPEs to the topic of the professional development of science teachers give a birth to several projects, activities and products made by participants in their school. Like for instance: preparation of a science-theater show of a subject about Antarctic exploration performed by students 11 years old, a photo exhibition "Above and below the ice" (realized by ENEA), conferences for the local community, a competition for students, training courses for teachers (included in the plan ISS Teaching Experimental Sciences) on the subject of climate change and Polar Sciences, educational materials produced during the participation in the XVIII Italian Expedition in Antarctica.

The purpose of this work is to illustrate some of these products and the results of a survey carried among the participants to the SPEs. The authors will describe the benefits of this kind of experience on their professional development and on dissemination of polar research outcomes.

## Antarctic Bottom Water flow pathway inferred from geomorphology and seismic stratigraphy of the George V Land margin

De Santis L.\*<sup>1</sup>, Caburlotto A.<sup>1</sup>, Donda F.<sup>1</sup>, Lucchi R. G.<sup>1</sup>, Presti M.<sup>1</sup>, Accettella D.<sup>1</sup>, Geletti R.<sup>1</sup>, Wardell N.<sup>1</sup>, Colizza E.<sup>2</sup>, Candoni O.<sup>1-2</sup>, Tolotti R.<sup>3</sup>, Macri P.<sup>4</sup> & Giorgetti G.<sup>5</sup>

1. Istituto Nazionale di Oceanografia e di Geofisica Sperimentale, Trieste. 2. Dipartimento di Matematica e Geoscienze, Università di Trieste. 3. Dipartimento di Scienze della Terra, dell'Ambiente e della Vita, Università di Genova. 4. Istituto Nazionale di Geofisica e Vulcanologia, INGV, Roma. 5. Dipartimento di Scienze Fisiche, della Terra e dell'Ambiente, Università di Siena.

Corresponding email: [ldesantis@ogs.trieste.it](mailto:ldesantis@ogs.trieste.it)

Keywords: swath bathymetry, seismic reflection, Italian Antarctic Program.

Swath bathymetry and seismic reflection profiles collected by the Italian Antarctic Program (PNRA WEGA and MOGAM projects), combined with Australian (CSIRO) oceanographic measures (Williams et al., 2010) and benthic fauna sampling (Post et al., 2010), in the offshore of the George Vth Land, document evidence of bottom water cascading currents and turbidity currents inside continental slope canyons.

The continental slope is incised by canyons heading to shelf edge sills and bounding sedimentary ridges of Miocene age. Dense shelf water forms in coastal polynya and is exported off the shelf break to form the Adélie Land branch of the Antarctic Bottom Water (ALBW, Rintoul et al., 2008). This bottom water is detected by CTD and mooring measurements up to about 3200m of depth, in the Jussieu canyon and further to the west. The speed of the ALBW is enough to transport fine sand and silt from shallow to deep water as documented by sea bed sediments. Similar bottom currents activity is recorded also during Quaternary glacial and interglacials (Caburlotto et al., 2009, Macri et al., 2005) with source in the George V Land rocks and in the continental shelf (Damiani et al., 2006).

The meandering character of the Jussieu canyon and the sediment wave field on its eastern ridge, would suggest that they likely formed under the action of downslope, continuous, bottom current, since the early Pliocene (Escutia et al., 2010).

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## U-Pb SHRIMP zircon dating of magmatic rocks dredged from the South Tasman Rise (Australia)

Fioretti A.M.<sup>1</sup>, Bergomi M.<sup>2</sup>, Caironi V.\*<sup>3</sup>, Korsch R.J.<sup>4</sup>, Tunesi A.<sup>2</sup> & Visonà D.<sup>5</sup>

1. CNR - Istituto Geoscienze e Georisorse Padova. 2. Dipartimento di Scienze dell'Ambiente e del Territorio e di Scienze della Terra, Milano Bicocca. 3. Dipartimento di Scienze della Terra A.Desio, Università degli Studi di Milano. 4. Geoscience Australia, Canberra, ACT, Australia. 5. Dipartimento di Geoscienze, Università di Padova.

Corresponding email: [valeria.caironi@unimi.it](mailto:valeria.caironi@unimi.it)

Keywords: South Tasman Rise, U-Pb SHRIMP zircon, AGSO cruise 147.

The South Tasman Rise (STR) consists of the west- and east-South Tasman Rise, which are submerged continental fragments that were part of the East Gondwana Continent. The STR formed following the extension between Antarctica and Australia that generated the Tasmanian Gateway. It is located between Tasmania and Antarctica and represents a vital, but often overlooked, link to understand the geological evolution of both North Victoria Land and Tasmania. Reconstruction of Gondwana shows that STR was contiguous to several continental fragments that are now thousands of km apart. Because of its central location in the plate boundary framework that developed within East Gondwana, the STR underwent all the major tectonic events that led to the dispersal of Gondwana. The STR is therefore a centrepiece in understanding the complex tectonic history of this region.

Extensive sampling of STR rocks took place during AGSO cruise 147. Investigation on the metamorphic rocks of the STR pointed out interesting correlations with rocks from the Wilson Terrane and the Lanterman Metamorphics (Antarctica) and from Tasmania (Berry et al., 1977).

Based on this evidence, and aiming at clarifying the correlation between mainland Australia, Tasmania and Antarctica, we undertook a detailed petrologic and geochronologic study on magmatic rocks dredged at 10 different sites from South Tasman Rise. Seven of these rocks yield Cambrian ages in the range 487-507 Ma, consistent with the Ross-Delamerian orogen; one sample is a granite gneiss of late Proterozoic crystallization age (ca. 740 Ma), which corresponds to the Wickham event (Tasmania) or Beardmore orogen (Antarctica); one sample has Grenville age (Fioretti et al., 2005); and one sample is Late Devonian (ca. 363 Ma), an age that is well represented in Australia, Tasmania and Antarctica.

Petrographic observation, geochemical investigation and zircon typologic study are presented here to characterize these rocks, and to test their possible correlation with coeval rocks in Antarctica and Australia.

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## **Dome C: a potential site where to find a 1.5 million year “oldest ice” record of climate and greenhouse gases from Antarctica**

Frezzotti M.\*<sup>1</sup>, Urbini S.<sup>2</sup> & Zirizzotti A.<sup>2</sup>

1. ENEA, Roma. 2. INGV, Roma.

Corresponding email: [massimo.frezzotti@enea.it](mailto:massimo.frezzotti@enea.it)

Keywords: Paleoclimate, ice core, Dome C, Antarctica.

After the success of EPICA, the European Project for Ice coring in Antarctica which, at Dome C (East Antarctica) has provided access to climate and environmental records covering the last 800 ka, the international ice core community, under the auspices of International Partnerships in Ice Core Sciences (IPICS), is now engaged in the challenge to obtain the oldest possible ice core record from Antarctica. An ice core record reaching back to or towards 1.5 Ma ago would be a major step forward in understanding Quaternary climate, and would further our understanding of the relationship between greenhouse gases and climate.

Throughout the EPICA era, climate cycles of roughly 100 ka years held sway. Marine sediments show that just before this time, cold and warm periods alternated instead on a timescale of 40 ka years. Understanding this change would provide a key to understanding the more recent variability in other words, to understand why our present climate is as it is. Proposed causes include a trend in CO<sub>2</sub>, and the effect in data of opposing changes in the two polar regions.

In order to attain the goals, two or more cores will be required in order to provide replication in a regime where flow disturbance is possible. Horizontal ice flow should be avoided as much as possible, as ice transported over long distances in the bottom hundred meters of ice is prone to flow disturbances. Based on ice thickness, bedrock topography, accumulation rate and basal temperature, the likely search region is the ice divide of East Antarctica, with a region south of Dome C provoking particular interest; other areas should also be researched (Dome F, Dome B, Dome A and their ice divide area).

After the current planning stage, a broad area geophysical survey and a season of shallow drilling are needed in any candidate region. This will provide enough data for a more targeted modelling effort that will provide candidate sites. Multinational consortia would be expected to form in order to tackle each candidate site. Before being confirmed as an “oldest ice” site, each candidate should undergo more detailed local survey and we would also recommend the drilling of a 600 m core to reach the last glacial maximum before heavy equipment is committed.

## **Significance of extreme glacimarine sedimentation on the NW Barents Sea continental margin**

Lucchi R.G.\*

OGS, Istituto Nazionale di Oceanografia e Geofisica Sperimentale, Trieste.

Corresponding email: [rglucchi@inogs.it](mailto:rglucchi@inogs.it)

Keywords: ice stream dynamics, plumites, deglaciation.

The post Last Glacial Maximum depositional history of the Storfjorden and Kveithola trough-mouth fans in the northwestern Barents Sea has been investigated within two coordinated Spanish and Italian projects in the framework of the International Polar Year (IPY) Activity 367, NICE STREAMS.

Sediment facies analysis allowed the distinction of a number of depositional processes whose onset appears closely related to ice stream's dynamics, oceanographic patterns, and sea-level changes in response to climate change. Highly-consolidated glacial diamicton, deposited during glacial maxima on the upper slope, indicating ice streams grounded at the shelf edge. Massive release of IRD was associated to increased calving rates with possible outer ice streams lift off and collapse at the inception of deglaciation. The presence of a several meter-thick sequence of interlaminated sediments deposited by subglacial outbursts of turbid meltwater (plumites) indicates rapid ice streams' melting and retreat. Crudely-layered and heavily-bioturbated sediments deposited in the later stages of deglaciation by contour currents under climatic/environmental conditions favorable to bioproductivity.

The extreme sedimentation rate of 3.4 cm a<sup>-1</sup> calculated for the plumites from the upper-slope area indicates a massive, nearly instantaneous (less than 150 years), terrigenous input corresponding to an outstanding meltwater event. We indicate these interlaminated sediments to represent the high-latitude marine record of Meltwater Pulse 1a (MWP-1a).

## Extreme depositional events on the NW-Barents Sea continental margin

Lucchi R.G.<sup>\*1</sup>, Colmenero-Hidalgo E.<sup>2</sup>, Siervo F.J.<sup>3</sup>, Sagnotti L.<sup>4</sup>, Barcena M.A.<sup>3</sup>, Melis R.<sup>5</sup>, Morigi C.<sup>6</sup>,  
Villa G.<sup>7</sup>, Urgeles R.<sup>8</sup>, Camerlenghi A.<sup>1</sup> & Rebesco M.<sup>1</sup>

1. OGS-Trieste. 2. Facultad de CC. Biológicas y Ambientales, Universidad de León, Spain. 3. Department of Geology, University of Salamanca, Spain. 4. INGV-Roma, Italy. 5. Dipartimento di Matematica e Geoscienze, Università di Trieste. 6. Dipartimento di Scienze della Terra, Università di Pisa. 7. Dipartimento di Fisica e Scienze della Terra, Parma. 8. Institut de Ciències del Mar, CSIC-Barcelona, Spain.

Corresponding email: [rglucchi@inogs.it](mailto:rglucchi@inogs.it)

Keywords: Barents Sea, plumites, MWP-1a.

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## Post-LGM palaeoclimatic changes derived from diatom census counts in the Western Ross Sea area (East Antarctica)

Mezgec K.\*<sup>1-2</sup>, Colizza E.<sup>2</sup>, Melis R.<sup>2</sup> & Lucchi R.G.<sup>3</sup>

1. Dottorato in Scienze della terra, ambientali e polari, Dipartimento di Scienze Fisiche, della Terra e dell'Ambiente, Università di Siena. 2. Dipartimento di Matematica e Geoscienze, Università di Trieste. 3. OGS (Istituto Nazionale di Oceanografia e di Geofisica Sperimentale) Trieste.

Corresponding email: [karinmezgec@hotmail.com](mailto:karinmezgec@hotmail.com)

Keywords: Diatoms, Ross Sea, palaeoclimate.

The Ross Sea is one of the most important region of the Southern Ocean since it is involved in the formation of dense, saline and super-cooled water masses (the High Salinity Shelf Water – HSSW and the Ice Shelf Water - ISW). These water masses descend into the deep ocean to form Antarctic Bottom Water (AABW) which plays a key role in the global thermohaline circulation and, in turn, in the global climate system.

Four marine sediment cores and two box cores have been selected along a transect, considering the possible preferential path of the HSSW, passing across the Joides Basin Trough, on the continental shelf (cores ANTA99-cJ5 and ANTA99-cJ3), and reaching the Central Basin, a confined depositional system located at the mouth of Joides Basin (cores ANTA95-c98, KI13-c1 and box cores KI13-bc4, KI13-bc2). Core ANTA99-cJ5 was partly studied within the ESF-PNRA HOLOCLIP (Holocene climate variability at high-southern latitudes: an integrated perspective) Project, while all other cores have been analysed in the framework of the PNRA-ROSSLOPE (Past and present sedimentary dynamic in the ROSS Sea: a multidisciplinary approach to study the continental SLOPE) Project. Multidisciplinary analyses were performed in order to study the past oceanographic and climatic evolution of the Western Ross Sea occurred during the post-LGM deglaciation phases. Both cores collected in the Joides Basin are characterized by diatomaceous mud with high abundance of *Chaetoceros* Hyalochaete resting spores (CRS) at the base of the sequence that indicate the beginning of the glacial retreat. The subsequent up-core increase in *Fragilariopsis curta* suggests the establishment of seasonal sea ice associated with the Ross Ice Shelf retreat.

The cores collected on the continental slope are, instead, characterized by gravelly-silty-sand to clayey silt with mixed-age diatom species that are present at the base of the sequence with high relative abundance of *Eucampia antarctica* spores which could be linked with sea ice. On the other hand the upper part of the core is rich in post-glacial diatom species with an increase in *F. kerguelensis* which suggests open ocean conditions with reduced sea ice presence.

A comparison between the diatom assemblages identified in the cores allowed us to suggest a paleoclimatic and paleoenvironmental reconstruction of the Western Ross Sea area after LGM, and to highlight the glacial/interglacial transition on the basis of diatom's species abundance variations through the cores.

## Sources and properties of aerosol particles upon Ny-Ålesund (Svalbard Islands): results of integrated vertical profile measurements and electron microscopy analyses

Moroni B.\*<sup>1</sup>, Cappelletti D.<sup>2</sup>, Ferrero L.<sup>3</sup> & Bolzacchini E.<sup>3</sup>

1. Dipartimento di Ingegneria Civile e Ambientale e Centro di Eccellenza SMAArt, Università di Perugia. 2. Dipartimento di Chimica, Biologia e Biotecnologie, Università di Perugia. 3. Centro di Ricerca POLARIS, Università di Milano-Bicocca.

Corresponding email: [b.moroni@tiscali.it](mailto:b.moroni@tiscali.it)

Keywords: mineral dust, SEM-EDS, OPC, miniDiSC, climate and environment.

Aerosols and their interactions with cryosphere, clouds and sea can have a significant impact on the radiation balance in the Arctic. The study of the nature, properties and vertical distribution of aerosol particles in the lower troposphere is, thus, essential to understand the key processes in the Arctic climatic system.

On these grounds, an intensive field campaign was carried out at Ny-Ålesund in spring 2011 and summer 2012 in the framework of the PRIN 2009 “ARCTICA” project. Size-segregated particle samples were collected both at ground level (~ 50 m a.s.l.) and along vertical profiles (up to ~ 1,000 m a.g.l.). In this latter case a helium-filled tethered balloon equipped with an optical particle counter (OPC), a nanoparticle monitor (miniDiSC) and a meteorological station was employed. Individual particle size, morphology and chemical composition were investigated by scanning electron microscopy coupled with energy dispersive microanalysis (SEM-EDS). The results were integrated with the results and elaborations of OPC and miniDiSC measurements along the vertical profiles.

Silicates, carbonates, metal particles, sulfate and chloride salts are the main particle groups in the samples. They are mostly from soil and from sea spray natural sources. The nature and properties of the particle types in the troposphere can greatly change depending on the pattern and evolution of air mass circulation during time. In particular the chemical properties of spinel- and Ti- metal oxides reveal distinct geological units of provenance. The geological record combined with air mass back trajectory evaluations and aerosol particle number concentration profiles provide valuable information for the identification of the particle source regions. Also, the concentration and the mineral chemistry of different particle types (*e.g.*, sheet silicates) show a vertical pattern and a seasonal trend in some instance due to air mass transfer and cloud formation. This fact provides some new information about turbulence in the very stably stratified regime of the polar region.

The properties of different particle types modulate the Arctic aerosol properties. In particular, the particle size distribution of sheet silicates (*e.g.*, illite) can have a great influence on the contact freezing probability and, thus, on the extent of ice nucleation on dust. On the other hand, the size and shape distributions of hygroscopic salt particles (*i.e.*, chlorides and sulphates) are such that they can have a significant radiative impact through direct influence on light scattering.

In conclusion, SEM analyses provide a good tool to find the nature and sources of particles, and to evaluate the aerosol properties. When combined with particle number concentration measurements it may help to unravel some aspects of the modelling of atmospheric processes such as dust inputs, particle behaviours, and spatial/temporal evolution of aerosol properties.

## **Syn depositional faulting in the Late Triassic succession of Kvalpynten, Edgeøya, East Svalbard**

Ogata K.\*<sup>1</sup>, Anell I.<sup>3</sup>, Braathen A.<sup>2-3</sup>, Osmundsen P.T.<sup>3-4</sup>, Smyrak-Sikora A.<sup>3</sup>, Husteli B.<sup>3</sup>,  
Olaussen S.<sup>3</sup> & Maher H.<sup>5</sup>

1 Dipartimento di Fisica e Scienze della Terra - Università degli Studi di Parma. 2. Department of Geosciences - University of Oslo. 3. Department of Arctic Geology - University Centre in Svalbard. 4. Geological Survey of Norway. 5. Department of Geology - University of Nebraska at Omaha.

Corresponding email: [kei.ogata@unipr.it](mailto:kei.ogata@unipr.it)

Keywords: East Svalbard, Late Triassic, Synsedimentary faulting, growth stratigraphy.

The Late Triassic De Geerdalen Formation, exposed in Kvalpynten on Edgeøya (East Svalbard) comprises two parts: a faulted array of half-graben basins with a complex stratigraphic architecture related to syn depositional faulting, and an overlying, less disturbed, deltaic or estuarine succession. The seismic-scale (ca. 8 km x 500 m) cliff exposure allows detailed analyses of the sedimentary architecture within individual half-grabens, along with the identification of sedimentary facies assemblages. The basin-bounding faults are generally E-W to NW-SE-trending, with a subordinate NE-SW trend. These faults show listric appearance, ductile character and displacements in the order of meters to tens of meters, flattening and soling out in the basal shale interval. Some more brittle, deeply rooted, sharp faults without evidence of rotation are also observed. The half-graben successions consist of unconformably stacked and interfingering composite sandstone bodies arranged in coarsening and thickening upward units up to tens of meters thick, reflecting different stages of fault growth. The component layered wedges of fine-grained sandstones, heterolithic strata and mudstones thicken towards the footwall and are overlain by sandstone units that show apparent lateral progradations in the hanging wall direction. These are, in turn, capped by several meters of thick, massive sandstone wedges that thicken towards the footwall. The sedimentary structures observed in the composite sandstone units are: 1) symmetrical wave ripples, 2) reworked current ripples and 3) small-scale, trough- (sigmoidal?) and planar cross-bedding. Bidirectional foresets has been observed locally, and hummocky cross-stratified beds occur within the mudstones, especially in the lower half of the succession. Heterolithic intervals are commonly intercalated within the composite sandstone bodies, displaying wavy, lenticular and/or flaser bedding. The overlying draping sandstones display more laterally continuous bedsets, channel infills and localized meter-scale clinofolds. The main inferred sediment transport is approximately towards the west, consistent with the overall direction indicated by larger bedforms. The sedimentary unit draping the half-grabens appears also to have been sourced from the east. In this framework, the lower De Geerdalen Formation exposed at Kvalpynten reflects mixedshallow marine conditions with combined tidal to distal deltaic/estuarine influence that prevailed within the half-grabens, whereas a west-northwestward deltaic progradation seems to characterize the upper part. The origin of these structures has been recently attributed to the reactivation of Paleozoic basement-rooted fault zones during the Uralide foreland deformation, in turn promoting the development of the shallower synsedimentary faults in the upper Triassic section (Anell et al., 2013).

Anell I., Braathen A., Olaussen S., Osmundsen P.T. 2013. Evidence of faulting contradicts a quiescent northern Barents Shelf during the Triassic. *First Break*, 31, 67-76.

## **Tectonic and topographic evolution of an oblique rifting shoulder: the South Ross Sea region, Antarctica**

Olivetti V.\*<sup>1</sup>, Rossetti F.<sup>1</sup>, Balestrieri M.L.<sup>2</sup>, Cornamusini G.<sup>3</sup> & Talarico F.<sup>3</sup>

1. Dipartimento di Scienze - Università di Roma Tre. 2. IGG-CNR sez Firenze. 3. Dipartimento di Fisica e Scienze della Terra e dell'Ambiente, Università di Siena.

Corresponding email: [valerio.olivetti@uniroma3.it](mailto:valerio.olivetti@uniroma3.it)

Keywords: tectonics, Antarctica, topography.

Ross sea region shows unique tectonic peculiarities on Earth: one of the largest Cenozoic intracontinental rift, the West Antarctic Rift System (WARS), and one of the highest extensional/rift flank mountain belt, the Transantarctic Mountains (TAM). The TAM is a mountain belt some thousands meters high that encompasses the western shoulder of the WARS, marking the boundary with the East Antarctic craton. The present-day knowledge of the WARS structure and evolution has been obtained mainly by seismic and geophysical studies, which reveal a complex, N-S trending horst and graben architecture. The rifting evolution is commonly considered polyphase, starting in the early Cretaceous linked to the Gondwana break-up and followed by a major Cenozoic phase, at c. 50-40 Ma. Rifting activity was accompanied by diffuse alkaline magmatism of the McMurdo Volcanic Group since Oligocene times. Tectonic evolution of the TAM is strongly coupled to WARS evolution. In fact, change from orthogonal to oblique rifting, right-lateral transcurrent tectonics and recent rifting activity have been documented by the integration of onshore and offshore data. Therefore, in order to shed light into the modes of rift propagation and evolution it is critical to define the tectonic framework linking the TAM shoulder structure to that of the WARS. Here we present new structural data from the Royal Society Range, collected during the XXVIII Italian Expedition in Antarctica. The Royal Society Range, located ca. one hundred km south of the McMurdo station, is a part of the TAM shoulder in south Victoria Land, facing a major volcanic district. In the field, the major faults are roughly N-S oriented but NNE-SSW and NW-SE orientation are also observed. The fault zones exhibits up to several meters thick, steeply-dipping damage zones, with kinematic indicator attesting for the dominant right-lateral strike-slip fault motion. Extensional structures are also reported. Structural data has been integrated with topography analysis. In fact, in hyper-arid polar environment, where erosion is very limited, topography may be a direct result of tectonic vertical movements. The regional topography is typified by a high mean elevation, which shows maximum values distributed along the rift flank. Swath profiles parallel to rift flank shows large wave-length undulation of the topography. The long wave length topography points out that the more uplifted chain sector occurred at the intersection between the NW-SE and the N-S fault systems. We then propose that the interplays of the two fault systems are the first-order cause of the tectonic architecture of the Royal Society Mountains architecture and development of the Mc Murdo volcanism.

## Evolution of the Transantarctic basin from Trias to Jurassic: relations between magmatism, bio-events and paleoclimate

Pertusati P.C.<sup>1</sup>, Albani R.<sup>1</sup>, Carosi R.<sup>2</sup>, Montomoli C.\*<sup>1</sup>, Ribecai C.<sup>1</sup>, Santacroce R.<sup>1</sup> & Zanchetta G.<sup>1</sup>

1. Dipartimento di Scienze della Terra - Università di Pisa. 2. Dipartimento di Scienze della Terra - Università di Torino.

Corresponding email: [chiara.montomoli@unipi.it](mailto:chiara.montomoli@unipi.it)

Keywords: Beacon Supergroup, Paleoclimate, bio-events.

The post Ross orogeny tectonic evolution of the Northern Victoria Land (Antarctica) involves the development of a Transantarctic basin on the margin of eastern Gondwana during the Middle Paleozoic that persisted until the initial stage of Gondwana break-up, during the Early Jurassic. The Gondwana break-up is associated to the development of the large Ferrar Igneous Province, characterized by a thick sequence of flood basalt (Kirkpatrick Basalt) and related sill and dolerite intrusions (Ferrar Dolerite) (Elliott, 2013).

Extensive stratigraphic and palynological works have been done on the sedimentary sequence resting unconformably over the metamorphic basement (Beacon Supergroup) (Pertusati et al., 2006, Bomfleur et al., 2014 and references therein) and on the overlying Kirkpatrick Basalt (Elliott, 2013 and reference therein) cropping out north of the Italian Antarctic Station.

During the XXVIII scientific expedition extensive field work has been conducted in the southern outcrops of the 1:250.000 sheets "Mt. Joyce" and "Convoy Range". The Beacon supergroup and overlying basalts have been studied and sampled. Two stratigraphic sections have been detailed studied: "Ford Peak" (Mt. Joyce) and "The Mitten" (Convoy Range).

Palynological analysis have been carried out on samples from both sections. All processed samples from "Ford Peak" section seem to be barren. In the samples from "The Mitten" section a rich and well preserved late early to middle-late Triassic microflora has been identified.

Also in the southern area two volcanic episodes have been recognized: the lower one associated to volcanoclastic deposits and breccias, including volcanic e sub-volcanic clasts, and the upper one characterized by extensive lava flow. All the sequences have been intruded by doleritic sills and dikes.

Preliminary isotopic analyses on the organic fractions of the different units seems to show consistent variability (in the order of more than 5‰), which may suggest important environmental changes possibly associated with general reorganization of carbon cycle. If this signal is a persistent feature which can be correlated to global events need to be verified with a larger regional isotopic dataset in the future.

Bomfleur B., Schoner R., Schneider J.W., Vierech L., Kerp H. & McKellar J.L. 2014. From the Transantarctic Basin to the Ferrar Large Igneous Province New palynostratigraphic age constraints for Triassic-Jurassic sedimentation and magmatism in East Antarctica. *Review of Paleobotany and Palynology*, 207, 18–37.

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## **Polar marine diatoms: key markers for Cenozoic environmental shifts. Sedimentary and paleo-environmental reports from Antarctic continental margin (Ross Sea, Wilkes Land and Prydz Bay)**

Tolotti R.\*<sup>1</sup>, Bonci C.<sup>1</sup>, Crosta X.<sup>4</sup>, Caburlotto A.<sup>2</sup>, Colizza E.<sup>6</sup>, Corradi N.<sup>1</sup>, De Santis L.<sup>2</sup>, Harwood D.<sup>3</sup>,  
Lucchi R.G.<sup>2</sup>, Lodolo E.<sup>2</sup> & Salvi G.<sup>5</sup>

1. Dipartimento di Scienze della terra, dell'ambiente e della vita (DISTAV), Università di Genova; 2. Istituto Nazionale di Oceanografia e Geofisica Sperimentale (OGS), Trieste; 3. Department of Earth and Atmospheric Sciences, University of Nebraska – Lincoln USA. 4. UMR-CRS 5805 EPOC, Université Bordeaux 1, Avenue des Facultés 33405 Talence Cedex, Bordeaux, France; 5. Museo Nazionale dell'Antartide (MNA), Trieste; 6. Dipartimento di Matematica e Geoscienze (DMG), Università di Trieste.

Corresponding email: [raffaella.tolotti@unige.it](mailto:raffaella.tolotti@unige.it)

Keywords: Polar marine diatoms, Cenozoic biostratigraphy, paleoceanography.

Marine diatoms are sensitive to water-mass distribution and their physical-chemical and biotic preferences affect their biogeographical distribution. In sedimentary records, although altered by secondary processes such as dissolution, they track the primary signal formed in surface water. This makes them the major biostratigraphic and environmental markers in the Southern Ocean as they record sea-surface temperatures, sea ice and other parameters useful for paleoceanographic and paleoclimatic reconstructions (Jordan et al. 2010; Leventer et al., 2010; Crosta, 2011; Escutia et al., 2011). We present three case studies of diatom biostratigraphy and paleoceanographic reconstructions performed on Antarctic sediments recovered from: 1) Pleistocene-Holocene sequences in the Ross Sea and Wilkes Lands, with evidences of glacial/deglacial-interglacial phases (PNRA and IMAGES-CADO Projects in Atlantic and Australian Sectors) (Caburlotto et al., 2010; Tolotti et al., 2013) and 2) Late Eocene-Early Miocene sequences in Prydz Bay, with preliminary micropaleontological results and biostratigraphy related to the greenhouse/ice-house transition (ODP Project in the Indian Sector) (Lagabrielle et al., 2009; Suto et al., 2012).

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## Water-soluble trace and rare earth elements in Arctic aerosol as tracer of different sources

Turetta C.\*<sup>1</sup>, Zangrando R.<sup>1</sup>, Barbaro E.<sup>1</sup>, Gambaro A.<sup>1,2</sup>, Gabrieli J.<sup>1</sup> & Barbante C.<sup>1,2</sup>

1. Istituto per la Dinamica dei Processi Ambientali - CNR Venezia. 2. Dipartimento di Scienze Ambientali Statistica e Informatica – Università Ca' Foscari Venezia.

Corresponding email: [clara.turetta@idpa.cnr.it](mailto:clara.turetta@idpa.cnr.it)

Keywords: trace elements, rare earth elements, arctic aerosol.

The elemental composition of water-soluble size-fractionated airborne particulate matter was investigated in order to better understand the distribution of water-soluble fraction of trace elements (TE) and of rare earth elements (REE) among different particulate sizes. Samples were collected at a polar station in the Svalbard Islands (78 55 07 N, 11 53 30E) from 19 April to 14 September 2010. A five-stage high volume cascade impactor Model TE-235 equipped with a TE-6070 PM10 size selective head (Tisch Environmental Inc.) was used at a flow rate of 68m<sup>3</sup> h<sup>-1</sup>. This sampler allows the collection of five size classes of airborne particles (aerodynamic diameter ranges of 10–7.2 µm, 7.2–3.0 µm, 3.0–1.5 µm, 1.5–0.95 µm, 0.95–0.49 µm), plus particles smaller than 0.49 µm collected by a background filter. Sample collection, treatment, and area are reported in two previous papers (Scalabrin et al., 2012; Zangrando et al., 2013). Analyses were carried out using a Sector Field Inductively Coupled Plasma- Mass Spectrometer (SF-ICP-MS, Element2 Finnigan-MAT, Bremen, Germany), coupled with a fully-integrated inlet system (Apex, AHF analysentechnik, Tübingen, Germany), on acidified samples (ultrapure nitric acid, Romil@UPA, Cambridge, UK).

TE and REE were measured in water-soluble fractions with the aim of recognising reliable tracers of specific sources which may prove crucial to cost-effective strategies of air pollution control. Water-soluble trace metals and elements were exploited as tracers to identify such individual sources. The use of water-soluble elements helps us to consider only the anthropogenic components of PM (Birmili et al., 2006; Fernández-Espinosa et al., 2004; Song et al., 2001). The trace element content of aerosols sampled in the most remote areas of our planet, primarily due to long range transport, gives valuable information on the global transport of particulates and on the contribution of human activities to air pollution.

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Zangrando R., Barbaro E., Zennaro P., Rossi S., Kehrwald N.M., Gabrieli J., Barbante C., Gambaro A. 2013. Molecular Markers of Biomass Burning in Arctic Aerosols. *Environ., Sci., Technol.*, 47, 8565-8574.

## Presence and size distribution of water-soluble organic compounds in the Antarctic aerosol

Zangrando R.\*<sup>1</sup>, Barbaro E.<sup>1-2</sup>, Vecchiato M.<sup>3-1</sup>, Kehrwald N.<sup>2</sup>, Gambaro A.<sup>1-2</sup>, Barbante C.<sup>1</sup>

1. Istituto per la Dinamica dei Processi Ambientali-CNR. 2. Università Cà Foscari di Venezia, Dipartimento di Scienze Ambientali Informatica e Statistica. 3. Università degli studi di Siena, Dipartimento Scienze fisiche, della Terra e dell'ambiente.

Corresponding email: [roberta.zangrando@idpa.cnr.it](mailto:roberta.zangrando@idpa.cnr.it)

Keywords: biomass burning, amino acids, Antarctica.

The organic fraction is an important part of particulate matter in the atmosphere, and water-soluble Organic compounds (WSOC) constitute between 40 and 60% of organic carbon. WSOC have great environmental importance, as they can reduce the surface tension of aqueous solutions by influencing the hygroscopicity of the aerosol and consequently the particles' ability to act as cloud condensation nuclei (CCN), with consequences on the optical properties of the aerosol, the air quality, and climate.

Our scientific activity in Antarctica had the purpose of obtaining further information about the formation, chemical composition and transport processes of aerosols. The study was conducted over 5 campaigns, two of which at the Mario Zucchelli Station (MZS) (29 November 2010-18 January 2011 and 3 November 2004-10 January 2005), two at Concordia Station (Dome C) (19 December 2012- 28 January 2012 and 7 December 2012-26 January 2013), and during an oceanographic cruise on the Ross Sea (13 January -19 February) 2012.

The Arctic aerosol samples were collected using a high volume sampler PM10 TE- 6070, equipped with a 5-stage cascade impactor Model TE -235. The 6 aerosols fractions collected ranged between 10.0 and < 0.49 μm at the Antarctic bases of MZS and Dome C. During the oceanographic cruise, atmospheric particulate matter (Total Suspended Particles, TSP) was collected using a TE5000 High Volume Air sampler (both samplers are produced by Tisch Environmental Inc., Cleves, OH).

In the aerosols samples, we determined the levels and particle size presence of the following compounds: levoglucosan and methoxyphenols (vanillic acid, isovanillic acid, homovanillic acid, syringic acid, coniferil aldehyde, ferulic acid, syringaldehyde, p-coumaric acid, vanillin), as biomass burning markers and 36 amino acids as indicators of primary production.

## SESSIONE S5

**Climate change and the Earth System: understanding the past,  
analyzing the present and predicting future scenarios**

### *CONVENORS*

*S. Galeotti (Univ. Urbino)*

*A. Provenzale (CNR-ISAC Torino)*

*C. Smiraglia (Univ. Milano)*

## Response of calcareous nannofossils to the Middle Eocene Climatic Optimum (IODP Site U1410, NW Atlantic)

Agnini C.\*<sup>1-2</sup> & Costa A.<sup>1</sup>

1. Dipartimento di Geoscienze, Università di Padova. 2. Department of Geological Sciences, Stockholm University, Sweden.

Corresponding email: [claudia.agnini@unipd.it](mailto:claudia.agnini@unipd.it)

Keywords: calcareous nannofossil, MECO, IODP Site 1410.

Here we present preliminary data on the response of calcareous nannofossils to the Middle Eocene Climatic Optimum (MECO) as recorded at IODP Site U1410 (NW Atlantic). The MECO is a global warming phase occurred at ca. 40 Ma with an estimated duration of ca. 500kyr. This event represents a temporary inversion in the long-term cooling, which initiated ca. 50 Millions of years ago after the Early Eocene Climatic Optimum. The MECO is characterized by a 4 to 6 °C increase in temperature both in surface and deep-sea waters. This interval seems to be associated with a global minimum in carbonate accumulation rate at least in deep depositional settings, which in turn implies a temporary shoaling of the calcite compensation depth (CCD; Bohaty et al., 2009). Though copious geochemical datasets (e.g.,  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ , ...) are now available from different sites/areas we still lack to understand how this event might have affect the marine biosphere. In this context, we have focused our attention on calcareous nannoplankton, which are one of the main component among marine primary producers and play a key role in the geochemical carbon cycle. To date, there is essentially a dearth of data on the response of calcareous phytoplankton to this remarkable perturbation in climate and carbon cycling. The high-resolution study of calcareous nannofossil assemblages performed at IODP Site U1410 across the MECO could thus potentially give important clues on paleoenvironmental changes such as increase/decrease in temperature and nutrient availability. One of the main goals of this study, and perhaps the most interesting, is to understand if the MECO is able to produce global and/or permanent changes in calcareous nannoflora or it only causes local and/or temporary modifications in calcareous nannofossil assemblages. Preliminary results show that some species/genera are more sensitive than others and this results in a differential response of taxa to the altered conditions present during the MECO. In particular, the appearance and disappearance as well as variations in abundance of species belonging to genera *Sphenolithus* and *Dictyococcites* (e.g., Base *Dictyococcites bisectus*, Base *Sphenolithus obtusus*, Top *Sphenolithus furcatolithoides* and Top *Sphenolithus spiniger*) provide a series of bioevents all interestingly occurring around the MECO (Agnini et al., in press). In the next future, these paleontological data will be compared with  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  records looking for possible causal relationships changes in the paleoenvironmental conditions and modifications in calcareous nannoflora.

Agnini C., Fornaciari E., Raffi I., Catanzariti R., Pälke H., Backman J., Rio D. 2014. Biozonation and biochronology of Paleogene calcareous nannofossils from low and middle latitudes. *Newsletters on Stratigraphy*, 47(2), 131-181.  
Bohaty S.M., Zachos J.C., Florindo F. & Delaney M.L. 2009. Coupled greenhouse warming and deep-sea acidification in the middle Eocene. *Paleoceanography*, 24(2), PA2207, doi:10.1029/2008PA001676.

## Marine sediment cores: archive of the Mediterranean Basin. A tool for Holocene climatic and environmental studies

Alberico I.<sup>1</sup>, Ferraro L.<sup>1</sup>, Lirer F.\*<sup>1</sup>, Anzalone E.<sup>1</sup>, Vallefucio M.<sup>1</sup>, Bonomo S.<sup>1</sup>, Cascella A.<sup>2</sup>, Petrosino P.<sup>3</sup>,  
Insinga D.D.<sup>1</sup>, Barra R.<sup>4</sup> & Marsella E.<sup>1</sup>

1. Istituto per l'Ambiente Marino Costiero - CNR, Napoli. 2. Istituto Nazionale di Geofisica e Vulcanologia, Pisa. 3. Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università degli Studi di Napoli Federico II, Napoli. 4. Associazione Comitato Ev-K2-CNR, Bergamo.

Corresponding email: [fabrizio.lirer@iamc.cnr.it](mailto:fabrizio.lirer@iamc.cnr.it)

Keywords: marine sediment cores, paleoproxies, database, spatial analysis, Mediterranean Sea.

Natural archives as tree rings, ice cores and marine sediments are remarkable sources to recover quantitative information on past climate at regional and global scale necessary to reconstruct high-resolution climatic sequences for the last millennia (IPCC, 2013 and references therein).

In this framework, the NextData project has been proposed to develop an infrastructure to retrieve, store and share climatic data from land and marine areas of the Mediterranean Basin.

The analysis of marine data infrastructures, which manage data of *in situ* and remote observations of the seas (GeoSeas, 2014; ICSU World Data, 2014; NOAA, 2014), highlighted that the online data of marine sediment cores are mainly descriptive information rather than quantitative analysis results (e.g. stable isotope data, planktonic foraminifera quantitative data, etc.) and only few of them are typified by references of scientific works. The goal of the NextData archive is to list the type of useful proxies which record the *Holocene* climatic changes and share them with scientific community. At this aim a conceptual and logical model was defined in order to publish the metadata on SHARE Geonetwork (<http://geonetwork-evk2cnr.org/webapp/>, last connection: December 2013) and the quantitative data on WDB-Paleo (<https://github.com/wdb/wdb>, last connection: January 2014).

The study area encompasses about 6,000 marine sediment cores, of which 600 were discussed in papers dealing with paleoclimate issues of the Holocene. The highest percentage of these papers concern the planktonic foraminifera (33%) and stable isotopic data (28%), followed by benthonic foraminifera, calcareous nannoplankton, dinoflagellates and AMS <sup>14</sup>C proxies, which are discussed in the 15% of these papers. Furthermore, the analysis performed with the algorithms of spatial analysis implemented in a Geographic Information System environment, made it possible to assess the geographical distribution of paleoproxies and to draw maps, which can represent a tool to support paleoclimatic and paleoenvironmental studies. Planktonic foraminifera, stable isotope and AMS <sup>14</sup>C datasets cover the whole Mediterranean Basin; they display a density higher along the coastline of the Italian peninsula than in other Mediterranean zones. The calcareous nannoplankton and pollen data show a higher density in the Eastern Mediterranean Basin.

Moreover, we illustrate the role of the geographical distribution of tephra layers or AMS <sup>14</sup>C data as proxies that supply constraints for age modelling of marine sequences (Lowe et al., 2007), mostly aimed at evaluating the synchrony/diachrony of the climatic changes in the Mediterranean area (Lowe, 2011).

IPCC (Intergovernmental Panel on Climate Change). Fifth Assessment Report – Climate Change 2013. <http://www.ipcc.ch/report/ar5/> (last connection: 3/02/2014).

Lowe D.J. 2011. Tephrochronology and its application: A review. *Quaternary Geochronology*, 6 (2), 107-153

Lowe D.J., Blockley S., Trincardi F., Asioli A., Cattaneo A., Matthews I.P., Pollard M. & Wulf S. 2007. Age modelling of late Quaternary marine sequences in the Adriatic: towards improved precision and accuracy using volcanic event stratigraphy. *Cont. Shelf Res.*, 27, 560-582.

## Ground deformation analysis exploiting surface and sub-surface displacement measurements

Allasia P.<sup>1</sup>, Ardizzone F.<sup>2</sup>, Cignetti M.\*<sup>1</sup>, Giordan D.<sup>1</sup>, Guzzetti F.<sup>1</sup>, Manconi A.<sup>1</sup> & Manunta M.<sup>3</sup>

1. CNR IRPI, Torino. 2. CNR IRPI, Perugia. 3. CNR IREA, Napoli.

Corresponding email: [francesca.ardizzone@irpi.cnr.it](mailto:francesca.ardizzone@irpi.cnr.it)

Keywords: monitoring, SAR interferometry, climate changes.

Different geological processes produce deformation of the ground surface. Geological phenomena that can result in ground deformation include earthquakes, subsidence, volcanic activity, glacial rebound, and landslides. In particular, there is a systematic lack of information on the effects of climate and environmental changes on the frequency and the intensity of landslides and their triggering phenomena (Huggel et al., 2012). The problem is particularly severe in mountain areas, where natural and human-driven climatic and environmental changes may alter significantly the frequency and the intensity of the slope processes. We present HAMMER project, developed in the framework of NextData project (<http://www.nextdatapoint.it/>) that intends to close this gap by collecting accurate and long term time series of ground surface and sub-surface deformation, and analysing eventual changes of the deformation trend associated with meteorological and climatic variables over time, focus on some study area in Italian Western Alps, Apennines, Pyrenees and Andes. The different physiographic setting guarantees an analysis of different geomorphological, geological and structural setting in order to take in account different type of phenomena.

The project involves two main actions, a first that includes the collection of meteorological and climate time series and of pre-existing ground displacement data obtained by *in situ* monitoring such as Total Stations, GPS receivers, inclinometer, and by the space-borne based measurements such as Differential SAR Interferometry (DInSAR) technique. The *in situ* monitoring technique provides ground deformation time series with very high temporal sampling, allowing for the reconstruction of the evolution of single landslide phenomena over time, while the DInSAR technique let to study the landslide phenomena at regional scale, to recognize the areas presenting ground deformation anomalies where to focus for a better understanding of the on-going physical processes. An integration of DInSAR and *in situ* measurements can be considered as a useful approach to analyse landslide phenomena at a different spatial (regional vs. local) and temporal (month/weeks vs. days/hours) resolution (Davalillo et al., 2014), in order to better evaluate the behaviour of different instable slope areas, and also to find eventual relationship between meteorological and climatic variables and ground movements. The second part of the project includes the realization of new DInSAR products in two new test areas that will be useful to test and validate the statistical relationship.

García-Davalillo J., Herrera G., Notti D., Strozzi T., Álvarez-Fernández I. 2014. DInSAR analysis of ALOS PALSAR images for the assessment of very slow landslides: the Tena Valley case study. *Landslides*, 11, 225-246.

Huggel C., Clague J. J., Korup O. 2012. Is climate change responsible for changing landslide activity in high mountains?. *Earth Surf. Process. Landforms*, 37, 77-91.

## **A novel integrated method to describe dust and fine supraglacial debris and their effects on ice albedo: the case study of Forni Glacier, Italian Alps**

Azzoni R.S.\*<sup>1</sup>, Senese A.<sup>1</sup>, Zerboni A.<sup>1</sup>, Maugeri M.<sup>2</sup>, Smiraglia C.<sup>1</sup> & Diolaiuti G.<sup>1</sup>

1. Università degli Studi di Milano, Dipartimento di Scienze della Terra "A. Desio". 2. Università degli Studi di Milano, Dipartimento di Fisica

Corresponding email: [robertosergio.azzoni@unimi.it](mailto:robertosergio.azzoni@unimi.it)

Keywords: Supraglacial debris and dust, Glacier melting area, ice albedo, SEM, Alpine glaciers.

Recently, evidence for significant tongue darkening on retreating glaciers has been drawing increasing attention. This peculiar surface phenomenon in part depends on the exposure of ice surface to layers of dust and coarser rock debris. The consequent effect is a remarkably decreasing of albedo, due to the presence of light absorbing particles. We investigated the characteristics of sparse and fine debris coverage at the glacier melting surface and its relation to ice albedo. In spite of the abundant literature dealing with dust and black carbon deposition on glacier accumulation areas (i.e.: on snow and firn), few studies that describe the distribution and properties of fine and discontinuous debris and black carbon at the melting surface of glaciers are available. Furthermore, guidelines are needed to standardize field samplings and lab analyses thus permitting comparisons among different glaciers. We developed a protocol to i) sample fine and sparse supraglacial debris and dust, ii) quantify their surface coverage and the covering rate acquiring high resolution digital images, iii) describe composition and sedimentological properties and its temporal and spatial evolution, iv) measure ice albedo and v) identify the relationship between ice albedo and fine debris coverage (Azzoni et al., accepted). The procedure was tested on the Forni Glacier surface (northern Italy), when the fine debris and dust present had marked variability in space and time (along the glacier tongue and from the beginning to the end of summer) thus influencing ice albedo: in particular the natural logarithm of albedo was found to depend on the percentage of glacier surface covered by debris. Debris and dust analyses indicate generally a local origin (from nesting rockwalls) and the organic content was locally high, suggesting that further analyses are required to describe its sources. Nevertheless the finding of some cenospheres suggests an anthropic contribution to the superficial dust as well. The fine debris presents marked variability, increasing its surface coverage from the beginning to the end of summer and thus influencing ice albedo. Moreover, the effect of liquid precipitation on ice albedo was not negligible, but short lasting (from 1 to 4 day long), thus indicating that also other processes affect ice albedo and ice melt rates and then some attention has to be spent analyzing frequency and duration of summer rainfalls for better describing albedo and melt variability.

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Azzoni R.S., Senese A., Zerboni A., Maugeri M., Smiraglia C. & Diolaiuti G. (accepted). A novel integrated method to describe dust and fine supraglacial debris and their effects on ice albedo: the case study of Forni Glacier, Italian Alps. The Cryosphere Discussion.

## **A challenge for a better understanding of the high mountain environment: the new Italian Glacier Inventory**

Azzoni R.S., D'Agata C., Maragno D., Diolaiuti G. & Smiraglia C.\*

Università degli Studi di Milano, Dipartimento di Scienze della Terra "A. Desio".

Corresponding email: [claudio.smiraglia@unimi.it](mailto:claudio.smiraglia@unimi.it)

Keywords: Glacier Inventory, Remote Sensing, Italian Alps.

A new Glacier Inventory is an indispensable scientific and practical requirement in Italy due to the importance of evaluating the present glacier coverage and the recent changes driven by climate. Furthermore Alpine glaciers represent a not negligible water and tourist resource to be managed and promoted thus requiring the knowledge of the actual distribution, size, features and evolution.

On the Italian side of the Alps is located more than a fifth of the entire Alpine glaciation with glacier distribution on all the sectors of the chain, from Maritime to Julian Alps. The first Italian Glacier Inventory dates back to 1959-1962. It was compiled by the Italian Glaciological Committee (CGI) in cooperation with the National Research Council (CNR); this first inventory was mainly based on field data coupled with field photographs and high resolution maps. The Italian glaciation resulted to be spread into 824 ice bodies which altogether were covering 518 km<sup>2</sup>. Moreover in the Eighties a new inventory was compiled to insert Italian data into the World Glacier Inventory (WGI); aerial photos taken at the end of the Seventies and at the beginning of the Eighties were used as the main source of data. During the last decade the largest part of the Italian Alpine Regions have produced regional and local glacier inventories, moreover the actual need is now to obtain a complete and homogeneous picture of the Italian glaciation which encompasses and enhances the already available regional and local data and all the new updated information coming from new sources of data. To take up this challenge an unique homogeneous glacier database has been developed, including the main fundamental parameters and features, such as glacier name, national inventory code, former WGI code, coordinates, surface area (minimum size 0.01 km<sup>2</sup>), glacier type, aspect (following the guidelines of the World Glacier Monitoring Service summarized by Paul et al., 2010). The identification of the Italian glacier bodies and the evaluation of glacier area and main features have been performed by analyzing aerial orthophotos acquired in the time frame 2005-2011 (pixel size 0.5 m X 0.5 m) and processing high resolution satellite images.

From the performed analyses the whole Italian glaciation consists in 896 ice bodies covering a surface area of 368.3 km<sup>2</sup>. Considering the glacier surface, the Italian region featuring the widest ice coverage is Valle d'Aosta (133.6 km<sup>2</sup>). Moreover the highest number of glaciers per region is found in Lombardy (241 ice bodies). From the new Italian glacier inventory it results that Italian glaciation mainly consists in small ice bodies (mean glacier area of 0.4 km<sup>2</sup>) featuring a dominant North aspect and only a very small number of wide glaciers is still present (i.e. 3 glaciers >10 km<sup>2</sup>) resembling the ancient huge Alpine glaciation.

Paul F., Barry R.G., Cogley J.G., Frey H., Haeberli W., Ohmura A., Ommanney C.S.L., Raup B., Rivera A. & Zemp M. 2010. Recommendations for the compilation of glacier inventory data from digital sources. *Annals of Glaciology*, 50(53), 119-126.

## **Application of CMIP5 global climate models to the fire danger indices evaluation across the Greater Alpine Region: skill assessment and future projections**

Barbarino S.\*<sup>1-2</sup>, Cane D.<sup>2</sup>, Von Hardenberg J.<sup>1</sup>, Pelosini R.<sup>2</sup> & Provenzale A.<sup>1</sup>

1. ISAC, Institute of Atmospheric Sciences and Climate, CNR, Torino. 2. Arpa Piemonte, Regional Agency for Environmental Protection, Torino.

Corresponding email: [s.barbarino@arpa.piemonte.it](mailto:s.barbarino@arpa.piemonte.it)

Keywords: Fire potential, climate change, RCP emission scenarios.

Wildfires represent a rather significant phenomenon across Central and Southern Europe. Besides the Mediterranean basin, regarded as the zone most prone to such events, in recent years the Alpine regions have also started to be affected by an increasing number of forest fires, in particular during summer: these events are characterized by severity and intensity. In addition, current climate projections depict the Alps as one of the regions that will suffer particularly from the expected enhancement of temperature in the future, thus raising the suitable conditions for the ignition of forest fires.

Besides the operational aspects, as the monitoring and management of fire events, preventive interventions represent the key point for fighting wildfires. Currently, the assessment of fire risk worldwide is provided by fire danger indices: they require weather conditions as input variables, and the calculation of such indices give information on potential fire behaviour.

In this study, we investigate the application of 7 global climate models available in the fifth phase of the Coupled Model Intercomparison Project (CMIP5) in order to evaluate fire potential in the coming decades over the Greater Alpine Region: we take into consideration the Canadian Fire Weather Index and the Fine Fuel Moisture Code, based on the Canadian Forest Fire Danger Rating System.

A preliminary analysis is addressed to the skill assessment of these Earth System models in describing mesoscale phenomena as wildfires. For this purpose, we conduct a comparison between the input weather fields (required for fire indices calculation) from CMIP5 historical runs and the corresponding ERA-INTERIM reanalysis dataset, which is here regarded as a benchmark. The same kind of evaluation is carried out among the fire weather indices, computed by employing the two different dataset.

After verifying such models, we take into account the CMIP5 simulations resulting from the application of the new emission scenarios - the Representative Concentration Pathways RCP26, RCP45 and RCP85 - to evaluate changes in fire risk and fire potential over the Alpine regions across the whole 21st century.

As a general overview, the application of these selected CMIP5 global climate models enable us to obtain comparable results with the reanalysis dataset. In addition, they give reasonably realistic and stable fire potential projections for the future, even as far as the end of the century.

## **Reworked coccoliths: proxy to reconstruct Volturno hydrographic basin runoff variation**

Bonomo S.\*<sup>1</sup>, Cascella A.<sup>2</sup>, Alberico I.<sup>1</sup>, Ferraro L.<sup>1</sup>, Lirer F.<sup>1</sup>, Vallefucoco M.<sup>1</sup>, Anzalone E.<sup>1</sup> & Marsella E.<sup>1</sup>

1. Istituto per l'Ambiente Marino Costiero - CNR, Napoli. 2. Istituto Nazionale di Geofisica e Vulcanologia, Pisa.

Corresponding email: [sergio.bonomo@cnr.it](mailto:sergio.bonomo@cnr.it)

Keywords: Paleoclimatology, Calcareous Nannofossils, Runoff Reconstruction.

Coccoliths are the thin calcite platelets forming the exoskeleton of the coccolithophores, which are one of the main groups of marine phytoplankton. These photosynthetic organisms directly depend on environmental parameters within the photic zone of the oceans (e.g. temperature, salinity, sunlight), which makes them excellent proxy for climate changes (Baumann et al., 2005). Coccolithophores have one of the most abundant fossil record: their long evolutionary story (Late Triassic - present day), high evolutionary turnover, and phenomenal abundance in marine sediments have made them ideal fossils for high-resolution biostratigraphic studies (Bown 1998). The reworked specimens generally disturb the biostratigraphic signal of a coccoliths assemblage. In shelf-dominated and river-dominated areas, the reworked coccoliths can provide information about land-ocean dynamic, sediment transport, and allow to account the continental terrigenous fluxes which are useful for paleoclimatic studies (e.g. Di Stefano and Incarbona, 2004; Ferreira et al., 2008). We present a work in progress study in which we compare the distribution pattern of reworked coccoliths recovered in the C5\_SW core *versus* the runoff model simulation (from 1951 to 2013 - CIRCE project) for the Volturno river hydrographic basin. The aim of this research is to achieve a new algorithm that will allow to extend the reconstruction of the variations of Volturno runoff up to 2000 years ago. The C5\_SW core was recovered at 92m depth in the Gulf of Gaeta during the NextData\_2013 cruise (NextData project - Paleoclimatic Data from Marine Sediments – WP1.5). The high resolution study of the first ~30 cm of the core (1 cm sample spacing), identified a broad correspondence between the reworking fluctuations and the runoff model data. These preliminary results would confirm the reliability of the reworked coccoliths to estimate the runoff quantitative fluctuations in the past.

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## The role of $p\text{CO}_2$ on climate and biogenic calcite production during the Aptian

Bottini C. \*, Erba E. & Tiraboschi D.

Dipartimento di Scienze della Terra, Università degli Studi di Milano.

Corresponding email: [cinzia.bottini@unimi.it](mailto:cinzia.bottini@unimi.it)

Keywords: Nannofossils, Aptian,  $\text{CO}_2$ .

The late Barremian - early Aptian time interval was marked by intense volcanic activity related to the Ontong Java Plateau (OJP) thought to have induced a global perturbation in the ocean-atmosphere system culminating in the early Aptian Oceanic Anoxic Event (OAE) 1a, an episode of widespread organic matter burial in oxygen-depleted oceans. This extreme event represents a “natural experiment” useful to decipher the ecosystem response to large injection of  $\text{CO}_2$ , relevant for the understanding of future global climatic changes, the biota response and how pre-perturbation conditions can be restored. Several studies have been conducted on OAE 1a providing evidence for a progressive reduction in the production of biogenic carbonate accompanied by higher surface-water fertility and major warming interrupted by transient cooler interludes.

In our study, we aimed at a better understanding of the role of  $p\text{CO}_2$  on the climatic variability during OAE 1a as well as on the production of calcite from calcareous nannoplankton. In addition, we intended to understand how, either the biota and the climate, recovered after OAE 1a and which conditions were imposed during the middle-late Aptian. We present a reconstruction of surface water paleotemperature, fertility and calcite paleofluxes through the Aptian (~121 to ~113 Ma) based on the calcareous nannofossil record from Italy (Cismon and Piobbico cores) and Pacific Ocean (DSDP Site 463). The nannofossil data were correlated with temperature proxies (oxygen isotopes,  $\text{TEX}_{86}$ ) and trace metal concentrations.

In the studied sites we identified similar and coeval variations in nannofossil calcite paleofluxes as well as in the abundance of temperature and fertility indicators, which well correlate with the geochemical data, thus suggesting global drivers inducing these variations. We found evidence for a direct connection between OJP activity,  $\text{CO}_2$  emissions and global warming in the early phase of OAE 1a accompanied by a decrease in calcification rates. Cooling events occurring during OAE 1a, were probably promoted by temporary  $\text{CO}_2$  sequestration due to burial of organic matter although under persisting OJP volcanism. The end of OAE 1a coincides with the vanishing of OJP activity and a marked cooling accompanied by a relative recovery in carbonate fluxes. The late Aptian was probably marked by at least two main volcanic phases related to construction of the Hikurangi and Kerguelen Plateaus, affecting biogenic calcite production but promoting cooler temperatures. A stasis in volcanism allowed a recovery of paleofluxes during the *Nannoconus truittii* acme, although paleofluxes never reached pre-OAE 1a values. We conclude that, during the Aptian, abnormal volcanic activity directly affected the climate and the ocean at global scale. Coccolithophores were forced to face excess  $\text{CO}_2$ , climatic changes and variations in surface water fertility and acidification, but survived and adapted to extreme paleoenvironmental conditions.

## **Evaluation of climate patterns in a regional climate model over Italy using long-term records from SYNOP weather stations and cluster analysis**

Calmanti S.<sup>1</sup>, Dell'Aquila A.\*<sup>1</sup>, Maimone F.<sup>2</sup> & Pelino V.<sup>2</sup>

1. ENEA, UTMEA-CLIM. 2. CNMCA, Italian Air Force.

Corresponding email: [alessandro.dellaquila@enea.it](mailto:alessandro.dellaquila@enea.it)

Keywords: Regional Climate models, Weather station data, Cluster analysis.

In the framework of NEXTDATA project activities, we have assessed the ability of a regional climate model – the ENEA-PROTHEUS system - to produce intermediate scale patterns of atmospheric variability over the Italian peninsula. This area, with its complex orography and coastlines, is a particularly interesting test-bed for regional climate models (RCMs) ability in reproducing sub-regional climate patterns.

We compare the output of a high-resolution RCM with 40 years of weather data from 64 weather stations from the Italian National Air Force network. Climatic zones have been identified by using the Ward's method for cluster analysis for minimum and maximum temperature and rainfall. The model is able to generate realistic spatial patterns of the observed clusters, the skill depending on the considered variable. The closest match between model and observations is occurs for the daily minimum temperature. The maximum temperature shows an unrealistic summer peak for most of the clusters. Consistently, the model produces too many strong warm events during summer. The model shows also a tendency to overestimate total rainfall especially during spring and early summer.

The frequency and intensity of extreme events are well captured only in the case minimum temperature for Alpine and mountain weather stations.

## Estimation of hydrological Uncertainty in the analysis of climate change for two mountain basins in Italy

Camici S.\*, Brocca L. & Moramarco T.

Research Institute for Geo-Hydrological Protection, CNR, Perugia.

Corresponding email: [s.camici@irpi.cnr.it](mailto:s.camici@irpi.cnr.it).

Keywords: Climate changing, hydrological uncertainty, Global Circulation Models.

Many climatic extremes are changing and decision-makers express a strong need for *reliable* information on future changes over the coming decades as a basis for adaption strategies. The Report of Intergovernmental Panel on Climate Change (IPCC, 2012) about potential effects of climate change highlights that "projected precipitation and temperature changes imply possible changes in floods, although overall there is low confidence (a 2-10% probability) in projections of changes in fluvial floods". However, the estimation of the future changes in the frequency and magnitude of floods is not an easy task and the low confidence is due to the *limited evidence* and because the causes of regional changes are complex, being related not only to changes in climate forcing, but also to basin characteristics.

Global circulation models (GCMs) provide the climate change scenario that are used as input for hydrological models. However, for small/medium catchments (2) the spatial/temporal resolution of GCMs (>10000 km<sup>2</sup> and daily time step) is inadequate for forcing a hydrological model and downscaling is required. This can be achieved by downscaling approaches as statistical, e.g. bias correction, or dynamical, e.g. using regional climate models (RCMs) nested in GCM. Moreover, sub-daily time step of rainfall and temperature is required for meaningful hydrological simulation. This can be obtained through stochastic weather generators that, finally coupled with continuous rainfall-runoff models, allow analyzing the hydrological impact of climate change. As each step in this chain introduces uncertainty, the reliability of climate change impact studies might be limited.

Based on that, the main objective of this study is to assess the uncertainty of the modeling chain, i.e., GCM-downscaling-weather generator-rainfall runoff model, by analyzing the statistic of the errors between the modeled and observed data at each step. The following procedure, already tested in previous studies, is here applied. 1) The outputs of different GCMs and of statistical downscaling approach are collected. 2) Long-term hourly time series of rainfall, temperature and discharge are generated through stochastic weather generators coupled with a continuous rainfall-runoff model. 3) The simulated annual/monthly maxima discharge are extracted for the present period and compared to the observed data. This procedure is applied to two mountain basins located in the Umbria and Tuscany/Liguria regions, the Chiascio and Magra catchments, respectively, considered as pilot areas for the NextData Project funded by the Italian Research Council. Different GCMs (HadCM3, ECHAM5-OM, PCM, CMCC-CM, etc.) are considered for the analysis. The assessment of the uncertainty in the different component in the modeling chain is investigated as a function of the basin characteristics and of the selected GCM.

## Glaciers One-Time. The Society Protagonist of the Research

Casarotto C.\*

MUSE - Museo delle Scienze Sezione di Geologia e Paleontologia, Trento.

Corresponding email: [christian.casarotto@muse.it](mailto:christian.casarotto@muse.it)

Keywords: Photographic comparison, glaciers, research and society, enhancement mountain environment.

The project *Glaciers one-time* has been proposed to the whole community involving the citizenship in a scientific research program. All are invited to take photographs of the modern Italian glaciers with the exact points of view of historical photographs, and to make photographic comparisons. The photographic comparisons in fact are the basis to carry out comparative studies on the health of our glaciers, seen as valuable indicators for the assessment of climatic conditions and their evolution over time.

With the aim of encouraging the community to approach, re-discovery and develop the mountain environment, the project did not give detailed information relating to the photographed glaciers; so the citizens are encouraged to identify of the glacier and the location of the places from which to take the photo. The project was characterized by a involvement of society in the world of research, to the enhancement of the Italian Alps, as an incentive to attend and rediscover the mountains, transmit to the society the meaning and importance of research, and ensure that the research becomes an important process useful for the growth of the individuals and the community.

Steps of the project:

1. identification of the national network, Scientific and Mountaineering Committee;
2. selection of 75 glaciers and their historical photographs, published on the website of the project [www.ghiacciaidiunavolta.it](http://www.ghiacciaidiunavolta.it), in collaboration with the Italian Glaciological Committee;
3. forwarding of the produced photographs, via the website, to the MUSE. A total of 173 photographs was archived. The Scientific Committee conducted the appropriate assessments to extrapolate the best pictures. The committee worked to extract, through photographic comparison, the changes in landscapes and portraits of the glacial retreat. All the best comparisons with the glaciological analysis are on the website [www.ghiacciaidiunavolta.it](http://www.ghiacciaidiunavolta.it).

All the best pictures are shared within the network and posted online to make them available to the entire community that can see and rediscover the importance of their work. With the contribution of the Italian Geological Society, a publication will collect the best photographic comparisons with qualitative/quantitative analysis and geological and geomorphological descriptions of some routes to the “discovery of the glaciers”.

The purpose is to disseminate the valuable material contributing to an epochal debate. The photographic comparison of alpine glaciers, portrayed in historical times and today with the same frame and location, documents a strategic issue in an endangered planet. The glacier is in fact our wealth and the development of mankind can not in any way be separated from its conservation. A century of climate changes in the Alps is a long part of human history that we can trace back, rediscovering the charm of the alpine landscape and its greater glaciers in the past.

## **Interaction between Late-Quaternary climate changes and volcano activity on the stratigraphy of the eastern flank of Mount Etna (Eastern Sicily)**

Catalano S., Pavano F., Romagnoli G., Sturiale G. & Tortorici G.\*

Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Sezione di Scienze della Terra, Università di Catania.

Corresponding email: [gtortoric@libero.it](mailto:gtortoric@libero.it)

Keywords: Mount Etna, climate changes, epiclastic deposits.

The volcanostratigraphic succession exposed along the eastern flank of Mt. Etna, in eastern Sicily, is the result of the interaction between the emplacement of the lava flows and of distinct clastic horizons.

The older volcanics are represented by subalkaline lavas, interleaved within Middle Pleistocene marine clays. The first subaerial products are represented by a sequence of alkaline lavas (225-132 ka; Gillot et al., 1994), characterized by deeply entrenched valleys filled by clastic deposits (Acireale Lahars), which are modelled by a major erosional surface, grading to the OIS 5.5 (125 ka) marine terrace. Younger (125-60 ka) volcanic horizons, exposed in the walls of a large caldera depression (Valle del Bove), are modelled, at the top, by an unconformity surface that is associated with clastic deposits (Milo Formation). Finally a clastic horizon (Chiancone alluvial fan)(15-7.5 ka; Calvari & GropPELLI, 1996), that lies above a main unconformity, separates the Würmian alkaline lavas (40-15 ka) from the Holocene and historical ones.

The older interbedded clastic horizons are represented by several tens of meter thick deposits, exhibiting textural features typical of epiclastic (debris-flow) deposits. These levels are made of plurimetric matrix-supported conglomerate in a well cemented muddy-sandy matrix and by fine tuff with rare centimetre-sized conglomerate elements. Generally, they are associated with coarse grained, poorly sorted and unconsolidated breccias, composed of a wide range of angular to sub-rounded lava blocks and scoriae, in a slightly consolidated matrix, indicating a debris-avalanche origin. The Holocene conglomeratic alluvial fan, showing dm-sized boulders, conceals the topography modelled on the pre-15 ka volcanics.

The volcanics chronological constraints together with the geometric relation between lava horizons and analysed clastic deposits indicate that these latter developed in short periods of few ka. During these periods, coinciding with major deglaciations that have accompanied the sea-level rises towards the OIS 5, 3 and the Holocene, the exogenous processes largely prevailed on lava flows accumulation. Consequently, dominant gravity-induced mass transport and alluvial processes have remobilised huge volumes of detritus. This evidence confirms that the maximum effectiveness of agents on the landscape have characterised in the past the periods of rapid sea-level rise rather than the entire periods of the sea-level highstands, thus suggesting that the increase of precipitation and the recurrence of heavy rain falls have been strictly related to climate crises induced by the main deglaciation processes.

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## Climatic changes and human adaptation in southern Arabia. The case study of the Gebel Qara rock shelters (Sultanate of Oman)

Cremašchi M.\*<sup>1</sup>, Zerboni A.<sup>1</sup>, Zanchetta G.<sup>2</sup>, Regattieri E.<sup>2-3</sup>, Isola I.<sup>4</sup>, Crassard R.<sup>5</sup> & Charpentier V.<sup>6</sup>

1. Università degli Studi di Milano, Dipartimento di Scienze della Terra "A. Desio". 2. Università degli Studi di Pisa, Dipartimento di Scienze della Terra. 3. IGC-CNR, Pisa. 4. INGV, Pisa. 5. CNRS, UMR 5133 Archéorient, Maison de l'Orient et de la Méditerranée, Lyon, France. 6. Inrap & CNRS, UMR 7041 ArScAna, Maison de l'Archéologie et de l'Ethnologie, Nanterre, France.

Corresponding email: [mauro.cremaschi@unimi.it](mailto:mauro.cremaschi@unimi.it)

Keywords: Holocene climate changes, Human response, Sultanate of Oman.

The limestone massif of Gebel Qara (Salalah, Sultanate of Oman) hosts a large number of karst cavities preserving sedimentary infilling and superposed speleothems. The sedimentary infilling of rock shelters also includes anthropogenic deposits dating to the pre-Neolithic Arabian period (Fasad Lithic Complex); for that reason, the caves of the Gebel Qara represent a valuable archive to study the regional nexus between climatic changes and cultural dynamics during the early and middle Holocene. The preliminary results obtained from the analyses of the samples collected during a novel survey (year 2013) are shortly discussed. Within several rock shelters, the stratigraphic sequence is composed, from the bottom to the top, by angular breccias associated with loessic sediments, overlaid by anthropogenic sediments and calcareous tufa. Loess was brought to the Gebel Qara by northern wind from the Nejd desert and it covers also the surfaces outside the rock shelters. This phase is dated, to c. 9950 years cal BP; despite the harsh environmental settings, at that time the Gebel Qara was exploited by groups of hunter and gatherers. At c. 9400 years cal BP sediments within rock shelters highlight a main climatic change toward more humid environmental conditions. Deposits belonging to this phase consist of colluvial sediments rich in terrestrial gastropods. Moreover, the occurrence within the deposits of Fasad points (Arabian late Epipalaeolithic) confirms that Gebel Qara was intensely exploited and human groups possibly contributed to the formation of the archaeological record. In fact, we suggest that the high concentration of land snails may be due to intentional gathering and deposits are interpreted as *escargottieres*. After this phase of human occupation, anthropogenic sediments were sealed by flowstones, which deposition occurred between c. 8960 and 4200 years BP (U/Th age); speleothems cover the last part of the early Holocene and the middle Holocene. Geochemical analyses on calcareous tufa show an increasing trend of the oxygen and carbon values towards their top, thus an evolution of the local climate toward drier conditions. The stratigraphic record represented in the Gebel Qara rock shelters indicates that in this time span the climate of the area changed from a dry conditions, dominated by northern winds, to a wet climate dominated by the southern monsoon circulation, and back again to moderately drier conditions. The shelters were occupied by groups of the Fasad culture only during the early arid phase and were almost completely deserted later; on the contrary, during the VII–V millennia BP Neolithic communities occupied the plain of Salalah, the margins of the mangroves, and the coastal dunes. Finally, the Gebel Qara was re-occupied again in historical times at the decline of the wet period.

## Increasing seasonality during the Early Pleistocene in the Mediterranean Sea

Crippa G.\*<sup>1</sup>, Angiolini L.<sup>1</sup>, Felletti F.<sup>1</sup>, Frigerio C.<sup>1</sup>, Leng M.J.<sup>2-3</sup>, Raineri G.<sup>4</sup> & Stephenson M.H.<sup>5</sup>

1. Dipartimento di Scienze della Terra 'Ardito Desio', Università degli Studi di Milano. 2. NERC Isotope Geosciences Laboratory, British Geological Survey, Keyworth, UK. 3. Centre for Environmental Geochemistry, School of Geography, University of Nottingham, UK. 4. Riserva Naturale Geologica del Piacenziano, Castell'Arquato. 5. British Geological Survey, Keyworth, UK.

Corresponding email: [gaia.crippa@unimi.it](mailto:gaia.crippa@unimi.it)

Keywords: seasonality, sclerochronology, Early Pleistocene.

The Early Pleistocene is an epoch characterized by several climatic oscillations, with its lower and upper boundaries coinciding respectively with the beginning of the Northern Hemisphere Glaciation and the Middle Pleistocene Transition.

During this time interval, the Mediterranean region was strongly affected by rapid climatic changes, the expression of which is clearly recorded by the biotic evolution in fossil archives. One of the most important of these biotic events is the appearance of the boreal guest *Arctica islandica* at the beginning of the Calabrian Stage, indicating that climatic deterioration had started to affect the Mediterranean Sea.

The Arda River marine succession, cropping out in Western Emilia, Northern Italy, continuously covers the Early Pleistocene time interval; it represents an ideal setting to study the climatic oscillations of the Early Pleistocene and, in particular, to understand how seasonality varies during these climate changes. It consists mainly of sandstones intervals, cyclically alternated with siltstones, claystones and very rich fossiliferous beds, deposited in a tectonically active setting during phases of advance of fan deltas affected by high-density flows triggered by river floods.

The geochemical signature registered in bivalve shells can be used as an archive of global change in seawater composition and temperature, as these organisms record in their calcium carbonate shells the primary seawater isotope composition, with little or no vital effect. To reach this goal, sclerochemistry has been undertaken on pristine bivalve shells belonging to the species *Glycymeris inflata*, *Glycymeris insubrica* and *Arctica islandica* collected from several stratigraphic horizons throughout the Arda River marine succession. One of the main outcomes of these analyses is the recognition of an increase in the amplitude of the oscillation of the oxygen isotope ratio from the base to the top of the section. This suggests an increase in seasonality in the Early Pleistocene, during the deposition of the succession, which become more pronounced toward the Middle Pleistocene Transition. These results also offer the opportunity to unravel the interplay among the different factors affecting the oxygen isotope record, i.e. salinity, temperature and glacial advance and retreat.

## Impact of early Eocene hyperthermals ETM2, H1 and I1 on planktic foraminiferal assemblages: the case study of the Tethyan Terche section (northeastern Italy)

D'Onofrio R.\*<sup>1</sup>, Luciani V.<sup>1</sup>, Giusberti L.<sup>2</sup>, Fornaciari E.<sup>2</sup> & Sprovieri M.<sup>3</sup>

1. Dipartimento di Fisica e Scienze della Terra, Università di Ferrara. 2. Dipartimento di Geoscienze, Università di Padova. 3. Istituto per l'ambiente marino costiero (IAMC) (CNR), Campobello di Mazzaara.

Corresponding email: [roberta.donofrio@unife.it](mailto:roberta.donofrio@unife.it)

Keywords: Early Eocene hyperthermals, planktic foraminifera, Tethyan setting.

The Terche section is an upper Paleocene-lower Eocene succession deposited in a bathyal setting of a continental margin of the central-western Tethys (Venetian Prealps, northeastern Italy). This section contains three well-exposed and expanded marly-clay units corresponding to intervals of negative carbon isotope excursions. Calcareous plankton biostratigraphy allow us to correlate them to the early Eocene hyperthermals ETM2 (~53.7 Ma), H2 (~53.6 Ma) and I1 (~53.3 Ma). The so-called hyperthermals are rapid (<200 kyr), short-lived peak-warming events characterizing the early Paleogene climate variability. They are superimposed to a long-term warming, which culminated at the Early Eocene Climatic Optimum, EECO (~49 Ma), and related and to major global carbon-cycle perturbations, the most extreme of which is the well-known Paleocene-Eocene Thermal Maximum. A large data set is essential to understand nature, causes and consequences of the global climatic changes during this crucial time of Earth history. To the present, perturbations produced by hyperthermals are rather well documented in terms of isotopic variations whereas their influence on the biota is still largely unexplored. The record from the Tethyan Terche section represents therefore a significant case study. Marked changes in planktic foraminiferal abundances correlate to the marly-clay units and suggest abrupt, though transient, episodes of environmental perturbations that resulted in improved eutrophication of the sea-surface waters coupled with intense warmth. The increased surface-water eutrophication during hyperthermals was forced by strengthening of the hydrological cycle and increased weathering, as a consequence of an expanded greenhouse effect that improved nutrient availability in the surface waters. These conditions favoured the acarininids, able to temporarily colonize warmer deeper and nutrient-richer waters previously occupied by subbotinids. The highly specialized, warm-indices morozovellids, that should largely share the same habitat with acarininids, do not show significant changes except for a temporary but substantial increase in abundance at the ETM2 and I1 onsets. We hypothesize that the first phase of warming favoured morozovellids until the enhanced hydrological cycle increased eutrophic conditions, detrimental for morozovellids but better tolerated by acarininids. Calcareous plankton variations during the hyperthermals in a deep-water setting could however be affected by selective dissolution susceptibility due to the lysocline rise associated to these events. The planktic foraminiferal fragmentation index, which gives indication on degree of carbonate dissolution, shows very low values in correspondence to the marly-units of the Terche section. This suggests that, modifications of the assemblages can be mainly considered as genuine. The marked decrease of carbonate content within marly-clay units can be thus largely attributed to dilution rather than dissolution.

## Overcoming the paradigm of the destruction of Nasca culture due to a Mega-El Niño event: a clue from the stratigraphic survey at Cahuachi (Peru)

Delle Rose M.<sup>1-2</sup> & Renzulli A.\*<sup>3</sup>

1. Consiglio Nazionale delle Ricerche, ISAC, Lecce. 2. IBAM-IMAA-CNR, 2012 Peru mission. 3. Dipartimento di Scienze della Terra, della Vita e dell'Ambiente. Università degli Studi di Urbino Carlo Bo.

Corresponding email: [alberto.renzulli@uniurb.it](mailto:alberto.renzulli@uniurb.it)

Keywords: Climate change, Hydrological sensitivity, Sedimentology, Petrography, Epistemology.

Cahuachi, the largest adobe ceremonial site in the world, is located on the coastal desert of Peru (Nasca Province), one of the driest zone of the Earth. It was the main centre of the Nasca culture (Orefici, 2012). In the nineties, an hypothesis of destruction of the site due to a Mega-El Niño event, based on a geological reconstruction, was proposed by Grodzicki (1990). Although some questions arose among the scientific community about this catastrophic interpretation (Bonavia, 1995), such a hypothesis finally led to believe that Cahuachi was covered by a huge flood that would have deposited conglomerates even on top of the highest buildings.

A stratigraphic section was measured in correspondence of the bedrock of the "Pirámide Sur" at Cahuachi. The section consist of mudstones, siltstones, sandstones and conglomerates. Our sedimentologic and petrographic studies clearly allow us to correlate the whole sedimentary deposits to the local geology, as defined by Montoya et al. (1994). The investigated succession can be referred to the Changuillo Formation having an Upper Pliocene-Lower Pleistocene age (Montoya et al., 1994) rather than to the Holocene alluvial terraces (Grodzicki, 1990). The conglomerate deposits at the top of the section could be also interpreted as a lateral facies of the base of Canete Formation and unequivocally underlie the ceremonial buildings. Most likely, Grodzicki and his collaborators had not good exposures of the bedrock and interpreted these deposits as a recent alluvial terrace, also following a subjective aerial photo interpretation (Ostaficzuk, 1990). The epistemological implications of the geological interpretations are evident.

The hydrogeological hazard assessed at Cahuachi (e.g. the occurrence of *huaycos*, debris flows triggered by extreme rain events) and the intense local earthquake activity are consistent with the influence of hydrological and seismic damages on the decline of the Nasca culture as asserted by Orefici (2012). However, the geological observation allow us to overcome the paradigm of the Nasca culture destruction due to a Mega-El Niño event.

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## **Reconstructing the past, detecting the actual features and modelling the future evolution of glaciers. The main outcomes of the SHARE STELVIO Project (Stelvio National Park ) as a contribution to understand the Alpine cryosphere evolution**

Diolaiuti G.\*<sup>1</sup>, Bocchiola D.<sup>2</sup>, Vuillermoz E.<sup>3</sup>, D'Agata C.<sup>1</sup>, Maragno D.<sup>1</sup>, Senese A.<sup>1</sup>, Azzoni R.S.<sup>1</sup>,  
Confortola G.<sup>2</sup>, Manzata E.<sup>4</sup>, Garavaglia R.<sup>2</sup> & Marzorati A.<sup>2</sup>

1. Università degli Studi di Milano, Department of Earth Sciences "A. Desio". 2. Politecnico di Milano, Department Civil and Environmental Engineering. 3. Ev-K2-CNR, via San Bernardino 145, 24126, Bergamo. 4. FLA (Lombardy Foundation for the Environment – Fondazione Lombardia per l'Ambiente), Milano.

Corresponding email: [guglielmina.diolaiuti@unimi.it](mailto:guglielmina.diolaiuti@unimi.it)

Keywords: glaciers, Stelvio National Park.

We analyzed a representative subset of Alpine glaciers (i.e.: 43 ice bodies) located in the Stelvio National Park under the umbrella of the SHARE STELVIO project i) to reconstruct their recent geometry changes (over a time frame of half a century); ii) to describe their actual features, present distribution and size; iii) to model the expected evolution under different climate change scenarios up to the end of the XXI century. The study embraced different competences and skills, from glaciology to remote sensing and climatology and permitted to describe past and present conditions of a not negligible fresh-water resource and to forecast its possible evolution. The geometry changes, which were derived from remote sensing investigations (mainly high resolution orthophotos), depicted a glacier surface area decrease of about 40% in the time frame 1954-2007 and an ice volume loss of 766 x 106 m<sup>3</sup> in the period 1981-2007. These values result well crosschecked with field glacier data collected on some selected glaciers of the Stelvio National Park since the second half of the XX century. Moreover for some glaciers were also available data describing bedrock and surface geometry since the beginning of the past century. These information permitted to apply a 1D flow model driven by mass balance perturbations which were evaluated on the base of a simple mass balance model. The flow model permitted to reconstruct past extent of glaciers and to forecast the future evolution up to the end of the XXI century. Under climate scenarios derived by ECHAM6 and EC models, our results suggest that the actually widest Italian valley glacier, Forni, will experience a reduction of about 80% with respect to its present size by 2080.

## **Snowmelt mass and energy balance on a steep slope**

Ferraris S.\*, Previati M., Pognant D. & Canone D.

DIST - Politecnico e Università di Torino.

Corresponding email: [stefanof32@gmail.com](mailto:stefanof32@gmail.com)

Keywords: snow, mountain hydrology.

Climate change will in some situations radically change the distribution of energy fluxes between soil and atmosphere. At the elevation of the seasonal snowline the expected increases in air temperature will lead to more rapid melting of the snowpack, thus influencing surface albedo and temperature. Also, the temporal distribution of the flow of rivers and the recharge of aquifers will be influenced.

An experimental site at about 1700 meters altitude is operated since 2010. Both energy and mass data are collected. During several snowfalls the energy provided by the solar radiation was able to melt the whole snowpack in a few hours. The melting of the snow cover explains a large part of the lack of closure of the energy balance. After the snow melting, the energy closure had a downward trend, perhaps because of the greater role of the unknowns related to energy in soil.

Instead, mass balances show a good closure for the individual event. The data deteriorates but remains acceptable if we consider the snow water equivalent values measured at the raingages. The latent flux after the snowfall is an element of complexity in the analysis of balance equations, but it cannot be considered negligible.

Air temperature, soil temperature, wind speed (and the interactions between them) also provide energy for melting, further accelerating the melting process.

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## NextData sixty years ocean reanalysis for the Mediterranean Sea

Fратиани C.\*<sup>1</sup>, Simoncelli S.<sup>1</sup> & Pinardi N.<sup>2</sup>

1. Istituto Nazionale di Geofisica e Vulcanologia, Gruppo Nazionale di Oceanografia Operativa. 2. Dipartimento di Fisica e Astronomia, Università di Bologna.

Corresponding email: [claudia.fratianni@bo.ingv.it](mailto:claudia.fratianni@bo.ingv.it)

Keywords: ocean reanalysis, validation, quality metric.

Historical records of the ocean variability are currently required by different research and institutional users and private companies for the management of the marine environment, risk assessment and sustainable exploitation of the marine resources. Historical observations are too sparse in space and time to be used alone for understanding the ocean climate variability.

The combination of information from numerical models and observations, utilizing data assimilation techniques, can provide more accurate information than observation - only or model - only. The production of the ocean reanalysis is a recent activity which started in the middle of the nineties (Lee et al., 2009) and it is now an established activity in several research and operational oceanographic centres.

This paper will present the first NextData MedSea reanalysis for the past 60 years and the methodology used.

The numerical model is based on the Nemo code, the data assimilation scheme is variational and all historical in-situ and satellite observations are used. The NextData MedSea reanalysis is forced with atmospheric surface variables from an AMIP dataset (Cherchi and Navarra, 2007). This paper will also present the assessment and measures of the quality of MedSea products versus the previous version of the Mediterranean Reanalysis. The data are openly and freely accessible at the web site: <http://medsearr.bo.ingv.it/>.

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## Status of the Phase I CORDEX activities and perspectives for the development of Phase II

Giorgi F.\*

Abdus Salam International Centre for Theoretical Physics (ICTP), Trieste.

Corresponding email: [giorgi@ictp.it](mailto:giorgi@ictp.it)

Keywords: Regional Climate Modeling, Climate Change, Uncertainties.

The COordinated Regional Downscaling EXperiment (CORDEX) has been developed with the purpose to assess and improve regional downscaling techniques (regional climate models, RCMs, and statistical downscaling, SD) and to produce a new generation of multi-model based 21st century regional climate projections for use in Vulnerability, Impact and Adaptation (VIA) studies. The CORDEX Phase I framework (Giorgi et al. 2009) envisioned large domains covering all land areas of the globe at an intermediate horizontal resolution of ~50 km.

A number of groups worldwide have already completed relatively large sets of RCM simulations over different domains, and the analysis of these experiments is providing important information on the behavior of the models and on the value of this multi-model based information for the characterization of the uncertainty underlying regional projections. In particular, the regional model RegCM4 (Giorgi et al. 2012) was used at the Abdus Salam International Centre for Theoretical Physics (ICTP) to produce a set of 34 projections over 5 CORDEX domains, Mediterranean, Africa, South Asia, Central America and South America. Fields from three global climate models (GCMs) were employed to drive the RegCM4 for two greenhouse gas concentration scenarios, RCP4.5 and RCP8.5. These simulations, called the CREMA (CORDEX REgCM hyper-MATrix) experiment were complete also as part of the NextDATA project of the Consiglio Nazionale per la Ricerca (CNR). In the first part of this paper I will provide a summary of the key issues emerging from the first results of the Phase I CORDEX effort, using illustrative examples from the CREMA and other regional efforts. These issues include the added value provided by RCMs, the analysis of multi model ensembles for the characterization of uncertainties and the collection and dissemination of large amounts of climate model data.

Based on the lessons learned from the Phase I activities, the RCM and broader downscaling communities are now discussing the design of the second phase of the CORDEX project. In the second part of the paper, I will thus describe the main elements of this discussion in order to elicit comments and contributions to this debate.

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## Past-to-present metamorphic CO<sub>2</sub>-degassing in the Himalayan orogen and its influence on the long-term global climate changes

Groppo C.\*<sup>1</sup>, Rolfo F.<sup>1-2</sup>, Mosca P.<sup>2</sup>, Ferrando S.<sup>1</sup>, Costa E.<sup>1</sup>, De Stefanis E.<sup>1</sup>, Laiolo M.<sup>1-3</sup> & Kaphle K.P.<sup>4</sup>

1. Department of Earth Sciences, University of Torino. 2. IGG – CNR, Torino, Italy. 3. Department of Earth Sciences, University of Firenze. 4. Central Department of Geology, Tribhuvan University, Kathmandu, Nepal.

Corresponding email: [chiara.groppo@unito.it](mailto:chiara.groppo@unito.it)

Keywords: orogenic CO<sub>2</sub> cycle, long-term global climate changes, metamorphic-CO<sub>2</sub> degassing.

Decarbonation reactions occurring during regional metamorphism in “large-hot” collisional orogens are an important source of atmospheric CO<sub>2</sub>, able to influence global climate through geologic time (Gaillardet & Galy, 2008). The Himalayan belt is the most prominent orogen on the Earth, where tectonic and erosional processes are still active today, and it is a likely candidate for the production of a large amount of metamorphic CO<sub>2</sub> that may have caused changes in long-term climate of the past, present and near future. Although some attempts of quantitative estimating metamorphic CO<sub>2</sub> degassing from the Himalaya have been made (e.g. Evans, 2011), considerable uncertainties still remain and the influence of the Himalayan orogeny on the past and present climate is highly debated.

We present the results of several research Projects focused on the study of metamorphic CO<sub>2</sub>-producing processes which occurred - and still occur - during the Himalayan orogeny.

The petrologic study of the CO<sub>2</sub>-source rocks (i.e. calc-silicate rocks) currently exposed on the Earth surface, is the key to investigate the metamorphic CO<sub>2</sub> flux in the past. Fieldwork activity performed by our research group in the eastern Himalaya highlighted that calc-silicate rocks are widespread in the Greater Himalayan Sequence (GHS) and occur as: dm- to m-thick layers or boudins (main assemblage: Pl+Cpx+Qtz+Grt) within medium- to high-grade metapelites in the structurally lower GHS, vs. tens to hundreds of meter thick layers (main assemblage: Kfs+Cpx+Cal+Scp+Pl+Qtz±Zo) within anatectic gneisses in the structurally upper GHS. Preliminary petrologic data demonstrates that both Grt- and Scp- bearing calc-silicate rocks may act as CO<sub>2</sub>-source during prograde heating, releasing internal-derived CO<sub>2</sub>-rich fluids through Grt forming reactions and Scp consuming reactions. The study of fluid inclusions occurring in the major rock-forming minerals is in progress and will provide direct constrains on nature and composition of the involved CO<sub>2</sub>-rich fluids.

Appealing clues for a contemporary metamorphic CO<sub>2</sub> production in the Himalayas are represented by the occurrence of CO<sub>2</sub>-rich hot-springs and related high CO<sub>2</sub> soil flux along major tectonic discontinuities of the Himalayan belt. Preliminary geochemical and isotopic data from selected hot-springs confirm the deep metamorphic decarbonation origin already suggested by previous authors.

The present study suggests that a reliable estimate of the past and present metamorphic CO<sub>2</sub> flux from the still active Himalayan orogen is a fundamental task for reconstructing the variations of atmospheric composition over geological time and their possible impacts on regional and global climate.

Evans K.A. 2011. Metamorphic carbon fluxes: how much and how fast? *Geology*, 39, 95-96.

Gaillardet J. & Galy A. 2008. Himalaya-carbon sink or source? *Science*, 320, 1727-1728.

## **A record of the Atlantic Multidecadal Oscillation in the magnetic properties of Alpine lakes**

Lanci L.\*<sup>1</sup> & Hirt A.M.<sup>2</sup>

1. DiSBef, Università di Urbino. 2. Institute of Geophysics, ETH-Zurich, Switzerland.

Corresponding email: [luca.lanci@uniurb.it](mailto:luca.lanci@uniurb.it)

Keywords: Atlantic Multidecadal Oscillation, Alpine Lakes, Rock-magnetism.

We studied rock-magnetic data of lake sediments from the Alpine region that were previously recognized as sensitive climate proxy records whose time resolution is sufficiently high to resolve the decadal climate variability. The analysis of these climate proxies during the last ~2500 yr, using a variety of spectral methods, show a common, statistically significant periodicity band with a period of about 60 yr, which is characteristic of the Atlantic Multidecadal Oscillation (AMO). Frequency-filtered signal from the Alpine lakes records co-vary with the instrumental record of the AMO over the last 110 yr with a negligible phase shift. The possible influence of solar irradiance in the putative AMO frequency bands was tested and ruled out. Comparison of the amplitude of the AMO signal with that of the Younger Dryas/Holocene transition suggest that AMO fluctuations played a significant role in pacing the variability of the Alpine climate variability after the Holocene thermal maximum.

## A multiproxy geochemical record of the early Aptian Selli event (OAE1a) from the platform carbonates of southern Italy

Lechler M.<sup>1</sup>, Jenkyns H.C.<sup>2</sup>, Owens J. D.<sup>3</sup>, Pogge von Strandmann P.A.E.<sup>4</sup>, Lyons T.W.<sup>5</sup>,  
Prosser G.<sup>1</sup> & Parente M.\*<sup>6</sup>

1. Dipartimento di Scienze, Università degli Studi della Basilicata, Potenza. 2. Department of Earth Sciences, University of Oxford, Oxford, UK. 3. Geology & Geophysics (G&G) Department, Woods Hole Oceanographic Institution, Woods Hole, USA. 4. Department of Earth Sciences, University College London, London, UK. 5. Department of Earth Sciences, University of California, Riverside, USA. 6. Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse (DiSTAR), Università di Napoli "Federico II".

Corresponding email: [maparent@unina.it](mailto:maparent@unina.it)

Keywords: OAE1A, geochemical proxies, carbonate platforms.

Several events of rapid global warming, seemingly triggered by huge injections of CO<sub>2</sub> into the atmosphere, have been recognized in the geological record. They are associated with perturbations in biogeochemical cycles and severe palaeoenvironmental disturbances. Some of these events, known as Oceanic Anoxic Events (OAEs), are marked by widespread deposition of organic-rich facies in epicontinental and oceanic basins under oxygen-depleted conditions.

The deep-marine organic-rich and carbonate-free facies, which are the hallmark of OAEs, are poor archives for some precious geochemical proxies that are preserved in carbonate minerals: examples include lithium isotopes and carbonate-associated sulphur isotopes. Shallow-water carbonates may fill some important gaps in our knowledge of OAEs, by offering an high resolution archive of these proxies and by documenting the response of shallow-marine tropical ecosystems to CO<sub>2</sub>-triggered global warming and ensuing palaeoenvironmental perturbations.

This study has focused on the early Aptian OAE1a (Selli Event, ca 120 Ma.), one of the most important Mesozoic OAEs. Sulphur isotopes, redox-sensitive elements (Ce/Ca, Ce/Ce\* and Mn/Ca) and lithium isotopes have been analysed in lower Aptian shallow-marine carbonate sections from southern Italy. The goal is to determine the relative extent of oxygen-depleted water masses in the oceans and the role of weathering as both an OAE initiator (via nutrient supply) and terminator (via CO<sub>2</sub> sequestration).

The lithium isotope ratio of seawater is mainly controlled by continental silicate weathering and high- and low temperature alteration of oceanic crust. With CO<sub>2</sub>-forced increasing weathering rates of silicates at the onset of OAEs, a shift to lighter isotopic values is expected. In fact, the studied sections record decreasing lithium isotopes to a minimum value, coincident with the negative spike in carbon isotopes preceding the onset of OAE1a. The increase in silicate weathering, in conjunction with organic-carbon burial, contributed to the drawdown of atmospheric CO<sub>2</sub>.

The concentration of cerium in seawater increases with decreasing oxic sinks in the oceans. Therefore, a higher Ce/Ca ratios and a more positive Ce anomaly is expected during OAEs. Manganese enrichments are usually formed in pore-waters rich in Mn<sup>2+</sup> with appropriate levels of carbonate alkalinity. However, it has been observed that during OAEs manganese is depleted in many deep-marine organic-rich and carbonate-poor facies, whereas shallow-water platform carbonates are enriched. As expected, in the studied sections, cerium and manganese show a positive shift during OAE1a, indicating the expansion of oxygen-depleted water-masses into shallow-water regions.

The sulphur-isotope composition of the oceans is largely dependent on the input via hydrothermal fluxes and weathering of sulphur-bearing minerals and the output via gypsum and pyrite burial. The precipitation of gypsum affects mainly the sulphur concentration in seawater and has only a minor isotopic effect. Conversely, the formation of sulphides from microbial sulphate reduction produces isotopically light pyrite. An overall positive correlation of carbon and sulphur isotopes during the early Toarcian and the Cenomanian–Turonian boundary OAEs suggests enhanced pyrite burial under euxinic conditions. A similar pattern can be recognised during the OAE1a in the platform carbonates of southern Italy.

## **An innovative approach to high-resolution summer-temperature reconstructions for the last centuries using large tree-ring datasets from the Central Alps**

Leonelli G.\*<sup>1</sup>, Coppola A.<sup>2</sup>, Baroni C.<sup>2</sup>, Salvatore M.C.<sup>2</sup>, Pelfini M.<sup>1</sup>

1. Department of Earth Sciences - University of Milan, Italy. 2. Department of Earth Sciences - University of Pisa, Italy.

Corresponding email: [giovanni.leonelli@unimi.it](mailto:giovanni.leonelli@unimi.it)

Keywords: Temperature reconstruction, tree rings, Central European Alps.

Since the last decades validated datasets of instrumental records of monthly temperature and precipitation are available to the scientific community. For Europe and the Alps in particular, these time series cover nearly seamless about 2.3 and 1.5-2 centuries of temperature and precipitation data, respectively. For the less recent periods, however, most of the meteorological data derives only from stations located in the cities or in urbanized areas, whereas the high-altitude environments are underrepresented. High-resolution land surface temperature from these environments which are primarily impacted by variations in climatic regimes may be derived from the trees growing there, that may record century-long climatic information with annual resolution. Indeed, most of the annually-resolved climatic reconstructions performed for periods prior to instrumental records are largely based on tree-ring information.

With the aim of providing century-long information on past climatic variability in the 1° x 1° grid point Lat. 46° N, Long. 10° E (Central Alps, comprising the Ortles-Cevedale and the Adamello-Preseana Groups), nearly 20 tree-ring chronologies have been constructed with dendroclimatic purposes from University of Milan and University of Pisa (Leonelli et al. 2009; Coppola et al. 2013). For the same grid point another 9 chronologies were added to the previous dataset, for a total of about 800 individual series of tree-ring growth covering the period from nearly 1300 up to 2008 A.D. Instead of considering all the individual series collected within each site and then modeling responses to climate and performing the temperature reconstruction using the site chronologies (canonical reconstruction), we used an innovative approach which points at using only those series that are highly sensitivity to summer temperature. For this purpose, over the period covered by the temperature instrumental record, we selected only those series presenting highly significant year-to-year synchronicity with the HISTALP summer (JJA) temperature series and the Pearson's correlation > 0.3. After this selection, the recent portion of the Highly Sensitive To Temperature (HSST) chronology was constructed. This chronology was elongated through the pre-instrumental period up to 1274 A.D. following the same approach of series selection previously applied, using the chronology itself as reference. The obtained HSST chronology is the basis for the high-resolution reconstruction of past JJA temperature over the considered Alpine region and presents a satisfactory signal stability up to 1430 AD.

Understanding past climatic variability in the Alps and providing century-long high-resolution temperature reconstructions may be extremely useful for modeling past climatic variability in remote sites and for correctly predicting the future impacts of ongoing climate change on the Alpine environment and its resources.

Coppola A., Leonelli G., Salvatore M.C., Pelfini M. & Baroni C. 2013. Tree-ring-based summer mean temperature variations in the Adamello-Preseana Group (Italian Central Alps), 1610-2008 AD. *Clim. Past*, 9, 211-221.

Leonelli G., Pelfini M., Battipaglia G., Cherubini, P. 2009. Site-aspect influence on climate sensitivity over time of a high-altitude *Pinus cembra* tree-ring network. *Climatic Change*, 96 Issue 1/2, 185-201.

## Paleoclimatic changes occurred during the last two millennia in the central and south Tyrrhenian Sea: a contribution of NEXTDATA project

Lirer F.\*<sup>1</sup>, Margaritelli G.<sup>1,8</sup>, Vallefucio M.<sup>1</sup>, Agnini C.<sup>2</sup>, Anzalone E.<sup>1</sup>, Bellucci L.<sup>3</sup>, Bonomo S.<sup>1</sup>, Capotondi L.<sup>3</sup>, Cascella A.<sup>4</sup>, Di Rita F.<sup>5</sup>, Ferraro, L.<sup>1</sup>, Insinga D.D.<sup>1</sup>, Magri D.<sup>5</sup>, Marsella E.<sup>1</sup>, Pappone G.<sup>6</sup>, Petrosino P.<sup>7</sup>, Rettori R.<sup>8</sup>, Sorgato S.<sup>1</sup>

1. Istituto per l'Ambiente Marino Costiero (IAMC) – Consiglio Nazionale delle Ricerche, Napoli 2. Dipartimento di Georisorse – Università degli Studi di Padova, Padova 3. Istituto Scienze Marine, ISMAR– CNR, Consiglio Nazionale delle Ricerche, Bologna 4. Istituto Nazionale di Geofisica e Vulcanologia (INGV), Pisa 5. Dipartimento di Biologia Ambientale – Botanica, Università La Sapienza di Roma, Roma 6. Dipartimento di Scienze e Tecnologie - Università degli Studi di Napoli “Parthenope”, Napoli 7. DISTAR - Dipartimento di Scienze della Terra, dell’Ambiente e delle Risorse – Università degli Studi “Federico II”, Napoli 8. Dipartimento di Fisica e Geologia – Università di Perugia, Perugia

Corresponding email: [fabrizio.lirer@iamc.cnr.it](mailto:fabrizio.lirer@iamc.cnr.it)

Keywords: Tyrrhenian Sea, last 2k, paleoclimate, planktonic foraminifera, oxygen stable isotope.

At present temporally and spatially high-resolution climate information / reconstruction from marine archives is still limited. This is much more evident in the Mediterranean basin. The new high-resolution (decadal to century scale) time-series recovered in the central and south Tyrrhenian Sea represent thus an important contribution.

In particular, a high-resolution integrated study carried out in the central and south Tyrrhenian Sea have enabled identification of several climatic periods during the last two millennia. We focus on four shallow water marine records recovered with the R/V Urania at water depth of 93 and 118 meters (Gulf of Gaeta) and 103 meters (Gulf of Salerno).

Planktonic foraminifera distribution combined with oxygen stable isotope data performed on planktonic foraminifer *Globigerinoides ruber*, illustrates four major environmental changes during the last 2000 years: Roman period / Dark Age transition; Dark Age / Medieval Climatic Anomaly transition; Medieval Climatic Anomaly / Little Ice Age transition and Little Ice Age / Industrial period transition.

The high-resolution of the  $\delta^{18}\text{O}$  *G. ruber* record from four shallow water marine cores document a good correlation, even if small differences are present, probably related to the influence of the major rivers (Sele and Volturno rivers) in the study area. In particular, the  $\delta^{18}\text{O}$  signals illustrate the alternation of warm / wet and cold / dry events during the last 2000 years.

The Roman period is characterised by two warm intervals alternated with two cold ones which correlates *Globigerinoides quadrilobatus* and *Globorotalia inflata* maxima, respectively. The Dark Age period documents a warm phase with maxima in *G. ruber* followed by a cold ones with increase in *G. inflata* abundance. The Medieval Classic Anomaly period represents a quite complicate interval where the  $\delta^{18}\text{O}$  *G. ruber* signature document a general shift towards dry / cold condition interlayered by short warm phases characterised by peaks in *Globigerinoides ruber* pink. The Little Ice Age period documents more cool condition with a strong increase in *Globoprotalia truncatulinoides* abundance while the Industrial period is strongly dominate by the increase in warm oligotrophic *G. quadrilobatus* abundance.

*We acknowledge financial support from the Italian Project of Strategic Interest NEXTDATA (<http://www.nextdataproject.it>) “A national system for recovery, storage, accessibility and dissemination of environmental and climatic data from mountain and marine areas”.*

## **The lost archipelago in the Adventure Plateau (Sicilian Channel)**

Lodolo E. \*, Civile D. & Zecchin M.

Istituto Nazionale di Oceanografia e di Geofisica Sperimentale (OGS) – Trieste.

Corresponding email: [elodolo@ogs.trieste.it](mailto:elodolo@ogs.trieste.it)

Keywords: Adventure Plateau, shallow banks, palaeogeographic reconstructions.

The sea-level rise following the Last Glacial Maximum (LGM), defined as the most recent interval in Earth history when global ice sheets reached their maximum volume, has radically altered the pre-existing geography, pushing back the former shorelines. The effect of this eustatic change was particularly intense and dramatic in the flat lands and in shelves, such as the Sicilian Channel. High-resolution bathymetric maps and seismic profiles (Chirp lines and 2-D multichannel seismic reflection profiles) show that the Sicilian Channel, now lying at water depths rarely exceeding 150 m, has been emerged several times during its geological history, the last being the Early Holocene, when km-sized islands punctuated the north-western sector of the Sicilian Channel - the Adventure Plateau - forming a broad archipelago. Many of these islands, now located at water depths ranging from -10 to -40 m, are composed of highly deformed Miocene sedimentary rocks (Talbot, Ante-Talbot, Nereo, and Pantelleria Vecchia banks), others represent submarine Pleistocene volcanic edifices (Galatea, Anfitrite and Tetide banks). The sedimentary cover in all of these banks is virtually absent. The analyses of high-resolution seismic profiles allowed to identify the post-LGM morphological markers associated to the marine transgression, represented by specific and distinct erosional features. Combining swath bathymetric data with the high-resolution seismic profiles, we have generated two palaeogeographic maps of the former Adventure Archipelago at two specific time frames of the Early Holocene, corresponding to a former sea-level of -60 m and -42 m, respectively. Maps clearly show that in a few hundred years, the geography of the archipelago has changed dramatically, so much so that some islands have disappeared, and some have fallen by more than 80% of their former size. This was an extremely rapid and profound event in the recent geological history of the Northern Hemisphere, which has undoubtedly influenced the distribution of ancient human settlements along the coast, especially in the lowland areas in the vicinity of ancient shorelines.

## Recently deglaciaded areas, permafrost and natural instability in the Orco and Lanzo valleys (NW Italy)

Lucchesi S.\*<sup>1</sup>, Chiarle M.<sup>1</sup>, Bertotto S.<sup>1-2</sup>, Fioraso G.<sup>3</sup> & Nigrelli G.<sup>1</sup>

1. IRPI-CNR, Torino. 2. Dipartimento di Scienze della Terra, Università di Torino. 3. IGG-CNR, Torino.

Corresponding email: [stefania.lucchesi@irpi.cnr.it](mailto:stefania.lucchesi@irpi.cnr.it)

Keywords: Climate change, glaciers, permafrost.

The radical changes caused by glacial masses in the past and still present are accompanied by equally important morphological changes in the previously glaciated areas.

A first attempt of quantifying the effects of climate change in the Anthropocene was carried out for the Orco and Lanzo Valleys, through a detailed geomorphological analysis and interpretation of traditional aerial photos and digital orthophotos, available at a variety of scales and for different years.

This analysis showed that between 1850 and 2006 the overall number of glaciers in the studied area has decreased by 64% which correspond to a reduction of glaciated area of 78% compared with the glacier extent during the peak of the LIA (58.8 km<sup>2</sup>) (Lucchesi et al., 2014).

The areas of recent deglacialization are currently characterized by the outcropping of new large rock surfaces, by extensive and impressive moraines and till, or by the presence of lakes. Overall 13.5 km<sup>2</sup> (corresponding to 28%) of the areas of recent deglacialization are characterized by the outcropping of rock, 33.9 km<sup>2</sup> (71%) are covered by glacial deposits (till), fluvio-glacial or gravitational sediments (slope debris, landslides) and 0.6 km<sup>2</sup> (1.3%) are occupied by lakes in 2006.

The environment of recent deglacialization is morphologically very young and dynamic, more exposed than others to extremely fast remodeling processes, especially for the areas covered by glacial deposits. For instance, on 24 September 1993, after an intense rainstorm, a large portion (800,000 m<sup>3</sup>) of the frontal moraine of the Mulinet Glacier was removed by a huge debris flow that traveled 4.5 km downstream.

Nevertheless, recently deglaciaded areas are in part affected by the presence of a more or less pervasive and continuous permafrost (Mair et al., 2011). The presence of permafrost has a stabilizing effect on rock and debris slopes. Under a warming climate, permafrost degradation can become one of the most relevant factors contributing to the development of instability processes (in particular rock falls and debris flows).

For this work, we met the geomorphological information obtained for the deglaciaded areas (type and extent of outcropping materials), with the permafrost distribution map realized in the framework of the PermaNet project for the European Alps. As a result, we were able to make a first estimate of debris areas and volumes prone to instability, or ready to be mobilized by surface water runoff.

Lucchesi S., Bertotto S., Fioraso G. & Chiarle M. 2014. Little Ice Age and contemporary glacier extent in the Western and South-Western Piedmont Alps (North-Western Italy). *Journal of Maps*, 10(3), 409–423.

Mair V., Zischg A., Lang K., Tonidandel D., Krainer K., Kellerer-Pirklbauer A., Deline P., Schoeneich P., Cremonese E., Pogliotti P., Gruber S. & Böckli L. 2011. PermaNET. Permafrost Long-term Monitoring Network. *Interpraevent*, Synthesis report, 1(3), 1-24.

## **New regional climate simulations using RegCM4 over the CORDEX South Asia domain**

Mariotti L.\*, Bacer S. & Giorgi F.

Earth System Physics Section - The Abdus Salam International Centre for Theoretical Physics (ICTP), Trieste – Italy.

Corresponding email: [mariotti@ictp.it](mailto:mariotti@ictp.it)

Keywords: climate simulations, precipitation, downscaling.

We present two new high-resolution regional climate simulations over the CORDEX South Asia made with the latest version of the Regional Climate Model RegCM4. The simulations have been performed at 25 km and 12 km of horizontal resolution using the ERA-Interim boundary conditions. The simulated results are compared with the monthly mean surface observations for temperature and precipitation over the entire domain.

The rainy season during the June-July-August-September (JJAS) over India shows a bigger improvement using a different parameterization of the MIT-Emanuel convection scheme for land and ocean. Another big improvement has been found with the UW PBL scheme (Bretherton and McCaa, 2004).

The model shows in JJAS season a slight cold bias over the mountain compared with CRU dataset, instead in Indian land area the pattern of the temperature is well represented. The monsoon precipitation over the Indian continent is reasonably represented.

A good agreement was found from the comparison between RegCM4 with the IMD dataset by studying the area weighted average values time series of monthly accumulated rainfall (cm) in Indian land area.

## NextData Project: development of a web system for climate and paleoclimate data sharing

Melis M.T.\*<sup>1-2</sup>, Locci F.<sup>1</sup>, Dessi F.<sup>3</sup>, Frigerio I.<sup>4</sup>, Strigaro D.<sup>4</sup>, De Amicis M.<sup>4</sup> & Vuillermoz E.<sup>2</sup>

1. Dipartimento Scienze Chimiche e Geologiche, Università di Cagliari. 2. Ev-K2 CNR, Bergamo  
3. CNR-ISAC UOS Torino. 4. Geomatic Laboratory, Università di Milano Bicocca, Milano.

Corresponding email: [titimelis@unica.it](mailto:titimelis@unica.it).

Keywords: Geonetwork, Spatial Database, climate data.

This study is dedicated to the development of a webGIS service platform for the environment data sharing, which is carrying out in the framework of the Italian national project NextData. This project is supported by Ministry of Education, Universities and Research and a part is mainly dedicated to the study of climate change in the last 2000 years in the Mediterranean area. The system is based on the integration between the open source metadata cataloguing system provided by Geonetwork and a dedicated new database called WDBPALEO.

Scope of this work is to show the design, the development and the implementation of the Environmental Data System (EDS). The EDS is designed up to now to store data from two sources: high altitude automatic stations and non-polar ice cores and marine sediment cores (Melis et al., 2013). Since 2005, the Ev-K2 CNR Committee has promoted an integrated environmental project named SHARE (Station at High Altitude for Research on the Environment) focused on the mountain regions as primary indicators of climate change. Originally launched as a system of measurements in environmental and earth sciences in the Himalaya-Karakorum region, SHARE has later expanded its network to Europe (Apennines and Alps), Africa (Rwenzori Mt) and more recently to South America (Andes).

The EDS is split in two parts: WDB and WDBPALEO database system: the first is dedicated to the storing of high altitude data from Automatic Weather Stations (AWS) of SHARE Network, and the second to paleoclimate data from non-polar ice cores and marine sediment cores. These two data sources (AWS and cores) would be the base of a timeline history for a global past climate reconstruction.

The scientific interest of this service is the possibility to access into the same website to the data acquired from the network of highest altitude stations for actual climate analysis and provision and data from paleoclimate samples acquired from non-polar glaciers and sea cores. The service for the first time shares these data in a downloadable standard format for all researchers and describes with the metadata catalogue all the necessary information for the correct use of these data.

The structure to store and share data, from database to Web GIS application, is based on open source software tools and they are free, useful and very capable. The present database is released with GNU license and it could potentially be customized and shared it without limitations.

Melis M. T., Dessi F., Locci F., Bonasoni P., Vuillermoz E. 2013. Share Geonetwork: a web-service platform for environmental data sharing. Proc. SPIE 8795, First International Conference on Remote Sensing and Geoinformation of the Environment (RSCy2013), 87951V (August 5, 2013) <http://dx.doi.org/10.1117/12.2027602>.

## **GIS analysis to apply theoretical Minimal Model on glacier flow line and assess glacier response in climate change scenarios**

Moretti M.\*, Mattavelli M., De Amicis M. & Maggi V.

Dipartimento di Scienze dell'Ambiente e del Territorio e di Scienze della Terra, Università degli Studi di Milano-Bicocca.

Corresponding email: [m.moretti8@campus.unimib.it](mailto:m.moretti8@campus.unimib.it)

Keywords: Glacier, Model, GIS.

The development of theoretical work about glacier dynamics has given rise to the construction of mathematical models to assess glacier response in climate change scenarios. Glacier are sentinels of climate condition and the Project of Interest NextData will favour new data production about the present and past climatic variability and future climate projections, as well as new assessments of the impact of climate change on environment. The aim of this specific research program is to develop and apply theoretical models to understand, evaluate and reproduce glacier response in different climate scenarios. These models try to reduce the complexity of a glacier dynamics in a simple description based on physics laws: the background of the numerical algorithms. To investigate glacier evolution we used Minimal Glacier Model (Oerlemans J., 2011): this class of models does not explicitly describe spatial distribution of quantities like ice thickness, basal water pressure, sliding velocity and the glacier evolution is calculated from an integrated continuity equation over the entire volume, based on the perfect plasticity principle. The state variable is glacier length. The analysis is composed also by theoretical equation to estimate mean thickness of glacier (Linsbauer A., 2012), useful to minimal model parameters, that starts from the evaluation of elevation range and slope. In minimal model it is also necessary an exhaustive study about geomorphology of the glacier through the related Digital Elevation Model (DEM) using a GIS. Throw DEMs, it is possible to reconstruct the evolution of area and volume of the glacier with a multitemporal analysis and draw the flow lines that follow the accumulation-ablation dynamic, on which the model is applied. During this work an algorithms were developed to extrapolate from DEMs all the feature of interest to run model and to conduct a complete geomorphometric analysis on glacier. The model input data set are given by the mass balance and the Equilibrium Line Altitude. We relate these with winter precipitation and summer temperature using a theoretical fit as a transfer function of climate forcing on glacier behavior. This meteorological values are recovered in global atmospheric reanalysis or climate model, focusing on the area around the glacier of interest. The first step is the presentation of the model validation on historical real series of glacier parameter and dimension, followed by the run of this validated models to estimate the evolution of glacier in future scenarios.

Linsbauer A., Paul F. & Haberli W. 2012. Modeling glacier thickness distribution and bed topography over entire mountain ranger with GlabTop. *Journal of Geo. Res.*, 117, F03007.

Oerlemans J. 2011. *Minimal Glacier Models*. Igitur, Utrecht University.

## Generation and use of high-resolution climatic data for hydrological and impact studies

Palazzi E.\*, Terzago S., Turco M., Pieri A., D'Onofrio D., von Hardenberg J. & Provenzale A.

Istituto di Scienze dell'Atmosfera e del Clima (ISAC-CNR) Torino.

Corresponding email: [e.palazzi@isac.cnr.it](mailto:e.palazzi@isac.cnr.it)

Keywords: Climate Projections, Downscaling, Impact studies.

Estimating the expected impact of climate change on hydrometeorological risk, ecosystem functioning, snow and glacier melt and water availability requires climate projections with high spatial and temporal resolution.

Global Climate Models (GCMs) capture the dynamics and the main processes of the climate system, the feedbacks and the inter-relationships between different variables required for large-scale projections of future climate, but their spatial resolution, currently no higher than 70-120 km (IPCC, 2013), is too coarse for hydrological applications and impact studies at the local scale.

In the framework of the Italian Project of Interest NextData ([www.nextdataport.it](http://www.nextdataport.it)), a suite of dynamical and statistical downscaling methods is being implemented and applied to coarse resolution observational, reanalysis and model data to generate the climatic information at the resolutions appropriate for driving hydrological, rainfall/runoff, impact and assessment models. We are performing dynamical downscaling experiments by running, in climatic mode, the non-hydrostatic Weather Research and Forecasting (WRF) model nested into both reanalysis and GCM data at spatial resolutions down to 4 km. Statistical and stochastic downscaling methods are also being implemented to be applied downstream of the global or regional simulation outputs. In the former case we use methods such as the analogue Model Output Statistics (Turco et al., 2011); in the latter case, the RainFARM stochastic downscaling procedure is applied to long-term regional climate model precipitation data, as it was recently done in D'Onofrio et al. (2014).

In this contribution we present one application of the three downscaling methods outlined above, with particular attention on their suitability for applications in complex mountainous regions (e.g., the Great Alpine Region).

The validated downscaled outputs will be made available through the NextData Project portals and they will be tailored for rapid use, becoming an open national database of forcing conditions for impact models and studies (water resources, risk assessment, ecosystems) and for assessment tools.

D'Onofrio D., Palazzi E., von Hardenberg J., Provenzale A., Calmanti S. 2014. Stochastic Rainfall Downscaling of Climate Models. *J. Hydrometeor.*, 15, 830-843.

IPCC, 2013. *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change.* 2013.

Stocker TF, Qin D, Plattner G-K, Tignor M, Allen SK, Boschung J, Nauels A, Xia Y, Bex V, and Midgley PM (eds.) Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 1535 pp.

Turco M., Quintana-Seguí P., Llasat M.C., Herrera S., Gutiérrez J.M. 2011. Testing MOS precipitation downscaling for ENSEMBLES regional climate models over Spain, *J. Geophys. Res.*, 116, D18109.

## **Orbitolinid-rich intervals and their relations with the OAE1a in the carbonate platforms of central and southern Italy**

Parente M.\*<sup>1</sup>, Di Lucia M.<sup>2</sup>, Lechler M.<sup>3</sup> & Frijia G.<sup>4</sup>

1. Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse (DiSTAR), Università "Federico II" Napoli. 2. RPS Energy, Woking, United Kingdom. 3. Dipartimento di Scienze, Università of Basilicata, Potenza. 4. Institut für Erd- und Umweltwissenschaften, University of Potsdam, Germany.

Corresponding email: [maparent@unina.it](mailto:maparent@unina.it)

Keywords: OAE1a, orbitolinid larger foraminifera, carbonate platforms.

Orbitolinid larger foraminifera are key microfossils for the biostratigraphy of Barremian-Aptian Tethyan carbonate platforms. They have been also used as harbingers of palaeoenvironmental change. At the northern margin of the Tethyan Ocean, in the Urganian carbonate platform, transient blooms of flat conical orbitolinids have been commonly interpreted as a signal of increased nutrient input, causing the shift from the Urganian-type photozoan carbonate factory to the heterozoan carbonate production mode and, eventually, platform drowning. Building on this widely accepted concept, controversies have then arisen between authors emphasizing geologically rapid environmental changes, leading to the deposition of nearly isochronous orbitolinid-rich beds on a supraregional scale and those favouring the idea of progressive environmental deterioration, leading to the deposition of non-correlatable orbitolinid beds. Other authors have considered sea-level changes as the main control, interpreting marls with flat orbitolinids as repeatedly occurring at maximum flooding intervals.

The occurrence of similar orbitolinid-rich beds has long been known also in the carbonate platforms of central and southern Tethys. The lack of a reliable chronostratigraphic framework hindered the interpretation of their time-significance until carbon isotope stratigraphy came to the scene.

In this work we discuss the chronostratigraphic distribution and the palaeoenvironmental meaning of flat orbitolinid-rich beds in the shallow-water carbonates of central and southern Italy, integrating our data on several sections of the Apennine and Apulian carbonate platforms with a review of published data. We use a combination of chemostratigraphy (carbon and strontium isotope stratigraphy) and biostratigraphy to build a high resolution age-model for the studied sections and to put our data in the framework of global palaeoenvironmental changes during the late Barremian-early Aptian, with particular emphasis on the OAE1a (Selli event, ca 120 Ma).

## Holocene climate dynamics in the Eastern Italian Alps: a multi-proxy study from an ombrotrophic bog

Poto L.\*<sup>1</sup>, Gabrieli J.<sup>1</sup>, Segnana M.<sup>2</sup> & Barbante C.<sup>1</sup>

1. CNR- IDPA Istituto per la Dinamica dei Processi Ambientali, Venezia. 2. Università Ca' Foscari di Venezia, Dipartimento di Economia, Venezia.

Corresponding email: [luisa.poto@unive.it](mailto:luisa.poto@unive.it)

Keywords: Ombrotrophic bog, Holocene, climate changes.

Paleoclimate and paleoenvironmental studies in the north-eastern Italian Alps have been hampered by the rarity of well-preserved high-altitude deposits and the lack of high-resolution multi-proxy records with adequate chronological control. Here we present the first complete Late Glacial to Holocene peat succession from the Dolomites (Danta di Cadore, Belluno, Italian Alps). We collected a 7 m core and evaluated the potential of the ombrotrophic Val di Ciampo peat deposit (1400 m a.s.l.) as an archive of environmental and climate change. The depth-age scale is based upon independent <sup>14</sup>C and <sup>210</sup>Pb dates and combined with peat stratigraphy demonstrates that the peat core covers more than 13,200 years (cal BP), extending back to the end of the last part of the Late Glacial. We determined bulk density, inorganic matter content, pore water pH, conductivity, Ca/Mg ratios, and Ca, Sr and Ti trends to identify changes in trophic conditions through the bog. The boundary between ombrotrophic and minerotrophic conditions occurs at approximately 400 cm below the surface and demonstrates that this core is the longest Eastern Alpine ombrotrophic record yet obtained, corresponding to 7,000 years cal BP.

Chronological constraints on the course of deglaciation in the Southern Alps are fewer than those available for the Northern slope of the Alps. For the Piave basin, the mode and timing of deglaciation are well-defined only for its mid-part, while no data are available for the upper section. In such a context of very limited data, the oldest radiocarbon age (13,110-13,330 years cal BP) represents a very valuable result, providing clear evidence that, during the Bölling-Alleröd interstadial, the upper part of the Piave Glacier was ice-free, and that the retreat process of the Piave Glacier from the Last Glacial Maximum was very rapid.

Pollen assemblages at the transition from the Late Glacial to the Early Holocene were studied at high resolution. In this time frame, pollens show that thicker forests of Gymnospermeae were present during the Bölling-Alleröd interstadial (at approximately around 13,200 years cal BP), and were reduced by the climatic cooling of the Younger Dryas (12,600 - 11,500 years cal BP), when a more open type of vegetation spread. Then, with the beginning of the Holocene, forests developed again with the expansion of warmth-requiring species.

Moreover through chemical analyses (Inductively Coupled Plasma Mass Spectrometry, ICP-MS and X-ray Fluorescence Core Scanner, XRF-CS) we reconstructed the main trends in atmospheric depositions that characterized the Holocene providing information about climate-related changes in the atmospheric composition and about the impact of human activities on the environment.

The high-resolution chemical data of this peat archive improves our understanding of European Alpine Holocene climate variability and the relationship between natural climate fluctuations and anthropogenic climate change during the present interglacial in the Dolomites.

## Two thousand years of atmospheric metal depositions recorded by the ombrotrophic peat bog of Danta di Cadore (North-Eastern Italian Alps)

Poto L.\*<sup>1</sup>, Gabrieli J.<sup>1</sup>, Segnana M.<sup>2</sup> & Barbante C.<sup>1</sup>

1. CNR-IDPA Istituto per la Dinamica dei Processi Ambientali, Venezia. 2. Università Ca' Foscari di Venezia, Dipartimento di Economia, Venezia.

Corresponding email: [luisa.poto@unive.it](mailto:luisa.poto@unive.it)

Keywords: ombrotrophic bog, mining activity, Dolomites.

The Eastern Italian Alps are located near one of the areas in the world with some of the longest records of extreme environmental use by human activity. In this area, paleo-climate studies are hampered by the lack of high-resolution multi-proxy records with adequate chronological control. With this project, we propose to reconstruct Holocene climatic and environmental variations in the Eastern Italian Alps using an ombrotrophic peat bog record from the Dolomites (Danta di Cadore, 46°34' N, 12°33' E, 1400 m a.s.l., Belluno province).

The study of global climatic change require a holistic and multi-proxy approach to better understand several complex and often non-linear relationships. In the Italian Alps our study on peat cores represents the first attempt where a multi-proxy approach is applied, and here we report our first results. A 7.0 m peat sequence was extracted in Danta di Cadore. The depth-age scale, based upon independent <sup>14</sup>C and <sup>210</sup>Pb dates and modeled with the *Clam* method (Blaauw, 2010), demonstrates that the archive covers more than 13,200 years (cal BP).

The investigation of atmospheric deposition during the Holocene is extremely important because it provides information about climate-related changes in the atmospheric composition and about the impact of human activities on the environment. With this aim, the concentration of 44 trace elements have been determined with the Inductively Coupled Plasma Mass Spectrometry ICP-MS at a resolution of 1 cm on the first meter of the bog, and X-ray Fluorescence Core Scanner (XRF-CS) analysis was applied on the entire peat sequence (2.5 mm of resolution).

Trace elements and heavy metals concentrations provide important information about how mining activity that has characterized the history of the Cadore region since the Middle Ages. Pb, Ag, Cd concentrations and Enrichment Factors (EFs) were determined. Concentration levels and EFs of several trace elements correspond quite well to the documented chronology about mining activity in the Cadore region, indicating that the Val di Ciampo bog recorded the development and the history of mining exploitation at least at a regional scale. In particular, the Pb, Ag and Cd maximum concentrations are recorded between the 1950s and 1980s, a time interval which corresponds to the highest activity of the mining sites.

In addition lead isotopes ratios were measured to identify natural and anthropogenic sources of Pb emissions. Results show an increase of Pb deriving from fuel combustion over the last decades that gradually overlies the impacts of mining activity. The decreasing <sup>206</sup>Pb/<sup>207</sup>Pb trend reached its minimum value of 1.153 in the 1990s and then increased again. In these years, Italy started to follow EU rules to limit global pollutants in the atmosphere, and finally banned leaded fuels in 2002.

This multi-proxy approach that integrates, using new chronological insights, chemical physical and biological features of the core, improves our understanding of Eastern Alpine Holocene climate, helping to delineate biotic and abiotic responses to climate dynamics during the present interglacial.

Blaauw M. 2010. Methods and code for 'classical' age modeling of radiocarbon sequences. *Quaternary Geochronology*, 5, 512-518.

## **Environmental analysis of a sensitive area (sea national park) by a geoindicator network. An additional approach in environmental monitoring in Liguria**

Pucci V.\*<sup>1-2</sup>, Gaggero L.<sup>1</sup> & D'Acqui R.<sup>2</sup>

1. Dipartimento di Scienze della Terra dell'Ambiente e della Vita, Università di Genova  
2. Agenzia Regionale per la Protezione dell'Ambiente Ligure (ARPAL).

Corresponding email: [valerio.pucci@unige.it](mailto:valerio.pucci@unige.it)

Keywords: Geoindicators, environmental monitoring, sustainable development, AMP Bergeggi island.

Relevant geoindicators among the IUGS checklist of 27 were addressed to a sensitive Ligurian area (The Bergeggi island national marine park), to achieve a time - integrated dataset of environmental parameters beyond those related with the “state of environment” annual report. It was possible thanks to the present geomonitoring in Liguria region that corresponds to national and EU normative (e.g. Italian D.Lgs. 152/06, Dir. 2000/60/CE, etc.) and where high resolution and/or time integrated data acquisition is active. The Geoin project is i) a tool considered over a longer time scale than current State of the Environment (SOE) scale, and ii) environment monitoring beyond Civil Protection (emergencies) needs.

The following steps were carried out:

1) selection of sustainable indicators within the IUGS checklist and analysis of the present Ligurian monitoring network. Our selection was addressed to observation of significant features of the National marine park of Bergeggi island and adjoining areas, both for environmental equilibria and economic and social issues. The selected geoindicators were:

- Shoreline position
- Surface water quality
- Subsurface temperature regime
- Sediment composition

2) data acquisition, validation and statistical computing from the present ARPAL, SIRAL and UNIGE site specific databases. Particularly we focused chemical and physical data on different environmental matrixes;

3) elaboration and analysis of new time series (2000-2009) about pH, saturation dissolved oxygen rate and sea water temperature (2000-2014), coastline displacement (1944-2010), sea sediments chemical quality (2008-2012) data;

4) assessment of local effect, like descending trends of pH and dissolved oxygen rate or positive tendency in sea water temperature, in the perspective of global climate change or interference between anthropogenic activities and coastal dynamics (like differential displacement of the coast line and discontinuous presence of different polluting substances settled on the sea floor);

5) design of technical improvements to the present monitoring network and suggestions on deployment of new recording tools.

## The last 2000 years in the Dolomites (Eastern Italian Alps): climate and environmental dynamics inferred from pollen and geochemical analyses

Segnana M.\*<sup>1</sup>, Gabrieli J.<sup>2</sup>, Poto L.<sup>2</sup>, Festi D.<sup>3</sup>, Oeggli K.<sup>3</sup> & Barbante C.<sup>2</sup>

1. Dipartimento di Economia, Università Ca' Foscari Venezia. 2. CNR-IDPA Istituto per la Dinamica dei Processi Ambientali, Venezia. 3. Istituto di Botanica, Università di Innsbruck, Austria.

Corresponding email: [michela.segnana@unive.it](mailto:michela.segnana@unive.it)

Keywords: Holocene, Dolomites, peat bog, pollen analysis, geochemical analysis.

Today the Earth is facing a rapid climate change with an unequivocal global warming of the climate system (IPCC, 2013). Giving the complexity of this system, ruled by natural forcing and affected by anthropogenic impacts, a complete understanding of its variability is still needed. In this framework paleoclimate research may largely contribute to infer new data providing information about the Earth's climatic history.

The ombrotrophic Coltrondo peat bog (46°39'28.37''N 12°26'59.17''E, Eastern Italian Alps) is here studied with the main objective to reconstruct past climatic and environmental variations. A multi-proxy approach is selected, where physical, geochemical and biological proxies are analyzed to investigate different facets of the ecosystem. Focusing on the first meter of the core, which spans about 2000 years, a high-resolution pollen, non pollen palynomorphs and microcharcoal profile is realized, coupled with geochemical analyses obtained with ICP-MS (Inductively Coupled Plasma-Mass Spectrometer) and XRF-CS (X-Ray Fluorescence core scanner), trying to disentangle between human and natural induced changes.

Biological and chemical information obtained will also be compared with other archives from the alpine chain in order to give new insights and build scenarios for future climate changes in the Alps.

Moreover with this research we aim to achieve quantitative information of past climatic dynamics, in order to reconstruct atmospheric temperature variations in this area, adding valuable information at the already existing global data-set on temperature reconstruction (PAGES 2k Consortium, 2013).

IPCC 2013. Climate Change 2013. The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 1535 pp.

PAGES 2k Consortium, 2013. Continental-scale temperature variability during the past two millennia. *Nature Geoscience*, 6, 339–346.

## **A comparative analysis of different modelling approaches to evaluate high resolution glacier melt from meteo and energy data**

Senese A.\*<sup>1</sup>, Vuillermoz E.<sup>2</sup> & Maugeri M.<sup>3</sup>

1. Dipartimento di Scienze della Terra "A. Desio", Università degli Studi di Milano. 2. Ev-K2-CNR, Bergamo  
3. Dipartimento di Fisica, Università degli Studi di Milano.

Corresponding email: [antonella.senese@unimi.it](mailto:antonella.senese@unimi.it)

Keywords: Ice and Snow Melt Model, Bare and Buried Ice, Alpine and Himalayan Glaciers.

Different modelling approaches physically based will be compared to evaluate their effectiveness in predicting high resolution ice and snow melt. The study considers both the complete surface energy budget (Oerlemans, 2000; Senese et al., 2012) computed from meteo and energy data acquired at the glacier surface through Automatic Weather Stations (AWSs) and several enhanced T-index models (Hock, 2003; Pellicciotti et al., 2005) driven by air temperature and energy data. Moreover in the case of supraglacial debris occurrence (i.e. buried ice) the conductive heat flux along the debris layer (Nicholson and Benn, 2006; Mihalcea et al., 2008) was derived from meteo and energy input values as well.

The different model outputs are compared and discussed against measured melt rates. Moreover for each attempt some sensitivity tests were performed as well and the obtained results are reported and discussed. Last but not least the suitability of each method to be spatially distributed is considered and discussed.

The case studies of our analyses are Forni Glacier (Italian Alps) and Changri Nup Glacier (Nepal) where supraglacial AWSs have been running thus acquiring meteo and energy data in the framework of the SHARE (Stations at High Altitude for Research on the Environment) Program (pilot projects named SHARE STELVIO and SHARE PAPRIKA, respectively).

Nicholson L. & Benn D.I. 2006. Calculating ice melt beneath a debris layer using meteorological data. *Journal of Glaciology*, 52 (178), 463-470.

Hock R., 2003. Temperature index melt modelling in mountain areas. *Journal of Hydrology*, 282 (1-4), 104-15.

Mihalcea C., Mayer C., Diolaiuti G., D'Agata C., Smiraglia C., Lambrecht A., Vuillermoz E., Tartari G. 2008. Spatial distribution of debris thickness and melting from remote-sensing and meteorological data, at debris-covered Baltoro glacier, Karakoram, Pakistan. *Annals of Glaciology*, 48, 49-57.

Oerlemans J. 2000. Analysis of a 3 years meteorological record from the ablation zone of Morteratschgletscher, Switzerland: energy and mass balance. *Journal of Glaciology*, 46 (155).

Pellicciotti F., Brock B., Strasser U., Burlando P., Funk M. & Corripio J. 2005. An enhanced temperature-index glacier melt model including the shortwave radiation balance: development and testing for Haut Glacier d'Arolla, Switzerland. *Journal of Glaciology*, 51 (175), 573-587.

Senese A., Diolaiuti G., Mihalcea C. & Smiraglia C. 2012. Energy and mass balance of Forni Glacier (Stelvio National Park, Italian Alps) from a 4-year meteorological data record. *Arctic, Antarctic, and Alpine Research*, 44 (1), 122-134.

## **PaleoProxy Data Base (PPDB): A comprehensive geodatabase to archive and manage paleoproxies data**

Strigaro D., Mattavelli M.\*, Frigerio I. & De Amicis M.

Dipartimento di Scienze dell'Ambiente del Territorio e della Terra, Università degli studi di Milano Bicocca.

Corresponding email: [m.mattavelli3@campus.unimib.it](mailto:m.mattavelli3@campus.unimib.it)

Keywords: paleo proxies, geodatabase, webGIS.

Glaciers are sentinels of climate and environmental change, many marine regions pollen and other biological and geological entities can provide information on past climate variations. The Project of Interest NextData will favour the implementation of measurement networks in remote mountain and marine areas and will develop efficient web portals to access meteorological and atmospheric composition data, past climate information from ice and sediment cores, biodiversity and ecosystem data, measurements of the hydrological cycle, marine reanalyses and climate projections at global and regional scale. In this work a methodology to recover, store, access and disseminate paleoproxies data is presented. Studied proxies are ice and marine cores, sediment cores, tree rings, speleotems (Bradley R. S. 1999). To reach this goal an accurate bibliography research were accomplished to collect data and metadata that were essential to study a suitable methodology to design a correct conceptual scheme between entities to build PPDB structure. The data cover the globe, and while most span the last few millennia, some datasets extend back in time 100 million years. Most of the data are time series of geophysical or biological measurements. The importance to implement a unique database for paleoproxy derived from the necessity of paleoclimate scientists to have a structure that permit the data interoperability to develop new analysis methods based on multi proxy data such as the creation of Italy climatic maps of the last 10-15 ky BP. Furthermore in most cases there is not a geodatabase structure behind data. In PPDB data are not only well stored to permit data interoperability but there are a more efficient and accurate queries to retrieve more detailed informations. Data collected in the spatial geographic database are integrated in an information system through web services as Web Map Service (WMS), Web Feature Service (WFS) to share the geospatial information according to technical specifications proposed by Open Geospatial Consortium (OGC) and INSPIRE directive in order to maximize data interoperability. A web portal is built to retrieve raw data about proxy. The software architecture is based on open source structures, S.O Ubuntu GNU/Linux 12.04 LTS server with implementation of FTP, SSH, Apache Tomcat services and PostgreSQL with PostGIS extension for geospatial database. The metadata information are stored in the Nextdata metadata portal, a catalog system of data and metadata.

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## Present conditions and future projections of the Alpine snow cover

Terzago S.\*, von Hardenberg J., Palazzi E. & Provenzale A.

ISAC, Institute of Atmospheric Sciences and Climate, CNR, Torino.

Corresponding email: [s.terzago@isac.cnr.it](mailto:s.terzago@isac.cnr.it)

Keywords: snow, Alps, climate change.

Snow cover plays a key role in the climate of high elevation areas. Changes in the snow spatial/temporal distribution and thickness may affect energy, radiation and hydrology budgets at the Earth surface. In particular, a reduction in the snow amount and duration has a direct effect on water resources availability for downstream populations. The major rivers in Europe such as the Po, Rhine, Rhone and Danube are fed by a network of tributaries that originate in the Alps, making this mountain chain a crucial element in the hydrological cycle of a wide region. A shift in Alpine climatic regimes, particularly in winter precipitation and snowpack duration, would impact heavily on the river systems originating in that area, affecting life and socio-economic structures of populations living within the mountains and downstream.

Several studies analyzed snow variability and trends considering long term time series at national (e.g., Scherrer et al. 2013; Laternser and Schneebeli 2003; Valt et al. 2005), regional (e.g., Terzago 2012) or local spatial scale (e.g. Schoner et al. 2009).

In this work we present an overall picture of snowfall and snow depth features over the Greater Alpine Region drawn from the major available gridded datasets originating from different sources: (i) the snowfall reconstruction dataset (Chimani et al. 2011) derived from HISTALP precipitation and temperature surface observations, (ii) the ERA-INTERIM reanalysis (Dee et al. 2011), (iii) the CFSR reanalysis (Saha et al. 2010), and (iv) the simulations of the state-of-art Global Climate Model EC-Earth (Hazeleger et al. 2011). We present and compare the spatial patterns of snowfall and snow depth, their temporal variability on the historical period and we explore EC-Earth projections for the XXI century in RCP4.5 and RCP8.5 scenarios.

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## Impact of climate change on fires in a Mediterranean region

Turco M.\*<sup>1</sup>, Llasat M.C.<sup>2</sup>, von Hardenberg J.<sup>1</sup> & Provenzale A.<sup>1</sup>

1. Institute of Atmospheric Sciences and Climate, Consiglio Nazionale delle Ricerche, Torino. 2. University of Barcelona, Barcelona, Spain

Corresponding email: [m.turco@isac.cnr.it](mailto:m.turco@isac.cnr.it)

Keywords: Climate change, Regional impact scenarios, Mediterranean Forest fires.

We investigate the impact of climate change on wildfires in a Mediterranean environment (NE Spain). This goal has been achieved through these three supporting steps.

First, we examine a homogeneous series of forest fires in the period 1970–2010. Our analysis shows that both the burned area and number of fire series display a decreasing trend. A possible driver of the observed fires trend is the increasing effort to fire management. For instance, after the big fires in the 1980s, fire management strategies were improved, with an increase in fire prevention and fire fighting measures, on a European and Spanish level (Turco et al, 2013a).

Secondly, we analyse the links between fires and climate drivers in order to better understand their interactions and to develop parsimonious statistical models. These models consider coincident (i.e. same year) temperature and precipitation values, as proxies for the climatic factors that affect fuel flammability, and antecedent climate variables, as proxies for the climatic factors that influence fine fuel availability and connectivity. Our out-of-sample tests confirm that these relatively simple regression models have predictive ability for summer fires in Catalonia (Turco et al, 2013b).

Finally, we apply the climate-fire models to estimate the possible fire response to observed climate trends and to regional climate change projections. We show that a transition toward warmer conditions has already started to occur and it is possible that they continue by mid-century. The climate trends lead to a positive trend for the number of fires. While the actual trend is negative, climate forcing alone would have led to a positive trend in NF. This suggests that, in the absence of fire management, we would have had a significant increase in NF. The climate change impact on the burned area is more complex. Its response to climate trends is slightly negative (although not statistically significant) possibly because the direct effect of climate in regulating fuel flammability is balanced by the indirect effect of climate on fuel structure.

Overall, our study advances the understanding of the impact of climate change on wildfires in Mediterranean environments and help to identify key actions in adaptation strategies.

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## **Dendrochronological and dendroisotopic patterns from trees affected by glacier meltwater: the case study of Lago Verde ice-contact lake (Miage Glacier, Italy)**

Vezzola L.C., Leonelli G.\* & Pelfini M.

Dipartimento di Scienze della Terra, Università di Milano.

Corresponding email: [laura.vezzola@unimi.it](mailto:laura.vezzola@unimi.it)

Keywords: Dendrochronology, dendroisotopic signals, glacier meltwater, debris-covered glaciers.

An increase of the glacier runoff in glacierized mountain catchments has been largely recognized as a consequence of the increasing temperature trends since the last century which induce an intensification of the melting processes. Even if less impacted and with different responses to the climatic inputs, also debris-covered glaciers like e.g. the Miage Glacier (Mt. Blanc Massif, Western Italian Alps), undergo this dynamics. In particular, the debris coverage of the glacier surface is responsible of changes in ablation rates and in meltwater discharge, which typically influence glacier streams, ice-contact and proglacial lakes. When the tongue of debris-covered glaciers reaches altitudes below the treeline, trees may colonize the surroundings of the glacier terminus as well as the glacier surface, thus opening the possibility of assessing, for instance, the influence of lake water-level changes and of past glacier runoff events.

Recently, some researches have been carried out in the proglacial area of the Miage Glacier, on *Larix decidua* Mill. specimens located close to a small ice-contact lake called Lago Verde, characterized by a great water variability inducing frequent conditions of partial tree submersion. The results show that i) lake water-level changes negatively influence tree-ring growth: trees frequently reached by the lake water show narrower tree rings compared to trees located farther from the lake shores. Moreover, a positive relationship between the residual chronology at the treeline and June temperature was detected, whereas a weaker relationship was found at the Lago Verde, and this pattern may be related to the lower altitude of the Lago Verde, compared to the treeline. ii) Tree-ring cellulose of trees fed by glacial meltwater is significantly more depleted in  $\delta^{18}\text{O}$  than the one of trees fed only by precipitation (Leonelli et al., 2013).

Overall, the signals of environmental changes detected in the tree rings around the lake opens the possibility to characterize the areas mostly affected by lake water-level changes on a temporal scale and of reconstructing past major glacier runoff events on the medium- to long-term.

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## **Spring snowfall and river discharge trend and low-frequency variability over Alps**

Zampieri M.\*<sup>1</sup>, Scoccimarro E.<sup>1-2</sup> & S. Gualdi<sup>1-2</sup>

1. CMCC, Bologna. 2. INGV, Bologna.

Corresponding email: [matteo.zampieri@cmcc.it](mailto:matteo.zampieri@cmcc.it)

Keywords: Alps, snowfall, river discharge, Po River, Rhine, Rhone, Danube.

We present a twofold analysis of long-term trend and variability of different factors affecting the hydrological cycle over the Alps in spring. The study is based on datasets derived from observations for the last 150 years. In one case we focus on snowfall flux, which we found shifting between two different regimes in concert with the Atlantic Multidecadal Oscillation.

This teleconnection is explained by a mixture of changes in circulation and by local climatic feedbacks. Moreover, we analyzed the timing of the river discharge peaks relative to the main Alpine rivers, finding similar features of low frequency variability, and a common anticipation tendency of more than two weeks per century, probably explained by a change of seasonality of total precipitation.

## **SESSIONE S6**

### **Understanding carbonate sedimentary systems and diagenesis: new concepts and innovative approaches**

*CONVENORS*

*F. Jadoul (Univ. Milano)*

*O. Borromeo (Eni S.p.A.)*

*M. Parente (Univ. Napoli Federico II)*

## **Effects of changing accommodation space on a flat-topped, high relief carbonate platform: controls on facies distribution and sedimentary processes during a sea-level fall (Ladinian-Carnian, Southern Alps, Italy)**

Berra F.\*, Binda M. & Jadoul F.

Università degli Studi di Milano, Dipartimento di Scienze della Terra "A. Desio".

Corresponding email: [fabrizio.berra@unimi.it](mailto:fabrizio.berra@unimi.it)

Keywords: Triassic, carbonate platform, sea-level fall.

Subaerial exposure of carbonate platforms are recorded by different elements, whose study is able to define the changes in facies type and distribution on the platform top. One interesting case study is represented by the Calcare Rosso of the central Southern Alps (Lombardy), that records a major sea-level fall on the top of a high relief carbonate platform (Esino Limestone) occurring close to the Ladinian-Carnian boundary. The study of the distribution of the exposure-related deposits documented the existence of three major facies associations: 1) residual soils ("terra rossa" type), 2 to 10 m thick, locally associated with thin lenses of conglomerates (from angular to subangular mainly centimetric clasts) with black pebbles and, locally, weathered vulcanites; 2) chaotic breccia lenses irregularly distributed in the uppermost part of the Esino Limestone carbonate platform (up to about 20 m from the platform top), interpreted as collapse breccias in karstic setting; 3) inter-supratidal carbonate cycles with dissolution and development of paleosols and tepee structures (up to 50 m thick).

The distribution of these facies is controlled by the facies distribution in the Esino Limestone. Facies 1 and 2 typically characterize the core of the platform: these facies cover the inner platform facies of the Esino Limestone, whereas facies 3 covers the reef-upper slope facies of the underlying prograding facies of the Esino Limestone. The thickness of facies 3 rapidly closes from the rim to the core of the platform. The observed facies distribution reflects differences in the accommodation space and sedimentary processes from the rim to the core of the carbonate system, controlling thickness and facies association of the Calcare Rosso. The highest accommodation space (documented by facies 3) close to the platform rims could be ascribed to compaction-induced subsidence, due to the compaction of the basinal sediments (resedimented, well-bedded fine-grained calciturbidites) covered by the prograding slope facies of the Esino Limestone and/or to tectonic control possibly related to volcanic activity.

The subaerial exposure of the top of the high-relief, flat topped platform of the Esino Limestone caused a major karstification in the core of the platform and a discontinuous alternation of sedimentation and karstic events on the more subsiding platform edge. Processes related to subaerial exposure (mostly karst dissolution) strongly enhanced the original porosity of the deposits, but it was rapidly followed by early cement precipitation (the early origin of these cements is documented by cathodoluminescence and geochemical data). The early-diagenetic cementation rapidly occluded the karst-related porosity, strongly reducing the permeability of the unit shortly after its deposition. Porosity of this system is only partly preserved in the upper slope-reef belt of the Esino Limestone, later affected by selective dolomitization.

## **The Persichini “marbles” of the Ligurian Briançonnais: a historical stone material with a renewed scientific interest**

Bertok C.<sup>1</sup>, Borghi A.<sup>1</sup>, d’Atri A.\*<sup>1</sup>, Martire L.<sup>1</sup>, Massaro G.<sup>1</sup> & Piana F.<sup>2</sup>

1. Dipartimento di Scienze della Terra, Università di Torino. 2. CNR-IGG, Istituto Geoscienze e Georisorse, U.O. Torino.

Corresponding email: [anna.datri@unito.it](mailto:anna.datri@unito.it)

Keywords: Persichini "marbles", Siderolitico, historical stone material.

The Persichini “marbles” are more or less intensely recrystallized polichromous carbonate rocks widely used in Baroque sacred architecture in Torino and southwestern Piemonte as columns, balustrades and internal facings.

These rocks pertain to the Mesozoic succession of the Ligurian Briançonnais domain and in particular came from a thin and discontinuous stratigraphic horizon comprised between the top of the Middle Triassic peritidal dolostones of the Dolomie di San Pietro dei Monti formation and the Middle Jurassic platform limestones of the Calcarei di Rio di Nava formation. This horizon, characterized by a vivid reddish colour, is well known under the name Siderolitico and is interpreted as the result of the karstification of the Triassic platform related to the uplift of the Briançonnais domain during the Latest Triassic-Early Jurassic rifting.

In spite of the large use as an ornamental stone, very few studies were carried out on its sedimentologic, petrographic and geochemical aspects in the Ligurian Briançonnais. This paper reports the first results of a study we are carrying out on the remnants of the historical extraction sites in the Tanaro Valley in the frame of the ProGeo Piemonte Project that is aimed to the enhancement of different aspects of the geological heritage of Piemonte region.

The Persichini show a great variability in colour and texture ranging from reddish, clay- and hematite-rich carbonate rocks to clast-supported breccias with up to dm-large clasts, consisting of angular to rounded fragments of the Triassic dolostones, and a reddish carbonate matrix. The base boundary of these rocks is quite irregular and locally shows cup-shaped, concave-up morphologies clearly pointing to surficial karstic dissolution features. Irregular bodies of complex, polyphase, clast-supported, cement-bearing breccias penetrating the underlying Triassic dolostones suggest repeated fracturing and fluid circulation events. A significant aspect of the Persichini is a pervasive recrystallization, mainly related to dolomitization, which made these karstic sediments very hard and compact and suitable for the realization of both ornamental and load-bearing architectural elements. Microscopic evidence documents that such dolomitization occurred in an early diagenetic stage and may be correlated to dolomite occurring within Middle Jurassic limestones of nearby areas (Marguareis Massif) and interpreted to be of hydrothermal origin.

## **High-frequency carbonate cycles and diagenetic features of Lower Jurassic peritidal carbonates in the Calcare Massiccio Formation (Cornicolani Mountains, central Apennines)**

Brandano M.<sup>\*1-2</sup>, Corda L.<sup>1</sup>, Tomassetti L.<sup>1</sup> & Testa D.<sup>1</sup>

1. Dipartimento Scienze della Terra, Università Roma La Sapienza. 2. Istituto di Geologia Ambientale e Geoingegneria (IGAG) CNR, Area della Ricerca di Roma 1.

Corresponding email: [marco.brandano@uniroma1.it](mailto:marco.brandano@uniroma1.it)

Keywords: Calcare Massiccio, peritidal cycles, cyclostratigraphy.

This work presents a revised analysis of the small-scale cyclicity of the Lower Jurassic shallow-water carbonates known as Calcare Massiccio in the Cornicolani Mountains (Latium, Central Apennines) which represent an isolated intrabasinal structural-high platform, within the pelagic Sabina Basin. The Calcare Massiccio is here characterized by a cyclical peritidal sedimentation and is overlain by condensed pelagic deposits.

This work focuses on the environmental changes recorded in this structural high domain. Detailed logging of vertical sections and on facies analysis, sedimentary sequences are defined according to cyclostratigraphic concepts.

Three facies associations have been recognized: LF-A grainstone to packstone with ooids, oncoidal rudstone to floatstone, LF - B Peloidal wackestone to packstone, with birdseyes, laminated bindstone, LF-C Pisolitic-peloidal wackestone and extensive sheet-cracks. These facies are arranged in cyclically repeated meter-scale shallowing upward cycles bounded by LF-C facies. Each cycle may show different internal trends and may be bounded by different surfaces, such as subaerial exposure or marine flooding surfaces with non-Waltherian facies shifts.

Four main types of calcite cements were recognized: isopachous fibrous cement around oncoids and bioclasts; drusy mosaic cement infilling the intergranular space and the dissolution cavities; crusts of radial fibrous cement infilling large sheet cracks; blocky cement occluding the large space between the sheet crack crusts.

Six main peaks have been identified in the power spectra of the investigated sections: peak 1 at a frequency of 0.330995 (3.12 m), peak 2 at 0.380177 (1.8 m), peak 3 at 0.307043 (1.35 m), peak 4 at 0.158386 (0.97 m), peak 5 at 0.090113 (0.83 m) and peak 6 at 0.088033 (0.61 m).

The most prominent peaks are consistent with the Milankovitch cyclicity, however peaks not related to orbital parameters have been recorded.

We propose a dominant allocyclic control on the development of the studied Calcare Massiccio cycle stacking. However it cannot be ruled out a tectonic and, to a lesser extent, an autocyclic signal. Indeed the extensional tectonics, related to the Early Jurassic rifting stage affecting the passive margin of the Adriatic plate, could partially influence the Calcare Massiccio deposition.

## Quantifying the contribute of seagrass carbonate factory from Paleocene to Present

Brandano M.\*<sup>1-2</sup>, Cuffaro M.<sup>2</sup>, Gaglianone G.<sup>1</sup>, Mateu-Vicens G.<sup>3</sup> & Petricca P.<sup>1</sup>

1. Dipartimento Scienze della Terra, Università Roma La Sapienza. 2. Istituto di Geologia Ambientale e Geoingegneria (IGAG) CNR, Sez. Sapienza, c/o Dipartimento Scienze della Terra, Università Roma La Sapienza. 3. Càtedra "Guillem Colom Casasnovas" Edifici Guillem Colom Casasnovas, Universitat de les Illes Balears, Palma de Mallorca, Spain.

Corresponding email: [marco.brandano@uniroma1.it](mailto:marco.brandano@uniroma1.it)

Keywords: Seagrass, carbonate factory, plate reconstruction.

Seagrass produce extensive submarine meadows in the euphotic zone along temperate to tropical coastlines worldwide. Seagrass meadows host a diverse array of organisms dwelling either as epiphytic forms or as infaunal forms. Many of these organisms possess a calcareous skeleton (i.e., echinoids, molluscs, bryozoans, foraminifers, red algae), which contributes to the role of the seagrasses as carbonate-sediment factories. Since the impact of the carbonate production and accumulation in the global carbon cycle is of fundamental importance to the Earth's climate, this work aim to taste the efficiency of this factory by quantifying the epiphytic carbonate production of a *Posidonia oceanica* seagrass from southern Tyrrhenian shelf (Maratea, Southern Italy). Fifteen shoots of *Posidonia oceanica* were sampled, dried and burned to calculate the weight of epiphytic calcareous portion. Successively the shoot density range was measured as well as leaves size to obtain a range of the epiphytic carbonate production of Tyrrhenian shelf and compared with other Mediterranean localities. The average carbonate production of *Posidonia oceanica* meadows of Tyrrhenian shelf is  $400\text{gr/m}^{-2}, \text{year}^{-1}$ .

As seagrasses appeared during Late Cretaceous times, and were widespread throughout the Paleogene and Neogene, we want to investigate the contribute of the seagrass carbonate factory from Paleocene to the Present, quantifying the rations of coast development during this time lapse. For this purpose, we propose to test global plate tectonic reconstructions, obtained with recent rotation vectors relative to the mantle, over several time intervals, selected as much as possible to correspond with key lithospheric plate reorganizations.

## Paleontological applications of resedimented skeletal materials

Coletti G.\* & Basso D.

Dipartimento di Scienze dell'Ambiente del Territorio e di Scienze della Terra, Università di Milano.

Corresponding email: [g.coletti@campus.unimib.it](mailto:g.coletti@campus.unimib.it)

Keywords: resedimentation, transport, paleoecology.

Continental margins are one of the main zone of carbonate production. In this environment two separated styles of accumulation occur: framework production and loose grain deposition. While the biogenic framework is likely to resist to wave and current impact, skeletal grains and fragments may be transported outside the platform in to the deep-water depositional realm. Offshore sediment export account for 25% - 50% of rimmed shelf gross carbonate production (Hubbard et al., 1990; Ryan et al., 2001). Resedimented material represents an important budgetary factor which should be carefully considered. Skeletal grains transported toward the basin may have a remarkable preservation potential, and then they can be useful for various paleontological applications. In paleoecological studies, transported skeletal remains might provide information on the shallow-water environment where they were produced, in the eventuality that the platform deposits become lost or unobservable (Nebelsick et al., 2001). In particular biogenic nodular concretions, such as rhodoliths, bind skeletal particles of their formation environment during their growth. This "stored" material holds vital information on the carbonate factory where the coated grains developed, even when they are displaced from their native zone. Paleontological analyses on the rhodoliths from the Pietra da Cantoni Group of Piedmont Tertiary Basin proved that the grain association trapped within rhodoliths carefully depict rhodolith formation environment. Erosion of outcropping limestone formation is another source of carbonate debris toward deep-water setting. Limestone fragments may reenter sedimentary cycle as any other rock fragment, but they preserve, even in small volume, a wealth of useful information. Fossil association may be used to constrain the age of the formation in which they are found or, due to their peculiar characteristics, they may be helpful in provenance studies. Limestone fragments characterized by an heterozoan carbonate association of Late Eocene age, found in the Como Conglomerate of Gonfolite Lombarda Group, suggest a likely sediment supply to the Gonfolite basin also from the area of the Ternate Formation, which present a fossil association highly comparable to the one observed in the fragments.

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## **Facies analyses and depositional architecture of mixed siliciclastic-carbonate succession in a fault-controlled extensional basin (Miocene, Southern Tuscany, Central Italy)**

Croci A.\*<sup>1</sup>, Della Porta G.<sup>1</sup> & Capezzuoli E.<sup>2</sup>

1. Earth Sciences Department, Milano University. 2. Department of Physics, Earth and Environmental Sciences, Siena University.

Corresponding email: [andrea.croci@unimi.it](mailto:andrea.croci@unimi.it)

Keywords: Continental carbonate, Miocene, Southern Tuscany.

The extensional Neogene Albegna Basin (Southern Tuscany, Italy) includes several hydrothermal travertine units of Pliocene to Holocene age. During the Messinian, a fault-controlled basin (nearly 4 km<sup>2</sup>) was filled by precipitated carbonate and detrital siliciclastic strata, nearly 150 m thick. This continental carbonate succession was investigated to define its geometry, lithofacies types, and depositional environments, and to characterize the variety of precipitated carbonate fabrics.

The mixed carbonate-siliciclastic succession has a wedge-shaped geometry thinning northward. Carbonates are in centimetres to a few decimetres thick beds and include nine facies types: 1) crystalline dendrite cementstone, precipitated from spring-derived hydrothermal water, while flowing and degassing CO<sub>2</sub>; 2) sub-rounded radial crystalline grains grainstone consists of millimetre size lozenge crystals arranged around a nucleus of dense micrite; 3) clotted peloidal micrite and microsparite boundstone, forming irregular framework to centimetre-thick dendrites, of possible microbially mediated precipitation; 4) layers of laminated boundstone consisting of wavy laminae up to 2 mm thick of clotted peloidal micrite, leiolitic micrite and microsparite, including lens-shaped elongated subhorizontal porosity; 5) coated gas bubble boundstone, consisting of sub-spherical or elongated micritic coatings around porous structures a few millimetres in size; 6) raft rudstone which are flat horizontal carbonate structures precipitated in standing hydrothermal water pools; 7) calci-mudstone, made by leiolitic micrite; 8) peloidal skeletal packstone/grainstone, containing shells and coated algae; 9) coated reed boundstone, which consists of carbonate precipitated around phytoclasts and stems.

Four depositional units are identified in the succession. Unit 1, at the base, represented a travertine terraced slope, which laterally passed into a distal pond. Unit 2 is characterized by metre to decametre-thick beds of breccias alternating with metre to decimetre-thick travertine lenses. These lenses are interpreted as deposited in shallow travertine ponds. The breccia beds, interpreted as alluvial fan deposits, have clasts derived from the outcrops of Mesozoic substrate uplifted during the Apennine Orogeny. Unit 3 includes an association of siltstones, sandstones and conglomerates; the occurrences of a channel-shaped geometry in the southern part of the outcrop and silty clay layered beds in the northern part, suggest the interpretation of a fluvial system and adjacent alluvial plain deposits. The top Unit 4 is characterized by a renewed deposition of travertine, rich of coated reed boundstone and peloidal skeletal grainstone. The succession records a shallowing-upward evolution from Unit 1 to Unit 3 and a rise of the base level with Unit 4.

These results help to assess architectural patterns in interpreting the evolution of continental extensional basins in which hydrothermal activity occurs.

## REE patterns from Sinemurian (Lower Jurassic) siliceous sponge mounds (Djebel Bou Dahar, High Atlas, Morocco)

Della Porta G.\*<sup>1</sup> & Webb G.E.<sup>2</sup>

1. Dipartimento di Scienze della Terra, Università degli Studi di Milano. 2. School of Earth Sciences, The University of Queensland, Brisbane, Australia.

Corresponding email: [giovanna.dellaporta@unimi.it](mailto:giovanna.dellaporta@unimi.it)

Keywords: microbial carbonates, REE geochemistry, Jurassic.

Marine microbialites serve as seawater rare earth element and yttrium (REE+Y) proxies through many intervals of Earth history, but questions remain about the partitioning of REEs into different coeval carbonate phases, syn-depositional contaminants and redistribution during diagenesis. Microbialites, cements and background sediments were analysed for stable isotopes and trace element geochemistry in Sinemurian (Lower Jurassic) mid- to outer ramp siliceous sponge microbial mounds (High Atlas, Morocco). REE+Y were analysed using laser ablation-inductively coupled plasma-mass spectrometry. Automicrites, non-luminescent radial fibrous (RF) cement and brachiopods have stable isotope values comparable to published Early Jurassic marine values. Luminescent blocky sparite (BS) cements with lighter stable isotope values are interpreted as burial cements. Allomicrite has intermediate isotopic values consistent with diagenetic alteration during burial. Early marine RF cement has shale-normalized (REE+Y)<sub>sn</sub> patterns with characteristics of oxygenated seawater, whereas BS cement has high concentrations and (REE+Y)<sub>sn</sub> patterns very unlike seawater (bell-shaped, middle MREE-enriched with lower Y/Ho ratios). Allomicrite has relatively high REE concentrations with flatter (REE+Y)<sub>sn</sub> patterns and lower Y/Ho ratios that may reflect shale contamination and incorporation of particulate matter rich in light LREE from the water column. Automicrites include three subclasses distinguished on the basis of petrography and (REE+Y)<sub>sn</sub> patterns. Clotted peloidal automicrites (AM1) have (REE+Y)<sub>sn</sub> patterns consistent with seawater, but with higher concentrations. Other clotted peloidal to leiolitic automicrites with sponge spicules (AM2) have flatter (REE+Y)<sub>sn</sub> patterns with variable Ce anomalies. Leiolitic automicrites (AM3) have patterns similar to the allomicrite. Microbialites and early marine cements preserved seawater-like REE+Y patterns despite subsequent stabilising diagenesis. However, some AM2 automicrites, enriched in LREE, but lacking accompanying increased lithophile elements, suggest that LREE enriched particulate matter was incorporated into them.

This study confirms that Early Jurassic marine REE distributions were comparable to late Palaeozoic, Late Jurassic and Holocene distributions. LREE enrichment in some automicrites highlights the occurrence of a LREE-enriched contaminant here interpreted to be particulate carbonate and/or organic matter that preferentially scavenged LREEs while descending through the water column prior to sedimentation and incorporation into the automicrites. Incorporation of these particles significantly affects otherwise robust marine REE patterns in microbialite within a relatively clean carbonate environment. The seawater-like (REE+Y)<sub>sn</sub> patterns and prevalent negative Ce anomalies of marine cement and microbialites suggest that the siliceous sponge mounds accumulated in a well-oxygenated ramp setting.

## The Mila Member of Noto Formation: an integrated method to characterize a Triassic microbial reservoir rock (SE Sicily, Italy)

Felici E.\*<sup>1</sup>, Frixia A.<sup>1</sup>, Maragliulo C.<sup>1</sup> & Cirilli S.<sup>2</sup>

1. Eni e&p. 2. Università di Perugia.

Corresponding email: [elena.felici@eni.com](mailto:elena.felici@eni.com)

Keywords: Mila Mb.-reservoir, microbial-margin, hydrothermal-dolomitization.

The efficiency of the Sicily Triassic petroleum system has been proved in the Mila and Irminio oil Fields, drilled by Bimmisca, Vallazza, Cozzo Scalia and Carrubo wells.

During Rhaetian a microbial margin set up (Mila Mb. of Noto Fm.) between the Noto Fm. lagoon domain and the Streppenosa Fm. basin. Seismic interpretation indicate that this margin was NE-SW oriented. Thin pelagic episodes, in both Mila Mb. and Noto lagoon domain, indicate episodes of transgression.

We integrated different methodologies to generate a complete picture of depositional environment and diagenetic evolution of Mila Mb. Macroscopic and microscopic analyses, including facies observation, enable to perform a stratigraphic correlation of the studied cores. To reconstruct the depositional microenvironment, we focused our study on microbialites, using Riding (2011) and Flugel (2008) classifications.

*In the lower portion, Carrubo presents laminated fine grained or coarse agglutinated stromatolite facies and sparry crusts*, typical of intertidal environment. Cozzo Scalia is mainly characterized by low energy subtidal *thrombolitic* facies, grading upwards to an intertidal setting showing *stromatolite agglutinated* facies. Vallazza presents intertidal *dendrolites* facies passing upwards to a subtidal *thrombolitic* facies.

Above, the microfacies distribution shows a great vertical and lateral variability, due tectono-eustatic factors, that modified the accommodation space and morphology of sea floor during time.

According to the wells geographical position, Vallazza drilled the outer Mila margin (towards Streppenosa basin), Carrubo is in its inner part (towards Noto Fm. tidal – lagoon) and Cozzo Scalia is between them.

The diagenetic study has been performed using different methodologies: optical microscope and cathodoluminescence observations on polished thin sections, porosity evaluation and isotopic analysis. The petrographic analysis pointed out the occurrence of early and late diagenesis process, that can be summarized in two phases; the former testified by an early cementation with fibrous, radial and fascicular cements and an early fine grained dolomitization; the latter is linked to burial diagenesis, with precipitation of blocky cements and hydrothermal dolomitization (saddle dolomite). The hypothesis of hydrothermal processes was confirmed by isotopic analysis on cements ( about -9 ‰) and fluid inclusions (90-100°C).

The poor Mila reservoir properties are due its micritic nature and are improved by hydrothermal dolomitization close to the major faults.

The study demonstrates that hydrothermal dolomitization and karst development considerably improve the reservoir characteristics of microbial mounds and that the structural control on the reservoir body is fundamental during its diagenetic history.

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## **Climate vs. sea level change on the generation of carbonate depositional sequences: the case of the Carnian (Late Triassic) of the Dolomites**

Gattolin G.\*<sup>1</sup>, Gianolla P.<sup>2</sup>, Breda A.<sup>3</sup>, Franceschi M.<sup>4</sup> & Preto N.<sup>3</sup>

1. ENI, E&P division, San Donato Milanese (MI). 2. Department of Fisica e Scienze della Terra, Università di Ferrara  
3. Dipartimento di Geoscienze, Università di Padova. 4. Museo delle Scienze, Trento.

Corresponding email: [giovanni.gattolin@eni.com](mailto:giovanni.gattolin@eni.com)

Keywords: carbonate-platform-demise, climate-change, sea-level-change.

A global episode of climate change is documented worldwide at low latitudes in the Carnian (Late Triassic), which involved increased rainfall and possibly global warming. This climatic event apparently caused the demise of km-scale microbial-dominated high-relief carbonate platforms in the Alpine region. Sedimentary facies analysis, coupled with geological 3D modeling, is applied to constrain the sequence stratigraphy of this stratigraphic interval in the Dolomites (North-eastern Italy) in which a complex interaction between sea level and climate change was observed. This multidisciplinary approach enabled to disentangle the timing of climate change vs. sea level fluctuation, and their effects on the shallow water carbonate depositional system. The climatic event is identified by the increase of siliciclastics and predates a drop of sea-level, marked by subaerial exposure surface. After the increase in the siliciclastic input, a period of coexistence of m- to tens of m-scale microbial carbonate mounds and loose arenaceous carbonates is documented. The subsequent sea-level fall led to the definitive disappearance of microbialites, and shallow water carbonates definitively switched to ramps dominated by loose carbonate sediment. Thus, the demise of the Upper Triassic microbial dominated high-relief platforms of the Dolomites can be interpreted as a multi-step process: a climate event coeval with the demise of the km-scale platforms, and then a fall of the sea level coeval with the definitive disappearance of microbial carbonates. The climate-induced crisis of the Early Carnian shallow water carbonate system of the Dolomites generated a geological surface similar to a drowning unconformity, even though a transgression was not taking place. The sudden infilling of basins at the end of the Early Carnian was the result of the climatic induced switch from high-relief carbonate systems characterized by steep slopes to a gently inclined ramp, during a time of low subsidence rate. The evolution of carbonate systems of the Dolomites at the end of the Early Carnian is not predictable by the knowledge of sea level change only, further highlighting a known caveat of the sequence stratigraphy of carbonates: namely, that ecological changes determine significant modifications in depositional geometries. This case study may serve as a conceptual model for the sedimentary evolution of carbonate systems subject to ecological crisis that do not evolve in platform drowning because of a lack of accommodation.

## Lithogenic importance of calcareous nannofossils in the Late Triassic the case of the Pizzo Mondello section (Monti Sicani, Sicily)

Gilardoni S.E.\*, Erba E., Casellato C.E., Balini M. & Muttoni G.

Dipartimento di Scienze della Terra "A. Desio", Università degli Studi di Milano.

Corresponding email: [silvia.gilardoni@unimi.it](mailto:silvia.gilardoni@unimi.it)

Keywords: Triassic, nannofossils, micrite.

Calcareous nannofossils are micrometric calcitic parts (coccoliths/nannoliths) of coccolithophore exoskeleton. They first appeared in the Middle Triassic and ~12 coccolith-nannolith taxa are known in the Upper Triassic. However, calcareous nannofossils became lithogenetically significant only after Early Jurassic times, so that the origin of the pre-Jurassic micrites is still unclear.

The Upper Triassic Pizzo Mondello section (Sicily), which is one of the candidate sections for the definition of the Carnian/Norian boundary, has been selected to quantify the contribute of calcareous nannofossils to the pelagic micrite through quantitative analysis of 70 ultra-thin sections (7µm thick) using a polarized light microscope, at 1250X magnifications. Abundances were collected counting all specimens in 1 mm<sup>2</sup>.

We identified eight morphotypes of nannoliths (A, B, C, D, E, F, G, H). Results indicate that the most common morphotypes are A, C and E. Morphotypes B and F are attributed to *Thoracosphaera* sp. and morphotypes E to *Prinsiosphaera triassica*. Morphotype A has been documented by Preto et al. (2012) and morphotype G is similar to *P. triassica* but differs in having a diagenetic crust. The other morphotypes are not attributable to known taxa.

Average abundance is around 200 specimens/mm<sup>2</sup>; however, double values were detected in the Carnian/Norian boundary interval, while much lower abundances were observed in the upper part of the section. Morphometry was used to calculate area, volume and mass of each nannolith. Results show that morphotypes A and F are the most calcified, while morphotypes D, H and C are the less calcified. We estimated fluxes of each taxon considering abundance, volume/mass and sedimentation rates. Morphotypes A and F control total abundance and flux variations. The other morphotypes contribute less to the micrite, because are smaller and less abundant.

In the lower part of the section there is a correspondence between abundances, fluxes and nodularity (Balini et al., 2010): highest abundances and fluxes correspond to intense nodularity, while gradually lower values are linked to the decrease of nodularity. As the total abundance is proportional to nodularity, we infer that condensation with preferential dissolution of the thinnest components of the micrite, concentrated bigger and dissolution-resistant forms. Calcareous nannofossils did not contribute significantly to the micrite in the Upper Triassic as they constituted up to 14% in area, but they were already important components in pelagic sedimentation.

Balini M., Bertinelli A., Di Stefano P., Guaiumi C., Levera M., Mazza M., Nicora A., Preto N. & Rigo M. 2010. The Late Carnian-Rhaetian succession at Pizzo Mondello (Sicani Mountains). *Albertiana*, 39, 36-57.

Preto N., Willems H., Guaiumi C. & Westphal H. 2012. Onset of significant pelagic carbonate accumulation after the Carnian Pluvial Event (CPE) in the western Tethys. *Facies*. DOI 10.1007/s10347-012-0338-9.

## **The evolution of the Miocene platform-basin system in the northern Apennines (Italy): what can we learn from seep-carbonates**

Grillenzoni C.\*, Conti S., Fioroni C., Fontana D. & Salocchi A.

Department of Chemical and Geological Sciences- University of Modena and Reggio Emilia.

Corresponding email: [claudia.grillenzoni@unimore.it](mailto:claudia.grillenzoni@unimore.it)

Keywords: seep-carbonates, Miocene, northern Apennines.

Cold seep-carbonates documenting the expulsion of fluids enriched in methane have been identified in a variety of basin margins and tectonic-sedimentary settings. A number of geological factors influences methane seep activity, but primarily regional and local tectonics, mainly at the deformation front of accretionary prism and inner foredeep. Tectonics constrains the fluid circulation system, with faults and fractures serving as conduits and channelling water and methane up to the seafloor. Recent studies suggest that seep-carbonates occurrence is also controlled by climatic changes and their formation seems to correlate with cold periods and sea level low-stand. A drop of the hydraulic pressure on the plumbing system during sea level lowering in glacial phase could increase methane flows at seeps, inducing carbonate precipitation. The correlation between methane-derived carbonates and climate has been recently suggested for the Miocene of the northern Apennines by means of a sedimentological and biostratigraphic study of seep-carbonates and the enclosing hemipelagic marls (Vicchio Formation) (Fontana et al., 2013). The study suggests a correlation between the carbonate precipitation and the middle Miocene glacial cooling event (Mi3b). The triggering of the ascent and emission of methane-rich fluids may be related to the eustatic fall and in turn to the water pressure drop. A detailed stratigraphic and biostratigraphic study of seep-carbonates and enclosing marls in foredeep deposits of the Tuscan-Romagna Apennines has allowed a precise dating of seepage in slope and basinal successions. The analysis of the  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  records of carbonates,  $\delta^{13}\text{C}_{\text{org}}$  excursion of organic matter and TOC on the marls enclosing the authigenic carbonates has been performed in order to verify a correlative trend in correspondence of the climatic cooling event. A paleoecological study on benthic foraminifera assemblages has also allowed to detail these peculiar environments. The events defined from this study in basinal deposits have been correlated with depositional changes and discontinuity surfaces in the adjacent temperate-type carbonate platforms, and have contributed to the definition of modes and rates of the demise of carbonate deposition. The identification of cold phases and lowering of sea level in slope-basinal deposits and their detailed timing, may be a useful tool for correlation between deep depositional setting and coeval shallow-water successions. This approach may also provide important constrains in the reconstruction of the evolution of the Miocene platform-basin system in this complex compressive setting of the northern Apennines.

Fontana D., Conti S., Grillenzoni C., Mecozzi S., Petrucci F. & Turco E. 2013. Evidence of climatic control on hydrocarbon seepage in the Miocene of the northern Apennines: The case study of the Vicchio Marls. *Marine and Petroleum Geology*, 48, 90-99.

## Bioconstructions in cryptic cave environments: a consortium between bacteria and polychaeta

Guido A.\*<sup>1</sup>, Mastandrea A.<sup>1</sup>, Rosso A.<sup>2-3</sup>, Sanfilippo R.<sup>2</sup>, Tosti F.<sup>4</sup>, Riding R.<sup>4</sup> & Russo F.<sup>1</sup>

1. Department of Biology, Ecology and Earth Sciences, University of Calabria, Cosenza. 2. Department of Biological, Geological and Environmental Sciences, Catania University. 3. National Inter-University Consortium for the Sciences of the Sea (CoNISMa), Catania. 4. Department of Earth and Planetary Sciences, University of Tennessee, Knoxville, USA.

Corresponding email: [aguido@unical.it](mailto:aguido@unical.it)

Keywords: bioconstructions, bacteria, polychaeta.

Pendant bioconstructions occur within submerged caves of the Plemmirio Marine Protected Area in SE Sicily, Italy. These rigid structures, termed biostalactites, were syngenerated lithified by clotted-peloidal micrite that has a high bacterial lipid biomarker content with abundant compounds derived from sulfate-reducing bacteria. The main framework builders are polychaete serpulid worms, mainly *Protula* with subordinate *Semivermilia* and *Josephella* (Guido et al., 2013, 2014). These polychaetes have lamellar and/or fibrillar wall structure. In contrast, small agglutinated terebellid tubes, which are a minor component of the biostalactites, are discontinuous and irregular with a peloidal micritic microfabric. This distinctive association has been reported in several ancient deposits, such as Oxfordian and Upper Jurassic reefs, and in Late Jurassic to Early Cretaceous platform margin facies. The same composition of the clotted peloidal micrite and agglutinated polychaete tubes suggests that calcification, promoted by bacterial sulfate reduction (BSR), is utilized by the terebellids to help develop their tubes. The bacteria obtain nutrients for growth from decaying metazoan organic matter, and the worms utilize the microbial induced peloids to form their skeletons. This commensal symbiosis may not be restricted to grain-poor environments but, as suggested by the widespread occurrence of *Terebella*-like tubes in the geological record, might be a favored mechanism of tube construction, considering the close physical and ecological relationship of worms and sulfate-reducing bacteria in these bioconstructions.

Guido A., Heindel K., Birgel D., Rosso A., Mastandrea A., Sanfilippo R., Russo F. & Peckmann J. 2013. Pendant bioconstructions cemented by microbial carbonate in submerged marine caves (Holocene, SE Sicily). *Palaeogeogr., Palaeoclimatol., Palaeoecol.*, 388, 166–180.

Guido A., Mastandrea A., Rosso A., Sanfilippo R., Tosti F., Riding R., Russo F. 2014. Commensal symbiosis between agglutinated polychaetes and sulfate reducing bacteria. *Geobiology*, 12, 265-275.

## **Large scale detachments along low-angle slope depositional systems: the Tithonian disconformity of Eastern Sardinia ramp carbonates (Jurassic Southern European passive margin)**

Jadoul F.\*<sup>1</sup>, Della Porta G.<sup>1</sup> & Lanfranchi A.<sup>2</sup>

1. Earth Sciences Department, Milan University. 2. Oolithica Geoscience Ltd, Cheltenham UK.

Corresponding email: [flavio.jadoul@unimi.it](mailto:flavio.jadoul@unimi.it)

Keywords: Carbonate ramp, slope failure, Upper Jurassic.

Large-scale submarine unconformities and megabreccias are widely documented along the North Atlantic passive margin, in seismic lines but poorly described in outcrops. In the Jurassic southern European passive margin the collapse of siliciclastic and carbonate deposits resulted in the exposure of Mesozoic strata along erosional escarpments and the formation of large-scale submarine unconformities on the continental shelf.

This study focuses on the geometry and the depositional facies associated with a wide erosional submarine unconformity at the top of an Upper Tithonian outer ramp to basinal marly and lime-succession (Pedra Longa Fm.) from the Late Jurassic passive margin of Eastern Sardinia. These basinal strata accumulated adjacent to an exposed Mesozoic carbonate structural high facing the Alpine Tethys. The Eastern Sardinia Jurassic palaeogeography comprises a persistent shallow-water carbonate high separating a northern and a southern intraplateau basin. Relative sea-level fluctuations generated vertically-stacked transgressive-regressive units and basinward progradation of shallow-water ramp carbonates from the late Callovian to the Tithonian. The studied erosional unconformity is located at the base of the youngest carbonate progradational unit (Bardia Fm.) and marks a sharp boundary between relatively deep, outer platform strata and shallow water facies. This disconformity, cutting through the bedding with an angle up to 15°, is recorded only in the southern basin where it was traced over an area of 6.5 x 2.5 km. Narrow (3-6 m wide, 2-4 m thick) erosional canyon and chaotic polygenic megabreccia lenses (up to 15-20 m thick) are common distally basinward where the underlying lime-mudstones are up to 30 m thick. Breccia clasts include the underlying marly limestones and shallow-water carbonates. In the proximal detachment area the underlying basinal succession is strongly reduced (6-13 m thick), contains minor erosional surfaces, sedimentary dikes, soft deformations, and intraformational breccias pockets or it may locally be completely eroded.

The kilometre-size areal occurrence of the unconformity, its restriction to the intraplateau basin succession, the occurrence of megabreccias in a low-relief depositional system and the presence of sedimentary dikes suggest an extensional tectonic phase during the Late Tithonian. At present it is still uncertain if the studied unconformity results from the physiologic evolution of a passive margin succession, or if there is a local or regional contribution from the Tithonian geodynamic evolution of the Western Tethys-North Atlantic Oceans.

## **Coral bioconstruction variability in a small basin: the Burdigalian Bonifacio basin (South Corsica)**

Mazzucchi A.\*<sup>1</sup>, Bosellini F.R.<sup>2</sup>, Tomassetti L.<sup>1</sup> & Brandano M.<sup>1</sup>

1. Dipartimento di Scienze della Terra, La Sapienza Università di Roma. 2. Dipartimento di Scienze Chimiche e Geologiche, Università degli Studi di Modena e Reggio Emilia.

Corresponding email: [andrea.mazzucchi@uniroma1.it](mailto:andrea.mazzucchi@uniroma1.it)

Keywords: Coral bioconstructions, mixed carbonate-siliciclastic systems, Bonifacio Basin.

Coral-rich deposits and coral bioconstructions characterize the mixed carbonate-siliciclastic systems developed in the Bonifacio Basin during the Early Miocene. Accurate mapping on photomosaics allowed to document the internal organization of coral deposits as well as lateral and vertical facies relationships. Thin sections observation contributes to textural characterization and skeletal components identification.

Notwithstanding the small size of the basin (4 x 8 km) at least six types of coral bioconstructions and related depositional geometries are developed.

1) Above gently sloping substrate patch reefs occur in a wedge-shaped system. Siliciclastic facies characterizes the nearshore environment and carbonate production dominates the meso-oligophotic zone, where coral build-up passes basinward to the maerl facies.

2) In the pocket beach oysters and domal coral colonies rapidly colonize gravel and boulders of shoreface setting.

3) On rocky shore, coral buildup is organized in a lens-shaped structure showing a core mainly constituted by a relatively dense coral domestone with a moderate increase of platy corals in the upper part. A coral rubble associated with granitic cobbles and pebbles is locally present at the base of the structure.

4) Coral carpets developed in a patchy pattern on coarse skeletal sand of the shoreface environment.

5) Closer to the granitic basement, coral bioconstruction made up of a coral domestone that may developed on coastal conglomerate evolving basinward to a coarse hybrid sandstone with isolated large domal coral colonies.

6) Cross-bedded coral rudstone to floatstone formed at the base of clinoforms representing the failure of patch reefs developed on the shelf break of an infralittoral prograding wedge system.

The inherited topography produced by the Hercynian crystalline basement, together with the oceanography and the sedimentary processes acting in this small basin, are responsible for having produced such coral bioconstructions variability.

## **Isolated shallow-marine base-of-slope carbonate aprons in the Salento peninsula (Plio-Pleistocene, Apulia, Southern Italy)**

Meloni D.\*, Moretti M., Tropeano M., Gallicchio S., Sabato L. & Spalluto L.

Dipartimento di Scienze della Terra e Geoambientali, Università degli Studi di Bari "A.Moro".

Corresponding email: [demetrio.meloni@uniba.it](mailto:demetrio.meloni@uniba.it)

Keywords: Shallow-marine carbonate aprons, Plio-Pleistocene carbonates, Clinobeds.

A steep rocky slope characterizes the eastern coasts of the Salento peninsula (Southern Italy), where Cretaceous to Pleistocene limestones crop out. This rocky slope connects a wide flat area, about 100 m in elevation, to the cliffed coast of the Otranto Strait (Ionian Sea).

Stratigraphic and sedimentologic analyses have been carried out on an upper Pliocene-lower Pleistocene carbonate unit (the Calcarene di Gravina Fm.) cropping out along the coast inside some indentations of the rocky slope. This carbonate unit forms small isolated bodies with a variable thickness (up to several tens of metres), and is composed mainly of floatstones and packstones with coarse-grained bioclasts. Successions are characterized by long basinward-dipping well laminated and stratified clinobeds. These clinobeds are cut by irregular gullies (some meters in width), filled in their lower part by chaotic deposits (debris flow and slide deposits), and tens of meters in length slump scars. Backsets made up of fine- to medium-grained limestone fill the main slump scars.

Clinobeds developed thanks to grain flows, moving either bioclasts due to a local factory production (red algae, bryozoans, echinoids, brachiopods, planktonic foraminifers) or bioclasts coming from a shallower factory (benthic foraminifers; bivalves). The latter was hosted on the wide flat area today corresponding to the top of the Salento peninsula where upper Pliocene-lower Pleistocene carbonates are attributed to a different unit (the Uggiano la Chiesa Fm.).

The discontinuous presence of the studied carbonates at base of the rocky slope was an original feature. These deposits developed inside indentations of the rocky slope, inherited by faults, when the region was submerged. Isolated depositional systems corresponded to small shallow-marine aprons detached from upward-located coeval systems. These features simulate those ones of a distally steepened ramp, but facies distribution was induced by inherited morphostructural features of the bedrock rather than by the ability of the factories to produce an own depositional profile.

## A history of Triassic carbonate mud, from microbially influenced precipitation to pelagic biomineralization

Preto N.\*<sup>1-2</sup>

1. Dipartimento di Geoscienze, Università di Padova. 2. Leibniz Center for Tropical Marine Ecology (ZMT), Bremen, Germany.

Corresponding email: [nereo.preto@unipd.it](mailto:nereo.preto@unipd.it)

Keywords: microbial carbonates, pelagic carbonate, Triassic.

Carbonate mud in present oceans is mostly produced by calcareous nannofossils and, in shallow water settings, by disintegration of green algae. Until the Triassic, however, calcareous plankton did not exist and shallow water carbonate systems were often dominated by microbialites. Nevertheless, shelf and deep-water hemipelagic successions of the Italian Triassic are comprised of thick lime mudstone and wackestone successions. The origin of these carbonate muds is unknown. Some case studies are presented here in which the origin of Triassic carbonate mud was investigated.

Lower Triassic (Induan) mid-outer ramp successions of the Dolomites are mostly lime mudstone, deposited after the end-Permian extinction that killed all carbonate producers. The origin of these lime mudstones is thus enigmatic. SEM petrography and microprobe analyses were used to determine an originally aragonitic composition, and to exclude an origin from fragmentation of shells. These carbonates did not form as benthic microbialites either, and only bear biomarkers of bacteria. It is thus suggested that they precipitated directly from the water column of an aragonite sea, either abiotically or via bacterial influence.

Middle Triassic shallow water carbonate systems of Tethys are mostly made of benthic microbialites and marine cements. These abiotic and microbial carbonates should not produce loose carbonate sediment, however, surrounding basins witness the deposition of periplatform carbonate muds. Quantitative petrology (point counting on thin sections) highlight the presence of loose carbonate mud in shallow inner platform environments, along with aragonitic green algae. These might have exported significant amounts of fine carbonate to basins, similarly to the highstand shedding observed for recent Bahamian platforms. At the same time, however, the growth of the platform was ensured by a microbial carbonate factory, thus, carbonates of the platform and basin were both formed in shallow water, but their production was not entangled.

Periplatform carbonate mud deposition became widespread during the Late Triassic. Starting from the Late Carnian, these deep-water successions bear calcareous nannofossils (calcispheres) in rock-forming abundances. The onset of this pelagic carbonate deposition is sharp and coeval with a negative  $\delta^{13}\text{C}$  excursion and climate change episode, the Carnian Pluvial Event. By the Rhaetian, the pelagic lime mudstones of Sicily bears > 60% in volume of the calcareous nannofossil *Prinsiosphaera*.

The original mineralogy and provenance of fine carbonate in the Italian Triassic Tethys could only be disentangled by a combination of quantitative petrology, SEM and in-situ geochemical analyses. The results shed light on the dawn of pelagic carbonate sedimentation, that seems to occur in steps coeval with climatic and oceanographic crises in the Carnian and Rhaetian.

## **Sedimentary and early diagenetic carbonates from an Early Permian siliciclastic-dominated continental basin (Orobic Basin, Southern Alps, Italy): oncoidal beds and groundwater calcretes**

Tessarollo A.\*, Berra F. & Felletti F.

Dipartimento di Scienze della Terra "Ardito Desio", Università degli Studi di Milano.

Corresponding email: [andrea.tessarollo@unimi.it](mailto:andrea.tessarollo@unimi.it)

Keywords: Permian, Southern Alps, continental carbonates, groundwater calcretes.

In continental basins, carbonates are frequently related with lacustrine/palustrine depositional systems. Major controls on the abundance, mineralogy and type of carbonate are exerted by the geology of the catchment area, basin morphology and environmental/climate conditions. The study of continental carbonates (in terms of processes, i.e. inorganic precipitation, biogenic production, clastic accumulation or diagenetic precipitation) may provide important constraints on the paleoenvironmental interpretation of continental successions, significantly contributing to the understanding of the past climate conditions.

In the Orobic Basin succession, deposited during the Early Permian in a transtensive intramontane basin, different continental carbonates occur in the uppermost part (about 100m) of the succession, where they are intercalated within heterolithic facies (fine-grained sandstones, siltstones and shales). In order to characterize the succession three closely spaced stratigraphic sections have been measured.

In the studied sections two different types of carbonates have been described. The first carbonate type is mostly represented by tabular beds up to 50 cm thick, often laterally extensive over tens to hundreds of meter and typically characterized by oncoids up to 7 cm in diameter. At the microscope, oncoids often consist of alternating concentric layers of microbial micrite coatings and fibrous calcite rims, suggesting periodical modification of water conditions (short-time paleoclimate changes, possibly seasonal). The second carbonate type occurs as carbonate-cemented beds or aligned nodules, frequently with preserved original sedimentary structures. The presence of the carbonate cements is strictly related to the grain size, as they are present in the coarsest part (basal or middle) of the sandstone layers. Differential compaction of the nodules with respect to the surrounding sandstones suggests an early diagenetic origin, related to phases of progressive cementation/replacement of the siliciclastic framework, driven by the circulation of carbonate-rich water in the coarsest horizons.

The integration of sedimentological evidence from the siliciclastic and carbonate deposits contributes to a better reconstruction of the palaeoenvironment: this was a flat sheetflooded area, periodically developed in a shallow lake or pond that, during periods of reduced siliciclastic input, was the place for microbial growth and carbonate deposition. In addition, lateral influx and concentration of carbonate-rich groundwater within coarse (and thus highly permeable) horizons favored the subsurface growth of carbonate nodules and layers (groundwater calcretes). The inferred climatic conditions were semi-arid and seasonal.

## Nodules formation in Early Triassic fish-bearing beds from south-eastern China

Tintori A.\*<sup>1</sup>, Berra F.<sup>1</sup>, Jiang D.Y.<sup>2-3</sup>, Lombardo C.<sup>1</sup> & Meriggi G.<sup>1</sup>

1. Università degli Studi di Milano, Dipartimento di Scienze della Terra "A. Desio". 2. Department of Geology and Geological Museum, Peking University, Beijing, China. 3. State Key Laboratory of Palaeobiology and Stratigraphy (Nanjing Institute of Geology and Palaeontology, CAS), Nanjing, China.

Corresponding email: [andrea.tintori@unimi.it](mailto:andrea.tintori@unimi.it)

Keywords: fossil fishes, Early, Triassic, China.

Preservation in limestone nodules has been always seen as one of the best way to achieve very well preserved fossils, both invertebrates and vertebrates as formation of this carbonatic concretion is thought to start as soon as the organic remain arrive on the bottom. Though this kind of preservation is known from most of the Phanerozoic, vertebrates bearing nodules from marine environment are not so common (Late Devonian of Gogo -Australia, Early Cretaceous of Ceara - Brasil (possibly brackish or fresh water) and Gulmina -Morocco). However, during Early Triassic (Induan + Smithian) nodules enclosing fishes appear to be very widespread, being frequently found in Greenland, Spitsbergen, Madagascar and south-eastern China and less commonly in Canadian Rocky Mountains. Furthermore, it is very probable that in each of those areas fossiliferous nodule-rich levels are more than one, even if so far no detailed dating has been proposed apart from the Greenland ones. Recent field work in south-eastern China provide new information about three different sites with fish-nodules and nodules formation. First of all it is now proved that fossiliferous levels known in literature only by fishes preserved in nodules actually are rich also in fish specimens preserved in mudstone without any limestone concretion. Carbonatic nodules can also be devoid of macrofossils, even if they are found just a few cm above or below the fossiliferous ones. Detailed macroscopic and microscopic sedimentological observations on fossiliferous nodules highlighted the relationships between sedimentary structures between the nodule and the including rocks. The internal structure of the nodules has been analysed: nodules typically show an evident inner zonation, the central area surrounding the fossil remain being rich also in sparry calcite. The including rock is always a black, laminated, pure mudstone.

## The Lithothamnion Limestone of Bolognano Formation (Majella, Central Apennines): not only red algae

Tomassetti L.\*<sup>1</sup>, Brandano M.<sup>1-2</sup> & Petracchini L.<sup>2</sup>

1. Dipartimento Scienze della Terra, Università Roma La Sapienza. 2. Istituto di Geologia Ambientale e Geoingegneria (IGAG) CNR, Area della Ricerca di Roma 1.

Corresponding email: [laura.tomassetti@uniroma1.it](mailto:laura.tomassetti@uniroma1.it)

Keywords: litofacies, Majella, Miocene.

The Bolognano Formation represents the carbonate ramp succession of the Majella during the Oligocene- Late Miocene interval. The stratigraphic architecture of Bolognano Fm shows the presence of two lithostratigraphic units constituted by cross bedded calcarenites with *Lepidocyclina* separated by the cherty marly lithostratigraphic unit. The second *Lepidocyclina* unit is overlaid by bryozoan calcarenites passing basinward into hemipelagic marls. The uppermost carbonate unit is represented by the *Lithothamnion* limestone that directly lies on the bryozoan calcarenites in the Orfento Valley and on the hemipelagic marls in the northern sector of Majella (San Bartolomeo Valley, Cerratina area). In the Orfento Valley the base of the *Lithothamnion* limestone is characterized by a *Heterostegina*-rich horizon that unconformably overlaid the underlying bryozoan calcarenites. In the San Bartolomeo and Cerratina Valley the *Lithothamnion* limestone overlaid the hemipelagic marl unit. The *Lithothamnion* limestone is constituted by abundant red algae nodules, free-living branches, and rhodoliths that correspond to the “mäerl facies” associated with a seagrass meadows sediments and in the proximal sector locally with scattered corals, mainly developed at nucleus of the rhodoliths. This portion of the Bolognano Fm is also characterized by the occurrence of hummocky cross stratification interval or bed forms related to rip current channels produced by storm events. In these channels some well-preserved bones of marine mammals, mainly as vertebrae remains, have been recognized associates with a bivalve lag deposits. Upward the *Lithothamnion* limestone is characterized by an increase of fine terrigenous content with red algae growth forms dominated by thin crusts typically associated to fine grained substrate, indicating the gradual drowning of the *Lithothamnion* limestone that reaches its climax with the deposition of the overlying *Turborotalia multiloba* marls.

## Stratigraphic and petrographic analysis of the *Arabescato Orobico* dimension stone from the Brembana Valley (Calcare Rosso, Bergamasc Alps)

Vola G.\*<sup>1</sup> & Jadoul F.<sup>2</sup>

1. Dimension Stone and Building Material consultant. 2. Dipartimento di Scienze della Terra "A. Desio", Università degli Studi di Milano.

Corresponding email: [gabriele.vola@gmail.com](mailto:gabriele.vola@gmail.com)

Keywords: Calcare Rosso, Arabescato Orobico, carbonate petrography, applied stratigraphy.

The *Arabescato Orobico* is a very well-known historical-contemporaneous decorative stone and building material from the Bergamasc Alps, Italy. From the geological-stratigraphic standpoint it belongs to the Calcare Rosso, a characteristic polychromous carbonate, lenticular unit, latest Ladinian-Early Carnian in age. This unit, extensively studied in the past, is characterized by decimetre thick peritidal cycles (primary sediments) associated to plurimeter thick supratidal tepee, diagenetic breccia horizons, strongly modified by several, superimposed meteoric and marine early diagenetic processes with several cavities and tensional fracture generations filled in with dark grey fibrous hemispheroids (*raggioni*), grey isopachous calcitic cement crusts, internal calcitic and dolomitic sediments, and terra-rossa paleosols. The physical correlation of several stratigraphic sections outcropping along abandoned and active quarries of the Brembana Valley, permitted to divide the Calcare Rosso succession in three informal units (CR1, CR2, and CR3) on the basis of different markers horizons (unconformities, and terra rossa layers), and recognize a local very low angle onlapping geometry of this unit on the unconformity at the top of the Esino Limestone. The new stratigraphic scheme proposed for the median Brembana Valley shows partially heteropic facies between the upper portion of the Calcare Rosso (at least units CR2 and CR3) and the lower Breno Fm. and the same regional depositional setting. The carbonate petrography applied to the characterization of the commercial varieties available on the market, namely *Grigio*, *Grigio-Rosa*, *Rosa*, and *Rosso*, permitted to recognize eleven different commercial subtypes, and formulate a more coherent classification of the *Arabescato Orobico*, which can be used either in the stone sector, or in the conservation and restoration science, for distinguishing the *Arabescato Orobico* from different decorative stones with similar names or textures. The *Arabescato Orobico* commercial subtypes have been fully integrated within sedimentological facies analysis in the new stratigraphic-depositional model of the Calcare Rosso of the Brembana Valley, showing the lateral and vertical distribution of grey and red lithofacies associations, corresponding to Grigio/Grigio-Rosa, and Rosa/Rosso commercial types. Indeed the stratigraphic architecture of the unit is also suitable for evaluating available resources for new quarrying activity, or the recovery of currently abandoned quarries (Vola & Jadoul, 2014).

Vola G. & Jadoul F. 2014. Applied stratigraphy and carbonate petrography of the *Arabescato Orobico* dimension stone from the Bergamasc Alps (Calcare Rosso, Italy). Italian Journal of Geosciences, 133(2), 294-314 (DOI: 10.3301/IJG.2014.11).

## **SESSIONE S7**

### **Evaporite basins: facies, diagenesis and sequences**

*CONVENORS*

*A. Caruso (Univ. Palermo)*

*A. Di Stefano (Univ. Catania)*

## Deep biosphere secrets of the Mediterranean Salt Giant

Aloisi G.\*<sup>1</sup>, Lugli S.<sup>2</sup>, McGenity<sup>3</sup> T., Orcutt<sup>4</sup> B., Takai K.<sup>5</sup>, Treude T.<sup>6</sup> & Camerlenghi A.<sup>7</sup>

1. Laboratoire d'Océanographie et du Climat, Université Pierre et Marie Curie. 2. Dipartimento di Scienze Chimiche e Geologiche, Università degli Studi di Modena e Reggio Emilia. 3. School of Biological Sciences, University of Essex. 4. Bigelow Laboratory for Ocean Sciences. 5. Japan Agency for Marine-Earth Science and Technology (JAMSTEC). 6. Helmholtz Center for Ocean Research (GEOMAR).  
7. Osservatorio Geofisico Sperimentale.

Corresponding email: [galod@locean-ipsl.upmc.fr](mailto:galod@locean-ipsl.upmc.fr)

Keywords: IODP, Messinian Salinity Crisis.

One component of the IODP multi-platform drilling proposal called DREAM (Deep-Sea Record of Mediterranean Messinian Events), plans to investigate the deep biosphere associated to the Messinian Salinity Crisis (MSC) Salt Giant. We propose that the MSC Salt Giant, because of the variety of chemical environments it produces, has the potential to harbour an unprecedented diversity of microbial life with exceptional metabolic activity. Gypsum and anhydrite deposits provide a virtually unlimited source of sulphate at depths where oxidants are a rarity in other sedimentary environments. When reduced organic carbon comes into contact with these minerals there is the potential for a dynamic deep biosphere community of sulphate reducers to develop, with implications for sedimentary biogeochemical cycles and the souring of crude oil. But the thickness of the Messinian evaporites and the range of chemical environments it harbours poses fundamental questions: will the interaction of several extreme conditions of temperature, salinity, pressure and chemical composition limit the ability of microbes to take advantage of such favourable thermodynamic conditions? And has such a diverse set of physical and chemical environments fostered microbial diversity, rather than phylogenetic specialization, as recent research into deep Mediterranean brine systems seems to indicate? Over three kilometres in thickness, approaching the known temperature limits of life and with fluids precipitating carbonate, sulphate, halite and potash salts, microbes living within and around the MSC Salt Giant will be subject to the most exotic combinations of extremes, and have likely evolved yet unknown adaptations. Gypsum and Halite crystals contain fluid inclusions that are a micro-habitat in which microbes survive for tens of thousands, to possibly millions, of years, posing the fundamental question of cells devoting nearly all of their energy flow to somatic maintenance needs, rather than growth and reproduction, and opening new avenues for research for life on other planets. Fluid inclusions and the microbes they contain also inform us on the chemical and physical conditions of the sedimentary environment at the moment of deposition. This information will be key in deciphering the complex succession of paleoclimatic and hydrological events that led to the formation of the MSC Salt Giant. Drilling the MSC Salt Giant is an unprecedented opportunity to sample and investigate this highly reactive association of microbial communities, pore fluids and minerals which is the modern analogue for ancient deep biosphere communities developed in the salt giants of the geological past.

## High-resolution stratigraphy of the pre-evaporitic/evaporitic transition in the late Messinian Adriatic foreland domain

Amadori C.\*<sup>1</sup>, Cipollari P.<sup>1</sup>, Cosentino D.<sup>1</sup>, Florindo F.<sup>2</sup>, Caruso A.<sup>3</sup> & Lo Mastro S.<sup>1</sup>

1. Dipartimento di Scienze – Università Roma Tre. 2. INGV, Roma. 3. Dipartimento di Scienze della Terra e del Mare - Università di Palermo.

Corresponding email: [amadorichiara88@gmail.com](mailto:amadorichiara88@gmail.com)

Keywords: Messinian Salinity Crisis, Adriatic foreland, integrated stratigraphy.

One of the most spectacular evaporative event in the Earth history occurred in the Mediterranean Basin, during the late Messinian (Messinian Salinity Crisis, MSC), as a consequence of the restriction in the Atlantic-Mediterranean connection. Enclosed marine environments could record evaporative deposition undergo restriction in circulation coupled with climate forcing.

The aim of this paper is to investigate what happened in the sedimentary basin of the Adriatic foreland domain approaching the MSC by using an interdisciplinary study, which includes stratigraphy, paleontology, mineralogy, and magnetostratigraphy. The study area is the NW flank of the Maiella Mountains, where the MSC is well recorded by both the deposition of the Lower Evaporites and the post-evaporitic deposits of the Lago-Mare event. For getting a complete record of the pre-evaporitic/evaporitic transition in the study area, a 23m depth borehole was drilled starting from the 20cm-thick carbonate horizon (Calcare di Base) just at the base of the first gypsum cycle of the Lower Evaporites. Beneath the Calcare di Base, the sedimentary core recovered 3.8 m of dark clays rich in organic matter, punctuated by 5 carbonate-rich layers. The rest of the recovered sedimentary core is characterized by limestones and marly limestones rich in small lithotamnum, bryozoa, and benthic foraminifera, pertaining to the uppermost part of the Bolognano Formation. All the sedimentary core was analysed, collecting 5-10 cm thick samples.

The occurrence of the carbonate-rich layers within the dark clays allows us to recognize 5 sedimentary cycles, possibly forced by precessional cyclicity. Calcareous nannofossils show two peaks of *Sphenolithus abies* within the 2nd and 4th cycle from the top. Small *Reticulofenestra* and *Helicosphaera carteri* show one peak within the 1st cycle, as well as in the 3rd and 4th cycles. Among the planktonic foraminifera, *Turborotalita multiloba* shows a peak within the 4th cycle whereas *Orbulina universa* has two peaks, within the 3rd and 4th cycles. The uppermost 50cm of the sedimentary core are completely barren.

Although no major changes in lithology can be recognized in the fine-grained deposits, magnetic susceptibility decreases to extremely low values in the 1st and 2nd cycles, in the upper part of the sedimentary core. The depletion of magnetic minerals in this interval seems higher than can be attributed solely to dilution by magnetite-poor sediments, which implies that magnetite dissolution could have occurred. Our analyses on the paleontological record of the pre-evaporitic deposits in the Maiella foreland basin show results very similar to other pre-evaporitic Messinian successions from the Mediterranean Basin.

Finally, the calibration of the sedimentary core with the insolation curve allow us to confirm the precessional forcing of the sedimentary record in the Messinian Adriatic foreland basin during the pre-evaporitic stage.

## **Messinian evaporites in Sicily and nearby Ionian Sea: Linking basin tectonics, evaporite facies variations and their impact on subsequent deformation**

Butler R.W.H.<sup>1</sup>, Maniscalco R.\*<sup>2</sup>, Sturiale G.<sup>2</sup> & Grasso M.<sup>†</sup>

1. Geology and Petroleum Geology, School of Geosciences, University of Aberdeen. 2. Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania.

Corresponding email: [maniscal@unict.it](mailto:maniscal@unict.it)

Keywords: Salt tectonics, thrust-top basins, Messinian, Sicily, Ionian Sea.

Messinian evaporites in the seabed of the modern Mediterranean are generally inferred to influence the structure of the overlying Plio-Quaternary sediments. Hummocky deformation of these sediments (so-called “cobblestone” morphology) characterizes much of Mediterranean sea-floor. With improvements in seismic imaging, it is increasingly evident that original stratigraphic variations in evaporite formations can play important roles in their deformation. Critical in this regard is the relative abundance of halite, together with other high-solubility salts, and the less soluble calcium sulfates and carbonates. Our aim is to demonstrate the length-scale of variations in evaporite stratigraphies deposited in thrust-top basins and how these variations have controlled subsequent deformation of these basins. We use Messinian examples that integrate outcrop observations with extensive subsurface data from Sicily to provide new structural interpretations and apply these insights to interpret seismic data (in the absence of well control) from the nearby Ionian Sea. These Messinian basins are excellent sites for studying lateral variations in evaporite successions and their subsequent deformation. Two areas of the Sicilian thrust system are used here, linked to three major mine areas (Realmonte, on the south coast; Corvillo and Mandre in the centre of the island). Thrust-top mini-basins control fractionation of carbonate-evaporite facies that then continue to influence post Messinian deformation. Gypsum and carbonate units develop broad single-layer buckle-fold trains, wavelengths reflecting layer thickness. The development of deformation appears limited by bending resistance at fold hinges – which can be overcome by syn-tectonic erosion. In contrast, the thick halite deposits that accumulated in growth synclines have deformed with short-wavelength folds and distributed strain. These structures can display rapid lateral variations over length scales of a few hundred metres. Similar structural styles – with buckle fold trains passing laterally into more homogeneously shortened, short wavelength folding - are evident on seismic data from the buried Messinian interval beneath the Ionian sea. Using the Sicilian outcrop as analogues, the structural styles for the Ionian may be used to infer evaporite type in these subsurface examples and assist interpretation of evaporites beneath the sea-bed of Mediterranean.

## Depositional processes of Messinian evaporite-basins in the Adriatic foredeep (Northern Marche)

Capuano N.\*

Dipartimento di Scienze della Terra, della Vita e dell'Ambiente (DiSTeVA) - Università di Urbino "Carlo Bo".

Corresponding email: [nicola.capuano@uniurb.it](mailto:nicola.capuano@uniurb.it)

Keywords: Messinian, northern Marche, evaporite-basins.

Detailed analyses of new stratigraphic sequences allow some important considerations on the tectonic pulses that controlled the basins evaporite-deposits infill during the Messinian salinity crisis in the north-Marche foreland. In particular, a survey has been carried out on evaporitic facies of three "syn-tectonic" basins, known as: Sapigno Basin, Pietrarubbia Basin and Montecalvo in Foglia Basin, genetically related to tectonic-stratigraphic evolution stages of the Adriatic foredeep system.

Sapigno Basin - The stratigraphic sequence is dominated by clastic gypsum accumulation. Grain-size, texture and sedimentary structure suggest en-mass resedimentation processes, evolving from slides to debris flow, slumping and turbidity current. In this case, the coeval erosion and depositional processes were in concomitance with intra-Messinian tectonic pulses.

Pietrarubbia basin - The stratigraphic sequence includes laminated carbonate-evaporite facies (Calcare di Base) and gypsum-laminae facies; the transition with the overlying gypsum-breccia facies is marked by erosional discontinuity (Capuano, 2009). The northern and southern sector of the basin show gypsum-laminated-reddish facies, indicative of well oxygenated conditions within the basin. The central portion of the basin consists of dark-gray gypsum-laminated facies, indicative of oxygen reduction favored by water stratification in a more distal setting. Moving from NW to SE, the depth of the basin increases as shown by the increasing thickness of the accumulated evaporite deposits, from 30 m in the northern sectors to 100 m in the central sector. Facies association and thickness distribution testifies the syn- and post-evaporitic transition. The laminate evaporite-carbonate and gypsum-laminae facies are characteristic of depositional processes in shallow-water coastal environments passing to shelfal settings, whereas the chaotic gypsum deposits (i.e. breccie and megabreccie bodies), prograde above the slope and en-mass resedimentation in deep-water settings.

Montecalvo in Foglia basin - The basal unit is characterized by the presence of laminated evaporite-carbonate facies and gypsum-laminae facies. The upper unit consists of carbonate-olistoliths and gypsarenite facies. The gypsum-laminae structures result from traction currents. The transition with the overlying gyps-arenite and carbonate-olistoliths is marked by the so-called Messinian erosional surface (5.60 Ma). The gypsum-arenite facies (Castelcavallino, Pallino, Cà Lorenzi sections) show sedimentary structures formed by turbidity currents and resedimentation mechanisms, with paleocurrent structures indicating a NW-SE direction of the flow. Gypsum breccia and large blocks of carbonate-olistoliths, moving downslope under the action of gravity, associated with an important phase of erosion, was favoured by internal thrust activity, and subsequent resedimentation into deeper-water setting.

The depositional sequence recorded in Messinian evaporite basins over the Marche area, exhibit differences of facies, thickness, depositional trends and cyclical organization which result from synsedimentary tectonic processes leading to the emplacement of the northern Marche foredeep. Despite differences related to the local geodynamic settings, these basins experienced a common Late Messinian history that supports the development of clastic evaporites in deep-water setting. The Pietrarubbia and Montecalvo in Foglia basins show similar trends in term of structural evolution and changing depositional environments.

Capuano N. 2009. Note illustrative della carta geologica d'Italia alla scala 1:50.000, foglio 279, Urbino. Serv.Geol.It. ISPRA.

## Formation and accumulation of Messinian evaporites in the Caltanissetta Basin (Sicily) by “supercritical out-salting”: reasons for a Tethys serpentinite connection

Carbone S.<sup>1</sup>, Scribano V.\*<sup>1</sup> & Manuella F.C.<sup>2</sup>

1. Dipartimento di Scienze Biologiche, Geologiche e Ambientali (DBGA), Università degli Studi di Catania. 2. Via Dell'Oro, 137 – Catania.

Corresponding email: [scribano@unict.it](mailto:scribano@unict.it)

Keywords: Evaporite, Supercritical fluids, Serpentinites, Sicily.

Vai (2003) suggested that the area presently occupied by Sicily was a deep marine basin belonging to the ultra-slow spreading Ionian-Tethys Ocean, Early Permian in age. The study of the Hyblean xenolith suite and the reappraisal of geophysical data (Manuella et al., 2013) indicate that the unexposed basement of the Hyblean-Pelagian foreland consists of serpentinitized peridotites and minor gabbros, suggesting the existence of oceanic core complex structures (Scribano et al., 2006). Accordingly, the abundance of serpentinites in the oceanic roots of Sicily and its offshore areas hints at the presence of huge amounts of water and evaporite-like salts (probably about 10.5 kg of salts per m<sup>3</sup> of serpentinitized peridotite) in the Tethys basement of Sicily, as a result of the seawater-driven serpentinitization (Manuella, 2011). Regarding the Caltanissetta Depression, a thick succession of evaporites (Gessoso-Solfifera Group) was deposited in a Miocene marine basin, during Messinian. The most popular climate evaporite theory suggests that deep salt water basins, having restricted communication with the open ocean, dried out and filled up several times, forming a thick sequence of salts. This explanation may be realistic for a salt thickness of few tens of meters (Hovland et al., 2014). Differently, the Caltanissetta succession consists of 250 m of outcropping gypsum and carbonates and about 1000 m of buried chlorides. Therefore, we put forward the hypothesis that supercritical fluids, deriving from the massive dehydration of serpentinites due to a geothermal rise, may have remobilized the buried Triassic evaporites as saline brines (supercritical out-salting model; Hovland et al., 2014), during Messinian. These saturated brines were emplaced as hot “geysers” forming hypersaline ponds at the sea bottom (Hovland et al., 2014), as presently observed in the numerous deeps in the Red Sea floor.

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## **Carbonate deposition and diagenesis in evaporitic environments: the evaporative and sulphur-bearing limestones during the settlement of the Messinian Salinity Crisis in Sicily and Calabria (Southern Italy)**

Caruso A.\*<sup>1</sup>, Pierre C.<sup>2</sup>, Blanc-Valleron M.M.<sup>3</sup> & Rouchy J.M.<sup>3</sup>

1. Dipartimento di Scienze della Terra e del Mare- Università di Palermo. 2. CNRS-UMR 7159, LOCEAN- Université Pierre et Marie Curie (Paris), France. 3. CNRS-UMR 5143 - Muséum National d'Histoire Naturelle (Paris), France.

Corresponding email: [antonio.caruso@unipa.it](mailto:antonio.caruso@unipa.it)

Keywords: Messinian Salinity Crisis, Evaporites, Mediterranean.

The depositional and diagenetic processes involved in the formation of diagenetic carbonates in the evaporitic environment of the Messinian Salinity Crisis (i.e., calcare di base, sulphur-rich limestones and intragypsum carbonates) are investigated in central Sicily and Calabria basins. Strong sedimentary differences are observed between the studied sections that reflect specific depositional and diagenetic evolution in interconnected sub-basins resulting from the fragmentation of the Central Sicilian and Calabrian domains by active synsedimentary tectonic activity. These carbonates formed diachronously in restricted perched sub-basins, during the transitional period between the restricted marine conditions of the Tripoli Fm represented by diatomite/marls alternations and the generalized hypersaline settings of the Messinian Salinity Crisis. The primary peloidal and microbial limestones interbedded with gypsum layers succeed rhythmically with no major discontinuity to the restricted marine deposits of the upper Tripoli Fm. The former structure, mineral composition and chemistry of the primary carbonates were intensely transformed by the superimposition of early to late diagenetic processes that occurred in different ways according to the considered sub-basin. The first diagenetic step was the intensive development of interstitially grown gypsum and halite crystals from trapped saturated brines that locally led to the formation of true salt beds. Processes of bacterial sulphate reduction occurred in local depocentres where anoxic bottom waters favoured microbial processes fuelled by biogenic methane and crude oil. These processes caused calcite replacement of gypsum (scattered crystals to massive laminated or selenitic layers) and formation of native sulphur concentrations. Migration of hydrocarbon and H<sub>2</sub>S-rich fluids caused the epigenetic dissemination of sulphur and late diagenetic carbonate replacement of gypsum. Later influxes of continental waters were responsible for dissolution of the halite crystals and their replacement by sparry calcite. The vugs resulting from the molar volume changes, during both the gypsum/calcite conversion and halite dissolution, commonly remained empty or were filled with calcite, celestine, fibrous silica, anhydrite, secondary gypsum, and even native sulphur. The former accumulation of soft and incompetent fine-grained carbonate and gypsum sediments was strongly destabilized by this succession of volumetric changes resulting from multistep mineral replacements and fluidisation processes. Their superimposition easily explains the vuggy and boxwork-like textures, collapse features, in-situ brecciation and lateral displacement which are responsible for the chaotic organisation and lateral variability of these deposits, without necessarily involving basin-scale re-sedimentation as debris flows. Moreover, the disturbances of the sedimentary successions were aggravated by their inclusion in a pile of plastic sedimentary units (tripoli, gypsum and salt) that intensely reacted to active synsedimentary tectonic deformations (faulting, folding and local thrusting), to salt tectonics and solution collapse.

## Two Volcanic tephra layers within the upper Messinian succession of Tuscany (inner northern Apennine – Italy): $^{40}\text{Ar}$ - $^{39}\text{Ar}$ dating and implications on evaporitic and post-evaporitic stratigraphy

Da Prato S.\*<sup>1</sup>, Foresi L. M.<sup>1-2</sup>, Laurenzi M. A.<sup>1</sup>, D'Orazio M.<sup>3</sup>, Zanchetta G.<sup>1-3-5</sup>, Aldinucci M.<sup>4</sup>,  
Martini I.<sup>2</sup> & Sandrelli F.<sup>2</sup>

1. IGG-CNR Pisa 2. Dipartimento di Scienze Fisiche, della Terra e dell'Ambiente, Università di Siena. 3. Dipartimento di Scienze della Terra, Università di Pisa. 4. Perecon AS, c/o Økoplán AS, Bergen. 5. IGAG-CNR Montelibretti, Roma.

Corresponding email: [simone.daprato@igg.cnr.it](mailto:simone.daprato@igg.cnr.it)

Keywords: upper Messinian, tephra layers, Tuscany.

Two volcanic tephra layers have been found intercalated in the upper Messinian sediments of the Migliarino and Pignano sections, located in the Fine and Volterra-Chiusdino neogenic–quaternary basins, respectively (inner Northern Apennines). The Migliarino section (90 m thick), about 2 km SE of Rosignano Marittimo town, consists of 13 beds of alabaster gypsum alternating with mudstones. Lugli et al. (2010) consider the first eleven beds as primary gypsum deposited during the evaporitic Messinian phase. The tephra layer is intercalated to laminated clay between the 10th and 11th gypsum beds.

The Pignano section (130 m thick) is located about 7 km W of the Volterra town and consists of alternations of conglomerates, clayey sands and clays with rare secondary gypsum. The volcanic tephra is located at about 85 m from the base of the section and it is characterized by laminated clay covered by sand deposited in a distal delta-front environment.

The igneous fraction of the two tephra layers consists of crystal fragments of prevailing fresh, zoned oligoclase and sanidine, and subordinate quartz and brown mica. This latter phase is replaced to variable extent by chloritic products and Fe-Ti oxihydroxides. In both tephra layers the igneous crystal fragments have sharp edges. In the Migliarino tephra layer the igneous crystals are dispersed in an argillaceous yellowish matrix plus brown iron hydroxides. The Pignano tephra layer has a topmost part constituted by finer-grained crystal fragments and by abundant “Y”-shaped dark and clear fragments, likely representing altered volcanic glass shards, in a dominant argillaceous matrix. The lower portion is made of alternating crystal rich and argillaceous 1-5 mm-thick layers. The nature and composition of the mineral phases occurring in the Migliarino and Pignano tephra layers point to a highly evolved nature of the original magma.

Sanidine single-crystal laser fusion  $^{40}\text{Ar}$ - $^{39}\text{Ar}$  analyses of the two volcanoclastic levels give weighted average ages of  $5.52 \pm 0.01$  Ma (1 $\sigma$  analytical) for Migliarino and  $5.52 \pm 0.01$  Ma for Pignano [age monitor: TCR sanidine, 28.34 (Renne et al., 1998); decay constants of Steiger & Jäger (1977)].

The comparison of these levels with others in the Northern Apennines, impose new constraints for the chronology of the primary evaporitic Messinian succession.

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Renne P.R., Swisher C.C., Deino A.L., Karner D.B., Owens T.L. & DePaolo D.J. 1998. Intercalibrations of standards, absolute ages and uncertainties in  $^{40}\text{Ar}/^{39}\text{Ar}$  dating. *Chemical Geology*, 145, 117-152.

Steiger R.H. & Jäger E. 1977. Subcommittee on geochronology: convention on the use of decay constants in geo- and cosmochronology. *Earth Planet. Sci. Lett.*, 36, 359-362.

## SESSIONE S8

### **Stratigraphic architecture and sedimentary basin evolution: controlling factors and implications for geo-resources exploration and exploitation**

#### *CONVENORS*

*G. Davoli (Eni , Milano)*

*A. Di Giulio (Univ. Pavia)*

*M. Tropeano (Univ. Bari)*

## **A volcanic stratigraphic marker in the continental shelf offshore the Volturno river (Northern Campania, Southern Italy): inferences from high resolution seismic stratigraphy and tephrostratigraphy**

Aiello G.\*<sup>1</sup>, Insinga D.D.<sup>1</sup>, Iorio M.<sup>1</sup>, Marsella E.<sup>1</sup> & Senatore M.R.<sup>2</sup>

1. IAMC-CNR Napoli. 2. Università degli Studi del Sannio, Benevento.

Corresponding email: [gemma.aiello@iamc.cnr.it](mailto:gemma.aiello@iamc.cnr.it)

Keywords: Volturno offshore, seismic stratigraphy, tephrostratigraphy.

A volcanic stratigraphic marker in the continental shelf offshore the Volturno river, located in the Northern Campania has been recovered and discussed through seismo-stratigraphic and tephro-stratigraphic data. The seismo-stratigraphic data include a Subbottom Chirp and Sparker seismic grid collected in the frame of research programmes on marine geological mapping of the continental shelf off Campania Region. Cores have been also collected for a better calibration of seismic profiles. Although several tephrostratigraphic studies have been carried out in Southern Italy, regarding in particular the Somma-Vesuvius and the Ischia and Procida offshore, only few of them have linked the geological aspects on tephrostratigraphy detected through geochemical, sedimentological and SEM analyses with high resolution seismic profiles. In the Ischia stratigraphic succession the oldest tephra layers are distinguished by a well preserved layer, thick about 30 cm, which is correlated with the Phlegrean products of the Campanian Ignimbrite event (39 ky B.P). The marine counterpart layer is named the C13 tephra layer in the Tyrrhenian sea. The sedimentological and petrophysical analysis of cores has evidenced the occurrence of a volcanic stratigraphic marker, corresponding to a highly continuous and parallel seismic reflector on the seismic sections. Seismo-stratigraphic analysis has evidenced that the volcanic level, interpreted as a tephra deposit is interlayered in transgressive system tract deposits, pertaining to the Late Quaternary depositional sequence, well detected in the whole Campania Tyrrhenian margin. The volcanic level, mapped on six seismic profiles, is located at different depths, ranging between 70 and 155 m below the sea bottom, interrupting in correspondence to the shelf break. Sedimentological and petrophysical analyses have shown that the tephra layer corresponding to the seismic reflector consist of a thick sandy deposit with pumiceous clasts, whose analysis in terms of tephrostratigraphy is still in progress.

## **The new frontier of the exploration activity in the Western Nile Delta: the example of oil discovery**

Calabrò R.<sup>1</sup>, Costantini A.\*<sup>1</sup>, Feltre L.<sup>2</sup>, Federici F.<sup>2</sup>, Mazzarelli M.<sup>2</sup> & Zambelloni G.<sup>1</sup>

1. Abu Qir Petroleum, Alexandria, Egypt. 2. Edison Spa, Milano.

Corresponding email: [aldo.costantini@edison.it](mailto:aldo.costantini@edison.it)

Keywords: Seismic interpretation, structural setting, source rock, oil field.

Abu Qir gas field is located in the western Nile Delta, 25 km off-shore Alexandria (Egypt). Since Edison acquisition in 2009, many studies have been performed to evaluate the residual hydrocarbon potential.

The Nile Delta area has been affected by both the Syrian Arc folding (Late Cretaceous – early Tertiary) and extensional tectonic events related to the opening of the Gulf of Suez and Red Sea (starting in the late Oligocene). These tectonic events, involved pre-Pliocene formations and generated a large normal faults, that bounded at North, the Abu Qir anticline. This structural setting influenced the deposition of the Abu Madi Fm (Late Miocene) characterized by sand with shale interval (thick 25-140 meters) and Kafr el Sheik Fm (Pliocene), formed by sandstones (thick 200 meters). These two formations represent the main reservoirs of the Abu Qir area.

Based on the maps coming from OBC 3D data interpretation, Edison carried out a new drilling campaign, which discovered a new oil accumulation in basal Kafr el Sheik Fm (BKES). In 2011, Edison started a new exploration phase with a new seismic acquisition (3D Multi-Azimuth - MAZ), that improve the quality of the previous interpretations. The available geophysical studies (AVO - amplitude variation with offset) have not yet fully clarified the oil upside potential.

However, the ongoing basin modeling 2D, the spectral decomposition and RGB blending visualization (Geoteric) processing are expected to improve the quality of imaging and to assess the presence of the source rocks, the location of the kitchen, the maturation and the migration process as well as the possible oil volumes associated to Abu Qir and Kafr el Sheik Formations.

## The deep coring of Cotignola (RA): new stratigraphic data of the Middle-Upper Pleistocene succession of the south-eastern Po Valley

Calabrese L.\*, Severi P., Ferrari V. & Bonzi L.

Servizio Geologico Sismico e dei Suoli, Regione Emilia-Romagna.

Corresponding email: [icalabrese@regione.emilia-romagna.it](mailto:icalabrese@regione.emilia-romagna.it).

Keywords: Po plain, middle-upper Pleistocene, coastal deposits.

The deep coring of Cotignola has provided valuable new information on the geological history of the SE sector of the Po Valley. Thanks to its 350 meters deep and location, the coring investigated portions of the Pleistocene succession that had never been directly observed and described before. It's located SW of Cotignola (RA) and carried out in spring 2013 on behalf of the Edison Stoccaggio S.p.A.. The site is above a buried structural high and the sequence consists of alternating sand, silt and silty clay. In agreement with the CARG Sheet 239 "Faenza", three main units were distinguished, belonging to the upper-middle Pleistocene: Upper Emilia-Romagna Synthem (AES), Lower Emilia-Romagna Synthem (AEI) and Imola Sands (IMO). The limits were defined through facies analysis and correlations with the established stratigraphic framework. The trend of the whole sequence is regressive. The Upper Emilia-Romagna Synthem (AES) consists of alluvial plain deposits and include fluvial channel fill, levee from proximal to distal, floodplain with the presence of swamps and paleosols and is organized into six sub-units, mostly coarsening upward.

The Lower Emilia-Romagna Synthem (AEI) records the transition from alluvial, to coastal plain and then marine-marginal environments. AEI is organized into five transgressive/regressive sub-units and the general trend is regressive. The Imola Sands consist mainly of fine sands and silts with sandy silts and silty clays and medium sands, even with pebbles. The facies associations testify marine platform, beach, transitional to continental environments. The sequence is organized into three sub-units. The AES continental facies have been observed in other sites of the Apennine plain and the recognized stratigraphy fits well with the existing geological model described in CARG Sheets of this sector. The sub-units of IMO, likewise, are comparable with members described in the literature (Amorosi et al., 1998). The marine-marginal and transitional facies associations of AEI, otherwise, have never been observed in this sector; in fact, AEI was described as purely continental succession, both in outcrops and in other cores.

In the lower AEI, two sedimentary cycles consisting of alluvial to coastal plain and then clear marine beach deposits are here observed. They pass both laterally towards the Apennine margin, and vertically in the upper AEI, to only continental environments and eastward they correlate with marine deposits.

The coring testifies that, between the Apennine margin and Cotignola, there was a paleo-coastline during the lower AEI time and also confirms CARG geological sections of this area, based on geophysical data and well logs.

Amorosi A., Caporale L., Cibin U., Colalongo M.L., Pasini G., Ricci Lucchi F., Severi P. & Vaiani S.C. 1998. The Pleistocene Imola Sands, northern Apennines foothills. *Giorn. Geol.*, 60, 83-118.

## Structural setting of Marne a Fucoidi formation in Adriatic Offshore (Zona B)

Casero P.<sup>1</sup>, Colucci F.\*<sup>2</sup>, Moia F.<sup>2</sup> & Rossato A.<sup>1</sup>

1. Petroleum Geologist. 2. Ricerca sul Sistema Energetico – RSE S.p.A. (Milano).

Corresponding email: [francesca.colucci@rse-web.it](mailto:francesca.colucci@rse-web.it)

Keywords: Marne a Fucoidi formation, Zone B, isochronous map, structural setting.

The paper reports the isochronous map (TWT-Two Way Times) of the Marne a Fucoidi (Cretaceous Inf.-Aptiano/Albiano) geological formation elaborated for the large region of the south-central offshore in the Adriatic sea known as Zona B. The map refers to the top of the geological formation which belongs to the Umbria-Marche geological succession.

This geological formation has been discovered in nearly all the perforations drilled during the hydrocarbon exploration in the Zona B of Adriatic offshore and it presents a modest thickness but is a clear geological identity in the evolution of the basin.

The studied geological domain lies almost entirely in Zone B and extends from the 44<sup>th</sup> parallel in the north almost to the Gargano promontory in the south and its area exceeds 22,000 sq. km. For the map realization, all the deep wells and 2D seismic reflection sections available within the VIDEPI project – Visibility of petroleum exploration data in Italy have been considered and processed ([www.videpi.com](http://www.videpi.com)). The map has been elaborated at 1:100,000 scale and the total area was divided into 5 different sub-areas on which the plane position of the available seismic reflection sections and the wells have been reported. A detailed grid has been designed and each nodes reports the TWT value deduced by the 2D seismic reflection sections calibrated with well data.

The 5 sub-areas were merged realizing the isochronous map which has been vectorized to make it useful in a GIS-Geographic Information System environment. The velocity field of the area has been realized and the average velocity of this geological formation is around 2550 m/sec and the experimental values range from 1950 m/sec of Gargano Mare 1 well and 3326 m/sec of Bonaventura 1 well and seismic velocity above 3000 m/sec were confined to north-west sector of the investigated area.

This map shows the deep structural shape of Umbria-Marche geological succession with the trend of principal anticlines and synclines and it can be helpful for supporting the exploration of new hydrocarbon and CO<sub>2</sub> geological storage reservoirs.

## **Deciphering depositional mechanisms and evolution of depositional bodies through architectural and textural analysis: the case of the Ussana Group (Late Oligocene – Early Miocene, Sardinia)**

Costamagna L.G.\*

Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari.

Corresponding email: [lucakost@unica.it](mailto:lucakost@unica.it)

Keywords: Continental deposits, Oligocene-Miocene, Sardinia.

In Central Sardinia the siliciclastic Ussana Group (formerly Ussana Fm, Pecorini & Pomesano Cherchi, 1969) gather together several formational units unconformably resting over older rocks. The group is related to the first opening of the Sardinian Rift in the Late Oligocene–Early Miocene and it deposited in high- to mid energy alluvial fan to fan deltas contexts forming short depositional systems and passing gradually to the marine environments of the Early Miocene terrigenous to carbonate Marmilla Fm. The tecto-sedimentary meaning of the group is related to high-energy environments due to tectonic steps created by the extensional tectonics along the sinking eastern rim of the Tertiary Sardinian Rift. The thickness and the features of the formational units forming the group may be highly variable according to the local morphotectonic situation, being comprised between 600 and 20-30 m. Detailed sedimentological investigations over the Ussana Group are hampered by the limited lateral persistence of the outcrops, preventing the precise reconstruction of single fan paleoenvironmental units. Nonetheless, in order to evidence the diverse depositional mechanisms of the Ussana Group deposits and to better define the depositional sub-environments, accurate architectural and textural analysis of some well-exposed outcrops have been carried on, leading to evidence inner, middle and outer fan sectors, even if related to different and not correlated fan bodies.

So, some good outcrops have been investigated in detail. The investigation has been performed using a modified version (Costamagna, 2009) of the Miall procedure for continental deposits (Miall, 1996; 2014). Thus, we managed to evidence channel (both single and amalgamated) and interchannel areas, to subdivide different channel and interchannel units, and to recognise diverse sedimentary sub-environments. Several types of depositional processes have been characterized: they may show massive to tractive features, so including all the terms of the depositional range comprised between debris flows and stream flows end members. Besides, the stacking pattern of the analyzed outcrops allows to infer qualitatively the local subsidence rate. The W/D rate of the single channels may suggest if avulsion or lateral migration processes prevailed, allowing also assumptions regarding the rainfall rate and the possibly ruling climate.

Costamagna L.G. 2009. Towards a depositional architecture restyling: a new/old way to look at fluvial deposits. 27th IAS Meeting of Sedimentology, Alghero (Italy), 20-23 September 2009, 117.

Miall A.D. 1996. *Geology of Fluvial deposits*. Springer, 584 pgs.

Miall A.D. 2014. *Fluvial Depositional Systems*. Springer, 318 pgs.

Pecorini G. & Pomesano Cherchi A. 1969. Ricerche geologiche e biostratigrafiche sul Campidano meridionale (Sardegna). *Mem. Soc. Geol. It.*, 8, 421-451.

## **Paleogene to Quaternary evolution of central Po basin: coupling sedimentation and tectonic control**

D'Ambrogi C.\*<sup>1</sup> & the Italian GeoMol Team [Cagnoni A.<sup>2</sup>, Ferri F.<sup>1</sup>, Maesano F.E.<sup>3</sup>, Molinari F.C.<sup>4</sup>, Monesi E.<sup>5</sup>,  
Piccin A.<sup>2</sup>, Scardia G.<sup>5-7</sup>, Torri G.<sup>6</sup>]

1. Servizio Geologico d'Italia - ISPRA, Roma. 2. Regione Lombardia, Milano. 3. coll. est. Servizio Geologico d'Italia - ISPRA, Roma. 4. Servizio Geologico, Sismico e dei Suoli - Regione Emilia Romagna, Bologna. 5. CNR IGAG, Roma. 6. coll. est. Servizio Geologico, Sismico e dei Suoli - Regione Emilia Romagna, Bologna. 7. Instituto Oceanográfico, Universidade de São Paulo, Brasil.

Corresponding email: [chiara.dambrogi@isprambiente.it](mailto:chiara.dambrogi@isprambiente.it)

Keywords: Po basin, 3D modeling, tectonic control, geopotentials.

A new seismic interpretation, performed in the framework of the EU funded GeoMol Project, allows to detail the evolution of a wide area (3,800 km<sup>2</sup>) in the central part of the Po basin.

The area runs along a NW-SE direction from Brescia to Mirandola, enclosing the Southern Alps thrust front, which evolves in the Lake Garda area from a E-W strike to the NNE-trending Giudicarie belt, and the external front of the Northern Apennines, the Ferrara arc. Between the two thrust fronts is the south-dipping Mantova Monocline.

The variability of the stratigraphic units, in terms of environment facies and thickness, is known, but the impressive dense seismic dataset (12,000 km, kindly provided by ENI S.p.A) analyzed for the GeoMol Project enables, through a 3D model and derived elaborations (restoration and thickness maps), to describe the steps of the sedimentary evolution and to detect the role of the tectonic structures on the basin architecture during the Paleogene-Quaternary time interval.

We recognized and modeled 10 main seismic horizons younger than the top Scaglia (late Cretaceous-Paleogene) and the main thrust systems. Chronological data from recent literature are used to better constrain the age of the younger five horizons, Pleistocene in age. The core of our basin analysis is a 3D model time-depth converted and constrained using 136 well stratigraphies.

The thickness maps derived from the 3D model describe the basin configuration as foreland of the Alps and then of the Apennines, and more in detail the changes in the architecture of the Apennine foredeep, where local depocentres have been detected. These depocentres are controlled by thrust activity up to the Pleistocene, which influenced the sedimentation history of the whole basin from the marine to continental environment.

Due to the large number of geometrical and chronological constraints, the thrust activity is particularly well documented during the Pleistocene. The resulting effects do not only exercise a control on the morphology of the basin, but also affect the drainage pattern of the Po River and its tributaries during the shelf progradation.

The result is a detailed 3D imagery of the central portion of the Po basin that points out the tectonic control on the different steps of the basin evolution. Moreover the 3D model will be the base for the assessment of the geothermal potential in the area, according to the common modeling and potential assessment workflows defined with the European partners and applied in the other pilot areas of the GeoMol Project.

*The project GeoMol is co-funded by the Alpine Space Program as part of the European Territorial Cooperation 2007-2013. The project integrates partners from Austria, France, Germany, Italy, Slovenia and Switzerland and runs from September 2012 to June 2015. Further information on [www.geomol.eu](http://www.geomol.eu).*

## **Climate control on the Pliocene-Pleistocene sedimentary flux in the Venice region**

Di Giulio A. \*, Forni V., Mancin N., Poggi M. & Toscani G.

Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia.

Corresponding email: [digiulio@unipv.it](mailto:digiulio@unipv.it)

Keywords: climate changes, erosion, detrital flux, Venice, Pliocene-Pleistocene.

The correlation between Cenozoic climate evolution and erosion of mountain belts is one of the main topics in the recent literature (e.g. Herman et al. 2013 and references therein). Several papers challenged it at a global scale by studying directly erosion rates measured through geochronology, or depositional rates in the surrounding basins assuming it as a reliable proxy of changing erosion rates on land. According to this literature, Cenozoic global climate changes results to have had a strong impact on erosion rate; nevertheless the reported data did not document how climate really affected erosion. Specifically, the m.y. scale resolution of both geochronologic and sedimentary data did not permit to recognize which of the known changes occurred in Cenozoic climate (long term cooling, increasing amplitude and changing frequency of climate cycles) mostly controlled erosion.

The presented research is based on the exceptional resolution of the stratigraphic record of the Venice well, integrated with that of Lido 1 well (Barbieri et al. 2007), extending down-section up to the unconformable Miocene-Pliocene boundary, in order to finely calibrate the seismic grid available in the area (courtesy of ENI), in turn used to unravel the detrital flux history in the region during the last 5 Ma with a chronological resolution sufficiently high for investigating the possible correlation with climate changes.

To this end, a 3D model of the Pliocene-Pleistocene architecture of the Venice region subsurface was reconstructed. A backstripping procedure was applied to each stratigraphic unit to decompact the obtained present-day sedimentary volume, thus obtaining the real detrital flux through time in the area. Collected data were then compared with the average oxygen isotopic ratio, the amplitude and the frequency of climate cycles in the corresponding time span.

What primarily merged is that the amplitude and frequency of climate cycles seem to play a major role in controlling detrital flux in the Venice region, while the long term cooling is subordinated (where present). In addition no significant increase of detrital flux in the region is recorded as a direct response of the supposed beginning of major Alpine glaciation in the Middle Pleistocene, and the related change of dominant erosion process from fluvial to glacial.

Barbieri C., Di Giulio A., Massari F., Asioli A., Bonato M. & Mancin N. 2007. Natural subsidence of the Venice area during the last 60 Myr. *Basin Research*, 19(1), 105-123.

Herman F., Seward D., Valla P.G., Carter A., Kohn B., Willet S.D. & Ehlers T.A. 2013. Worldwide acceleration of mountain erosion under a cooling climate. *Nature*, 504, 423-426.

## The northern Longobucco basin-margin architecture and evolution. Preliminary results

Fabbi S.\*, Santantonio M. & Aldega L.

Dipartimento di Scienze della Terra - Università degli Studi di Roma "La Sapienza".

Corresponding email: [simone.fabbi@uniroma1.it](mailto:simone.fabbi@uniroma1.it)

Keywords: Calabria, Jurassic stratigraphy, Paleoescarpments.

A geological mapping project in the Longobucco basin (Sila Greca-NE Calabria) is aimed at documenting its Mesozoic architecture and stratigraphic/tectonic evolution. Two different Mesozoic sedimentary successions are observed in the area, resting above the Hercynian crystalline and metamorphic basement (Santantonio, 2012 and references therein). The Longobucco Group (**LG**) documents sedimentation controlled by early Jurassic tectonics, and is made up of Rhaetian/Hettangian continental clastics, passing to Sinemurian mixed shelf limestones, Pliensbachian open shelf marls, and finally to >1 km-thick late Pliensbachian/early Toarcian siliciclastic turbidites. The Caloveto Group (**CG**) is a thinner succession, developed since the Pliensbachian around and on basement highs, and made of neritic carbonates, which were extended and drowned in the Toarcian to become unconformably (onlap) overlain and eventually buried by the late Toarcian-early Cretaceous marl/radiolarite/cherty limestone complex of the S. Onofrio Subgroup (**SOS**). Although resting on the same basement, neither outcrops documenting an original lateral contiguity of the two groups, nor the fate of the **LG** after the early Toarcian have ever been described in the literature. We herein offer a description and tentative interpretation of the northern margin of the Longobucco basin, based on preliminary data. South of the Colognati river the Pliensbachian marls and turbidites (**LG**) embed thick clastic wedges bearing boulders of granite, of conglomerates and of shelf limestone, forming a belt which should mark the basin margin, where the clast-sourcing formations had to be exposed along a submarine normal fault scarp. The footwall of this fault is seen at Mt. Scarborough and, at lower elevations, along the southern slopes of the Colognati valley, where the basement and its oldest sedimentary cap are exposed. Along the northern side of the Colognati valley, by contrast, the onlap of the **SOS** on the basement is interpreted as being a younger (and higher) escarpment tract. At Mt. Scarborough the basement forming the Pliensbachian escarpment is at the hangingwall of a thrust, having at the footwall the **SOS** and the younger escarpment tract. Field evidence suggests the existence of a stepped submarine paleomorphology formed by at least two main diachronous paleoescarpments. Remarkably, basinward with respect to the Pliensbachian escarpment, the siliciclastic turbidites change vertically into red marls and cherty limestones of the **SOS**. This represents the first direct evidence of post-early Toarcian development of the **LG**. Inferring a shared post-Toarcian stratigraphic evolution of the **LG** and the **CG** (the **SOS** represents its upper part) should imply that the **LG** and **CG** represent one basin, an hypothesis that will require further testing in the field.

Santantonio M. 2012. Mesozoic evolution of the Caloveto Group, NE Calabria. Rend. Onl. Soc. Geol. It., 21, 295-297.

## **Facies heterogeneity in hybrid event beds and its applied significance: insight from the Cretaceous Palaeocene Gottero Sandstone (NW Apennines, Italy)**

Fonnesu M.\*<sup>1</sup>, Felletti F.<sup>2</sup>, Houghton P.D.W.<sup>1</sup>, Patacci M.<sup>3</sup> & McCaffrey W.D.<sup>3</sup>

1. UCD School of Geological Sciences, University College of Dublin, Ireland. 2. Dipartimento di Scienze della Terra, Università degli Studi di Milano. 3. School of Earth Sciences, University of Leeds, UK.

Corresponding email: [marcofonnesu86@gmail.com](mailto:marcofonnesu86@gmail.com)

Keywords: Turbidites, Hybrid event beds, facies tract.

Hybrid event beds (HEBs) found in association with conventional turbidites characterise many ancient deep-water systems and are currently an important issue in hydrocarbon exploration on account of their unpredictability and the implications for reservoir quality. HEBs are a type of deep-water sediment gravity flow deposit that generally comprise a basal clean sandstone overlain by a variety of muddier and less-permeable sandy facies thought to be emplaced by combinations of cohesive debris flow, transitional and turbiditic processes as part of the same transport event. HEBs are commonly found in the outer and marginal parts of deep-water systems where they replace beds composed dominantly of clean sand up-dip over scales of kms to 10s km. Here we report that in addition to these broad patterns, important yet poorly understood short-length facies changes (over metres to 100s m) can occur, modifying the overall texture and reservoir characteristics at or beneath the typical spacing of production wells.

A very detailed sedimentological and stratigraphic study has been carried out in the well-exposed Cretaceous-Palaeocene Gottero Sandstone on M.Ramaceto involving more than 3000 m of logged sections in eight traverses each spaced between 255 and 910 m apart. Bed-type transition probabilities for the correlated beds together with sedimentological observations clearly define two distinct “facies tracts” involving hybrid event beds, and one for conventional turbidites. The HEBs were generated by relatively dense flows that were able to locally erode the substrate and acquire mud clasts that then disaggregated to release clays that promoted turbulence damping and generation of “linked-debrites”.

Detailed facies analysis combined with bed by bed correlations shows that marked lateral variations in the internal bed make-up of the HEBs occurs along depositional strike. This strike variability typically involves lateral changes in the proportions of the constituent bed divisions, in the texture of the debritic interval and in the scale of substrate blocks originally entrained by the flows. Generally, these changes occur without significant variation in the overall event bed thickness. The statistical evaluation of such facies transitions is used to develop a revised model of clean sand distribution in hybrid flow generated lobes, and to characterise the critical transition from up-dip turbidite-dominated intervals to the down-dip, HEB-dominated fringes.

The variable thickness and continuity of the basal clean sandstone and the rugosity on the contact between it and the overlying debrite have important implications for reservoir characterisation. Significant variability in bed character at interwell scale can be anticipated and the intra-bed rugosity may impact on drainage and sweep efficiency during hydrocarbon production, particularly in cases where the lower sandstone is locally completely replaced by debritic facies.

## **Sedimentation in the Tethyan pelagic realm during the Cenomanian: monotonous settling or active redistribution?**

Gambacorta G.\*<sup>1</sup>, Bersezio R.<sup>1-2</sup> & Erba E.<sup>1</sup>

1. Dipartimento di Scienze della Terra "A. Desio", Università di Milano. 2. CNR-IDPA, Milano.

Corresponding email: [gabriele.gambacorta@unimi.it](mailto:gabriele.gambacorta@unimi.it)

Keywords: bottom currents, calcareous pelagic contourites, Cenomanian, OAE, pelagic environment, Scaglia.

Sea bottom processes of the pelagic realm are still not completely understood and represent an intriguing subject (Rebesco & Stow, 2001; Knutz, 2008; Hernández-Molina et al., 2008; Shanmugam, 2008; Hüneke, H. & Rüdiger H., 2011). This paper focuses on the relationships between "normal" settling processes, redistribution of sediments and oceanographic parameters in a pelagic setting, during the Cenomanian. Five key Tethyan localities in the Cenomanian Umbria-Marche and Belluno Basins have been studied in order to understand the interplay among sea bottom processes that acted on the sea floor. The dataset consists of the mm-scale sedimentological description of the sections complemented by microfacies analysis on selected samples. Different sedimentological indications, such as presence of intraclasts, lined forams, pervasive plane-parallel lamination, suggest a continuous reworking under action of bottom-currents with varying intensity and direction. All the identified facies are here illustrated in detail and organized in a comprehensive schematic facies framework, the "facies matrix", that leads to recognize two depositional facies suites: the "settling dominated" and the "traction current dominated", under different oxygenation conditions. Our results suggest that settling of biogenic and inorganic particles represents the main source of pelagic sediments, but not the unique depositional process: under the action of sea-bottom currents of different intensity, sediments are continuously redistributed on the sea floor. All the collected evidences contribute to the proposal of a comprehensive depositional model for these reworked and redistributed fine-grained sediments, that represent true calcareous pelagic contourites. The model suggests that the identified traction-related facies can be used as a proxy for bottom current intensity and, indirectly, as an indicator of changing ventilation regimes at the sea floor through time.

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## **Po Plain–Northern Adriatic Sea Basin (Italy): basin-scale geological model of the Late Miocene–Middle Pleistocene succession**

Ghielmi M.\*<sup>1</sup>, Minervini M.<sup>1</sup>, Nini C.<sup>2</sup>, Rogledi S.<sup>3</sup>, Rossi M.<sup>1</sup>, Sules O.<sup>1</sup> & Vignolo A.<sup>4</sup>

1. eni spa - exploration & production division, San Donato Milanese (MI). 2. eni ghana exploration & production ltd., Accra (Ghana). 3. Geologo.  
4. eni NAOC, Abuja (Nigeria).

Corresponding email: [manlio.ghielmi@eni.com](mailto:manlio.ghielmi@eni.com)

Keywords: Northern Adriatic Sea, Po Plain, Messinian, Pliocene, Pleistocene, Tectono-sedimentary evolution.

A complex system of elongate foredeep depocenters, the Po Plain-Adriatic Foredeep (PPAF), developed in the eastern sector of the Po Plain and in the northern Adriatic Sea during the Late Miocene–Pleistocene. The PPAF is one of the most prolific area for hydrocarbon exploration in Italy and the most important for gas. In the last decades, this basin has been revised by Eni-Agip through several multidisciplinary studies. The large availability of subsurface data (including regional 2D and 3D seismic surveys and over 500 selected wells), the preservation and the relatively moderate structural deformation of the studied succession were key factors for the generation of a detailed three-dimensional geological model for the foredeep basins as well as for the related ramp/foreland area and thrust-top basins.

During the Late Miocene, Pliocene and Early Pleistocene a severe compressive deformation affected the northern Apennine as well as the PPAF area. The PPAF underwent 4 major phases of compressional deformation and depocenter migration in a NE direction towards the foreland and four regional tectonic unconformities were generated, namely: the Latest Tortonian, the Intra-Messinian, the Intra-Zanclean, the Gelasian Unconformities. As a consequence of these major deformation events, the foredeep shape was affected by a large variability in space through time, ranging from regular elongated shape to irregular shape, from simple foredeep to fragmented foredeep. According to these data, a new model for the Northern Apennine foredeep with two evolutive stages has been proposed.

The PPAF was a deep-marine basin with water depths usually exceeding 1000 m. Its succession mainly consists of thick sequences of turbidite deposits. Basin-scale, sand-rich, highly-efficient turbidite systems with longitudinal paleocurrents mainly directed to the southeast were largely predominant in the foredeeps. The clastic sediments supplying the PPAF foredeeps were mainly provided by large fluvio-deltaic systems located along the Alps margins of Lombardia and Veneto foreland. On the contrary, with the exception of the post-evaporitic Messinian, the northern Apennine belt acted only as a secondary sedimentary source for the PPAF.

In conclusion, the main results achieved by the Eni-Agip studies are: 1) the detailed reconstruction of the Messinian-Pleistocene tectono-sedimentary evolution; 2) the identification of 4 major compressional events in the Late Tortonian-Pleistocene interval; 3) a new sequence-stratigraphic model based on 4 allogroups (i.e. major stratigraphic units bounded at base and top by the regional tectonically-induced unconformities) and 10 component large-scale sequences; 4) a sedimentary model of the foredeep, piggy-back basins and foreland successions with the compilation of detailed basin-scale facies distribution maps; 5) a better definition of the main effective hydrocarbon plays of the area and of the related structural, mixed and stratigraphic traps.

## **Sedimentary evolution of fluvial systems from the Upper Carboniferous - Early Triassic of the Catalan Pyrenees: facies analysis as a tool for interregional correlations**

Gretter N.\*<sup>1</sup>, Ronchi A.<sup>1</sup>, López-Gómez J.<sup>2</sup>, Arche A.<sup>2</sup>, De la Horra R.<sup>3</sup>, Barrenechea J.<sup>2</sup> & Lago M.<sup>4</sup>

1. Department of Earth and Environmental Sciences, University of Pavia. 2. Instituto de Geociencias (CSIC,UCM), Madrid, Spain. 3. Departamento de Estratigrafía, Facultad de Geología, Universidad Complutense de Madrid, Spain. 4. Department of Earth Sciences, University of Zaragoza, Spain.

Corresponding email: [nicola.gretter@gmail.com](mailto:nicola.gretter@gmail.com)

Keywords: Permian, Middle Triassic, facies analysis, continental successions, Western Pyrenees.

The Upper Carboniferous–Early Triassic stratigraphic succession of Catalan Pyrenees consists of volcano-sedimentary Units that deposited in intracontinental sub-basins. The genesis of these troughs, starts with a post-collisional, strike-slip tectonic, followed by a Permian extensional setting with fluvial and lacustrine facies accompanied by extensive pyroclastic deposition. The beginning of the Triassic deposition is recorded by the onset of widespread extensional sedimentation. The development and evolution of the sedimentary system and its architecture has been reinvestigated through time and space, in order to obtain more detailed stratigraphical and sedimentological data on sedimentary facies, paleoenvironments and paleoclimatic changes.

In particular, we have focused our efforts on the description and the analysis of the “Permian red beds” due to their higher potential of correlation. Detailed outcrop-based tectono-stratigraphic analyses have been performed following the stratigraphic unit subdivision of Gisbert (1981). The fining-upward, 1000 m thick Late Carboniferous-Permian succession is mostly made up of conglomerates, sandstones and siltstones with intercalations of volcanics and volcanoclastic levels. It is organized into two main tectono-sedimentary sequences that groups five depositional units. Deposits pertaining to the first Tectono-sedimentary Unit (TSU1) consists of the mostly volcanic and volcanoclastic Grey Unit (Stephanian B-C), Transition Unit (TU, early-middle Autunian), and Lower Red Unit (LRU, late to post-Autunian). Both the TU and the LRU are fining upward clastic sequences dominated by lacustrine, alluvial fan and meandering river flood-plain deposits. Channels, overbank fines and palaeosols occur as the most representative architectural elements. The overlying Upper Red Unit (URU, Middle-? Late Permian) is bounded at the bottom and top by angular unconformities and possibly represents the second Tectono-sedimentary Unit (TSU2). The Buntsandstein deposits (Anisian) unconformably overlies the URU and consists of oligomictic quartz rich conglomerates followed by sandstones and shales; it is thought to represent the third TSU in this area. New vertebrate remains and tetrapod footprints findings in the LRU, URU and Buntsandstein, gave precious hints for a possible chronostratigraphic attribution.

The integration of detailed stratigraphic/sedimentological analyses with chronological constraints (new ages from recent literature) helped to compare and correlate this sector to likely close areas in Late Palaeozoic times. Accordingly, similarities can be found between the studied Permo-Triassic succession and the Lodévois, W Provence, Sardinian ones. On the contrary, the Iberian Ranges, Catalan Coastal Ranges and Southern Alps show major differences. This picture suggests significant elements to unravel the paleogeographic scenario and the crucial geodynamic evolution in this southern Peri-Tethyan sector.

## **Tectonics vs. sedimentation during the Sicilian orogenesis. The case history of upper Miocene terrigenous basins in the central-eastern Sicily**

Interbartolo F.\* & Sulli A.

Dipartimento di Scienze della Terra e del Mare- Università degli Studi di Palermo.

Corresponding email: [francesco.interbartolo@unipa.it](mailto:francesco.interbartolo@unipa.it)

Keywords: Syntectonic Basins, Facies Sequences, Fold and Thrust Belt.

The Sicilian Fold and Thrust Belt developed through two main tectonic events (Catalano et al., 2000), the earlier (middle-late Miocene) involving thin bodies of deep-water carbonates with shallow-seated deformation; the latter (latest Miocene–early Pliocene) determined deep seated deformation, where S-verging thrusts often associated with high-angle backthrusts affected thick carbonate platform units and induced the passive re-imbrication into the overlying deep-water carbonate, which generated late Miocene to Pliocene syn-tectonic basins (Avellone et al., 2010). In particular, during the late Tortonian to early Messinian these basins were characterized by sedimentation of continental to open marine clastics and shallow-marine carbonate sediments.

We studied in detail the facies sequences and structural features of the well exposed basin fill of the Polizzi Generosa, Resuttano and Catenanuova–Centuripe areas (central-eastern Sicily), in order to understand the interaction between tectonics and sedimentation in the evolution of these basins. The Polizzi basin rests on a syncline with NNE-SSW axis, dissected by NE-SW trending normal faults. It is filled by overlapping conglomeratic, sandy and clayey lithofacies, showing fining and deepening upward trend. The Resuttano basin lies on a syncline with NE-SW axis, cut by NW-SE normal faults and NE-SW reverse faults. In the lower part it consists of sands and silts with coarsening and shallowing upward trend, and in the upper part by overlapping conglomeratic to sandy lithofacies, showing heteropic relations and arranged in fining-deepening upward trend. Both basins show no evidences of syn-depositional tectonics.

The Catenanuova-Centuripe basin rests on a synform with E-W axis trend. It sets on the back of a main thrusts dipping toward N-NW and is constituted by syntectonic filling as shown by the growth structures diverging towards N. The sequence shows a coarsening- shallowing-upward trend, generally constituted by two heteropic lithofacies: one consists of clayey marls and quartz sands, and the other is constituted by quartz sands with thick conglomerate lenses.

We assert that in the Polizzi and Resuttano basins tectonics did not affect their fill, so they were filled and then deformed in response to deformation of the underlying deepest tectonic units during the late Tortonian. Therefore they are pre-tectonic basins formed between the first and the second event of the deformation (Avellone et al., 2010), while the Catenanuova-Centuripe basin was forming during the deep seated deformation.

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## Upper Miocene siliciclastic depositional systems in the central-eastern Sicily basins

Interbartolo F.\* & Sulli A.

Dipartimento di Scienze della Terra e del Mare- Università degli Studi di Palermo.

Corresponding email: [francesco.interbartolo@unipa.it](mailto:francesco.interbartolo@unipa.it)

Keywords: Facies Analysis, Delta System, Alluvial Deposits.

The Sicilian Neogene basins, developed in different positions above the Sicilian-Maghrebian orogen, above an often deformed moving substrate, are filled by continental to open marine sediments. In the Polizzi Generosa, Resuttano and Catenanuova–Centuripe areas (central and eastern Sicily), river-dominated braid/fan delta coarse-grained deposits represent a large amount of basin fill pertaining to the Terravecchia Formation (upper Tortonian–lower Messinian). Integrated stratigraphic and sedimentologic analyses were the key to reconstruct the main siliciclastic depositional environments during the late Miocene.

In the Polizzi area we distinguished two sectors, which have different facies associations: 1) fan delta conglomerates covered by middle to upper shoreface–amalgamated hummocky cross-stratified sandstones and offshore silty clays, 2) gravelly conglomerates braid plain and delta front sandy calcarenites, both facies sequences showing a fining upward trend.

In the Resuttano area upper Miocene sediments, from SW to NE, are made up of sandy/gravelly river-dominated delta front and prodelta clayey siltstones passing to braidplain gravelly conglomerates, arranged respectively in coarsening and fining upward trends.

In the Catenanuova-Centuripe area upper Miocene sediments are constituted by braidplain gravels, alluvial plain with ephemeral ponds facies and delta front/prodelta sands/silts with a coarsening upward trend.

We assert that in the Polizzi area the facies associations are arranged in two main depositional systems: the former is a fan delta system generated by grain flows and developed in a relatively short stretch, until the receiver basin. This depositional system evolves in a wave-dominated shoreface delta system when the environment changes, in response to sea level rise, with the deposition of well-sorted medium to coarse sands. The latter, related to a low-gradient delta system, is fed by a braided river system.

The depositional system in the easternmost Resuttano area consists in a braided river system fed by high-energy ephemeral streams, forming large alluvial plains crossed by not confined braided channels. The coarse deposits transported by rivers have formed a large shelf-type delta system with a well definite delta front and prodelta prograding westward.

In the Catenanuova-Centuripe the depositional system, is made up of upper alluvial plain crossed by amalgamated channels, and a distal alluvial plain characterized by distributary channels with coarse sand load, which gradually gave way to marine processes towards the delta front/prodelta area.

## **Depositional features of the Tufiti di Tusa Formation near the Nocara-Colobrarò Ridge (Southern Apennines, Basilicata)**

Lisco S., Fornelli A., Gallicchio S.\* & Moretti M.

Dipartimento di Scienze della Terra e Geoambientali, Università degli Studi di Bari "A. Moro".

Corresponding email: [salvatore.gallicchio@uniba.it](mailto:salvatore.gallicchio@uniba.it)

Keywords: Southern Apennines, volcanoclastic turbidites, submarine fan system.

The Tufiti di Tusa Formation (e.g. APAT, 2007) crops out along the front of the Southern Apennines Chain. It is made up of prevalent volcanoclastic turbidites related to a submarine fan system deposited in a trench type basin: this succession, in fact, records the sedimentary and tectonic processes during the early phases of the apenninic subduction in the Late Oligocene-Early Miocene. The succession shows a thickness of about 215 m and crops out along the front of the Southern Apennines near the Nocara-Colobrarò ridge in the Basilicata region; it lies stratigraphically on the Argille Variegate Group (APAT, 2007), is represented by siliciclastic, calciclastic and volcanoclastic turbidites and belongs to a tectono-stratigraphic Sicilide unit which overthrusts both Lagonegro Basin units and Miocene foredeep units. The lithostratigraphic and sedimentologic features observed along the studied section allowed us to recognize four different portions (from the bottom to the top, portions A, B, C and D), which show different facies associations. Each portion depicts a depocenter area characterized during its evolution by variable sediment inputs, depositional processes and turbidite systems. Portion A, 70 m thick, is made up of medium to thin bedded siliciclastic turbidites, interbedded with marls and clays; the facies associations are indicative of surge like turbidity flow deposited in a distal lobe environment. Portion B, 40 m thick, is made up of thick bedded and medium grained calciclastic turbidites and by thin bedded and fine grained siliciclastic arenites and shales. Facies association of this portion is representative both of calcareous concentrated density flow (referable to proximal depositional zone) and siliciclastic low density turbidity currents (of distal depositional zone). Portion C, 20 m thick, is made up of thin bedded and fine grained siliciclastic and calciclastic turbidite beds in which rare thick bedded and medium grained turbidites occur; the main facies association of this portion consists mainly of low density turbidity currents of distal depositional zone. Portion D, about 85 m thick, is made up of thick bedded and coarse grained volcanoclastic turbidites related to concentrated and hyperconcentrated turbidity flows of proximal depositional zone. The vertical distribution of the facies associations shows that the succession is made up of three heteropic and superimposed turbidite systems related to feeding areas located in different geodynamic setting. On the base of palaeogeographic features, the Tufiti di Tusa Fm. seems to record the evolution of a trench type basin gradually incorporated into an accretionary prism.

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## Reservoir quality assessment in tide-dominated strait-fill successions: a case study from the modern and ancient Messina Strait

Longhitano S.\*

Dipartimento di Scienze, Università degli Studi della Basilicata, Potenza.

Corresponding email: [sergio.longhitano@unibas.it](mailto:sergio.longhitano@unibas.it)

Keywords: tidal currents, tidal dunes, Pliocene-Quaternary, Messina strait, depositional zones, reservoir model.

Consideration on tide-dominated marine straits has greatly increased during this last decade due to their economic relevance, because many ancient strait-fill successions have revealed significant oil and gas reservoirs (Longhitano, 2013).

In this work the upper Pliocene-to-Present Messina Strait case study is presented with the aim to discuss the potential role of its strait-fill deposits in a reservoir characterization perspective.

The modern Messina Strait is a 3-km-wide marine passageway comprised between Sicily and Calabria. It is governed by currents flowing 2-to-3 m/sec axially to the strait and whose bi-directionality is determined by semi-diurnal tidal inversions between the two interlinked basins (Barrier, 1987). A high-resolution multi-beam survey acquired on to the modern strait bottom indicates the occurrence of a zone partitioning, where sediments are distributed with different features as result of the varying bed shear stress exerted by converging/diverging tidal currents.

The ancient Messina Strait tidal dynamics is recorded in 70-to-130-m-thick Plio-Pleistocene sedimentary deposits exposed in both the onshore margins. Many stratigraphic sections exhibit cross-stratified sandbodies which formed under hydrodynamic conditions very similar to those observable in the adjacent modern strait (Mercier et al. 1987).

The results of this comparison highlight the following conclusions: (i) tidal currents, which dominate across the modern strait bottom, may interact with waves or gravity-driven mass processes, generating specific lithofacies associations with different reservoir properties; (ii) some less relevant deposits, neglected in past studies, may indicate diagnostic depositional zones which are crucial in the reconstruction of ancient straits, especially for predictions on the position of sand-prone volumes; (iii) many oil-bearing cross stratified successions detected in play coming from the most promising hydrocarbon-prone zones of the world could be reinterpreted and, importantly, potentially re-evaluated at the light of such a new depositional model.

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## Provenance of Numidian sandstones of Southern Apennines: preliminary U-Pb spot dating on detrital zircons

Micheletti F.\*<sup>1</sup>, Fornelli A.<sup>1</sup>, Langone A.<sup>2</sup>, Perrone V.<sup>3</sup> & La Pietra I.<sup>1</sup>

1. Dipartimento di Scienze della Terra, Università degli Studi di Bari "Aldo Moro". 2. IGG-CNR Pavia. 3. Dipartimento di Scienze della Terra, della Vita e dell'Ambiente, Università degli Studi di Urbino "Carlo Bo".

Corresponding email: [francesca.micheletti@uniba.it](mailto:francesca.micheletti@uniba.it)

Keywords: U-Pb zircon data, Numidian, quartzarenites, Apennines.

The Numidian successions, cropping out in Southern Spain, Morocco, Algeria, Tunisia, Sicily and Southern Apennines, consist of turbidite sediments deposited in a deep marine basin in Early-Middle Miocene times. Several hypotheses about the origin of detritus were depicted and a provenance from north (European Plate) and from south (African Craton) was suggested. Age data on detrital zircons in Spain, North Africa and Sicily are available and all indicate Paleo- to Neoproterozoic ages (2.000-560 Ma; Thomas et al., 2010), whereas in Southern Apennines data about the age of Numidian zircons are missing. Consequently, detrital zircons of two samples of Numidian sandstones from Monteverde (AV) and Pietragalla (PZ) have been dated utilizing U-Pb spot analyses by LA-ICP-MS (IGG-CNR Pavia, Italy).

Petrographic features of these samples were already detailed in Fornelli (1998). They are coarse-grained quartzarenites having high compositional maturity and textural immaturity with a moderate sorting. The main minerals are quartz, K-feldspar, plagioclase and micas, while accessory minerals are zircon, tourmaline and glauconite. The matrix is prevalently silicatic and the cement is siliceous-ferruginous, formed by hydrous Fe-oxides, chalcedony and clay minerals.

SEM images of separated zircons evidenced three different zoning patterns: a) "magmatic zoning", b) presence of "xenocrystal cores" and c) "secondary textures". U-Pb spot dating were performed on 50 zircon crystals analysing 87 domains. 47 concordant ages ranging from Meso-Archean (3.047±13 Ma) to Cambrian (516±19 Ma) were measured. Majority of ages (n=22) are Paleo-Proterozoic (2.500-1.600 Ma), indicating an undoubted provenance of detritus from African Craton sources. The age cluster around 665 Ma suggests a relationship with Neo-Proterozoic granitic magmatism characterizing the West African Craton (Gasquet et al., 2005). It is very interesting that Hercynian and Alpine ages are missing; so a provenance of detritus from Hercynian or Alpine Chains, both exposed on large areas of the European Plate, can be excluded. The range of U-Pb zircon ages in Numidian sandstones from Southern Apennines, therefore, is fully similar to that from Spain, Morocco, Algeria and Sicily, suggesting a provenance from the same source-area, i.e. the African Craton (Thomas et al., 2010).

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## Geological evolution of the Adriatic Foreland between the Apennines and Dinarides

Minola M.\*<sup>1</sup>, Perotti C.<sup>2</sup> & Breciani I.<sup>2</sup>

1. Edison S.p.A. 2. Università degli Studi di Pavia.

Corresponding email: [matteo.minola@edison.it](mailto:matteo.minola@edison.it)

Keywords: Adriatic Foreland, seismic interpretation, Mid Adriatic Ridge.

Interpretation of 2D and 3D seismic data were performed in order to evaluate the structural configuration and relationships between the Apennines and Dinarides, from the Upper Triassic to the Pleistocene, in the whole Adriatic Sea, from the Gulf of Venice to the Otranto Channel. Some field analyses were also conducted in the Northern Apennines, in the River Secchia Valley, where the Burano Formation outcrops and is influenced by major transpressive lineaments: the results have been used as an analogue for the Adriatic offshore area. The main zone of deformation in the Adriatic Foreland is the Mid-Adriatic Ridge (MAR), a deformational belt NW-SE directed, that extends from the Ancona Promontory to the Grifone-1 well near the offshore of Bari. The MAR is formed by a variety of positive structures each with a core of anhydrites belonging to the Burano Formation as confirmed by several exploration wells, which reached the dolomitic and anhydritic members of the formation. Well correlation panels and seismic interpretation show that MAR deformed from the Oligocene. Different peaks of tectonic activity can be observed, the most important of which is Pliocene in age. The significant presence of anhydrites in the Adriatic Sea is also supported by the occurrence of well-defined diapiric structures (Jabuka and Vis) located along the Croatian side of the Adriatic Sea. These structures, and others highlighted by the seismic interpretation, appear to be aligned forming a new structural lineament parallel to the MAR. This lineament (here called "Dinaric Ridge") develops from the northwestern flank of the Dugi-Otok Basin to the offshore area of Montenegro. Moreover, two new NE-SW structural lineaments were identified in the study area respectively located south of Ancona Promontory and close to the Pescara Basin. Both are interpreted as left strike-slip faults and seem to have conditioned the angular relationships between MAR and Apennines front. These lineaments are often linked to structures of the MAR showing double vergences, or NW vergence, and to the presence of the Burano Formation in outcrop (Pta. Delle Pietre Nere, Sassalbo and the Secchia River Valley), and in the offshore subsurface (Mizar-2, Ernesto\_N-1, Famoso-1 and Stella-1 wells). A new hypothesis for the evolution of the MAR is finally proposed.

## **Slope instabilities on a steep carbonate apron system: the Plio-Pleistocene Calcarenite di Gravina Formation along the southern Salento peninsula (Southern Italy)**

Moretti M.\*, Meloni D., Tropeano M., Gallicchio S., Sabato L. & Spalluto L.

Dipartimento di Scienze della Terra e Geoambientali, Università degli Studi di Bari "A.Moro".

Corresponding email: [massimo.moretti@uniba.it](mailto:massimo.moretti@uniba.it)

Keywords: carbonate aprons, slope instabilities, slump and slide features.

Stratigraphic and sedimentologic analyses have been carried out on the upper Pliocene - lower Pleistocene Calcarenite di Gravina Fm., a carbonate unit cropping out along the coastal sectors of the eastern Salento Peninsula (Southern Italy). The Calcarenite di Gravina Fm. usually shows shoreface to offshore transition facies associations being a transgressive unit deposited mainly on a low-angle ravinement surface.

In the study area, the Calcarenite di Gravina Fm. crops out inside some indentations of the rocky slope (made up of tectonized pre-Pliocene units) showing very unusual sedimentological features. In fact, the Calcarenite di Gravina Fm. occurs in small isolated bodies with a variable thickness (up to several tens of metres), and is composed mainly of coarse-grained, bioclastic floatstones and packstones. The successions are characterized by long basinward-dipping well laminated and stratified clinobeds. The latter developed thanks to grain flows, moving either bioclasts due to a local factory production (abundant red algae and minor bryozoans, echinoids, brachiopods, planktonic foraminifers) or bioclasts coming from a shallower factory (benthic foraminifers and bivalves). These clinobeds are cut by irregular gullies (some meters in width), filled in their lower part by chaotic deposits (debris flow and slide deposits). Facies features and stratigraphic geometries of this carbonate unit indicate a deposition along a slope and at its toe.

The slope instabilities are recorded by the occurrence of both extensional and contractional structures developed in different sectors of the palaeoslope. Extensional features are located in the head of the local slope and are chiefly recorded by the existence of slump scar surfaces. They are tens of meters in length and are slightly basin-ward inclined. Backsets made up of fine- to medium-grained packstones fill the main slump scars. Normal faults with decimetric displacements also occur in the head sectors of the slope and involve limited parts of the clinobeds (for a maximum thickness of 0.30 m) recording a stage of incipient slump scar development. Contractional structures are recorded by thick slump sheets (until 3 m thick) located at the toe of the local slope. They show complex compressional features (folds, imbricated thrusts, etc.) representing the ending of the downslope slump transport. Isolated, isoclinal and asymmetrical folds (involving only few tens of centimetres) have been recognized in physical lateral continuity with the occurrence of small-scale scar surfaces.

A detailed description and measurement of all extensional and contractional structures have been carried out. Final data are reported in simple rose diagrams: 1) the measurement of fold axis and the main thrust surfaces in the thicker slump sheets show a nearly random orientation of these contractional structures; 2) extensional features (slump scars and small-scale normal faults) seem to be more adequate to evaluate the reliable orientation of the palaeoslope recording a more uniform distribution of structural elements in the rose diagrams; 3) the isolated, asymmetrical and isoclinal folds show a uniform orientation of their axis too. They seem to be the reliable compressional structures for the individuation of palaeoslope orientation.

Regarding the interpretation of possible trigger mechanism for the formation of slump scars, slump sheets and slide bodies, the action of sin-sedimentary tectonics (that we observe as growth-folds in the involved sedimentary units) cannot be discarded. Nevertheless, the clinobeds locally show an actual sedimentary slope inclined more than 30° indicating the presence of gravitationally-unstable systems: therefore, slope instabilities could be triggered by ordinary sedimentary processes that are able to produce the conditions to overcome the internal friction angle of the involved sediments.

## **Genesis and infill process of subglacial tunnel valleys: learnings from Quaternary case studies**

Moscariello A.\* & Benvenuti A.

Earth and environmental Sciences, University of Geneva, Switzerland.

Corresponding email: [andrea.moscariello@unige.ch](mailto:andrea.moscariello@unige.ch)

Keywords: subglacial tunnel valleys, Quaternary, Germany, Switzerland.

Subglacial tunnel valleys are commonly thought to be formed by meltwater flowing underneath large ice sheets hence difficult to observe and describe. Moreover, their sedimentary infill is often highly intricate and therefore difficult to predict. The detail study of ancient tunnel valley is therefore a way to understand the genetic and infilling processes of these still poorly known geological environments, which often represent important repository of natural resources such as groundwater, hydrocarbons and ores.

The study of the nature of the bedrock including the stratigraphy and structural characteristics, its relationship with the morphology of the base of the tunnel valley, and the accurate mapping of lithology forming the infill of the valleys, have provided new insight on the subglacial processes occurring at the base of tunnel valleys during their formation.

This study provides a first detailed analysis of this relationship in order to determine whether tunnel-valley location and morphology are controlled by the substratum. Tunnel valleys are incised preferentially into fine-grained layers, while the top of coarser-grained units commonly coincide with the tunnel-valley floor. This is explained by the occurrence of large water-pressure differences over fine-grained and impermeable layers along the flow-path of subglacial meltwater flowing through the substratum, from areas with high pore-water pressure towards areas with relatively low pressures in the vicinity of meltwater channels. These pressure differences might have been sufficient for the fracturing and fluidization of these layers and hence triggering and facilitating the subglacial erosion.

The detailed nature of the infill of tunnel valleys has been also studied in a couple of Pleistocene tunnel valleys in Hamburg (Germany) in the Southern North Sea and Swiss Plateau (Lake Geneva). These were investigated using both large amount of wells, 2D and 3D seismic data. The stratigraphic correlations and the resulting three-dimensional lithological model were used to assess the spatial lithological distributions and sedimentary architecture. The overall trend of the succession shows a progressive decrease in transport energy and glacial influence through time. Internal tunnel valley architecture is characterized by large clinoforms dipping upstream whose sedimentary and mineralogical nature have been investigated. They are interpreted as subglacial material being accumulated at the ice-front during momentary pulses of ice re-advance. During periods of stagnation, thick ice-proximal deposits accumulated at the ice margin, while during rapid recession, only a thin veneer of such coarse-grained sediments was deposited while a meltwater stream developed. The proposed model shows how the history of ice-sheet recession determines the position of coarse-grained depocentres, while the post-glacial history controls the deposition of fines through a progressive infill of remnant depressions.

## **Fluvio-deltaic coal-bearing reservoirs: new insights from outcrop and borehole data from Eastern Kentucky (US)**

Moscariello A.\*

Earth and environmental Sciences, University of Geneva, Switzerland.

Corresponding email: [andrea.moscariello@unige.ch](mailto:andrea.moscariello@unige.ch)

Keywords: coal-bearing reservoirs, fluvio-deltaic deposits, coastal plain deposits, Eastern Kentucky, Carboniferous.

The increased focus on exploration and development of unconventional resources in the last 5-10 years has led to a renewed interest in coal-bearing fluvio-deltaic and coastal plain deposits. The latter holds the majority of coal bed methane resources for which is important to understand the extension and subsurface architecture of coal seams. On the other side, coal-bearing sand rich successions still represent very important conventional reservoirs in NW Europe, Eastern Russia and NE China and the Asia-Pacific region. In all these cases, predictive model for sand and coal distribution in the subsurface are required to drive an effective and cost efficient hydrocarbon development strategy.

The Eastern Kentucky and West Virginia road network provide world-class exposures of Upper Carboniferous coal bearing successions where the interplay between sand and shale intervals and intervening coals can be studied in detail.

In this paper we present a summary of ongoing research recently carried out on the Pennsylvanian Hyden and Pikeville Formations where architecture and lateral facies variability of clastic deposits and associated coals can be observed and followed for several kilometers thanks to exceptional outcrop quality and dense borehole data from coal mining.

Specifically, this paper focuses on geometry and genetic significance of coal seams and heterolithic clinofolds intervals.

Coals, usually genetically associated with transgressive system tract lies often on top of channel-fill sandstone and under shale dominated intervals the latter recording the transition from a flooded coastal plain to shallow to deep marine environment. However coals are found as well draping irregular topographic surfaces where wide and relatively deep (10-20 m) incisions can be recognised. In this situations coals are typically overlain by channel fill sandstone forming the stratigraphical unit above. Often the sand is not eroding the underlying coal. In this cases, the coals are interpreted as forming during a low stand phase and thus possibly the true indicators of development of incised valleys.

Five to ten meters-high inclined beds made of mixed heterolithic successions of sandstones and shales are associated with both fluvial-dominated mouth bars and point-bars develop in large meandering river systems often developed within estuarine environment. This study highlights the typical 3D features of these deposits allowing the definition of sedimentological and stratigraphical criteria to distinguish these tow systems in the subsurface.

The Carboniferous succession of Eastern Kentucky is then compared with the coeval succession in the North Sea (The Netherlands) to highlight the importance of outcrop based analogues studies to help understanding the overall distribution of subsurface geology by providing practical criteria for a) carrying out a well-to-well correlation and b) reconstruct the overall 3D reservoir architecture.

## Baseline characterization and modeling of a fractured reservoir for potential CO<sub>2</sub> storage: the Longyearbyen CO<sub>2</sub> Lab case study

Ogata K.\*<sup>1</sup>, Senger K.<sup>2</sup>, Braathen A.<sup>3</sup>, Olausen S.<sup>4</sup> & Tveranger J.<sup>5</sup>

1. Dipartimento di Fisica e Scienze della Terra - Università degli Studi di Parma. 2. Electromagnetic Geoservices ASA – Norway. 3. Department of Geosciences - University of Oslo. 4. Department of Arctic Geology - University Centre in Svalbard. 5. Centre for Integrated Petroleum Research (Uni CIPR) – Norway.

Corresponding email: [kei.ogata@unipr.it](mailto:kei.ogata@unipr.it)

Keywords: Svalbard, geologic CO<sub>2</sub> storage, fracture-related fluid flow.

The aim of the Longyearbyen CO<sub>2</sub> Lab project is to develop an onshore, pilot-scale (ca. 60.000 of CO<sub>2</sub> tons/year) site for geologic sequestration of CO<sub>2</sub> in a tight, siliciclastic aquifer belonging to the upper Triassic-middle Jurassic De Geerdalen and Knorringfjellet Formations, located at 700-1000 m depth in Central Spitsbergen, Svalbard. We here present the baseline study of the target Mesozoic sedimentary succession, which integrates high-resolution structural and stratigraphic analyses of outcrop and borehole data. Through this integrated approach, we identified recurrent litho-structural and structural units (LSUs and SUs, respectively) on the basis of their fracture associations, lithologies and dominant sedimentary facies. A principal fracture set trending approximately E-W (J1) and a subordinate fracture set trending approximately N-S (J2) have been recognized. Subordinate systems of shear fractures (S1) trending roughly NE-SW and NW-SE, and a secondary low-angle, fracture set (S2) striking E-W to NW-SE have been observed. Their origin is interpreted as related to the far-field stress of the Paleogene West Spitsbergen fold-and-thrust belt. The identified units are thought to influence the local hydrogeologic regime due to the intrinsic variations in the matrix and fracture network properties. The architecture of the reservoir-caprock succession is thus segmented, with the vertical alternation of intervals characterized by varying 1) fracture porosity and permeability, 2) microfracturing-related matrix porosity, and 3) preferential subsurface fluid flow pathways. The moderate injectivity (ca. 45 mD/m) recorded during water injection tests suggests that CO<sub>2</sub> may potentially be injected and stored in the tight, naturally fractured reservoir of the Longyearbyen CO<sub>2</sub> Lab project, with a major contribution from the regional network of meso-scale fracture sets mapped and analyzed in both drill cores and outcrops. Due to the present day stress regime and the orientation of the most promising fracture systems (i.e. J1) in terms of possible fluid conductivity, we propose a NNW-SSE oriented horizontal drilling of the injector well at the reservoir level to optimize the fracture permeability and to maximize the related fluid flow. In the proposed framework we expect an E-W spreading of the injected buoyant plume with a focussed drift toward the E-NE, through horizontal and vertical diffusion within the finer- and coarser-grained intervals, respectively. The derived semi-quantitative results are recommended for the reservoir modeling efforts. Accordingly, the processed data were directly used as input parameters in the development of a static geological model of the unconventional target aquifer.

## Stratigraphic architecture of the Upper Miocene deposits of the Adana Basin (southern Turkey)

Radeff G.<sup>1-2</sup>, Cosentino D.\*<sup>1-3</sup>, Cipollari P.<sup>1-3</sup>, Schildgen T. F.<sup>1</sup>, Strecker M. R.<sup>1</sup>, Darbağ G.<sup>4</sup>, Gürbüz K.<sup>5</sup>

1 Dipartimento di Scienze, Università degli Studi Roma Tre, Italy. 2 Institut für Erd- und Umweltwissenschaften, Universität Potsdam, Germany 3 Istituto di Geologia Ambientale e Geoingegneria, CNR-Roma, Italy 4 Jeoloji Mühendisliği Bölümü, Kahramanmaraş Sütçü İmam Üniversitesi, Turkey 5 Jeoloji Mühendisliği Bölümü, Çukurova Üniversitesi, Turkey.

Corresponding email: [domenico.cosentino@uniroma3.it](mailto:domenico.cosentino@uniroma3.it)

Keywords: Stratigraphy of sedimentary basins, Messinian Salinity Crisis, Lago-Mare event, Geohistory, Southern Turkey.

The Adana Basin is a Neogene forearc basin developed close to the triple-junction among African, Arabian, and Eurasian plates. Its sedimentary record spans from Late Oligocene to Quaternary and shows evidence for the late Serravallian Arabia-Eurasia collision, as well as the late Messinian uplift of the Central Anatolian Plateau. The Burdigalian–Serravallian sandstones and limestones and the upper Tortonian–Messinian shales and evaporites of the Adana Basin have been considered as the reservoir and the seal of the eastern Taurus petroleum system, respectively. The recently proposed stratigraphy for the Messinian–Zanclean deposits of the Adana Basin allowed us to re-interpret some of the seismic profiles acquired in the basin by the Turkish Petroleum Corporation. The interpretation of the seismic profiles was constrained by data from surface geology and well logs. From our new interpretation, the geometries of the potential seal rock of the Adana Basin appear to be more complicated than previously reported. The anhydrites and black shales, recording the main evaporative event of the Mediterranean (Primary Lower Gypsum), are spatially discontinuous. The Resedimented Lower Gypsum, deposited above the first Messinian erosional event (MES1, about 5.56 Ma), outline a spatially confined sedimentary body showing a 3D lobe geometry. Using the seismic data we reconstruct the subsidence curve and the geohistory of the Adana Basin showing the main events that occurred in the area. At the Middle/Late Miocene transition the stratigraphy of the Adana Basin records an erosional surface which can be related to the collision between Arabian and Eurasian plates coupled with a global sea-level drop. An increase in the subsidence rate is shown at about 5.56 Ma: it corresponds to a period of increased sedimentation rate right after the drawdown of the Mediterranean base level and the formation of the MES1. At about 5.45 Ma, above a younger erosional surface (MES2) a major increase in subsidence rate is recorded, with the deposition of up to 1.6 km of fluvial deposit (conglomerates and marls of the Handere Fm) during the latest Messinian Lago-Mare event (5.45–5.33 Ma). The provenance analysis of the Handere Formation clasts documents that the majority of them is sourced from the Taurus Mountains. Compared with the clast composition of Quaternary terraces and with lithologies outcropping in the present-day catchments, we infer a major change in the drainage system to have occurred between 5.45 Ma and the Quaternary. All these observations support the hypothesis that the CAP southern margin was uplifting during the deposition of the Lago-Mare conglomerates, providing the large amount of material coevally sedimented in the Adana Basin in the latest Messinian. This study highlights the complexity of the Adana Basin geohistory and provides useful data for revising the Taurus petroleum system.

## **Tectonic evolution of the Cretaceous back-arc to foreland Neuquén Basin (Argentina) through a detrital multi-proxy provenance study**

Ronchi A.\*<sup>1</sup>, Di Giulio A.<sup>1</sup>, Sanfilippo A.<sup>1,2</sup>, Carrapa B.<sup>3</sup>, Balgord E.<sup>3</sup>, Ramos V.A.<sup>4</sup>

1. Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia, Italy; 2. School of Natural System, College of Science and Engineering, Kanazawa University, Japan; 3. Department of Geosciences, University of Arizona, USA; 4. Laboratorio de Tectónica Andina, Universidad de Buenos Aires, Argentina.

Corresponding email: [ausonio.ronchi@unipv.it](mailto:ausonio.ronchi@unipv.it)

Keywords: Andean subduction, foreland basin, sandstone petrology.

The Neuquén back-arc basin (Patagonia, Argentina) experienced a tectonic evolution closely linked to the changing dip of subduction of the Farallon Plate under the South American continental margin during the Cretaceous, between 36° and 41° S latitude. Specifically, the change from a retro-arc extensional setting to a foreland basin compressional one in the Neuquén Basin during mid Cretaceous time was controlled by changes in the absolute motion of South America related to the break-up of Western Gondwana and the opening of the South Atlantic Ocean (e.g. Ramos 2010).

The multi-proxy provenance study of continental Aptian to Santonian detritus is here used to resolve the evolution of the basin source active volcanism and exhumation patterns of sediment sources on both sides of the basin. Specifically, sandstone petrology is used to obtain a broad picture of different kinds of source rocks and their evolution through time. U/Pb detrital zircon geochronology performed both on grain rims and cores is used to better constraints the geologic units delivering detrital sediments to the basin. Finally, apatite fission track (AFT) thermochronology is used to determine the exhumation timing of source units.

Our results clearly show that the basin change from extensional to compressional tectonic regime was coupled with an abrupt switch in sandstone composition from continental block sandstones fed by the foreland region to magmatic arc sandstones fed by the Andean Cordillera, including syn-depositional volcanic products. This evolution is consistently recorded by sandstone framework grain composition and by an abrupt decrease of U/Pb rim ages of detrital zircons. This provenance picture progressively changes up-section with a progressive return toward prevailing basement sources recorded by the gradual shift of sandstone detrital framework toward continental-block provenance compositions, coupled with a progressive increase of Paleozoic U/Pb ages of detrital zircons including crystals with Proterozoic crystal cores. Combined with the Triassic-Jurassic fission AFT ages provided from the same stratigraphic levels, this is interpreted to be the result of a new source in the foreland basin from the stable Patagonian basement. Erosion of the Patagonian basement to the east is interpreted to be the result of the flexural uplift of the peripheral bulge caused by the Late Cretaceous thrust front migration into a compressional retro-arc foreland basin setting.

Ramos V.A. 2010. The tectonic regime along the Andes: Present settings as a key for the Mesozoic regimes. *Geological Journal*, 45, 2-25.

## **Geometries and modes of emplacement of the Tremiti diapir (Apulia offshore, southeastern Italy)**

Teofilo G.\*, Festa V., Tropeano M., Sabato L. & Spalluto L.

Dipartimento di Scienze della Terra e Geoambientali - Università degli Studi di Bari "Aldo Moro".

Corresponding email: [gianvito.teofilo@uniba.it](mailto:gianvito.teofilo@uniba.it)

Keywords: adriatic, basin analysis, salt tectonics, 3D modeling, Tremiti Structure.

The reinterpretation of public seismic profiles and the stratigraphic review of some exploration wells in the Adriatic offshore of Gargano (Apulia, southern Italy) allowed the detection of a kilometre-scale salt-anticline, the Tremiti diapir, within the larger Tremiti Structure. The use of Move<sup>TM</sup> (Midland Valley Ltd.) and Surfer<sup>®</sup> (Golden Software, Inc.) softwares, allowed both the 3D modeling and the reconstruction of the time-contour map of the salt surface.

The salt-anticline was generated by diapirism of Upper Triassic halite, drilled in the Ernesto Nord 1 well, at the bottom of a thick Mesozoic to Quaternary sedimentary succession. Both internal stratal patterns and shapes of Plio-Quaternary units, and the occurrence of an angular unconformity between early Tortonian and Pliocene rocks on the Tremiti Islands, suggest that halokinesis began during the late Miocene and is still active today. An ancient extensional SE-dipping fault, cutting an older Mesozoic low-amplitude salt-anticline, played an important role for the later emplacement of the Tremiti diapir. The reactivation as dextral strike-slip of the ancient SE-dipping fault favoured a "single flap" mode of emplacement along the northeastern portion of this fault. Whereas, in the southwestern sector, the plan view offset of the fault suggests the presence of a transfer zone, where transtension favoured piercing.

## **Synsedimentary structural control on basinal turbidites due to the segmentation of the foredeep (Marnoso-arenacea Formation, Miocene, Northern Apennines, Italy)**

Tinterri R.\*<sup>1</sup>, Tagliaferri A.<sup>1</sup> & Muzzi Magalhaes P.<sup>2</sup>

1. Dipartimento di Fisica e Scienze della Terra, Università di Parma. 2. Petrobras, Rio de Janeiro, Brasile.

Corresponding email: [roberto.tinterri@unipr.it](mailto:roberto.tinterri@unipr.it)

Keywords: foredeep, turbidites, basin confinement.

The Marnoso-arenacea Formation (MAF, Langhian-Tortonian) was deposited in an elongate, NW-stretched foredeep basin formed in front of the growing Northern Apennines orogenic wedge. It consists of a shoaling upward stratigraphic succession recording the progressive closure of the Apennine foredeep basin due to the propagation of thrust fronts toward the north-east. This thrust propagation produced a complex foredeep characterized by synsedimentary structural highs and depocentres and a progressive segmentation of the basin resulting in the uplift of the inner portions and north-eastward shifting of the main depocentres. The MAF stratigraphic succession, therefore, can be summarized in three stages: 1) an older and inner Langhian-Serravallian basin consisting of basinal turbidites controlled by subtle structural reliefs; 2) an intermediate Upper-Serravallian transitional phase characterized by mass-transport complexes and thick accumulations of sandstone lobes filling thrust-related structural depressions and 3) a younger and outer Tortonian basin filled by turbidity currents with a low degree of efficiency, due to flow decelerations induced by basin narrowing. Consequently, during this evolution, structural control and associated morphologic confinement increased over time, controlling the lateral and vertical distribution of turbidite facies. This work discusses the evolution of the MAF inner basin, focusing especially on the upper Serravallian transitional phase, which records the definitive closure of the inner basin and the deposition shifting to an outer basin. In this phase, a strong segmentation of the foredeep took place, due to the uplift of two important structures within the basin, which, based on a high-resolution stratigraphic framework, show coeval growth phases. These structures are represented by NW-SE oriented M. Castellaccio (Coniale) thrust-related fold and the Verghereto area to the SE. In such a situation, the vertical and lateral facies changes, associated with evident stratigraphic pinchings and onlap relationships and highlighted by a high-resolution physical stratigraphy with bed-by-bed correlations, have played a key role in showing this phase of strong foredeep segmentation and basin confinement.

## The Venetian-Friulian Basin: anatomy of a shared foreland basin

Toscani G.<sup>1</sup>, Marchesini A.<sup>2</sup>, Di Giulio A.\*<sup>1</sup>, Fantoni R.<sup>3</sup>, Mancin N.<sup>1</sup> & Zanferrari A.<sup>2</sup>

1. Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia. 2. Dipartimento di Chimica, Fisica e Ambiente, Università di Udine.  
3. ENI S.p.A-San Donato Milanese.

Corresponding email: [digiulio@unipv.it](mailto:digiulio@unipv.it)

Keywords: foreland basin, venetian-Friulian Basin, 3D model, geohistory.

We present a 3D model of the Venetian-Friulian Basin (VFB) subsurface architecture. The VFB infill is the result of the overlapping effects of three collisional systems developed in the area in different times and with different tectonic transport directions: the Dinaric system (Paleocene-Eocene), the eastern Southern Alps system (Middle Miocene-Holocene) and the Northern Apennines system (since Pliocene). The resulting architecture was reconstructed merging published data and more than 1400 km of seismic lines (ENI), that were interpreted and depth converted in order to obtain a 3D basin scale reconstruction of the following key surfaces: top Mesozoic carbonates, bottom of Chattian-Langhian sequence, bottom of Serravallian-Messinian sequence, Messinian unconformity, bottom Quaternary. The first result of this work is a 3D model describing the surfaces geometry.

In the subsequent work-step, paleobathymetric and geohistory analyses were performed in order to provide constraints for unravelling the evolutionary model of the basin. The interplay between deep processes (tectonics, lithospheric flexure, exhumation) and surface processes (uplift, erosion, deposition, base level changes) caused a continuous re-distribution of rock masses from the erosional to the depositional part of the complex collisional setting formed by the VFB itself and the surrounding belts.

During the Paleocene-Eocene, the VFB was the foreland basin of the Dinaric system; the effects of the Dinaric collisional tectonics caused a westward migration of the belt-foreland system. During this period, an important role was also played by the basin topography inherited from the Mesozoic rifting-drifting evolution of the Adriatic micro-plate. During Eocene-Oligocene the inherited topography of the basin was progressively smoothed by the gravity driven accumulation of clastic sediments supplied by both the Eastern Alps and Dinaric belt. This led to the complete erasing of the previous sea-bottom topography during latest Oligocene-early Miocene, when a shallow marine sedimentation occurred all over the basin.

The top of the Chattian-Langhian sequence provides the flat topographic surface that seals the previous basin flexure and is affected only by later deformations. During Middle-Late Miocene the northward flexure due to the load of eastern Southern Alps was filled by clastic sediments forming a southward thinning wedge whose northern part is currently exposed in the frontal sectors of the belt. This context was abruptly modified by the base level lowering linked to the Mediterranean salinity crisis during late Messinian. The whole basin experienced a subaerial erosion producing a basin-scale unconformity surface sealed by open marine sediments during Pliocene. In the Quaternary, the basin topography was progressively smoothed for the last time by Plio-Pleistocene sediments, which partially recorded the flexural effects of the Northern Apennines system on the VFB.

## The application of high-resolution sequence stratigraphy of clastic shelves to reservoir geology

Zecchin M.\*<sup>1</sup> & Catuneanu O.<sup>2</sup>

1. OGS (Istituto Nazionale di Oceanografia e di Geofisica Sperimentale), Trieste. 2. Department of Earth and Atmospheric Sciences, University of Alberta.

Corresponding email: [mzecchin@ogs.trieste.it](mailto:mzecchin@ogs.trieste.it)

Keywords: High-resolution sequence stratigraphy, Clastic shelves, Reservoir, Heterogeneity, Compartmentalization.

High-frequency clastic shelf sequences contain porous deposits, consisting of coastal to shallow-water sandstones and conglomerates, which may represent very good reservoirs, and therefore critical targets for exploration and production, as well as for fluid (hydrocarbon, water or CO<sub>2</sub>) storage. The study of these reservoirs, following a sequence stratigraphic approach, is essential to predict their features and distribution within systems tracts forming high-frequency sequences, which in turn compose higher-rank systems tracts and sequences (Catuneanu, 2006; Zecchin & Catuneanu, 2013). A critical aspect to improve the exploitability of the reservoirs is their heterogeneity, which directly affects the volume of the reservoirs and determine internal compartmentalization (Zecchin & Caffau, 2012). The heterogeneity can be primary, related to depositional processes influencing grain size and facies distribution, and secondary, related to diagenesis. In particular, the primary heterogeneity is referred to the facies variability from distal to proximal settings, to the accumulation of condensed shell beds, and to facies characteristics of bedsets (Zecchin & Catuneanu, 2013), whereas the secondary heterogeneity derives from diagenetic processes at sequence stratigraphic surfaces and facies contacts, and within sandbodies (Taylor et al., 2000). Both the distribution of reservoirs and their heterogeneity can be predicted following a high-resolution sequence stratigraphic approach (Morad et al., 2013; Zecchin & Catuneanu, 2013). Ultimately, the integration of subsurface data with the analysis of outcrop analogues is essential to better understand the features of clastic shelf reservoirs and to develop 3D models of fluid migration.

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## **SESSIONE S9**

### **Coastal environments: stratigraphy, resources and human impact**

#### *CONVENORS*

*A. Amorosi (Univ. Bologna)*

*S. Andreucci (Univ. Cagliari)*

*R. Pagliarulo (CNR-IRPI Bari)*

## **Rock cliff instability mechanisms and erosional processes along the Adriatic Salento coast (Southern Italy)**

Andriani G.F.<sup>1</sup>, Lollino P.<sup>2</sup> & Pagliarulo R.\*<sup>2</sup>

1. Dipartimento di Scienze della Terra e Geoambientali. Università di Bari "Aldo Moro". 2. IRPI-CNR Bari.

Corresponding email: [r.pagliarulo@ba.irpi.cnr.it](mailto:r.pagliarulo@ba.irpi.cnr.it)

Keywords: Cliff, failure, coastal recession.

The recent Ordinance of the Gallipoli Harbour Office and the Coast Guards with the consequent interdiction for any activities along more than 50 km of the Adriatic Salento coasts brought the widespread instability processes to the attention of the public opinion. The coastal morphology is characterized by vertical rock cliffs, locally with overhanging blocks, articulated in caps and promontories, stacks, inlets and beaches. The evolution of the coastal morphology of the Southern Apulian coasts is mainly related to the rock mass movements, erosion and weathering phenomena due to the abrasive action of the marine spray and the wave action at the cliff foots. A predisposing factor of the instability processes of the cliffs is represented by the outcropping geological formations made of poorly cemented Pleistocenic calcarenites and by the presence of ancient coastal quarries. The instability processes are represented by rock falls, block slidings and toppling. This paper is aimed at exploring the different causes that promote the instability processes and the possible landsliding kinematics, also by means of numerical modelling techniques. The knowledge of the cliff behavior may provide a valuable support for predicting the possible failure occurrence and modeling the coastal morphological evolution.

## Tidal notches in Mediterranean sea

Antonioli F.<sup>\*1</sup>, Lo Presti V.<sup>2-1</sup>, Anzidei M.<sup>3</sup>, Deiana G.<sup>4</sup>, Ferranti L.<sup>5</sup>, Furlani S.<sup>6</sup>, Mastronuzzi G.<sup>7</sup>, Orrù P.<sup>4</sup>,  
Pagliarulo R.<sup>8</sup>, Rovere A.<sup>9</sup>, Scicchitano G.<sup>10-11</sup>, Sansò P.<sup>12</sup>, Spampinato C.R.<sup>10</sup>, Sannino G.<sup>1</sup>, Vacchi M.<sup>13</sup>,  
Caruso A.<sup>14</sup> & De Sabata E.<sup>15</sup>

1. ENEA, UTMEA, Casaccia, Roma. 2. Dipartimento di Scienze della terra, Sapienza, Università di Roma. 3. INGV, Roma. 4. Dipartimento di Scienze Geologiche, Università di Cagliari. 5. DiSTAR - Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse Università di Napoli "Federico II". 6. Dipartimento di Matematica e Geoscienze, Università di Trieste. 7. Dipartimento di Scienze della Terra e Geoambientali, Università degli Studi "Aldo Moro", Bari. 8. CNR, IRPI, Bari. 9. Lamont Doherty Earth Observatory, Columbia University. 10. Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università degli Studi di Catania. 11. STUDIO GEOLOGI ASSOCIATI T.S.T., Misterbianco (CT). 12. Dipartimento di Scienze e Tecnologie Biologiche ed Ambientali, Università del Salento, Lecce. 13. OT-Med Labex, Europole de l'Arbois, batiment du CEREGE, Aix-En-Provence, France. 14. Dipartimento di Scienze della Terra e del Mare, Università degli Studi di Palermo. 15. MEDSHARK, Roma.

Corresponding email: [fabrizio.antonoli@enea.it](mailto:fabrizio.antonoli@enea.it)

Keywords: Tidal notch, Sea level rise.

“The most recent continuous sea level rise has resulted to the absence of a present-day notch” (Evelpidiu et al., 2012). This sentence, striking geomorphological and global significance, stimulated the collaboration of this large group of authors. In less than a year we visited and measured 73 sites in central Mediterranean sea (Italy, France, Croatia, Montenegro, Greece and Malta), with the aim to understand why tidal notches are still developing indeed.

The results of these observations have been used to understand: i, the exact position of mean sea level with respect to the notch; ii, the correlation between morphometry and meteomarine factors; iii, discuss the mechanisms that influence the genesis and evolution of tidal notch: chemical phenomena (mixing-corrosion), biological (erosion by intertidal organisms), mechanical (meteomarine) but also isostatic, tectonic and climatic factors. In addition to width and depth notch measures were detected: the presence or absence of biological reef as *Dendropoma* or *Litophyllum*, the possibility that these biological markers may interfere with the shape and the concavity of the notches, the depth of the cliff facing notches and wave exposition. The measures of width and depth notch were compared with a tidal model (maximum excursion) and some data tide gauge data.

Ours database which also includes few coastal areas with a bit tectonics, shows that the present day tidal notch, if in a stable area, is always present, apart from rare exceptions (2/73 sites) often due to local factors.

One of the main conclusion of this research is the strong correlation between local tide and the notch width very evident tides over 1 meter (extra-Mediterranean).

Evelpidou N., Kampolis I., Pirazzoli P.A. & Vassilopoulos A. 2012. Global sea-level rise and disappearance of tidal notches. *Global and Planetary Changes*, 92-93, 248-256.

## **A late Quaternary paleovalley system from the western Adriatic coast: insight from the Biferno coastal plain (Molise, Italy)**

Bracone V.\*<sup>1</sup>, Amorosi A.<sup>2</sup>, Campo B.<sup>2</sup>, D'Amico C.<sup>1</sup>, Rossi V.<sup>2</sup> & Roszkopf C.M.<sup>1</sup>

1. Dipartimento di Bioscienze e Territorio - Università degli Studi del Molise. 2. Dipartimento di Scienze Biologiche, Geologiche e Ambientali - Università di Bologna.

Corresponding email: [vito.bracone@unimol.it](mailto:vito.bracone@unimol.it)

Keywords: Paleovalley, Facies analysis, Biferno coastal plain.

Integrated sedimentological and paleontological (foraminifers, ostracods and molluscs) investigations of two continuous cores (38 m and 40 m long, respectively), along with stratigraphic correlations of well data, allowed to detect a paleovalley system, about 40 m thick and 2 km wide, in the subsurface of the Biferno coastal plain (Molise, Italy). This is the first onshore detailed documentation of a paleovalley system from the Adriatic Sea coast.

The valley system truncates a variety of marine (offshore to upper shoreface) and alluvial (fluvial-channel to floodplain) deposits. Fluvial-channel gravels are the youngest gravel deposits of pre-LGM age (31280±220 Cal BP). Floodplain facies characterize the interfluvial zones. The valley fill consists of six facies associations, including alluvial (fluvial-channel, crevasse-levee, floodplain and poorly drained floodplain), swamp and lagoon-estuarine deposits. Six radiocarbon dates provide a reliable chronological framework to the late Pleistocene-Holocene succession. At the valley bottom, late Pleistocene fluvial-channel gravels are overlain by floodplain clays and crevasse sands and silts. Organic-rich swamp clays are also locally present. This succession is in turn overlain by lagoon deposits, 2 m thick, recognised by log data at about 10 m depth. Facies distribution testifies to the rapid landward migration of the paleoshoreline, following the Last Glacial Maximum. The upper part of the succession exhibits a “regressive” trend, with alluvial (fluvial-channel and floodplain) and swamp clays. From a sequence stratigraphic point of view, the fluvial gravels in the lowermost part of the valley fill represent lowstand deposits (LST). A transgressive surface (TS) at the top of the fluvial-channel gravels marks the onset of a deepening-upward succession (TST). The shallowing-upward tendency recorded by fluvio-deltaic deposits onto lagoon deposits is interpreted to reflect highstand sedimentation (HST). It is apparent that late Quaternary glacio-eustatic fluctuations exerted a major control on the formation and sedimentary evolution of the paleovalley system.

## **Allogenic vs autogenic control of post-LGM infill architecture in the Ombrone paleovalley (Southern Tuscany, Italy)**

Breda A.\*<sup>1</sup>, Amorosi A.<sup>2</sup>, Rossi V.<sup>2</sup> & Fusco F.<sup>3</sup>

1. Department of Geosciences, University of Padova. 2. Department of Biological, Geological and Environmental Sciences, University of Bologna.  
3. Consultant palynologist.

Corresponding email: [anna.breda@unipd.it](mailto:anna.breda@unipd.it)

Keywords: Paleovalley, Lateglacial-Holocene, allogenic vs autogenic control.

The Ombrone paleovalley system (southern Tuscany) was incised during the last glacial global sea-level fall and then drowned and infilled during the subsequent Lateglacial-Holocene transgression. A detailed sedimentological and stratigraphic study of two cores drilled along the paleovalley axis, 5 km apart, led to the reconstruction of the post-LGM valley history, highlighting the role of autogenic dynamics versus allogenic forcing in shaping the stratigraphic infill architecture of the valley.

Stratigraphic correlation between the two cores highlights remarkable similarity in the lower valley fill, and otherwise a complete discrepancy in the upper valley fill succession. Above the paleovalley floor, about 60 m below the present sea-level, the basal fluvial deposits date back to 18 cal ky BP, providing an unusually high-resolution and almost continuous stratigraphic record of Lateglacial sedimentation. The onset of the Holocene is recorded in the study cores by floodplain deposits. Above, a deepening-upward succession reveals a retrogradational shift from alluvial to coastal facies during the ensuing sea-level rise.

Above the initial transgressive surface, the two cores record consistent distal to proximal facies changes. In core OM1 (seaward core) the deepening-upward trend is marked by the transition from inner to outer estuarine environments. In core OM2 (landward core), the emplacement of estuarine conditions is interrupted by a new advance of the continental environments. Mass flow deposits produced by high-energy flash floods inundating the floodplain are recorded. Above, the upper valley fill presents a fully continental record, with thick fresh-water swamp to lacustrine deposits. The anomalous succession observed in core OM2, with fresh-water facies stratigraphically equivalent to the fully estuarine facies observed in core OM1 and interpreted as the maximum deepening of the system, may reflect the position of core OM2 in a relatively confined segment of the Ombrone valley, just landward of the confluence with a tributary valley (Rispeccia paleovalley). Probably, a sudden sediment input from the tributary valley produced a topographic threshold, damming the main valley course and isolating its landward segment by the sea.

The Ombrone paleovalley case study demonstrates that, despite evident allogenic (eustatic/climatic) control on estuarine sedimentation, autogenic dynamics can locally overwhelm the allogenic signal over very short distances (a few kms), leading to the development of completely different stratigraphic architectures.

## Approaching coastal risk in Emilia-Romagna by using the geological model of the Holocene succession

Calabrese L.\*<sup>1</sup>, Perini L.<sup>1</sup>, Bonzi L.<sup>1</sup>, Correggiari A.<sup>2</sup>, Ferrari V.<sup>1</sup>, Luciani P.<sup>1</sup>, Remia A.<sup>2</sup> & Severi P.<sup>1</sup>

1. Servizio Geologico Sismico e dei Suoli, Regione Emilia-Romagna. 2. ISMAR, CNR Bologna.

Corresponding email: [lcalabrese@regione.emilia-romagna.it](mailto:lcalabrese@regione.emilia-romagna.it)

Keywords: coastal risk, Holocene, geological model.

The coast naturally is a dynamic environment where the boundary between land and sea is transitional and changeable; human activities are often concentrated in this thin strip, increasing fragility. In Emilia-Romagna region (ER), the geological and geomorphological characteristics of the coastal zone, combined with an intensive exploitation of resources generate critical phenomena such as beach erosion, marine ingression, subsidence and salt contamination of groundwater. The creation of a detailed stratigraphic model of the Holocene succession has helped to understand these problems and it has supported specific studies to promote prevention and protection actions that competes to the Region. The succession shows thickness ranging from 35 m to 20 m and is organized as transgressive/regressive sequence on Pleistocene deposits, with back-stepping barrier/lagoon systems and estuary at the base and then fore-stepping deltaic complexes and beach ridges (Correggiari et al. 1996; Amorosi et al. 1999). The geological model derived from the processing of a large amount of data, conduct by, experienced interpreters, using GIS software and 3D geological modeling programs. The model is constantly updated and refined as new data are acquired. At the base of the model are the Geognostic Database (GDB) of the ER, geological maps and studies of the CARG project and thematic investigations by ER. GDB, in particular, allows to integrate and compare heterogeneous data, i.e. cores, boreholes, well logs, penetrometric, geophysical and geoelectric tests; datings, petrographic and micro-paleontological analyses are also available. The recent acquisition near shore of 77 seismic lines, about 200 km, has supported land-sea correlations and extend the model to a poorly investigated coastal area.

Specific studies about coastal dynamics, subsidence and hydrogeology have been conducted, based on the geological model. In particular, it has allowed:

- to interpret the current erosion of deltaic cusps and rectification of the shoreline as a long-term process;
- to construct a geotechnical model to evaluate the contribution of compaction of Holocene succession to the coastal subsidence;
- to plan the network of 37 piezometers of phreatic aquifer and to interpret properly the data collected during the last 5 years of monitoring.

The model has proved to be a useful and advanced tool on several fronts. It is an implementable outcome and it would be applied to new fields such as the seismic risk in the coastal area.

Amorosi A., Colalongo M.L., Pasini G. & Preti D. 1999. Sedimentary response to Late Quaternary sea-level changes in the Romagna coastal plain (northern Italy). *Sedimentology*, 46, 99-121.

Correggiari A., Roveri M. & Trincardi F. 1996. Late Pleistocene and Holocene evolution of the North Adriatic Sea. *Il Quaternario*, 9, 697-704.

## ***Posidonia oceanica* seagrass meadows facies from western Mediterranean**

Gaglianone G.\*<sup>1</sup>, Frezza V.<sup>1</sup>, Mateu-Vicens G.<sup>2</sup> & Brandano M.<sup>1-3</sup>

1. Dipartimento di Scienze della Terra - Università di Roma "Sapienza". 2. Càtedra Guillem Colom Casasnovas - Universitat de les Illes Balears, Palma de Mallorca, Spain. 3. IGAG-CNR Area della Ricerca di Roma 1, Monterotondo Stazione, Roma

Corresponding email: [giovanni.gaglianone@uniroma1.it](mailto:giovanni.gaglianone@uniroma1.it)

Keywords: facies, mixing carbonate-siliciclastic, *Posidonia oceanica*.

Sedimentary facies characteristic of seven *Posidonia oceanica* meadows from western Mediterranean Sea were investigated. Six sampling sites are localised in Italy (Maratea, Ponza Island, Santa Marinella, Giglio Island, Osella and Alghero), and only one in France (Argentella, Crovani Bay, Corsica). These meadows are set up on soft and hard substrates, in areas subject to different weather and sea conditions, and characterised by various coastal landforms and terrigenous inputs derived from fluvial contributions or coastal erosional processes. Consequently, the role of *P. oceanica* meadows in the sedimentary processes was investigated in different contexts.

Sedimentological, geochemical and compositional analyses of 190 bottom samples, collected between 0 and 35 mwd, were performed and, finally, tested with a Q-mode cluster analysis. Five sedimentary facies have been recognised: terrigenous sands and gravels (F1), subdivided into two subfacies, terrigenous sands (F1a) and terrigenous gravelly sands (F1b), on a related *pocket beach* seagrass meadow; bioclastic sands (F2), characteristic of shallow meadow in a quite environment; gravelly sands (F3), recognised in shallow waters, subject to a significant wave motion; mixed siliciclastic-carbonate coarse sands (F4), typical infralittoral deposits controlled only by the waves; and, finally, sorted siliciclastic sands (F5), from shallow meadows affected by wave motion (subfacies F5a: moderately sorted siliciclastic sands) or fluvial inputs (subfacies F5b: well sorted siliciclastic sands).

Facies and subfacies are distinguishable on the basis of sorting, gravel content, abundance and maturity of clastic sediments, and weighted average of carbonate content. In all facies, the bioclastic fraction is dominated by foraminifers (typical epiphytic species, such as *Asterigerinata mamilla*, *Lobatula lobatula*, *Peneroplis pertusus* and *Rosalina bradyi*) and red algae, whereas other bioclastic components are very subordinate and show a variable distribution.

Only in the Maratea site (Basilicata, Southern Italy), the epiphytic carbonate annual production of seagrass meadow was evaluated taking into account independently the canopy and their common basal parts; in addition, the whole leaf bundles were assessed. The canopy carbonate content mostly coincides to known data; the carbonate production of the basal part of bundles is not well known and shows values higher than those of the leaves. On the whole, the epiphytic carbonate annual production per surface meadow unit was estimated around  $400 \text{ g m}^{-2} \text{ year}^{-1}$ .

## The *Sabellaria spinulosa* colonies in the Gargano coastal area: a temporary storage of beach sand in temperate reef constructions

Lisco S.<sup>1</sup>, Moretti M.\*<sup>1</sup>, Moretti V.<sup>2</sup>, Cardone F.<sup>3</sup> & Corriero G.<sup>3</sup>

1. Dipartimento di Scienze della Terra e Geoambientali, Università degli Studi di Bari "A.Moro", Bari

2. Dipartimento di Biologia, Università degli Studi di Bari "A.Moro", Bari. 3. Regione Puglia, Servizio Ecologia - Ufficio VIA, Bari.

Corresponding email: [massimo.moretti@uniba.it](mailto:massimo.moretti@uniba.it)

Keywords: *Sabellaria spinulosa*, reef, Gargano.

The sedentary polychaete *Sabellaria spinulosa* (Leukhart 1849) is a suspension feeder that builds tubes by cementing together terrigenous particles. Under a narrow set of environmental conditions, *S. spinulosa* can form reefs (consisting of hundreds or thousands of worm tubes) that can be very variable in height, size and patchiness. The more developed reefs form in areas with large and continuous supply of sand, turbulent water, nutrient availability and rocky seafloor sectors (that often represent the starting point of the reef formation). Reefs of *S. spinulosa* are restricted to shallow marine environments and are quite easily broken up by storm waves. Nevertheless, these reefs show a rapid growth after the wintery degeneration phases.

Recently, a large reef of *S. spinulosa* has been discovered and described with a multidisciplinary approach along the northern Gargano coast at (Torre Mileto, Southern Italy Adriatic sea). In this communication, we will detail only the main sedimentological data and results. Sampling procedures were carried out seasonally in four different times in a year of ecological/sedimentological monitoring survey. Three transects perpendicular to the coast were traced and monitored: the central one along the reef and the other two in the eastern and western soft substrate sectors, analysing and sampling foreshore and shoreface sediments (until depths of 5-6 m). In order to evaluate the kind of terrigenous particles that are involved in the worm tubes constructions, detailed granulometric and petrographic analyses were carried out on both reef and soft-sediment substrate samples. *S. spinulosa* seems to prefer grains with diameter comprised between 128 µm and 295 µm, nevertheless, between adjacent tubes, larger and smaller grains are trapped too. The size distribution of the grains incorporated in the reef have been compared with soft-sediment substrate grain-size: no appreciable differences have been detected. Furthermore, *S. spinulosa* seems to have not preferences on the grain composition. We have measured the same modal composition in the worm tubes and surrounding soft-sediments (mainly quartz, carbonate lithoclast and bioclast). More analyses have been carried out on other morphoscopic features (relationships between the tube diameters and D50 of worm tube sands, morphometric parameters of the trapped grains, etc.) trying to highlight the role of *S. spinulosa* in the selection of grains for the tube construction.

We have also evaluated the role of the reef in the mitigation of coastal erosion in this sector of the Gargano Promontory. The reef is made up of a 50% of terrigenous sediment, 30% of intergranular porosity and 20% of worm tubes. Field observations and the analysis of orthophotos of different periods show that the beaches that are located in eastern sectors with respect to the reef (in the direction of main longshore currents) are prograding or stable, while the western beaches seem to record only coastal erosion. The reef acts as physical barrier for storm waves and long-shore currents and represents a temporary storage of sandy sediments that can supply the beaches during main winter storm wave events.

## **Geomorphological evolution of the Venice littoral during the Holocene: impact of natural and human-induced processes**

Rizzetto F.\*

Istituto di Scienze Marine, Consiglio Nazionale delle Ricerche, Venezia.

Corresponding email: [federica.rizzetto@ismar.cnr.it](mailto:federica.rizzetto@ismar.cnr.it)

Keywords: Geomorphological evolution, coast, Venice.

The Venice littoral is composed by an alignment of barrier islands, which separates the lagoon from the Adriatic Sea. Water exchange between lagoon and sea occurs through three inlets, named, from north to south, Lido, Malamocco, and Chioggia, respectively.

Data acquired from recent multidisciplinary researches have allowed improving the knowledge about the geomorphological evolution of the coast. In particular, the present work is focused on the modifications of the littoral close to the Lido inlet, occurred during the Holocene and produced both by natural and anthropogenic processes. This area has been chosen as an example of highly dynamic environment, largely affected by human activities.

Multidisciplinary investigations allowed reconstructing the Holocene sequence of the region (Tosi et al., 2007) and identifying the ancient positions of the coastline in the past millennia. The morphological evolution of the coast has been well documented since the 14<sup>th</sup> century, owing to the good availability of historical maps. Despite errors of accuracy and precision, as the maps were realized exclusively through field measurements, these ancient documents have given a clear and direct evidence of the real past conditions of the littoral and have revealed the effects of the first human impacts on the coast.

With reference to more recent times, detailed and accurate information has been obtained from the analysis of satellite images acquired in the last decades and aerial photographs taken since the 1940s, which have documented rapid transformations, mainly induced by anthropogenic interventions.

Clear relationships exist among climate changes, coastal processes and morphological variations. Littoral modifications have occurred in response to both short-term events (i.e. waves, tides, storms, winds) and long-term events (sea-levels rise, land vertical movements). In historical times, humans have significantly influenced the variable contributions of these factors and have altered natural sediment supplies and transport pathways. Since the end of the nineteenth century, the construction of two jetties at the Lido inlet and coastal defences along the near littoral has seriously modified the beach morphodynamics; moreover, in combination with urbanization and other local anthropogenic activities, these structures have largely altered the environment and rapidly changed its geomorphological setting. At present, new important transformations are affecting this coastal area as a consequence of the MOSE project, a system of mobile gates installed at the three lagoon inlets to protect Venice from flooding.

Tosi L., Rizzetto F., Bonardi M., Donnici S., Serandrei Barbero R. & Toffoletto F. 2007. Note illustrative della Carta Geologica d'Italia alla scala 1:50.000. 128 Venezia. APAT, Dip. Difesa del Suolo, Servizio Geologico d'Italia, SystemCart, Roma.

## **The state of activity of the canyons in the Napoli Bay (Southern Tyrrhenian Sea - Italy), inferred by the analysis of morphometric parameters**

Roca M.\*<sup>1-2</sup>, Budillon F.<sup>2</sup> & Pappone G.<sup>1</sup>

1. Dipartimento Scienze e Tecnologie, Università degli studi di Napoli "Parthenope". 2. Istituto per l'Ambiente Marino Costiero - CNR, Napoli.

Corresponding email: [mariangela.roca@uniparthenope.it](mailto:mariangela.roca@uniparthenope.it)

Keywords: Morphometry of canyon system, Napoli Bay, Southern Tyrrhenian Sea.

Variations in the equilibrium profiles of submarine canyons (EP) are normally regarded as proxies for local tectonic/morphologic disturbance, cessation of sediment fluxes or sediment burial. Recent researches have also proved that under favorable conditions canyons may continue to transfer sediments to deep sea environments, regardless of sea level conditions, if sediment yield is upheld. We report on the state of activity of two adjacent canyon systems, Magnaghi (MC) and Dohrn (DC) canyons (Napoli Bay, Southern Tyrrhenian Sea), on the base of their morphometric parameters, derived by a Digital Terrain Model analysis. These canyons represent the major drainage pathways of shelf sediments towards the deep basins off Ischia and Capri island respectively, in particular of volcanic-clastic products from eruptive centers in the area. We measured significant values as A (catchment extension), S (slope gradient), T (thalweg depth), RL and LL (elevation of lateral levees), IS (index of sinuosity) and IC (index of curvature) to verify their state of activity. We observed that MC has achieved an equilibrium profile, according to Mitchell et al., 2005, even though it lacks of a fan system at the base of slope; the DC shows an irregular depth profile and displays a very large fan. A general tendency of the main axes of both canyons to anticlockwise deflection is observed together with a higher elevation of the right levees than the left ones, possibly driven by Coriolis forces (Cossu et al., 2013); however the main bends in thalweg course are not really gradient-driven meanders, but diversions controlled by local tectonic lineaments. The absence of a MC fan lobe, unforeseen so far, is here inferred to the emplacement of the Ischia Debris Avalanche 3.5 ky BP (De Alteriis et al., 2010), which most likely caused the removal of the fan. The DC graphs prove a deactivation of the southern tributary channel, a re-incision of the main channel and a successive burial of the northern branch, due to recent activity of Phlegrean Fields vents.

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Cossu R. & Wells M. 2013. The possible role of Coriolis forces in structuring large-scale sinuous patterns of submarine channel-levee systems. *Phil. Trans. R. Soc.* 371, no. 2004 20120366. doi: 10.1098/rsta.2012.0366.

Mitchell N.C. 2005. Interpreting long-profiles of canyon in the USA Atlantic continental slope. *Mar. Geol.*, 214,75-99.

## Recent evolution of a delta plain and a coastal zone: the Volturno delta system (southern Italy)

Ruberti D.\*<sup>1</sup>, Vigliotti M.<sup>2</sup>, Di Natale M.<sup>1</sup> & Ivaldi R.<sup>3</sup>

1. Department of Civil Engineering, Design, Construction Industry and Environment (DICDEA) - Second University of Naples, Aversa (CE). 2. Department of Environmental, Biological and Pharmaceutical Sciences and Technologies, Second University of Naples, Caserta. 3. Istituto Idrografico della Marina, Genova.

Corresponding email: [daniela.ruberti@unina2.it](mailto:daniela.ruberti@unina2.it)

Keywords: Campania Plain, Volturno delta system, coastal erosion, reclamation, historical cartography.

The Campania Plain has developed following the Holocene glacio-eustatic sea level rise after the Last Glacial Maximum. The establishment of the coastal progradational phase, in the last about 6000 ky BP, allowed the formation of a wave-dominated delta system of the Volturno River, with flanking strandplains forming beach-dune ridges partially enclosing lagoonal-marshy areas. The progradation of the Volturno alluvial delta created favourable conditions for the development of continental environments, characterised by marshes and wetland as an integral part of the alluvial flood plain within the lower Volturno delta system. The formation of a mature sand bar complex offshore caused a progressive isolation of the former coastal lagoonal area from the open Tyrrhenian Sea. About 2 ky cal BP, beach and lagoonal environments still persisted along the present coastal zone. Most of the marshy areas were reclaimed from 1811 until the early 1900s. As a result of the reclamation interventions, the development of agricultural and farming, with associated processing industries, took place as well as a strong urbanization. Among the morphological changes of the landscape induced by land reclamation, the Volturno River delta plain and related strandplain variation is perhaps the most striking. The analysis of the historical cartography and the comparison with recent maps up to the present, provide a sufficiently exhaustive picture of the evolutionary trend of the studied littoral. From the Roman times to the last century, the entire coastline has experienced progradational trends, with decreasing values from 100 m at 10 m per century, proceeding from southeast to northwest, with 15 m/year progradation speed recorded in the period 1809-1907. The GIS based comparison of georeferenced cartography has allowed to record the peak of progradation of the Volturno delta system during the 1800's, after which it began to evolve from cusped to arcuate in a strongly asymmetric form. In fact, the first anthropic interventions along coastline and the catchment area reduced the volume of sediment available for the sedimentary balance, so that in the last century the erosion at the delta mouth triangle was registered. The eroded sediments of the cusped delta apex were gradually stored by longshore transport along the lee-side; at the end, the shoreline has become parallel. In fact, from 1907 to 1954 the shoreline near the mouth area suffers erosion phenomena with a rate of about 2 m per year, with the left mouth area subjected to a less conspicuous retreat (about 1 m a year). From 1954 to 1982 the backward trend is continuing with values between 1 and 6 m/year in the right mouth area, and 1 to 19 m/year in left area. This phenomenon is partly due to massive urbanization and building of defensive works on the right side which have "hardened" the coast; conversely, the establishment of the nature reserve on the other side has left the coastal area exposed to the erosion process. The comparison between the results of bathymetric measurements conducted in the 1887 and in 1987 enabled a detailed assessment of the morphological changes occurred during the last century showing the sea bed most severely eroded near the wings of the Volturno river delta; by contrast, in the northern and southern parts more sediments were deposited offshore.

## Quaternary marine-to-freshwater ostracods and other invertebrates from the SE Sicily

Sciuto F., Rosso A. & Sanfilippo R.\*

Department of Biological, Geological and Environmental Sciences, University of Catania.

Corresponding email: [sanfros@unict.it](mailto:sanfros@unict.it)

Keywords: Quaternary, SE Sicily.

Lower Pleistocene marine to lacustrine sediments widely crop out along the SW edge of the Hyblean Plateau near the Cartiera Mulino (Vittoria), SE Sicily. Malacofaunas testify very shallow and sheltered marine palaeoenvironments referable to the muddy sands in sheltered areas (SVMC Biocoenosis) dominated by metaphytes. The current palaeoecological study focuses on further associated invertebrate groups, i.e. ostracods, bryozoans and serpulideans.

Ecological requirements of detected species joined to sedimentologic and taphonomic features allowed depositional environments to be defined, and palaeobasin evolution to be reconstruct.

Along a section, 6 metres thick, a total of 8 bulk-samples were collected, each showing variable species/specimen richness of different taxonomic groups, partly as a consequence of selective diagenesis.

In the basal part ostracods are elsewhere dominant, with prevailing *Aurila*, *Bairdia*, *Urocythereis*, *Costa* and *Graptocythere* species. Among serpulideans 6 species and a few specimens were recognised, *Vermiliopsis striaticeps* and *Janua pagenstecheri* being the most abundant. Bryozoans consist of 14 species with dominant *Crisia fistulosa* and other congeners. Evidences on the encrusting undersides of serpulid and bryozoan skeletons show plant casts. These bioimmurations testify a sea-grasses rich palaeoenvironment, in agreement with palaeoecological data gained through molluscs and the presently studied groups. The presence of the bryozoan *Cryptosula pallasiana* and the incidence of teratologic specimens of *Elphidium* in the upper portion could testify a slight shallowing and a salinity decrease upwards.

Central layers completely lack in studied benthic groups and nearly entirely include reworked deep-water planctonic foraminifers, clearly resulting from Lower Pliocene (Trubi Formation) to Lower Pleistocene sediments.

The top part of the section only includes microfaunas, with ostracods belonging to *Ilyocyris bradii*, *Candona neglecta* and *C. angulata*. The abundance of these species, as well as presence of characean oogones, could testify an uplift of the palaeobasin and/or the onset of confined environments with lacustrine conditions.

## Quaternary coastal deposits of NW Sardinia (Italy): the anomalous position of MIS 7

Sechi D.\*<sup>1</sup>, Andreucci S.<sup>2</sup> & Pascucci V.<sup>3</sup>

1. Dipartimento di Scienze Naturali e del Territorio, Università di Sassari. 2. Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari.  
3. Dipartimento di Architettura, Design e Urbanistica, Università di Sassari.

Corresponding email: [dasechi@uniss.it](mailto:dasechi@uniss.it)

Keywords: Sardinia, MIS 7, Neotectonic.

The Quaternary stratigraphy of NW Sardinia (Mediterranean Sea) consists of different coastal deposits grouped into mainly 5 unconformity-bounded units (U0, U1, U2, U3a/b and U4) spanning from MIS 8 to MIS 3 (Pascucci, 2014).

The studied Late Pleistocene deposits crop out along an embayment (NW coast) southward-opened and confined between two NW-SE orientated normal faults. U1 (gravelly-beach deposit) rests unconformable on the bedrock at an elevation of +1.5 m (apsl) and correlated to the MIS 7. An erosive surface separates U1 and U2. This latter, consists of braided systems dated at 200±22 ka, thus related to the MIS 7/6 transition. On U2 rests unconformable U3a characterized by a sandy pocket beach system (~ 2 m apsl) and OSL dated at 130±11 ka (MIS 5e). Finally, the succession is capped by alluvial-fan deposits (U4) referred to the Last Glacial period.

Although, Sardinia has been considered tectonically stable since the early Pleistocene, the MIS 7 elevation at +1.5±1 m is several meters above the worldwide-accepted position. This cannot be explained with the only sea level eustatic variation, thus likely local uplift can be inferred. Moreover, this anomaly agrees to what several Authors reported for some late Pleistocene marine deposits and/or tidal notches along the Island coasts: such as the Orosei Gulf (E coast; Ferranti, 2006); Porto Paglia (SW; Battau, 2011) and San Giovanni di Sinis (W; Lecca and Carboni, 2007; Andreucci, 2009).

These evidences might suggest that a tectonic uplifting at regional scale affected the Sardinia at least before the MIS 5e (125 ka).

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## **SESSIONE S10**

### **Geomaterials and their likes: from Nature to technology and manufacturing**

#### *CONVENORS*

*G. Cruciani (Univ. Ferrara)*

*L. Gaggero (Univ. Genova)*

*P. Cappelletti (Univ. Napoli)*

## The “Modica” stone: study of salt damage and assessment of efficacy of different consolidants

Aloise P.\*<sup>1</sup>, Belfiore C.M.<sup>1,2</sup>, Crisci G.M.<sup>1</sup>, Fichera G.V.<sup>2</sup>, La Russa M.F.<sup>1</sup>, Pezzino A.<sup>2</sup> & Ruffolo S.A.<sup>1</sup>

1. Dipartimento di Biologia, Ecologia e Scienze della Terra (DiBEST), Università della Calabria. 2. Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Sezione di Scienze della Terra.

Corresponding email: [piergiorgio\\_aloise@libero.it](mailto:piergiorgio_aloise@libero.it)

Keywords: Sal crystallisation, nanomaterials, consolidation, limestone.

The deterioration of a stone material is strictly related to its pore structure that affects the interaction between surface and environmental agents, especially water that transports large amounts of salts into the stone. Indeed, salt crystallization, is one of the most dangerous weathering agents in porous building materials (Belfiore et al., 2012; La Russa et al., 2013). This damage depends on numerous factors: type and quantity of salt in the stone, the shape of crystals, the super saturation of the salt, the pore size and the force of repulsion between salt and the walls of the pores (Scherer, 2004; La Russa et al., 2013), characteristics of porous network and environmental conditions. Specifically, pore size distribution is considered as a principal factor controlling the uptake and transport of liquid within a stone, because it determines the degree of damage of a rock subjected to salt crystallization attack (Yu and Oguchi, 2010). In particular, the crystallization pressure of salt crystals, growing in confined pores, is found to be the main cause for damage (Steiger, 2005; La Russa et al., 2013). The conservation of such degraded stone is an important step in the field of restoration; therefore, an essential aim of the scientist is the correct choice of conservation strategies to be applied to each case study. Specifically, the consolidation of degraded stone materials represents a crucial issue in the field of restoration of cultural heritage: is used to improve the cohesion of weathered stone when serious decay patterns and in-depth cohesion loss are present, consequently increasing the mechanical strength of the rock. This contribution presents the results of a laboratory experimentation carried out on a limestone largely used in the Sicilian Baroque architecture, namely the *Modica stone* (Belfiore et al., 2012). Several specimens, collected from a historical quarry nearby the city of Modica were artificially degraded by salt crystallization tests (EN 12370, 2001). Then, degraded samples were treated with three different consolidating products: i) a suspension of nanolime in isopropyl alcohol, ii) a suspension of nanosilica in water, iii) ethyl silicate dispersed in white spirit. A systematic approach, including thin section observations mercury intrusion porosimetry (MIP), colorimetric analysis, peeling tests (ISO 11664-4:2008, 2008; Drdacky et al., 2012), point load test (ASTM D 5731, 2002) and scanning electron microscopy (SEM) analysis, was used to evaluate the correlation between salt crystallization and both microstructural and chromatic variations of the examined limestone as well as the efficacy of treatments. The consolidating behaviour of the tested products was also appraised by repeating salt crystallization tests after consolidation, in order to assess the resistance of treated stone against the crystallization pressure. Results showed that some treatments, although inducing an enhancement of stone cohesion, lead to an increase of the crystallization pressure, which could generate dangerous susceptibility to degradation.

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## Structural relaxation along solid solutions: from the crystal field theory to the polyhedral bond valence approach

Ardit M.\*<sup>1</sup>, Dondi M.<sup>2</sup> & Cruciani G.<sup>1</sup>

1. Dipartimento di Fisica e Scienze della Terra, Università di Ferrara. 2. ISTECCNR Faenza.

Corresponding email: [rdmttt@unife.it](mailto:rdmttt@unife.it)

Keywords: Structural relaxation, crystal field strength, polyhedral bond valence.

The degree of structural relaxation due to the isovalent substitution of cations along a solid solution can be evaluated by means of the structural relaxation coefficient,  $\varepsilon$ . This coefficient, defined as the measure of the mismatch between *average* and *local* bond distances at the crystallographic site where the substitution takes place, can vary between 0 and 1 (Urusov, 1992), i.e. from absent to total relaxation. Electronic absorption spectroscopy is one of the most common technique used in mineralogy to obtain local bond distances. Deconvolution of electronic spectra allows to calculate the crystal field strength ( $10Dq$ ) that, according to the crystal field theory, is proportional to the inverse fifth power of the mean distances from XRD (Langer, 2001). In a recent work (Ardit et al., 2014) it is unequivocally demonstrated, at least for Al $\leftrightarrow$ Cr substitutions at octahedral site, that  $\varepsilon$  inversely scales with the absolute difference between crystal field strengths of solid solution end-members. On the other hand, it is not always possible to obtain a complete solid solution, and the linear extrapolation of structural and optical parameters up to one of the end-members may lead to incorrect values. In light of this, a new approach based on the bond-valence method (Brown, 2002) has been developed to evaluate the lattice strain associated to different local arrangement of ligands at a coordination site (Dondi et al., 2014). In detail, it has been demonstrated that the  $BV_{sum_{obs}}/BV_{sum_{calc}}$  ratio linearly scales with  $10Dq$  (i.e. with the local bond distances of the involved crystallographic site). This ratio entails the observed bond-valence sum of polyhedra which share the oxygens coordinating a doped site ( $BV_{sum_{obs}}$ ) with respect to the bond-valence sum calculated from ideal bond distances for each polyhedron ( $BV_{sum_{calc}}$ ). In this contribution, the aspects of above will be discussed through different case studies (i.e. the effect of Cr<sup>3+</sup> and Co<sup>2+</sup> at octahedral and tetrahedral sites, respectively) and by a comparison of structures having a different atomic arrangement (i.e. the case of II-NaMP<sub>2</sub>O<sub>7</sub> pyrophosphates).

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## Non-destructive methods for stone materials characterization

Armienti P.\*<sup>1</sup> & Montagnini D.<sup>2</sup>

1. Dipartimento di Scienze della Terra, Università di Pisa. 2. Datageo Srl, Navacchio (PI).

Corresponding email: [armienti@dst.unipi.it](mailto:armienti@dst.unipi.it)

Keywords: Image Analysisism, Non destructive method, stone materials.

Technical properties of stone materials are strongly dependent on their textural organization: in this note we present some application of image analysis techniques developed at the DST of Pisa to solve petrologic problems in basic research fields, but of potential commercial interest. Both methods collect data on the smooth surface of a slab and are not destructive, not requiring the preparation of thin sections.

*Petrr*® is a technique which can be applied to coloured stones, like granites, in which each mineral phase has a distinguishable colour. *Panoptes*® applies to materials in which grains have identical optical properties. Both methods have been patented.

*Petrr*® is based on a cursory method which provides a quantitative modal analysis that derives from comparison of RGB spectra of whole rocks and single minerals. The test can be applied to diverse fields ranging from the certification of the colour of a composite material, to archeometry and study of the modality of fracturation upon load. *Panoptes*® is a sophisticated technique that applies the Snell law to detect grain boundaries in monomineralic rocks, allowing the accurate spatial determination of structural surfaces and the related Grain Size Distribution. We show an application related to the non destructive determination of the yield strength upon compression and flexure and a method for the individuation of blocks that may undergo spontaneous fracturing.

## Radiometric characterization of building materials from Eastern Sicily

Belfiore C.M.<sup>1</sup>, Fiannacca P.<sup>1</sup>, Lo Nigro L.<sup>2</sup>, Lo Nigro S.<sup>2,3</sup>, Marino M.C.<sup>4</sup>, Pezzino A.<sup>1</sup>, Spartà S.<sup>4</sup> & Viccaro M.\*<sup>1</sup>

1. Dipartimento di Scienze Biologiche Geologiche e Ambientali - Università di Catania. 2. C3SL s.r.l. - Spin Off dell'Università di Catania. 3. INFN - Sezione di Catania. 4. Servizio Fisica Sanitaria/SPPR - Università di Catania.

Corresponding email: [m.viccaro@unict.it](mailto:m.viccaro@unict.it)

Keywords: Building materials, radioactive nuclides, Eastern Sicily.

Regulation no. 305/2011 of the European Parliament and of the Council of March 9, 2011 sets the conditions for the commercialization of construction materials. According to the provisions of the Directive 2013/59/EURATOM of the European Council of December 5, 2013, which lays down basic safety standards for the protection against dangers arising from the exposure to ionizing radiations, it is recommended to develop a measurement protocol to be followed in radiometric characterization of building materials such as mortars, cements and stone materials. In particular, the accurate determination of the radionuclides U238, Th232 and K40 occurring in building materials is of primary importance. Eastern Sicily, chosen as the pilot site for the testing phase, is characterized by the presence of rocks that are frequently used as building materials which, for simplicity, can be grouped into three main geological domains: volcanic, sedimentary and crystalline basement. The diverse nature of the rocks of the three domains is reflected in their different compositional features in terms of major and trace element concentrations, also affecting the primary abundances of radioactive nuclides (for example, various isotopes of U, Th, K, Rn etc.). A simplified analysis of the geological context of eastern Sicily suggests that the basement rocks are potentially the richest in radionuclides (U <5 ppm, Th <23 ppm), followed by those belonging to the volcanic domain (U < 3 ppm, Th <17 ppm) and finally by the sedimentary ones (U <2.5 ppm, Th <8 ppm). The rocks of each of the three identified geological domains may also exhibit a compositional variability depending on structural and textural features such as grain size, mineral habit, shape and preferred orientation. In addition to these intrinsic rock features, other physical characteristics, such as the presence of porosity, open or closed, as well as the pore size may also exert an important control in determining the selective enrichment or depletion of specific elements. Although the extent and effectiveness of different processes in producing compositional anomalies in various types of rocks is not well known in quantitative terms, these anomalies appear to be very frequent in systems subjected to intense active tectonics responsible for fracturing processes at different scales (from micro-fracturing up to regional scale fault systems). The knowledge of how the chemical-physical characteristics of rocks of different nature may influence the production of such anomalies is today still rather limited. The presence of rocks with a wide spectrum of chemical and physical characteristics and the complex structural framework of eastern Sicily give therefore the possibility to investigate factors involved in the generation of anomalous concentrations of radioactive isotopes in rock types commonly used as building materials.

## Synthetic magnetic zeolites from waste materials: fly ash and red mud

Belviso C.\*<sup>1</sup>, Agostinelli E.<sup>2</sup>, Belviso S.<sup>3</sup>, Cavalcante F.<sup>1</sup>, Pascucci S.<sup>1</sup>, Peddis D.<sup>2</sup>, Varvaro G.<sup>2</sup> & Fiore S.<sup>1</sup>

1. Istituto di Metodologie per l'Analisi Ambientale - MAA-CNR, Tito Scalo (PZ). 2. Istituto di Struttura della Materia - CNR Area della Ricerca di Roma. 3. Università della Basilicata, Dipartimento di Scienze, Potenza.

Corresponding email: [claudia.belviso@imaa.cnr.it](mailto:claudia.belviso@imaa.cnr.it)

Keywords: fly ash, red mud, magnetic zeolites.

A new method is proposed to synthesise magnetic zeolites with suitable magnetic properties without the addition of iron oxide magnetic nanoparticles. The precursors employed for the synthesis are two waste materials, i.e. red mud (RM) and fly ash (FA), which are abundant, easy to recover and inexpensive. In addition, large amounts of FA and RM are deposited in landfills resulting in an increasing environmental problem.

The two waste materials were chosen because they both contain iron-based oxides, which are the most common magnetic materials used to induce magnetic properties in zeolites. RM is a waste material formed during the production of alumina when the bauxite ores are subjected to caustic leaching. RM are mineralogically characterised by the presence of iron oxides (i.e., primarily hematite and goethite with a minor boehmite component), while aluminium hydroxides, calcium oxides, titanium oxides, aluminosilicate minerals and sodalite occur as traces. However, the RM mineralogical composition varies due to the differences in the bauxite ores and the refining processes employed. The use of this waste material for zeolite synthesis has not been previously reported. FA is a by-product of thermal power plants and is used in concrete and cement manufacturing. FA is primarily composed of amorphous aluminosilicate and minerals, such as quartz and mullite. In addition, hematite, magnetite and carbon may also be present. More than half of FA is disposed of in landfills but in the last few years, much research has been focused on its use in solutions to environmental problems (Belviso et al., 2014) as well as for the synthesis of zeolites (Belviso et al., 2012).

The structural, microstructural and magnetic properties of precursors and synthetic zeolites formed from these two waste materials were investigated. Different types of zeolites were obtained for different FA/RM percentages and all of them possess sufficiently high magnetic moments to enable their easy separation from the solution using an external magnet. Therefore, the time consuming and expensive high performance centrifugation processes, which are typically employed to recover zeolites, can be eliminated.

The absorbance properties of the synthetic zeolites were determined by RO16.

Due to their properties, the synthetic newly-formed minerals can be used to solve water pollution problems and after their action they can be easily removed from solution.

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## Silicate glasses recycling: optimization of the procedure for tobermorite synthesis

Bernini F.\*, Malferrari D., Castellini E., Laurora A. & Brigatti M.F.

Department of Chemical and Geological Sciences, University of Modena and Reggio Emilia.

Corresponding email: [fabrizio.bernini@unimore.it](mailto:fabrizio.bernini@unimore.it)

Keywords: Tobermorite, Synthesis, Recycling.

Tobermorite identifies a group of layered-like calcium silicate hydrated minerals, with general formula  $\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot 4(\text{H}_2\text{O})$ , composed by the three polytypes plombierite, tobermorite and riversideite, which differ for the baseline periodicity (approximately 14.0, 11.3 and 9.30 Å, respectively) that is in relation with the different content of water molecules. Here, we aim at finding a system to recovery silicate glass from recycling through economically advantageous and ecologically sustainable synthesis of tobermorite.

Preliminary synthesis trials suggested the introduction of additives to enrich the calcium content and optimize the composition of the glass powder.

Different synthesis trials were performed varying: i) the ratio (weight/volume) between suitably corrected starting material and the alkaline solution simulating the hydrothermal environment; ii) the concentration of the alkaline solution; iii) the interaction time between the starting material and alkaline solution; iv) the reaction temperature; v) the reaction environment (open container or bomb); vi) the interaction mode (static or dynamic).

The main phases formed in all the synthesis trials are tobermorite 11Å in varying proportions depending on the treatment used and calcite. The quantitative mineralogical analysis of each phase was obtained using the Rietveld-RIR method and the employed structural models for the quantitative refinement are those defined by Battocchio et al. (2012), Bonaccorsi et al. (2005) and Merlino et al. (2001). The degree of crystallinity of tobermorite was evaluated according to the method proposed by Coleman (2005) which takes into account the shape of the peaks of the reflections (002), (220) and (222).

The main conclusions of this work are that at constant temperature of synthesis, the amount of formed tobermorite and its crystallinity increases when increasing the time of interaction. In 48 hours of interaction we obtained a compound characterized by the presence of about 60 w/w% of tobermorite. In all the tests, notwithstanding the synthesis conditions employed, the total amount of calcite that forms is almost constant and slightly higher than the starting quantity present in the glass. So the synthesis of tobermorite is an usefull process in recycling waste glasses.

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## Reactivity of fillosilicates kaolinite and montmorillonite towards $\mu$ -oxo complex of Fe(III) with phenantroline

Bernini F.\*, Malferrari D., Pignataro M., Castellini E. & Brigatti M.F.

Department of Chemical and Geological Sciences, University of Modena and Reggio Emilia.

Corresponding email: [fabrizio.bernini@unimore.it](mailto:fabrizio.bernini@unimore.it)

Keywords: montmorillonite, iron, phenantroline.

In the last decades many efforts have been devoted to functionalize clay minerals to impart them with specific properties, driven by the nature of the functionalising species and/or synergic effect resulting from the interaction. The best example of this trend is the synthesis and exploitation of pillared clays, organoclays, and clay mineral-polymer nanocomposites (Bergaya and Lagaly, 2011). In fact, clay minerals are particularly suited to host molecules able to exert a desired function: they are natural (not toxic), stable, biocompatible, available both as crystals and polydispersed powders. This is why the possibility to immobilize onto clays molecules having smart properties is still a goal of several current research, given the wide range of clay-functionalising molecules and properties that can be obtained.

The literature on Fe(III)-pillared clays is often lacking of a detailed description of the resulting structure; moreover, the loading of the materials starts from a mixture of iron species which makes heterogeneous also the iron speciation inside the mineral, dealing with partly hydrolyzed Fe(III) solutions. Here, we immobilize in a stable form a  $\mu$ -oxo Fe(III)-phenantroline complex  $[(\text{OH}_2)_3(\text{phen})\text{Fe}^{\text{III}}\text{OFe}^{\text{III}}(\text{phen})(\text{OH}_2)_3](\text{SO}_4)_2$  (phen= 1,10-phenantroline) onto kaolinite and montmorillonite with the aim of obtaining stable Fe(III)-modified materials in which the iron species present in the surface and/or in the interlayer of the clay minerals is clearly and univocally identified. We obtain this goal introducing onto clays an iron solution in which the Fe(III) is complexed by a phenantroline ligand: the complexation prevents Fe(III) precipitation and allows to work at weakly acid and neutral pH values in acetate buffer solution. The obtained Fe(III)-modified kaolinite and montmorillonite were analyzed through DR-UV-Vis, TG-mass and elemental analysis techniques which provides a full characterization of the obtained materials including the immobilized iron species. Preliminary results showing that the Fe(III)-phenantroline modified montmorillonite acts as a catalyst for the oxidation of guaiacol in the presence of hydrogen peroxide are also presented.

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## Characterization of CaO-based Sorbents for CO<sub>2</sub> capture: Sorbent Morphology and Reaction Kinetics

Biasin A.<sup>1</sup>, Zorzi F.<sup>2</sup>, Salviulo G.\*<sup>2</sup> & Strumendo M.<sup>1</sup>

1. Department of Industrial Engineering, University of Padova. 2. Department of Geosciences, University of Padova.

Corresponding email: [gabriella.salviulo@unipd.it](mailto:gabriella.salviulo@unipd.it)

Keywords: Carbon Capture and Storage(CCS), thermo-gravimetric analysis (TGA), in-situ X-Ray Diffraction XRD.

Among greenhouse gas emissions, anthropogenic CO<sub>2</sub> is widely recognized as the major contributor to global warming and climate change effects. Carbon dioxide emissions have rapidly increased due to the technological and industrial development and in the last decade the reduction of the CO<sub>2</sub> emitted by power generation industry (mainly the power plants based on fossil fuel combustion and coal gasification) has become an important worldwide scientific goal. Among the Carbon Capture and Storage (CCS) technologies, a promising cost effective CO<sub>2</sub> capture technique involves the utilization of calcium based solid sorbents. This approach exploits the reaction of calcium oxide (CaO) with CO<sub>2</sub> to form calcium carbonate (CaCO<sub>3</sub>) under operative conditions not reachable with other CCS technologies, namely at high temperatures. The carbonation reaction (CaO (s) + CO<sub>2</sub> (g) → CaCO<sub>3</sub> (s)) is reversible and hence this technology should be based on cyclic stages of carbonation and of calcination. However, it is well known that CaO-based sorbents are usually subjected to a marked decay in the CO<sub>2</sub> capture capacity after multiple calcination-carbonation cycles, and this loss-in-capacity is believed to be caused by the sintering and the loss of the available pore volume of the sorbent particles. In order to improve the capture capacity of CaO-based sorbents, it is important to deeply understand the mechanism of calcium oxide carbonation and the kinetics controlling this gas-solid reaction. The purpose of this project is to investigate the relationship between sorbent morphology (before carbonation) and carbonation kinetics. In the present work, calcium oxide carbonation kinetics was followed by means of thermo-gravimetric analysis (TGA), mainly using CaO samples previously obtained by several ex-situ calcination stages conducted in a muffle. A characterization of each sample (before the carbonation stage) was carried out utilizing BJH and BET methods for pore size distributions and specific surface areas estimation. X ray powder diffraction technique was used to collect specific information about the initial CaO crystallite size. Finally, the carbonation kinetic constants (intrinsic kinetic constant and diffusivity through the product layer) were obtained by fitting of TGA data at different temperatures and were correlated with the starting CaO crystallite size and the sorbent structural parameters (porosity, specific surface, “structural parameter”). Additionally, the evolution of the CaO sorbent crystallite size during the calcination was monitored using in-situ X ray diffraction (XRD), at different calcination temperatures and with different atmospheres.

## LightWeight Aggregates from industrial and c&D waste recycling: new perspectives for environment safeguard and energy saving

Cappelletti P.\*<sup>1</sup>, de Gennaro R.<sup>1</sup>, D'Amore M.<sup>1</sup>, Graziano S.F.<sup>1</sup>, Langella A.<sup>2</sup>, Zanelli C.<sup>3</sup> & Dondi M.<sup>3</sup>

1. Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università Federico II, Napoli. 2. Dipartimento di Studi Geologici ed Ambientali, Università del Sannio, Benevento. 3. ISTEC-CNR, Faenza.

Corresponding email: [piergiulio.cappelletti@unina.it](mailto:piergiulio.cappelletti@unina.it)

Keywords: Recycling, waste management, lightweight aggregates, energy efficiency.

Recent advancements in R&D of LightWeight Aggregates (LWA) are overviewed. Aggregates are natural or artificial cohesionless materials constituted by elements with different grain size. LWA must possess: i) a mass/volume ratio not higher than 2000 kg/m<sup>3</sup> for each single particle; ii) a bulk unit weight not higher than 1200 kg/m<sup>3</sup> (EN 13055-1). LWA historically used in architecture are natural products such as pumices, diatomites, etc. During the fifties, the growing market demand enhanced the production of new LWA obtained by the expansion by heating at high temperatures of some natural materials such as clays, vermiculite and perlite. Reference parameters necessary to achieve an expansion are the SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub> ratio and the fluxing oxides (Fe<sub>2</sub>O<sub>3</sub>+MgO+CaO+Na<sub>2</sub>O+K<sub>2</sub>O); actually, these factors are not sufficient to determine the real expansion of the material for which it is necessary the occurrence of gas developing substances at raw materials' softening temperature. Recent investigations demonstrate that it is possible to produce LWA by using other natural materials such as tuffs, ignimbrites and zeolitized epiclastites as well as industrial wastes and recycled materials (Kazantseva, 1997; de Gennaro, 2004; 2007; 2009). Promising results were obtained with porcelain stoneware and ornamental stone polishing muds which contain small amounts of abrasive (max 3%wt SiC) that is the expanding agent necessary for the bloating. Good results were obtained also by mixing these muds with zeolite-rich rocks: the LWA obtained show similar or even better features that those currently marketed and provide a good prospect for the production of lightweight structural concretes. The proposed process also accounts for environmental positive benefits as these wastes of the ceramic or stone industry (tuffs included) have no current applications and need to be landfill disposed. Glass is also a recycled material useful for the production of expanded aggregates with good technical properties in the cement industry (Ducman et al., 2002; Lebullenger et al., 2010). Expanding agents are calcium carbonate or chalk, sodium sulphate, mixture of iron oxide with carbon, silicium carbide and nitride compounds. Other industrial wastes tested in the LWA production are the fly ashes and sewage sludge from wastewater treatment plant (Cheeseman & Viridi, 2005; Ramamurthy et al., 2006). A further application sector is the manufacturing of lightweight cement-based insulating panels, to improve the energetic efficiency of buildings.

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## Nucleation of CAS by thermal treatment of Cs-clinoptilolite

Cerri G.\* & Brundu A.

Dipartimento di Scienze della Natura e del Territorio, Università di Sassari.

Corresponding email: [gcerri@uniss.it](mailto:gcerri@uniss.it)

Keywords: CsAlSi<sub>5</sub>O<sub>12</sub>, clinoptilolite, nuclear waste.

Clinoptilolite is a zeolite highly selective toward cesium cation, thus is employed for the decontamination of radioactive wastewater to remove Cs radioisotopes (Armbruster, 2001). Heating is one of the methods tested to prevent cesium release from spent clinoptilolite. Due to the high thermal resistance of this zeolite in Cs-form, temperatures up to 1000-1100 °C have been required to attain an almost complete cesium immobilization inside materials prevalently amorphous (Komarneni & Roy, 1981; Cappelletti et al., 2011). On the other hand, crystalline Cs-bearing phases like CsAlSi<sub>5</sub>O<sub>12</sub> (CAS) have been often indicated as potential host for cesium radioisotopes (Gatta et al., 2008). This paper shows the possibility to obtain CAS by thermal treatment of a Cs-clinoptilolite.

Following a procedure already tested (Brundu et al., 2008), a powder containing about 90 wt.% of clinoptilolite has been prepared with the same Sardinian zeolite-rich rock used by Cappelletti et al. (2011) (QXRPD analysis: Siemens D5000 diffractometer; Bruker Topas software). Clinoptilolite has been initially Na-exchanged (10 cycles in 1M NaCl solution; s/l = 30 g/l) then conducted in Cs-form (5 cycles; 0.5M CsCl). Chemical analyses (ICP-MS) of Na- and Cs-exchanged materials have been performed at Actlabs (Ontario, Canada).

Taking advantage of a TA-Instrument Q600, amounts of about 15 mg have been heated up to 1300 °C (10 °C/min; air flow 100 ml/min; no isothermal step at 1300 °C). Several experiments have been performed by varying the cooling time and/or by re-heating samples already treated. Tests have been repeated to check the results. Heated samples has been investigated with a Bruker D2 diffractometer using a zero-background sample holder. So far, the best CAS pattern is related to the material that followed the path: RT→1300°→RT (fast cooling)→1300°→RT (cooling: 10 °C/min). Basically, this sample has a structure totally crystalline.

The ideal reaction  $Cs_6Al_6Si_{30}O_{72} \cdot nH_2O \rightarrow 6CsAlSi_5O_{12} + nH_2O \uparrow$  summarizes the transformation of Cs-clinoptilolite.

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## Characterization of the pore system of commercial bricks: a new perspective combining 2D and 3D imaging and traditional methods

Coletti C.\*<sup>1</sup>, Maritan L.<sup>1</sup>, Mazzoli C.<sup>1</sup> & Cultrone G.<sup>2</sup>

1. Dipartimento di Geoscienze, Università di Padova. 2. Department of Mineralogy and Petrology - University of Granada.

Corresponding email: [chiara.coletti@studenti.unipd.it](mailto:chiara.coletti@studenti.unipd.it)

Keywords: Porosity, Computed micro-tomography, Image analysis.

During the firing process of bricks, mineralogical and textural changes transform the base clay into an artificial aggregate, characterized by significant porosity. Pore morphology, pore-size distribution and interconnection model influence the physical properties and represent important parameters to evaluate the predicting durability of bricks. Indeed, the porosity is the principal factor of connection between building materials and environment and entails the capacity of water storage and circulation and therefore, in combination with crystallization of soluble salts or stress due to freeze-thaw cycles, determines the decay behaviour. Four commercial bricks used also in restoration, with different compositions and firing temperatures, have been here analysed. Mineralogy and chemistry were studied by Field Emission Scanning Electron Microscopy (FESEM), X-ray Fluorescence (XRF) and X-ray Powder Diffraction (XRPD). Decay accelerated ageing tests were carried out to evaluate their resistance to frost and salt crystallization (UNI EN 12371, UNI EN 12370), while ultrasound was measured to check the elastic-mechanical characteristics and the structural anisotropy. The distribution of pore access size (in the 0.001–100  $\mu\text{m}$  range) was determined by means of Mercury Intrusion Porosimetry (MIP). More information was defined measuring water absorption and drying according to the method described in UNI EN 772-7 normative. Capillarity rise, drying index, apparent and real densities, open porosity and degree of connection of pores were calculated. Size, morphology and texture of pore matrix (closed and open porosity) was detected by the 2D digital image analysis (DIA), carried out processing back-scattered images acquired by Scanning Electron Microscopy (SEM), and by 3D models, obtained from computed micro-tomography ( $\mu\text{-CT}$ ). The present work represents a preliminary study based on a multianalytical approach that combines various methods which investigate different size and aspects of the pore system, in order to draft a more complete knowledge of the porosity of bricks and optimize new mix designs to use in restoration and in modern buildings. This will represent a starting point to define a protocol for quantification and parameterization of morphological features of voids, through 2D and 3D digital image processing techniques in view of restricting and substituting the traditional method of mercury intrusion porosimetry.

## Zn-biominerals: a perspective for environmental technologies to treat mine waters

De Giudici G.\*, Medas D., Podda F., Sanna R., Scorciapino M., Floris C. & Casu M.

Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari.

Corresponding email: [gbiudic@unica.it](mailto:gbiudic@unica.it)

Keywords: bioremediation, bioremediation, sustainability.

Since life flourishing, biological processes have been producing a profound impact on the Earth's environment (Hazen et al. 2008). Often, biomineralization processes respond to processes of life adaptation to extreme environments. Science and technology have advanced to the point where their relationship can now be explored in interdisciplinary studies. Thus, Nature offers many examples of sustainable materials that can be used in environmental and material science technologies.

An extracellular Zn-biomineralization seasonally occurs in Naraculi river in the mine area of Ingurtosu (Sardinia, Italy). This biomineralization is made of hydrozincite and has relevant environmental implication for the abatement of Zn transported by river water. The cyanobacteria *Scytonema sp.* is responsible for the hydrozincite biomineralization. Several different factors affect the Naracauli biologically controlled mineralization, and bioremediation technology should be calibrated to optimize many of these factors. However, the Naracauli biomineralization occurs extracellularly, thus it is intrinsically a good candidate to be synthesized from Zn adsorption and nanocrystal nucleation onto a template.

In this work, biomineral hydrozincite is investigated in order to assess molecular mechanism ruling nucleation and growth. Wanty et al. (2013) found that Zn is adsorbed onto organic filaments, and hydrozincite nanocrystals there nucleate and aggregate to form (100) flattened mesocrystals. Biologically produced hydrozincite was sampled and then analyzed by various techniques. Focusing Ion Beam was used to cut oriented thin slices comprising both organic filaments and hydrozincite mesocrystals. The thin slices were then investigated by HR-TEM imaging finding that the organic filaments are substantially made of an amorphous phase. Then, organic molecules were extracted from the biomineralization material and analysed by H-NMR finding the lipidic composition. Actually, the ongoing research is aimed to fully characterize the *Scytonema sp.* produced template, and then nucleate hydrozincite from adsorption of Zn onto a corresponding synthetic template.

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## Use and exploitation of Piemonte dimension stone (NW Italy)

Dino G.A., Borghi A.\*, d'Atri A. & Martire L.

Dipartimento di Scienze della Terra, Università di Torino.

Corresponding email: [alessandro.borghi@unito.it](mailto:alessandro.borghi@unito.it)

Keywords: dimension stone, quarrying activity, Piemonte.

Stone materials represent the direct evidence of history and cultural heritage of important Italian areas. In particular, Piemonte region (NW Italy), thanks to the vicinity to the Alpine chain, shows a strong presence of local stones for the construction of buildings and infrastructures. Here stone has been widely exploited and used in the historical and contemporary buildings, monuments and urban art (Borghi et al., 2013), but also for local applications, such as rural buildings and villages (e.g. mountain huts, barns, pastures), street furniture, flooring, paving, stairs of local buildings (Dino & Cavallo, 2014). Piemonte valleys are characterized by the presence of quarrying activities (closed and still in progress) and of working plants, so that villages and towns present in Piemonte valleys widely employed, with different techniques, local stones. These rocks are mainly connected to siliceous materials such as granites (Montorfano and Baveno granites, above all), gneisses (beole and serizzi from Verbano – Cusio – Ossola area; Luserna stone, Malanaggio Stone, Villarfochiardo Stone and Cumiana Stone from Cottian Valleys) and quartzite (*Bargiolina*), but also to marble (Palissandro from Crevoladossola, Candoglia and Ornavasso marbles) and biocalcarenites (Cantoni Stone). Local applications for rural villages, squares, city centres, etc.. have to be considered as “cultural heritage”, because stones represent local history and culture and must be preserved as heritage stone. Therefore, such local infrastructures and buildings have to be restored in the right way, by employing stones correctly quarried, worked and certified.

In this context, the local authorities have to foresee for public works and buildings refurbishment, mainly in the city centres and rural villages, the application of local materials, which could be classified as heritage stones (Cooper et al. 2013). In that way not only the local peculiar heritage would be preserved but also local economy would be improved.

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## **Waste recycling: opportunities and challenges for earth sciences**

Dondi M.\*

CNR-ISTEC, Istituto di Scienza e Tecnologia dei Materiali Ceramici, Faenza.

Corresponding email: [michele.dondi@istec.cnr.it](mailto:michele.dondi@istec.cnr.it)

Keywords: critical raw materials, inertization, waste recycling, stability of mineral assemblages.

The Raw Materials Initiative undertaken by the European Commission sheds light and draw a renovated interest on recovery, reuse and recycling of waste materials. This action is relaunched by the Horizon 2020 programme, where waste recycling is one pillar of the climate and resources societal challenges. The main objectives of these policies are: a) recovery of critical raw materials from wastes (through urban mining and mineralurgical processing); b) paving the way toward a zero-waste society (cannibalistic approach to industrial manufacturing, construction and demolition, municipal solid wastes); c) exploiting novel processes and materials, especially in high throughput sectors (e.g., cements, ceramics, glasses, building materials). Opportunities and role of Earth Sciences in the field of waste valorization are envisaged by overviewing the main technological hindrances and open questions in the track of more efficient processes and safer products. Examples entail knowledge and experimental approach close to Geochemistry, Mineralogy and Petrology. Relevant tasks concern: tracing useful elements in waste deposits; efficiency of technologies for the recovery of critical raw materials; modelling ion mobility and interaction with minerals; behaviour of elements during processing and after transformation into products; effective incorporation of hazardous components and their inertization; phase transformations which waste materials undergo along the processing; crystal chemistry of phases in waste-bearing products; making sense of new parageneses in waste-based materials; stability of mineral assemblages during thermal cycles; role of amorphous and glassy phases; predictive models to improve the mix design.

## Characterization of sustainable conglomeratic materials made with aggregates recycled from returned concrete

Ferrari G.<sup>1</sup>, Secco M.\*<sup>2</sup>, Valentini L.<sup>2</sup>, Surico F.<sup>1</sup>, Brocchi A.<sup>1</sup>, Torelli L.<sup>1</sup>, Squinzi M.<sup>1</sup>, Dalconi M.C.<sup>2</sup> & Artioli G.<sup>2</sup>

1. Mapei S.p.A., Milano. 2. CIRCe - Centro Interdipartimentale di Ricerca per lo Studio dei Materiali Cementizi e dei Leganti Idraulici, Dipartimento di Geoscienze, Università degli Studi di Padova.

Corresponding email: [michele.secco@unipd.it](mailto:michele.secco@unipd.it)

Keywords: Sustainable concrete production, multi-analytical characterization, numerical modeling.

Nowadays, one of the main waste materials produced by the ready-mix concrete plants is constituted by returned concrete, the residual amount of fresh concrete not poured to the building site and returned to the production plant by the truck mixer. Recently, a new technology has been developed to convert such waste into sustainable concrete aggregates, based on the utilization of two types of additives - a super-absorbing polymer (SAP) and a set accelerator - that transform fresh concrete into a solid, granular material constituted by a core of original coarse aggregate surrounded by a composite shell of sand and hydrated cement. In the present contribution, the results of a series of characterization studies based on both experimental and modeling approaches are reported, to investigate the properties of such materials at the fresh and hardened state.

One of the key technological issues related to the treatment of returned concrete with this procedure is related to the definition of the right period of curing, to obtain a material with both granular characteristics and proper mechanical properties. For the purpose, a series of numerical simulation with the VCCTL software developed by NIST were performed, to define the proper curing intervals according to temperature and concrete type.

Furthermore, a series of studies have been performed to investigate the chemical, physical and microstructural properties of the obtained granular materials. The standard characterization tests (density and absorption measurements, abrasion and freeze/thaw resistance determination, soluble chlorides and sulfates quantification) confirmed that such materials are fully utilizable as concrete aggregates. Furthermore, micro-analyses by X-ray micro-tomography and scanning electron microscopy (SEM-EDS) allowed to define the microstructural and micro-chemical characteristics of such materials, characterized by high density of the cement pastes and extremely good interfacial properties between the aggregate core and the surrounding composite shell.

Finally, the effects of recycled aggregates addition into conglomeratic materials of different strengths have been investigated by means of uniaxial compression tests, absorption tests and SEM-EDS micro-analyses. For the purpose, two types of granular materials have been produced, from original low strength and high strength concretes, respectively. Then, the resulting aggregates have been used with a 30% by weight degree of substitution to produce three concretes characterized by different compressive strength classes (low, medium and high, respectively). The results indicate that in no case the properties and the nominal strength class of the concretes are downgraded by the aggregate substitution. Furthermore, the water permeability properties of the final concretes are always significantly improved by the addition of the recycled aggregates. Such improvements in the technological properties of concretes are justified by a substantial absence of interfacial transition zones (ITZ) between recycled aggregates and surrounding cementitious matrices, as showed by SEM-EDS analyses.

## Breakdown of natural chrysotile and asbestos-containing waste by Self-propagating High temperature Synthesis (SHS)

Ferretti M.\*<sup>1</sup>, Gaggero L.<sup>2</sup>, Caratto V.<sup>2</sup>, Belfortini C.<sup>1</sup> & Musi L.<sup>1</sup>

1. Dipartimento di Chimica e Chimica Industriale, Università di Genova. 2. Dipartimento di Scienze della Terra dell'Ambiente e della Vita, Università di Genova

Corresponding email: [ferretti@chimica.unige.it](mailto:ferretti@chimica.unige.it)

Keywords: Chrysotile, asbestos-containing waste, inertisation.

The Asbestos-Containing Waste (ACW) represents, beside the urban solid waste, the most conspicuous typology in our country and the first among toxic wastes. In the perspective of reducing the environmental issue and to explore recycling of the breakdown products, we experimented the use of Self-propagating High temperature Synthesis (SHS), exploiting the highly exothermic and fast self-propagating high temperature alumino-thermic reactions (Munir, 1988; Gaggero et al., 2010).

Experimental procedures typically referred to the SHS method were adopted, taking advantage of the energy release of the highly exothermic reactions ignited by a relative low heat source. Reactants were selected between different oxide-metal couples (Hem+Mg; Mgt+Mg; Hem+Al) liable to activate the aluminothermic reaction and to break down the chrysotile. The successful experiments are based on the couples  $\text{Fe}_2\text{O}_3 + \text{Mg}$  and  $\text{Fe}_3\text{O}_4 + \text{Mg}$  varying some parameters as chrysotile or ACW abundance (from 45% to 65% weight), size of the pellet (diameter 13 and 25 mm, height from 7 to 70 mm) and weight of samples (from 2 to 100 g).

The process occurred in a reaction chamber with Ar inflow at ambient pressure. Chrysotile-reactant pellets were placed inside the chamber under a W coil that transferred the ignition energy from a power supply, turned off as soon as the reaction was ignited (after about 7s). After ignition, the average loss of weight of the sample resulted c. 4% that normalized to the percent of chrysotile in the pellet corresponds to a variable weight loss between 10 and 12%, likely corresponding to the dehydroxilation of chrysotile. As the toxic action of asbestos resides in habit, composition and size, inertization requires the structural change of mineral fibre. Following the combustive reaction, all experiments demonstrated effective in destructing the fibrous habit of chrysotile, turning its composition to stubby olivine grains. The asbestos inertization is particularly advantaged by the SHS process in comparison with conventional thermal treatments, due to fast reaction time, low activation energy and simple instruments, that positively reflect into time and costs of the process. Finally, the product of this transformation is liable to be re-used as second material.

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Munir Z.A. 1988. Synthesis of high temperature materials by Self-Propagating Combustion methods. Amer. Ceram. Soc. Bull., 67, 342-349.

## Experimental method for the deep cleaning of soluble salts from mortars and lithic materials

Ferretti M.<sup>1</sup>, Gaggero L.\*<sup>2</sup>, Torrielli G.<sup>1-2</sup> & Vicini S.<sup>1</sup>

1. Dipartimento di Chimica e Chimica Industriale, Università di Genova. 2. Dipartimento di Scienze della Terra dell'Ambiente e della Vita, Università di Genova.

Corresponding email: [gaggero@dipteris.unige.it](mailto:gaggero@dipteris.unige.it)

Keywords: Soluble salt extraction, mortars, frescos.

A common *in situ* alteration pattern in mortars and frescoes is the crystallization of soluble salts from solutions rising by capillarity or circulating in damp walls. If this pattern reveals overwhelming upon other environmental decay factors, the extraction of salts is the major restoration to operate on the artwork to recover its pristine conditions after a preliminary assessment and mitigation of the causes of soaking.

An innovative method has been assessed to enhance the quality and durability of decontamination by soluble salts, compared with conventional application of sepiolite or cellulose wraps.

The conventional application of cellulose or sepiolite requires casting a more or less thick layer of wrap on the mortar, soaking with distilled water, and waiting until dry. The soluble salts are then trapped within the wrap. A set of artificial samples reproducing the stratigraphy of frescoes was contaminated with saline solution of known concentration. The extraction by the new method (UNIGE patent under filing) was demonstrated by trapping the salts within layers of Japanese paper juxtaposed to the mortar; the extraction was operated in a significantly shorter time than with wraps (some hours vs. 1-7 days). Two cycles of about 15 minutes are effective in deep cleaning from contaminants. The decontamination was proved by conductivity tests on the juxtaposed Japanese paper.

In addition, we established that a considerable amount of soluble salts could be further extracted even after the conventional treatment, demonstrating that traditional wraps operate just a shallow cleaning, and soluble salts are liable to emerge as efflorescence affecting the conservation after restoration.

The optimum cleaning is obtained by finishing the innovative extraction with sepiolite/cellulose wraps. The innovative method decreases the time for accurate cleaning before consolidation and protection.

## **MSWI residues as unconventional source of critical raw materials: understanding possible easy ways to evaluate their occurrence and to obtain added-value products**

Funari V.\*<sup>1</sup>, Bokhari S.N.<sup>2</sup>, Meisel T.<sup>2</sup>, Vigliotti L.<sup>3</sup>, Dinelli E.<sup>1</sup> & Braga R.<sup>1</sup>

1. Dipartimento BiGeA - Sezione Geologia, Università di Bologna. 2. General and Analytical Chemistry - Montanuniversität Leoben, Austria. 3. Istituto di Scienze Marine, CNR, Bologna.

Corresponding email: [valerio.funari@unibo.it](mailto:valerio.funari@unibo.it)

Keywords: Critical raw materials, Waste, Substance flow analysis.

Critical raw materials (CM) are chemical elements and minerals such as Be, Co, Ga, Ge, In, Mg, Nb, Sb, Ta, W, Platinum Group Elements (PGE), Rare Earth Elements and Y (REY), fluorite, graphite, which are important for the technological development (European Commission, 2010) needed to achieve a low-carbon society.

Solid residues from Municipal Solid Waste Incinerators (MSWI) may represent an unconventional source of valuable chemical elements, as a continue flow stream (e.g.: Morf et al., 2012). In this contribution we will show that the CM content in bottom and fly ashes, which are the common MSWI outputs, and their estimated annual flow (t/a) are significant. Analyses were carried out by ICP-MS and XRF, reaching very low detection limits in order to evaluate the CM potential. Total CM (Ce, Co, Nb, Sb, Ta, W) in bottom ashes is 380 mg/kg; fly ashes contain 1022 mg/kg Sb, 49 mg/kg total other CM (Ce, Co, Nb, Ta, W). Bottom and fly ashes have an average concentration higher than 60 mg/kg SREY. The estimated substance flow shows that an hypothetical recovery is advantageous in bottom ashes for the most of the elements.

To further explore the CM potential of bottom ashes, we have considered the different granulometric fractions produced by simple gravitational sorting during their temporary storage as stockpiles. The substance flow analysis reveals that the bottom ash finer fraction (which forms the top layer) shows an overall enrichment in CM compared to the other coarser layers. The finer bottom ashes residing on the top of stockpiles, which can be sampled by simple visual inspection at the plant storage facility, seem to represent the most promising target for future recovery strategies. We are also investigating whether correlations with the mass specific magnetic susceptibility of the MSWI solid residues can be used as proxies for CM occurrence (and, hence, as a fast indicator of CM's relative availability). First results show that this parameter is related to the REE distribution.

On the short term, our data will help to bolster the attention on incinerated waste as an unconventional solution for raw materials supply. A comprehensive strategy has to be implemented to address the quantitative availability of CM through new prospecting technologies, as called for by the European Commission in its European Innovation Partnership in Raw Materials (EIP).

European Commission 2010. Critical Raw Materials for EU. Report of the Ad-hoc Working Group on defining critical raw materials. <http://ec.europa.eu/enterprise/policies/raw-materials/critical/>

Morf L.S., Gloor R., Haag O., Haupt M., Skutan S., Di Lorenzo F. & Boni D. 2012. Precious metals and rare earth elements in municipal solid waste--sources and fate in a Swiss incineration plant. *Waste Management*, 33(3), 634-644.

## Innovative, quantitative, *in situ* characterization of weathered building materials

Gaggero L.\*<sup>1</sup>, Scrivano S.<sup>1</sup>, Gisbert Aguilar J.<sup>2</sup> & Yus Gonzales A.<sup>1-2</sup>

1. Dipartimento di Scienze della Terra della Vita e dell'Ambiente, Università di Genova. 2. Departamento de Ciencias de la Tierra, Facultad de Ciencias, Universidad de Zaragoza, España.

Corresponding email: [gaggero@dipteris.unige.it](mailto:gaggero@dipteris.unige.it)

Keywords: Weathering, ablational decay, reproducible sampling.

The diagnostic of weathered rocks and mortars aims at deciphering processes that affect materials exposed under outdoor, indoor, buried environmental conditions, and at enucleating decay factors. However, the characterization of weathering intensity is mostly descriptive and non-quantitative (ICOMOS Glossary, 2008). The Fitzner indexes applied to arenites (Fitzner et al., 2002) and more recently to marbles (Scrivano et al., 2013) help the description. The current method of decay diagnostic (Drdácky & Slizková, 2014) was improved by a joint gravimetric + dynamometric measure of ablational decay products. It encompasses:

- i) Preparation of stubs for SEM analysis with adherent conductive carbon tape (surface area 1.3 cm<sup>2</sup>)
- ii) Weighing of stub + tape + its plastic envelope at 0.001 g precision
- iii) Connecting the stub to a pocket penetrometer
- iv) Non invasive sampling of the incoherent dust applying a constant pressure of 2 kgf for 1 minute, then packing away the stub without losing grains
- v) Weighing of stub + tape + weathering products + their plastic envelope at 0.001 g precision
- vi) Recast the weight of removed material
- vii) Addressing the weathering products to electron microscopy and or microanalysis.

Our quantitative peeling test was applied on a cladded wall in the Staglieno Monumental Cemetery in Genoa. The wall is 96 m long and shows weathering gradients due to a neighbouring interred stream and to different insulation. Slabs of Verde Polcevera opicalcite were tested in three different areas of the structure (samples c1-c5 collected to the E, samples c6-c10 at the centre, samples c11-c15 to the W). The results highlighted capillary rise up to 2 meters height (weight of samples: c3 = 0,009 g; c8 = 0,0224 g; c13 = 0,0063 g) and a more weathered central area (weight of samples: c6 = 0,0062 g, c7 = 0,0058 g, c8 = 0,0224 g, c9 = 0,0024 g, c10 = 0,0045 g). On the whole our protocol allows reproducible factual sampling. Moreover, if carried out on statistically significant population, the definition of Intensity of decay results categorized.

Drdácky M. & Slizková Z. 2014. *In situ* peeling tests for assessing the cohesion and consolidation characteristics of historic plasters and render surfaces. *Studies in conservation*, 0, 1-10.

Fitzner B., Heinrichs K. & La Bouchardiere D. 2002. Damage index for stone monuments. *Protection and conservation of the cultural heritage of the Mediterranean cities*, Proc. 5th Int. Symp. on the Conservation of Monuments in the Mediterranean Basin, 315-326, Sevilla.

ICOMOS-ISCS. 2008. *Illustrated glossary on stone deterioration patterns*. 78 pp.

Scrivano S., Gaggero L. & Taddei A. 2013. Alteration patterns of marble under different environmental exposures: a systematic approach from the Staglieno Monumental cemetery and museum collections in Genoa (Italy). In: *Proceedings of the 12th International Congress on Deterioration and Conservation of Stone*, New York, 22-26 October 2012. In press.

## Influence of minor elements on the clinkerization process

Galimberti M.\*<sup>1</sup>, Marinoni N.<sup>1</sup>, Dapiaggi M.<sup>1</sup> & Marchi M.<sup>2</sup>

1. Dipartimento di Scienze della Terra, Università degli Studi di Milano. 2. CTG S.p.A., Italcementi Group – Bergamo.

Corresponding email: [matteo.galimberti@unimi.it](mailto:matteo.galimberti@unimi.it)

Keywords: clinker, minor elements, in-situ high temperature X-ray powder diffraction.

Ordinary Portland cement clinker is nowadays usually produced by firing in a rotary kiln a blend of limestone and clay minerals up to 1400°C, where a melt is formed and clinkerization occurs (Taylor, 1990). This standard manufacturing process is very energy-consuming and pollutant, so the exploration of new techniques and methodologies is of primary importance, because of the growing knowledge in terms of environment preservation, paying particular attention to intensive quarrying of ore bodies and greenhouse gases emissions, together with a careful energy policy, oriented towards eco-saving and recycle. Usually, manufacturing 1000 kg of clinker requires 850000 kcal, 1700 kg of raw materials and emits 850 kg of pollutants, mainly carbon dioxide (van Oss & Padovani, 2003; Habert et al., 2009). A performed solution is represented by the use of wastes both as raw materials and alternative fuels, but this involves the occurrence of minor elements as impurities, which can enter the structure of main clinker phases.

Most common impurities are sulfur, magnesium and alkalis; individually, their behavior has been studied in details (Emanuelson et al., 2003), but a comprehensive and combined study lacks, even though they normally occur together at production plants. This research aims to study the behavior of the above-mentioned impurities together and their reciprocal interaction during the clinkerization process. Processing in situ High Temperature X-Ray Powder Diffraction (HT-XRPD) patterns, collected at different temperatures up to 1400°C, performing Rietveld refinement method will give a quantitative phase analysis, while observation and processing of scanning electron microscopy back scattered electrons images will make possible to determine porosity and cracks distribution in manufactured clinker.

Emanuelson A., Hansen S. & Viggh E. 2003. A comparative study of ordinary and mineralized Portland cement clinker from two different production units. Part I: composition and hydration of the clinkers. *Cem. Concr. Res.* 33, 1613-1621.  
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van Oss H.G. & Padovani A.C. 2003. Cement manufacture and the environment Part II: Environmental challenges and opportunities. *J. Ind. Ecol.* 7, 93-126.

## Alunite-bearing kaolin from Piloni di Torniella mine: a suitable raw material for the synthesis of metakaolin-based geopolymers?

Gasparini E.\*<sup>1</sup>, Tarantino S.C.<sup>1</sup>, Ghigna P.<sup>2</sup>, Riccardi M.P.<sup>1</sup> & Zema M.<sup>1</sup>

1. Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia. 2. Dipartimento di Chimica, Università di Pavia

Corresponding email: [elisa.gasparini@unipv.it](mailto:elisa.gasparini@unipv.it)

Keywords: Metakaolin-based geopolymer, alunite, texture.

Geopolymers are ceramic materials obtained at temperature lower than 150 °C by alkali activation of an aluminosilicate solid precursor of natural (*e.g.*, kaolin/metakaolin) or industrial (*e.g.*, fly ashes) origin. The increasing interest in these materials is related to their “eco-friendly” production process and good mechanical and chemical properties (see Duxson et al., 2007), which may vary depending on the kind of raw material and processing conditions.

Aim of this work is to investigate the possibility to employ low-quality natural kaolin, containing secondary minerals such as alunite, for geopolymer synthesis. Alunite is present in kaolin deposits deriving from trachyte, rhyolite, and similar potassium-rich volcanic rocks and normally hinders the use of these clays in the ceramic industry due to the release at about 600 °C of SO<sub>x</sub> gases which damage furnaces refractories.

Geopolymers have been synthesized from kaolin from Piloni di Torniella mine, supplied by Eurit s.r.l. The kaolin is composed of about 55 wt% quartz and feldspar, 40 wt% kaolinite and 5 wt% alunite, and was activated at 550 °C for 3 hours. This condition have been chosen in order to prevent alunite desulphation, although at this temperature the dehydroxylation of kaolinite is not complete and hence it is expected that a lower amount of it can actually react with alkali.

The heated raw material and a sodium silicate solution have been mixed in stoichiometric amount to allow the following molar oxide ratios of synthesised samples: SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 4.6 and Al<sub>2</sub>O<sub>3</sub>/(Na<sub>2</sub>O+ K<sub>2</sub>O) = 1. Geopolymer maturation conditions of 52 °C for 19 hours have been chosen according to the results of a previous study, where the synthesis conditions have been evaluated by the Design of Experiment approach on geopolymers synthesised from alunite-free kaolin.

The synthetic conditions allowed to obtain geopolymer samples characterised by high thermal stability and good mechanical properties, showing compressive strength higher than 80 MPa. A multi-technique approach has been used to characterize the synthesized geopolymers: (i) compressive strength test has been used as a qualitative tool to assess the success of synthesis reaction; (ii) X-ray powder diffraction and Fourier Transform Infrared - Attenuated Total Reflectance (FTIR-ATR) spectroscopy have been applied to investigate phase composition; (iii) optical and scanning electron microscopies have been used to study the textural features of geopolymers, at different lengths of scale; (iv) differential thermal analysis and gas pycnometry techniques have allowed to investigate the thermal stability and density of synthesised samples, respectively. The relationships among mineralogical, petrographic and physical features of geopolymers have been studied and related to sample strength. Furthermore, leaching tests have been carried out and the resulting materials have been characterised. The amount of sulphur in geopolymer samples has been measured, before and after the test, by using Scanning Electron Microscope - Energy Dispersive spectrometry technique. Inductively coupled plasma - optical emission spectroscopy has been used to evaluate the concentration of sulphate, related to alunite decomposition, in the leached solution.

Duxson P., Provis J.L., Lukey G.C., van Deventer J.S.J. 2007. The role of inorganic polymer technology in the development of ‘green concrete’. *Cement Concrete Res.*, 37, 1590-1597.

## Host-guest and guest-guest interactions in a new perylene dye - Zeolite L composite

Gigli L.<sup>1</sup>, Arletti R.<sup>1</sup>, Vitillo J.G.<sup>2</sup>, Martra G.<sup>3</sup>, Calzaferri G.<sup>4</sup>, Devaux A.<sup>5</sup>, Belser P.<sup>5</sup>,  
Quartieri S.<sup>6</sup> & Vezzalini G.\*<sup>7</sup>

1. Department of Earth Sciences, Turin. 2. Department of Science and High Technology, Como. 3. Department of Chemistry, Turin. 4. Department of Chemistry and Biochemistry, Bern. 5. Department of Chemistry, Fribourg. 6. Department of Physics and Earth Sciences, Messina. 7. Department of Chemical and Geological Sciences, Modena.

Corresponding email: [mariagiovanna.vezzalini@unimore.it](mailto:mariagiovanna.vezzalini@unimore.it)

Keywords: Zeolite L, perylene dye, ZL/tB-DXP composite, SR-XRPD, structure refinement, IR, UV-Vis.

In recent years dye-zeolite L (ZL) composites (Calzaferri, 2012; Devaux et al, 2013) attracted renewed interest in several fields. These materials, in fact, can mimic the biological blueprint of the natural photosynthesis, designing systems used in several applications as novel optical materials, with a large variety of different properties. They are employed as key components of promising devices to be used in technology for converting light into stored energy, in biology and diagnostics. Supramolecular organization inside the ZL nanochannels depends on the shape and size of the dye, on its orientation – in turn affected by zeolite geometric constrains – and on the extraframework content (e.g. cations, H<sub>2</sub>O molecules). Due to the influence of the involved guest-guest and host-guest interactions on the optical properties of dye-ZL systems, the study of their structure is a prerequisite for advancing our knowledge of such materials. In this work we have studied the ZL/tB-DXP composite (Devaux et al, 2013), prepared by loading ZL with a dye belonging to the perylene family. Specifically, we investigated the influence of water molecules on the host-guest interactions through an integrated approach based on IR spectroscopy and Synchrotron Radiation X-ray Powder Diffraction (SR-XRPD). The ATR-IR and FTIR spectra collected on the hydrated and dehydrated form of the ZL/tB-DXP composite showed strong shifts of all the dye peaks with respect to those collected on the pure dye. Moreover, in the hydrated form the shift is significantly higher than in the dehydrated one, giving a clear indication that the water molecules present in the channels strongly affect host-guest and guest-guest interactions. The crucial role of water molecules was also confirmed by a general blue shift observed in the diffuse reflectance UV-Vis spectra collected upon water removal.

The SR-XRPD data showed a slight increase of the unit cell volume of the ZL/tB-DXP composite respect to the as-synthesized ZL. The structural refinement revealed the presence of about 0.25 tB-DXP molecules per unit cell, aligned along the main 12MR channel of ZL, and interacting with the framework oxygen atoms via hydrogen bonds mediated by water molecules. Concluding, both the results of the IR measurements and of the structural refinement highlight the effective influence of the water molecules on the optical properties of ZL/tB-DXP composite.

Calzaferri G. 2012. Nanochannels: Hosts for the Supramolecular Organization of Molecules and Complexes. *Langmuir*, 28, 6216-6231.

## Topotactic and reconstructive changes at high pressure and temperatures from Cs-natrolite to Cs-hexacelsian: potential nuclear waste disposal materials

Hwang H.<sup>1</sup>, Seoung D.<sup>1</sup>, Gatta G.D.\*<sup>2</sup>, Blom D.A.<sup>3</sup>, Vogt T.<sup>3</sup> & Lee Y.<sup>1</sup>

1. Department of Earth System Sciences, Yonsei University, Seoul, Korea. 2. Dipartimento di Scienze della Terra, Università degli Studi di Milano. 3. NanoCenter & Department of Chemistry and Biochemistry, University of South Carolina, Columbia, USA.

Corresponding email: [diego.gatta@unimi.it](mailto:diego.gatta@unimi.it)

Keywords: Nuclear technology, Cs-zeolites, Cs-hexacelsian.

Synchrotron X-ray powder diffraction experiments have been performed on dehydrated Cs-exchanged natrolite in order to systematically investigate successive transitions under high pressures and temperatures. At pressures above 0.5(1) GPa using water as a pressure transmitting fluid and after heating to 100°C, dehydrated Cs<sub>16</sub>Al<sub>16</sub>Si<sub>24</sub>O<sub>80</sub> (deh-Cs-NAT) transforms to a hydrated phase Cs<sub>16</sub>Al<sub>16</sub>Si<sub>24</sub>O<sub>80</sub>·16H<sub>2</sub>O (Cs-NAT-II), which has a ca. 13.9% larger unit-cell volume (Lee et al., 2011; Seoung et al., 2013). Further compression and heating to 1.5(1) GPa and 145 °C results in the transformation of Cs-NAT-II to Cs<sub>16</sub>Al<sub>16</sub>Si<sub>32</sub>O<sub>96</sub> (anh-Cs-POL), a H<sub>2</sub>O-free pollucite-like triclinic phase with a 15.6% smaller unit-cell volume per 80 framework oxygen atoms (O<sub>f</sub>). At pressures and temperatures of 3.7(1) GPa and 180 °C, a new phase Cs<sub>1.547</sub>Al<sub>1.548</sub>Si<sub>6.452</sub>O<sub>16</sub> (Cs-HEX) with a hexacelsian framework forms, which has a ca. 1.8% smaller unit-cell volume per 80O<sub>f</sub>. This phase can be recovered after pressure release. The structure of the recovered Cs-HEX has been refined in space group *P6<sub>3</sub>/mcm* with *a* = 5.3731(2) Å and *c* = 16.6834(8) Å, and also been confirmed by HAADF-STEM real space imaging. Similar to the hexacelsian feldspar (*i.e.*, BaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>), Cs-HEX contains Cs<sup>+</sup> cations which act as bridges between the upper and lower layers composed of tetrahedra and are hexa-coordinated to the upper and lower 6-membered ring windows. These pressure- and temperature-induced reactions from a zeolite to a feldspar-like material are important constraints for the design of materials devoted to Cs<sup>+</sup> immobilization.

Lee Y., Lee Y. & Seoung D. 2010. Natrolite may not be a “soda-stone” anymore: Structural study of fully K-, Rb-, and Cs-exchanged natrolite. *Am. Mineral.*, 95, 1636-1641.

Seoung D., Lee Y., Kao C.-C., Vogt T. & Lee Y. 2013. Super-Hydrated Zeolites: Pressure-Induced Hydration in Natrolites. *Chem. Eur. J.*, 19, 10876-10883.

## HP-induced confinement and polymerization of ethylene glycol in high-Si mordenite

Leardini L.<sup>1</sup>, Quartieri S.\*<sup>1</sup>, Arletti R.<sup>2</sup> & Vezzalini G.<sup>3</sup>

1. Dipartimento di Fisica e Scienze della Terra, Università di Messina. 2. Dipartimento di Scienze della Terra, Università di Torino. 3. Dipartimento di Scienze Fisiche e Geologiche, Università di Modena e Reggio Emilia.

Corresponding email: [squartieri@unime.it](mailto:squartieri@unime.it)

Keywords: Zeolite mordenite, High-pressure polymerization, synchrotron XRPD, pressure-induced molecular intrusion.

The confinement and the high-pressure (HP) induced polymerization of organic molecules into microporous solids can be of paramount technological interest. Pressure is the most efficient tool to reduce intermolecular distances, thereby permitting continuous tuning of the corresponding interactions and allowing the chemical reactions to occur without the use of catalysts. In this work, the penetration of guest molecules under HP into a high-silica mordenite (HS-MOR, (SiO<sub>2</sub>)<sub>48</sub>•5 H<sub>2</sub>O, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ~ 200, s.g. Cmcm) in its protonated form was investigated by in-situ synchrotron X-ray powder diffraction (XRPD) using (16:3:1) methanol:ethanol:water (m.e.w.), (3:1) water:ethanol (w.e.), ethylene glycol (e.g.) and resorcinol (res.) as penetrating pressure transmitting media (PTM). The HP synchrotron XRPD experiments were performed in DAC at SNBL1 (ESRF, Grenoble). The powder patterns were collected in the following pressure ranges: Pamb - 11.8 GPa, Pamb - 2 GPa, Pamb - 8.8 GPa and Pamb - 8.5 GPa for m.e.w., w.e., e.g., and res., respectively. Other patterns were measured upon decompression. The evolution of the structural features was followed by full profile Rietveld refinements. The general results of this study are the following:

- i) penetration of guest species into the channels, even at very low P, has been observed for all the tested PTM;
- ii) the P-induced effects are partially reversible upon decompression;
- iii) In the P range Pamb-1.2 GPa, common to all the experiments, the volume contraction of HS-MOR compressed in e.g. (-1.47%) is higher than those registered in m.e.w., w.e. and res (-0.96%, -0.86% and -1.02%, respectively). However, on the overall investigated P range, the volume contraction undergone in e.g., m.e.w. and res. is rather similar. This suggests a slower penetration rate of the guest molecules when using ethylene glycol as PTM.

Of great interest is the formation, at about 1 GPa, of polymeric chains of ethylene glycol molecules (polyethylene glycol), running along the c-axis inside the 12-membered ring channels. An important aspect of this intrusion process is that it is partially irreversible upon pressure release. This HP-polymerization could represent a novel “green chemistry” route to industrial chemical synthesis, as the use of additional and polluting compounds is avoided (Santoro et al., 2013; Scelta et al., 2014).

Santoro M., Gorelli F. A., Bini R., Haines J. & van der Lee A. 2013. High-pressure synthesis of a polyethylene/zeolite nano-composite material. *Nature Comm.*, 4, 2564-2569.

Scelta D., Ceppatelli M., Santoro M., Bini R., Gorelli F. A., Perucchi A., Mezouar M., van der Lee A. & Haines J. 2014. High Pressure Polymerization in a Confined Space: Conjugated Chain/Zeolite Nanocomposites. *Chem. Mater.*, 26, 2249–2255.

## Synthesis and colouring performance of the $\text{CaCoSi}_2\text{O}_6$ pyroxene ceramic pigment

Mantovani L.\*<sup>1</sup>, Tribaudino M.<sup>1</sup>, Dondi M.<sup>2</sup> & Zanelli C.<sup>2</sup>

1. Dipartimento di Fisica e Scienze della Terra "M. Melloni" - Università di Parma. 2. Istituto di Scienza e Tecnologia dei Materiali Ceramici CNR-ISTEC – Faenza.

Corresponding email: [luciana.mantovani@unipr.it](mailto:luciana.mantovani@unipr.it)

Keywords: Ceramic pigment, pyroxene, colouring performance.

The pink coloured pyroxene  $\text{CaCoSi}_2\text{O}_6$  has been here synthesised as a possible ceramic pigment stable in very aggressive media like Ca and Zn-rich glazes and glassy coatings used in porous tiles. Pyroxenes was selected as a crystalline structure both for their six/eight-fold crystallographic sites where  $\text{Co}^{2+}$  ions can be accommodated, producing a pink colour and for the good stability to the alteration. The colour of the  $\text{Co}^{2+}$  compounds depends on the coordination geometry and the host lattice: if cobalt is in tetrahedral coordination the colour is deep blue while, if the coordination number is higher, six or eight, the hue swings to pink or violet (Mimani & Ghosh, 2000; Dondi et al. 2010). In ceramic science, the alternative Co-based pink colourant is frequently represented by the Co-olivine, but it does not remain stable in porcelainized glazes during firing (Llusar et al. 2001). Moreover,  $\text{CaCoSi}_2\text{O}_6$  pyroxene has a minor cobalt content per formula units respect to the Co-olivine, promoting minimization of the production cost and toxicity. The syntheses were performed through solid state method, mixing up powders of  $\text{Co}_3\text{O}_4$ ,  $\text{CaCO}_3$  and amorphous  $\text{SiO}_2$ ; different time and temperature of annealing were used to pinpoint the best synthesis condition for the formation of single phase  $\text{CaCoSi}_2\text{O}_6$ . The final product of the different annealing has been analysed by XRPD, SEM-EDS and the colour behaviour has been investigated (CIE-Lab). Syntheses made at temperature equal or lower than  $1100^\circ\text{C}$  produced a mixture of  $\text{CaCoSi}_2\text{O}_6$  (pyroxene),  $\text{Ca}_2\text{CoSi}_2\text{O}_7$  (Co-åkermanite), Co-olivine ( $\text{Co}_2\text{SiO}_4$ ) and  $\text{SiO}_2$  in different quantities. Co-åkermanite has one fourfold crystallographic site where  $\text{Co}^{2+}$  ions can be accommodated, thus ensuring its blue colour. The hiding power of blue Co in fourfold coordination is more intense than that in octahedral one; for this reason the presence of Co-åkermanite dominates the resulting colour, giving a deep blue hue even if it is present in small quantities. Increasing the temperature to  $1150^\circ\text{C}$  for about 24 hours, a single pyroxene phase with composition  $\text{CaCoSi}_2\text{O}_6$  is obtained: the final colour is a bright pink (CIE  $L^*=64$ ,  $a^*=23$ ,  $b^*=-9$ ). Technological tests were done for the resulting pigment  $\text{CaCoSi}_2\text{O}_6$  mixing them with glaze and glassy coating commonly used in the industrial tile making process. The final results showed that only in one case the  $\text{CaCoSi}_2\text{O}_6$  withstands the corrosion by melted glaze and acts as a pigment giving a pale-pink colour (CIE  $L^*=67$ ,  $a^*=8$ ,  $b^*=-14$ ). In the other cases the chemical attack caused a gradual leaching of  $\text{Co}^{2+}$  that dissolves into the glass, thus imparting a deep blue colouring (dye behaviour).

Mimani T. & Ghosh S. 2000. Combustion synthesis of cobalt pigments: Blue and pink. *Cur. Sci.*, 78, 892-896.

Fores A., Llusar M., Badenes J.A., Calbo J., Tena M.A., Monros G. Cobalt minimisation in willemite ( $\text{Co}_x\text{Zn}_{2-x}\text{SiO}_4$ ) ceramic pigments. *Green Chem.* 2000, 2, 93-100.

Dondi M., Zanelli C., Ardit M. & Cruciani G. 2011. Co-Doped Hardystonite,  $\text{Ca}_2(\text{Zn}, \text{Co})\text{Si}_2\text{O}_7$ , a New Blue Ceramic Pigment. *J. Am. Cer. Soc.*, 94, 1025-1030.

## Effects of soda-lime-silica waste glass on mullite formation kinetics and micro-structures development in vitreous ceramics

Marinoni N.\*<sup>1</sup>, Diella V.<sup>2</sup>, Pavese A.<sup>1,2</sup> & Francescon F.<sup>3</sup>

1. Dipartimento di Scienze della Terra "Ardito Desio", Università degli Studi di Milano – Milano. 2. Consiglio Nazionale delle Ricerche, IDPA, Sezione di Milano- Milano. 3. Ideal Standard International - C.O.E. - Ceramic Process Technology - Trichiana (BL).

Corresponding email: [nicoletta.marinoni@unimi.it](mailto:nicoletta.marinoni@unimi.it)

Keywords: soda-lime glass, sanitary-ware body, physical-mechanical features, kinetic analysis.

Several papers on the use of different waste glasses in industrial products have been presented proving that such refuses can be an alternative to the traditional raw materials (Bernardo et al., 2010). Among silica-rich wastes those from bottle banks have attracted much attention. Glass cullets (referred to as soda-lime or soda-lime-silica (SLS) glass) from urban waste consist mainly of silicon, sodium and calcium oxides. Thanks to its potential of low temperature viscous flow sintering, SLS glass can be considered as a good candidate for total, or partial, replacement of the natural fluxes (mainly Na-feldspar) in ceramic manufacturing. Souza et al., 2004 claimed that SLS glasses can substitute feldspar-based fluxes up to 5 wt% without affecting the technological features of the output but reducing the sintering temperature.

The use of SLS glass in the vitreous sanitary-ware ceramics provides an environmental safeguard by saving natural resources, and reducing the process energy consumption and CO<sub>2</sub> emissions. However it is still a matter of debate how SLS-glass affects the basic ceramic reaction kinetics. Much attention has been paid to porcelain-type technology, but comparatively little has been spent for vitreous sanitary-wares, which result from high-temperature treatments (~1230 °C) of the system clay-kaolinite-feldspar-quartz.

In the present paper, we discuss the introduction of SLS glass into the vitreous sanitary-ware ceramic phase-system in partial replacement of the traditional flux agent (Na-feldspar) focussing the attention on: (i) how SLS glass affects the sanitary-ware ceramic transformations at high temperature, in terms of mullite nucleation and growth; (ii) how SLS glass influences the micro-structures formation and the technological properties of the output, as a function of the firing time ( $t_f$ ) and temperature ( $T_f$ ).

The study was performed on samples with classical vitreous sanitary-ware compositions in which a fraction of feldspar is replaced by SLS glass. The mullite kinetics was investigated by isothermal runs using *in-situ* High Temperature X-Ray Powder Diffraction (HT-XRPD) and Scanning Electron Microscopy (SEM). Samples fired over a  $t_f$ - $T_f$  grid to mimic a ceramic body were then studied by means of XRPD and technological testing to measure the properties relevant to vitreous sanitary-ware ceramic technology.

Bernardo E., Scarinci G., Bertuzzi P., Ercole P. & Ramon L. 2010. Recycling of waste glasses into partially crystallised glass foam. *J. Porous. Mater.*, 17, 359-365.

Souza G.P., Rambaldi E., Tucci A., Esposito L. & Lee, W.E. 2004. Microstructural Variation in Porcelain Stoneware as a Function of Flux System. *J. Am. Ceram. Soc.*, 87, 1959-1966.

## Fuel-based pollutants removal from water: structural evidences of adsorption into high silica zeolites

Martucci A.\*<sup>1</sup>, Pasti L.<sup>2</sup>, Braschi I.<sup>3</sup> & Bagatin R.<sup>4</sup>

1. Dep. of Physics and Earth Sciences, University of Ferrara. 2. Dep. of Chemistry and Pharmaceutical Sciences, University of Ferrara. 3. Dep. of Agricultural Sciences, University of Bologna. 4. Research Center for Non-Conventional Energy - Istituto Eni Donegani Environmental Technologies, San Donato Milanese (MI).

Corresponding email: [mrs@unife.it](mailto:mrs@unife.it)

Keywords: Zeolites, fuel-based pollutants, adsorption.

Removal of fuel-based compounds from natural water is of considerable interest due to the harmful effects of these pollutants on the environment, even at very low concentration. Adsorption is a reliable technique to eliminate them from wastewaters due to the flexibility of the system, low energy and cheap operation costs (Braschi et al., 2012; Martucci et al., 2012; Pasti et al., 2012). The presence of natural organic matter can significantly affect organic pollutant adsorption by either competing for adsorption sites, or restricting access to (micro)pores.

In this work organophilic zeolites differing in topology, channel systems and free window apertures, and fuel-based-pollutants differing in chemical properties and molecular dimensions, were tested. Structural evidences of adsorption from dilute solutions into organophilic zeolite as well as the competitive role of humic monomers, the effect of the temperature in the adsorption processes will be discussed. The selected adsorbents were hydrophobic ZSM-5 and Y zeolites with high SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>. Kinetics and adsorption isotherm batch data were obtained via Headspace Solid Phase Microextraction-GC. X-ray powder patterns were collected before and after adsorption on a Bruker D8 Advance diffractometer with SOL-X detector. Thermal analysis were performed in air up to 900°C at 10°C/min. Infrared spectra were collected on a Thermo Electron Corporation FT Nicolet 5700 Spectrometer. This combined diffractometric, thermogravimetric, chromatographic and spectroscopic study allowed us to: 1) measure the sorption capacity of zeolites weighed against organic pollutants dissolved in water; 2) characterise the structure after contaminants adsorption; 3) localise the organic species in the zeolite channel systems; 4) highlight the role of humic monomers in the pollutants removal; 5) probe the interaction between the adsorbate and the zeolite framework. The very favorable adsorption kinetics along with the highly irreversible adsorption into zeolite pores make these cheap and environmental friendly materials applicable for the treatment of water contaminated with fuel-based pollutants.

Braschi I., Gatti G., Bisio C., Berlier G., Sacchetto V., Cossi M., & Marchese L. 2012. The Role of Silanols in the Interactions between Methyl tert-Butyl Ether and High-Silica Faujasite Y: An Infrared Spectroscopy and Computational Model Study. *Physical Chemistry C*, 116, 6943-6952.

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Pasti L., Martucci A., Nassi M., Cavazzini A., Alberti A., & Bagatin, R. 2012. The role of water in DCE adsorption from aqueous solutions onto hydrophobic zeolites. *Microporous and Mesoporous Materials*, 160, 182-193.

## Selective adsorption of biomolecules on mineral surfaces for nanotech applications

Moro D.\*, Ulian G. & Valdrè G.

Centro di Ricerca Interdisciplinare di Biomineralogia, Cristallografia e Biomateriali, Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Bologna.

Corresponding email: [daniele.moro@unibo.it](mailto:daniele.moro@unibo.it)

Keywords: Chlorite, glycine, scanning probe microscopy.

Mineral surfaces are good candidates as substrates for biotechnological applications because they may present at the nanoscale a wide variety of physico-chemical properties and surface nanostructures that can be used to actively condense and manipulate biomolecules (Valdrè et al., 2012). Recent advancement in highly spatially resolved experimental and theoretical methodologies (e.g., scanning probe microscopy, SPM, and quantum mechanical simulations) has widened the possible investigations of biological/organic matter interaction with mineral substrates, enabling both controlled surface modifications at the nanoscale and detailed prediction and characterization of surface properties. SPM is one of the best-suited techniques for the investigation at a single-molecule level of bio-surface interactions. Recent availability of high performance computing has increased the possibility to study quantum mechanically the interaction phenomena, extending the number of atoms involved in the simulation. In this contribution we present a detailed study of the interaction at the single-molecule level of the amino acid glycine with the (001) crystallographic plane of chlorite. Single glycine molecules were experimentally observed to selectively adsorb and condense on the (001) brucite-like surface of a freshly cleaved chlorite. Chlorite surface potential was ascribed to drive single glycine molecules to align along crystal sub-nm edges. We simulated the glycine interaction with the brucite-like (001) surface using the DFT/B3LYP-D\* functional and an all-electron basis set to aid the interpretation of the experimental results. In agreement to the SPM observations, the amino acid is strongly adsorbed by the mineral surface (binding energy of about -33 kJ/mol), with several hydrogen bonds established. The understanding and control of this kind of bio-mineral interaction is useful in specific applications, such as self-assembly, bio-nanopatterning and biomolecular arrays, and also in theories on prebiotic chemistry and origin of life (Hanczyc et al., 2007; Hazen et al., 2010; Valdrè et al., 2004).

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Hazen R.M. & Sverjensky D.A. 2010. Mineral surfaces, geochemical complexities, and the origins of life. *Cold Spring Harbor Perspect. Biol.*, 2, a002162.

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Valdrè G., Moro D., Hounsom C.M. & Antognozzi M. 2012. SPM nanolithography of hydroxy-silicates. *Nanotechnology*, 23, 385301.

## Polyphase ore deposition at the Montevecchio vein system, SW Sardinia

Moroni M.\*<sup>1</sup>, Ruggieri G.<sup>2</sup>, Lattanzi P.<sup>3</sup> & De Giudici G.<sup>3</sup>

1. Dipartimento di Scienze della Terra A. Desio, Università degli Studi di Milano. 2. CNR - Istituto di Geoscienze e Georisorse, Unità Operativa di Firenze. 3. Dipartimento Scienze della Terra, Università degli Studi di Cagliari.

Corresponding email: [marilena.moroni@unimi.it](mailto:marilena.moroni@unimi.it)

Keywords: Sardinia, sphalerite, fluid inclusions.

Montevecchio is among the biggest Pb-Zn mining districts in Sardinia. The mineralization is hosted in a 10 km-long, NE-SW-trending set of hydrothermal veins emplaced along steep fractures parallel and radial to the contact of the late Variscan Arburese granitoid complex. Host rocks are Paleozoic low-grade metapelites and metavolcanics variably affected by contact metamorphism. The Montevecchio vein system was extensively exploited for Pb, Zn and Ag with Bi, Sb, Cu, Cd and Ge plus Co and Ni as byproducts, between 1848 and 1973 by means of a network of galleries extending for over 100 km [reviewed in Biddau & al. 2001]. Reports about the detailed features of the Montevecchio veins are scarce and outdated. The mineralization was described as dominated by Ag-rich galena or Cd-rich sphalerite with minor tetrahedrite chalcopyrite, pyrite and accessory Ag-, Cd-, Co-Ni-rich sulfides and sulfosalts, in quartz, Fe-Mn-Mg-Ca carbonate and/or baryte gangue. Preliminary microthermometry revealed a complex history for the mineralization, with contrasting low-T (max 150°C) saline and high-T (>300°C) fluids reported in Boni & al.(2009). New micro-textural, chemical and thermometric studies on the Montevecchio veins confirm the complexity of the mineralization and suggest polyphase emplacement from epithermal to high-T, skarn deposition (with scheelite). Ore facies may be nominally “sphalerite only”, “galena only” or mixed. Coarse, zoned sphalerite exhibits chemical signatures where minor components (Fe, Cd, Mn, Ag, Sb, Ge, Cu, Pb) compete with Zn in the lattice according to variable patterns in different veins, not always compatible with what observed in literature. The controls on economic byproducts Cd, Ge and Ag are far from being obvious or clear. These metals may locally partition between sphalerite and sulfosalts during polyphase deposition, where sulfosalts are depending on galena abundance. In some cases sphalerite may be completely devoid of Cd and anomalously rich in Ag. Tetrahedrite composition ranges between Sb and As end-members, with Ag content depending on vein, assemblage and presence of Ag phases. In Cd-rich ore Cd-rich tetrahedrite inclusions in galena may occur. Galena is rich in sub- $\mu$  mono/polyphase sulfosalt blebs locally inducing selective low-T decomposition of galena close to unaltered sphalerite. Zn remobilization is however recorded by growth of late-stage Zn carbonate. The quartz, carbonate or baryte-bearing gangue assemblages equally show evidence of complex polyphase deposition.

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## Synthesis and characterization of wollastonite-2M by using a diatomite precursor

Novembre D.\*<sup>1</sup>, Pace C.<sup>1</sup> & Gimeno D.<sup>2</sup>

1. Dipartimento di Ingegneria e Geologia- Università di Chieti. 2. Dept. Geoquímica, Petrologia i Prospecció Geològica, Universitat de Barcelona, Spain.

Corresponding email: [dnovembre@unich.it](mailto:dnovembre@unich.it)

Keywords: diatomite, calcium silicate, wollastonite.

The calcium silicate wollastonite (CaSiO<sub>3</sub>) presents two structurally quite different forms; the phase stable above 1150°C called pseudowollastonite or α-wollastonite and the phase stable below 1150°C called β-wollastonite (Hesse, 1984). Wollastonite 2M (Parawollastonite) represents a low temperature polytype with monoclinic symmetry.

Due to its acicular particle shape, whiteness, fluxing properties and absence of volatile components, wollastonites are in general applied with success in the fields of tile factories, paint, paper and vinyl tile manufactures and also as a substitute of asbestos (Justness, 2012). Synthesis of wollastonite is referred to the solid phase reaction method (Grigoryan et al., 2010), the hydrothermal process (Grigoryan et al., 2008), the sol-gel method (Villegas et al., 1988) and the molten salts technique (Trubnikov et al., 1989).

Solid phase reaction synthesis of wollastonite 2M by a natural rock precursor as source of amorphous silica and CaCO<sub>3</sub> has been here achieved. Chemical treatments were carried out on a diatomitic rock from Crotone (Calabria, Italy) in order to measure its reactive silica and CaCO<sub>3</sub> contents. Synthesis was performed at 1000° C, ambient pressure and for the duration of two hours, by the mixing of the diatomitic rock with a natural limestone as source of additive CaCO<sub>3</sub> and sodium carbonate as triggering agent.

Chemo-physical, crystallographical, morphological characterization and infrared and nuclear magnetic resonance (<sup>29</sup>Si) experiments were carried out. Estimation of the amorphous phase in the synthesis powders was performed through the quantitative phase analysis using the combined Rietveld and reference intensity ratio methods, resulting in a final product of 95.2% wollastonite 2M.

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## The effect of mineralizers on tridymite stabilization

Pagliari L.\*<sup>1</sup>, Dapiaggi M.<sup>1</sup>, Pavese A.<sup>1</sup> & Francescon F.<sup>2</sup>

1. Dipartimento di Scienze della Terra- Università degli Studi di Milano. 2. Ideal Standard International - C.O.E. - Ceramic Process Technology.

Corresponding email: [lucia.pagliari@unimi.it](mailto:lucia.pagliari@unimi.it)

Keywords: mineralizers, silica polymorphs, energy efficiency.

The H-T silica polymorphs are known to be tridymite and cristobalite, crystallizing at 870 and 1470°C respectively, as reported in the stability diagram proposed by Fenner (Fenner, 1913). Nonetheless, there has been a lot of discussion over the last century about whether tridymite could or not be considered a stable phase in the pure silica system: when pure quartz is heated, the transformation that usually happens is the direct crystallization of cristobalite, without the intermediate formation of tridymite (Pagliari, 2013, just as an example). However, if any mineralizing agent is added to quartz, tridymite can stabilize and grow, helped by the presence of impurities, such as Na, Ca and K atoms, which accommodate in the large voids of the structure (Buerger, 1954; Flörke, 1956; Holmquist, 1958; Stevens, 1997). Some authors (Flörke, 1986; Stevens, 1997) proposed also that tridymite cannot nucleate if a cristobalite nucleus is first formed.

The present study is about the kinetics and mechanism of tridymite formation starting from pure quartz powders of different grain sizes (D50 of 24, 11 and 3 µm), mixed with 20% aqueous sodium or potassium hydroxide solution. After preliminary *ex-situ* experiments at 900, 1000, 1100 and 1200°C for 1 and 6 hours, necessary to give an idea of the tridymite formation temperature, isothermal analyses were carried out with a Philips X'Pert diffractometer equipped with the hot chamber Anton-Paar HTK 16 MSW. Data collections were performed at different temperatures, depending on the grain size of the starting quartz, and lasted about 10 hours, time required to tridymite to form completely.

Evaluations on the influence of grain size of the raw material, use of mineralizers, temperatures and dwell times of the firing process could be done. The main results are the following: (i) cristobalite crystallization is promoted by the presence of a mineralizer, which decreases the temperature of its formation (compare with Pagliari); (ii) smaller grain sizes of the starting quartz boost the reactions, as already found by Pagliari; (iii) tridymite forms just after a previous nucleation of cristobalite, in agreement with literature; (iv) quartz can be completely replaced by tridymite at 1200°C, avoiding the undesired  $\alpha$ - $\beta$  quartz transformation in the process of ceramic production. From the knowledge of these aspects, industries can obtain an important advice on how to improve their energy efficiency, so recommended nowadays.

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## Crystal structure of the mineral-derived titanosilicate compound BaTiSi<sub>2</sub>O<sub>7</sub>

Palermo A.<sup>1</sup>, Viani A.<sup>2</sup>, Zanardi S.<sup>3</sup>, Gualtieri A.F.\*<sup>1</sup> & Cruciani G.<sup>4</sup>

1. Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia. 2. Institute of Theoretical and Applied Mechanics of ASCR, Centrum of Excellence Telč, Czech Republic. 3. ENI s.p.a., Refining & Marketing Division, San Donato Milanese (MI). 4. Università Dipartimento di Fisica e Scienze della Terra, Università di Ferrara

Corresponding email: [alessandro.gualtieri@unimore.it](mailto:alessandro.gualtieri@unimore.it)

Keywords: BTS2, titanium, photoluminescence, twinning, Rietveld.

Because of their optical, photo-luminescence (PL), and afterglow properties, barium titanosilicates are compounds of great interest for functional materials and light-emitting devices (Takahashi et al., 2012). Some of them are natural minerals (e.g. Ba<sub>2</sub>TiSi<sub>2</sub>O<sub>8</sub>, mineral fresnoite and BaTiSi<sub>3</sub>O<sub>9</sub>, mineral benitoite), but others can be synthesised finding inspiration from natural analogues. In this work, the crystal structure of synthetic BaTiSi<sub>2</sub>O<sub>7</sub> (BTS2), displaying peculiar orange PL emission, was solved for the first time from X-rays powder diffraction data. Results indicate that its structure is a distortion of the tetragonal form of the natural mineral suzukiite (?-BaVS<sub>2</sub>O<sub>7</sub>) with Ti in place of V (Liu and Greedan, 1994). BTS2 has been synthesized through conventional solid state reaction methods. Although BTS2 crystals invariably show complex twinning patterns, the structure solution and Rietveld structure refinement were attempted using two synchrotron diffraction datasets. BTS2 was found an indivisible intergrowth of monoclinic and triclinic crystals. The monoclinic phase has space group  $P2_1/n$  and unit cell  $a = 7.98355(31) \text{ \AA}$ ,  $b = 10.00843(37) \text{ \AA}$ ,  $c = 7.47952(27) \text{ \AA}$ , and  $\beta = 100.321(3)^\circ$  whereas the triclinic phase has space group  $P-1$  and unit cell  $a = 7.99385(4) \text{ \AA}$ ,  $b = 10.01017(5) \text{ \AA}$ ,  $c = 7.47514(3) \text{ \AA}$ ,  $\alpha = 90.084(8)^\circ$ ,  $\beta = 100.368(8)^\circ$ , and  $\gamma = 89.937(9)^\circ$ . The structure models obtained from this study confirm the presence of 5-fold coordinated Ti-atoms in a distorted pyramidal configuration, supporting existing theories for the explanation of PL orange colour in BTS2 (Takahashi et al., 2006). This compound can be considered as an example of intelligent exploitation of primary georesources for the realization of advanced technological materials in that its constituting elements are relatively abundant, and, unlike others PL synthetic compounds, no rare earth dopants are employed.

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## Synthesis of microcrystalline hydroxylapatite and influence of the growth kinetics on the crystal growth morphology

Pastero L.\*<sup>1-2</sup>, Aquilano D.<sup>1</sup> & Cámara F.<sup>1-2</sup>

1. Dipartimento di Scienze della Terra, Università degli Studi di Torino. 2. NIS - Nanostructured Interfaces and Surfaces Centre, Università degli Studi di Torino.

Corresponding email: [linda.pastero@unito.it](mailto:linda.pastero@unito.it)

Keywords: Hydroxylapatite, growth morphology, twinning.

Microsized hydroxylapatite ( $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ ) was synthesized under mild hydrothermal conditions ( $T=220^\circ\text{C}$ , autogenic pressure) by modifying the procedure proposed by Perloff and Posner (1956). The method involves the hydrolysis of a secondary calcium phosphate previously obtained (monetite,  $\text{CaHPO}_4$ ) into a tertiary calcium orthophosphate (hydroxylapatite). Crystals grown in this way were measured by X-ray powder diffraction using a D5000 Siemens diffractometer. They correspond to the pure hydroxylapatite (PDF 00-009-0432, Hodge et al. 1938), are morphologically monoclinic and show habit modifications strongly dependent on the growth rate and supersaturation of the system. In fact, smaller crystals exhibit an undeniable monoclinic morphology showing well developed forms belonging to some of the pinacoids expected from the ab-initio calculations about the equilibrium shape of the hydroxylapatite (Aquilano et al., 2014). The morphology becomes gradually more complicated when crystal size increases, because of the recurring twinning of the crystals. At a first glance, the biggest ones can be misinterpreted as hexagonal crystals because of their morphology, but a careful observation of the relative extension of the forms, of the orientation of the closing facets with respect to the “prisms” and of their surface character, will banish all doubts about their monoclinic symmetry. The final growth morphology differs significantly from the calculated equilibrium shape, but some of the expected forms can be found again, with a change in the relative size due to the growth regime in the presence of the solvent. This observation fits in with the hypothesis that the twinning of monoclinic hydroxylapatite polymorph could mime both structure and morphology of the hexagonal one engendering a mess of conjectures, found in literature, about twinning and symmetry of pure hydroxylapatite.

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## Characterization of geo-inspired binding materials from heat treated cement asbestos

Pollastri S.\*<sup>1</sup>, Viani A.<sup>2</sup>, Pérez Estébanez M.<sup>2</sup> & Gualtieri A.F.<sup>1</sup>

1. Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia. 2. Centre of Excellence Telč, Czech Republic.

Corresponding email: [simone.pollastri@unimore.it](mailto:simone.pollastri@unimore.it)

Keywords: Cement-asbestos, magnesium cement, recycling.

According to recent European directives, the need for environmentally friendly alternative solutions to landfill disposal of hazardous wastes, such as asbestos-containing materials, prompts their recycling as secondary raw materials; this concept known as “end of waste”, adopted by the European Commission on December 2005, regards under which conditions a waste could cease to be waste and could be regarded as a non-waste material. (Gualtieri et al., 2013). In this respect, this contribution describes recent results on the recycling of the high temperature products of cement-asbestos, in the formulation of magnesium phosphate cements (Viani & Gualtieri, 2014). This is an example of nature-inspired materials produced from recycled building materials; indeed, during thermal treatment, destruction of asbestos minerals and recrystallization processes leads to the formation of new phases that have their natural equivalents (Viani et al., 2013). The simultaneous formation of cementitious compounds represents a recycling opportunity for this class of hazardous wastes, bringing benefits in terms of energy requirements and preservation of natural resources in cement manufacturing.

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## **Occurrence of natural asbestos in the historical quarries where “greenstones” are exploited: the example of the Gimigliano-Mount Reventino Unit ophiolite terranes (Calabria, Southern Italy)**

Punturo R.\*<sup>1</sup>, Bloise A.<sup>2</sup>, Critelli T.<sup>2</sup>, Catalano M.<sup>2</sup>, Fazio E.<sup>1</sup> & Apollaro C.<sup>2</sup>

1. Dipartimento di Scienze Biologiche, Geologiche ed Ambientali - Università degli Studi di Catania. 2. Dipartimento di Biologia, Ecologia e Scienze della Terra - Università della Calabria.

Corresponding email: [punturo@unict.it](mailto:punturo@unict.it)

Keywords: Asbestiform minerals, ophiolite terranes, Calabria (Italy).

In order to assess the occurrence of asbestiform minerals within the ophiolitic sequence of the Gimigliano-Mount Reventino Unit (Calabria, southern Italy), a detailed mineralogical and petrographic investigation by means of Polarized Light Microscopy, X-ray powder diffractometry, Scanning Electron Microscopy combined with Energy-Dispersive Spectrometry, and Thermo Gravimetry together with Differential Scanning Calorimetry has been carried out.

Indeed, the main lithotypes that constitute the ophiolite sequence (i.e. metabasites and serpentinites) are exploited and marketed for building and ornamental purposes since prehistorical times (Punturo et al., 2004); for this reason, attention focused on the historical quarries with the main aim to detect the presence of asbestiform fibres which may be harmful for human health.

Results showed that, among the asbestos minerals contained in metabasites, tremolite is the main constituent followed by actinolite; moreover, other fibrous amphiboles (not regulated by the Italian law) occurring are crossite, glaucophane, hornblende and gedrite. As far as serpentinites, chrysotile is the dominant asbestos phase (Bloise et al., 2014; Punturo et al., 2013).

Obtained results hold environmental implications, since they can be used in order to take decisions for the realization of health protecting measures (e. g. during the road yards and quarry excavations) and may also provide data for the compulsory Italian mapping of natural sites, since the selected sites are characterized by the presence of the asbestos commonly known as NOA (naturally occurring asbestos) as well as by the occurrence of other fibrous minerals (e.g., antigorite) that are non- asbestos classified and, therefore, not regulated by law (e.g. DM 18/03/2003).

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## Temperature-induced transformations in ZSM-5 after 1,2-dichloroethane adsorption by “in situ” time resolved synchrotron powder diffraction

Rodeghero E.\*<sup>1</sup>, Martucci A.<sup>1</sup>, Cruciani G.<sup>1</sup> & Pasti L.<sup>2</sup>

1. Department of Physics and Earth Sciences, University of Ferrara. 2. Department of Chemistry, University of Ferrara.

Corresponding email: [elisa.rodeghero@student.unife.it](mailto:elisa.rodeghero@student.unife.it)

Keywords: ZSM-5, 1,2-dichloroethane adsorption, “in situ” time resolved synchrotron powder diffraction.

The aim of this work is to investigate the structural modifications in ZSM-5 during desorption of 1,2-dichloroethane (DCE) by ‘in situ’ time-resolved X-ray powder diffraction. DCE is an important environmental pollutant due to its high toxicity, inertness and widespread application in industry (Gavaskar et al. 1995). Recently, the effective adsorption of 1,2-dichloroethane from aqueous solutions onto highly siliceous ZSM-5 zeolite has been demonstrated by Pasti et al. (2012) by combining diffraction and gas chromatography.

In this work the step by step thermal desorption process of ZSM-5 organophilic zeolite (CBV28014, Zeolyst International, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ~280) loaded with DCE has been studied “in situ” by synchrotron radiation powder diffraction. Time-resolved diffraction data were collected (temperature range 25°-600°C) at the ID31 beamline at ESRF (Grenoble), using a fixed wavelength of 0.40003(1) Å. Kinetics and adsorption isotherm batch data were obtained via Headspace Solid Phase Microextraction -Gas Chromatography. Rietveld refinements were carried out on 19 consecutive powder patterns in the temperature range from 25°C to 600°C. The evolution of the structural features monitored by full profile Rietveld refinements reveals that a monoclinic (P2<sub>1</sub>/n) to orthorhombic (P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>) phase transition occurred at 70°C (Figure 1).

The decomposition and expulsion of DCE was accompanied by changes in the unit-cell parameters, as well as in the channel apertures. Complete DCE degradation and expulsion was achieved upon heating at about 300 °C. This kind of information is crucial for designing and optimizing the regeneration treatment of zeolite used as adsorbents in water and wastewater remediation treatment technologies.

Gavaskar A.R., Kim B.C., Rosansky S.H., Ong S.K., & Marchand E.G., 1995. Crossflow air stripping and catalytic oxidation of chlorinated hydrocarbons from groundwater Environ. Prog. 14, 33-40.

Pasti L., Martucci A., Nassi M., Cavazzini A., Alberti A., & Bagatin R. 2012. The role of water in DCE adsorption from aqueous solutions onto hydrophobic zeolites Microporous and Mesoporous Materials, 160, 182-193.

## **Thermal infrared investigation applied to the physical and mechanical characterization of some natural materials**

Sappa G.\* & Zuccato S.

Department of Civil, Building and Environmental Engineering, Sapienza University of Roma.

Corresponding email: [giuseppe.sappa@uniroma1.it](mailto:giuseppe.sappa@uniroma1.it)

Keywords: thermal infrared investigation, natural materials, physical and mechanical properties.

Thermographic investigation is a technique that allows to evaluate the temperature of surfaces by detecting the electromagnetic emissions of them (Tulipano L., 1976). This technique is based on the principle that any body with temperature, above absolute zero, emits electromagnetic radiation, which depend on the temperature of the body and the physical, chemical and geometrical properties of the surface. The goal of this paper was to evaluate potential applications of thermographic analysis to the characterization of natural materials, carried out at the scale of the laboratory sample (Gong W., 2011) We wanted, in fact, to give an evaluation on the possibility of use the observation and results obtained in laboratory, to study and interpret the termographic survey made at the scale of rock mass, considering and confronting mainly the values of thermal conductivity and dynamic elastic constant of the materials (He M.C. et alii, 2010). Initially they have been considered eight types of rock including: tuff, limestone, roman wall, basalt, sandstone. From these rocks they were obtained cylindrical specimens of various, but similar size, while it were evaluated, with appropriate procedures, various physical and characteristics, like specific weight, porosity and imbibition coefficient, the compressive strength of the samples, estimated by the Schmidt's hammer and the value of modulus of elasticity, determined by the mechanical wave propagation test across the specimen, using the specific sensors and an oscilloscope. Using the infrared camera it has been detected the temperature of various samples in thermal equilibrium with the environment and it has been calculated the behaviour of materials in respect of emissivity. Later, the specimens have been analysed in respect of the thermal flow, heating any specimens from the bottom by an electrical resistivity plane.

The warm-up phase, lasting about an hour, has been monitored by the camera, and they have been taken every minute of termography. The thermal images obtained from all these tests have been developed using a specific software, inserting reference points and areas in the image, from which has been possible to extrapolate the temperature data needed for the development and study of physical phenomena analysed. Some interesting results coming from these investigations are presented and discussed in this paper.

## **Lithiophorite and other Mn phases in a Messinian alluvial deposit of Sardinia: first considerations on REE and trace elements uptake capability**

Sinisi R.<sup>1</sup>, Mameli P.\*<sup>2</sup>, Oggiano G.<sup>2</sup> & Mongelli G.<sup>1</sup>

1. Dipartimento di Scienze, Università della Basilicata. 2. Dipartimento di Scienze della Natura e del Territorio, Università di Sassari.

Corresponding email: [mamelip@uniss.it](mailto:mamelip@uniss.it)

Keywords: Lithiophorite, Uptake, REE.

Mn oxides minerals are important scavengers of trace elements controlling the migration of heavy metals and radionuclides in the geosphere. In soils and laterites, as well as in other tropical sediments, Mn-bearing minerals commonly occur forming nodules, crusts, coatings on clasts, and/or Mn-rich horizons.

In northern Sardinia (western Italy) Mn oxides concentrations were found into Messinian alluvial conglomerates and residual clayey deposits. They occur as Mn-oxides and oxihydroxides locally forming the matrix of conglomerates, coatings covering the conglomerate clasts, and centimeter-size nodules scattered in the clays.

In this paper the preliminary data on mineralogical and chemical composition of Mn-oxides concentrations from the alluvial deposit of Scala Erre are provided with the aim to decipher the environmental conditions and chemical processes occurring during Mn oxides accumulation.

XRPD analysis showed that the main Mn phase of analysed samples is lithiophorite. Birnessite is also a significant component in most samples, whereas pyrolusite, todorokite, hollandite, and cryptomelane were detected in few samples only. Quartz, Fe-oxides and hydroxides (hematite and goethite), clay minerals (mainly kaolinite and scarce illite) and other phyllosilicates (muscovite and chlorite) complete the mineralogical association. ICP-MS and INAA analyses were performed on all samples showing a strong enrichment in transition metals, such as Co, Ni, Zn and Cu, a moderate enrichment in Ba, Y, U Pb and weak depletion in the other trace elements, compared to the GLOSS. Regarding the REE chondrite-normalised distribution patterns, some differences between nodules and the other Mn-rich samples were observed. Nodules are characterized by very high  $\Sigma$ REE values in the range of 1368.8 and 3398.5ppm; high values of LREE/HREE fractionation index ( $6.82 < (La/Yb)_ch < 9.96$ ); and strongly positive Ce anomalies (3.90)

Chemistry, particularly REE data, suggest possible different environmental conditions of precipitation. Ce anomalies are likely due to the presence of organic-rich and organic-poor fluids incoming during the formation of Mn phases, and the LREE/HREE fractionation was probably caused by a different geochemical behaviour of REE rather than a different REE uptake capability of Mn oxides.

## Theoretical and experimental characterization of pure and defective hydroxylapatite for biomedical applications

Ulian G.\*, Moro D. & Valdrè G.

Centro di Ricerca Interdisciplinare di Biomineralogia, Cristallografia e Biomateriali, Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Bologna.

Corresponding email: [gianfranco.ulian2@unibo.it](mailto:gianfranco.ulian2@unibo.it)

Keywords: Carbonated hydroxylapatite, surface electrostatic potential, vibrational properties.

In the biomedical field, much attention is paid on calcium apatites, because these minerals present many similarities with vertebrate bone tissues (Dorozhkin, 2009). In particular, the main component of the bone mineral phase is the hexagonal polymorph of hydroxylapatite [OHAp, space group  $P6_3/m$ ], which presents both anionic and cationic substitutions to stabilize its structure. The most abundant defect in biological OHAp crystals is the carbonate ion ( $\text{CO}_3^{2-}$ ), in a weight percentage ranging from 3% to 7%, depending on the function of the tissue and its age (Dorozhkin, 2009). The  $\text{CO}_3^{2-}$  may substitute both  $\text{OH}^-$  in the  $c$ -axis channel of apatite (type A) and the  $\text{PO}_4^{3-}$  group (type B), as confirmed by experimental (Fleet & Liu, 2003; Fleet & Liu, 2004) and theoretical studies (Ulian et al., 2013a; Ulian et al., 2013b; Ulian et al., 2014). Indeed, the normal modes of carbonate ion fall at different positions, according to the site occupied by the anion. In natural bone tissues, it is common to find both A and B defects at the same time. A deep knowledge of the hydroxylapatite surface biomimetic features is of utmost importance to understand organic biomolecular interactions. In our work, we studied by *ab initio* quantum mechanical approach the surface geometry, the vibrational (IR and Raman) features and the electrostatic potential of the (001) surfaces of both OHAp and defective carbonated hydroxylapatite (COHAp). Theoretical structural and spectroscopic data were compared to experimental XRD, IR and Raman ones with a very good agreement. These results can be very helpful to understand how the carbonate ion modulates the hexagonal OHAp features, information useful, for instance, to obtain more biocompatible materials for prosthetic implants.

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Fleet M.E. & Liu X.Y. 2004. Location of type B carbonate ion in type A-B carbonate apatite synthesized at high pressure. *J. Solid State Chem.*, 177, 3174-3182.

Ulian G., Valdrè G., Corno M. & Ugliengo P. 2013a. Periodic *ab initio* bulk investigation of hydroxylapatite and type A carbonated apatite with both pseudopotential and all-electron basis sets for calcium atoms. *Am. Mineral.*, 98, 410-416.

Ulian G., Valdrè G., Corno M. & Ugliengo P. 2013b. The vibrational features of hydroxylapatite and type A carbonated apatite: a first principle contribution. *Am. Mineral.*, 98, 752-759.

Ulian G., Valdrè G., Corno M. & Ugliengo P. 2014. DFT investigation of structural and vibrational properties of type B and mixed A-B carbonated hydroxylapatite. *Am. Mineral.*, 99, 117-127.

## Glass forming ability of sub-alkaline silicate melts

Vetere F.<sup>1</sup>, Iezzi G.<sup>\*2-3</sup>, Behrens H.<sup>1</sup>, Holtz F.<sup>1</sup>, Ventura G.<sup>3</sup>, Misiti V.<sup>3</sup>, Cavallo A.<sup>3</sup>, Mollo S.<sup>3</sup> & Poe B.T.<sup>2-3</sup>

1. Institute for Mineralogy, Leibniz University, Hannover, Germany 2. Dipartimento di Ingegneria & Geologia, Università G. d'Annunzio, Chieti, Italy 3. Istituto Nazionale di Geofisica e Vulcanologia, Roma, Italy.

Corresponding email: [g.iezzi@unich.it](mailto:g.iezzi@unich.it)

Keywords: silicate melts, nucleation, solidification, critical cooling rate, glass forming ability.

The glass forming ability (GFA) of natural silicate melts is still not well understood, although it is an important physico-chemical parameter to be accounted for in Earth and material sciences. In this study we quantified the GFA of natural sub-alkaline silicate melts *via* the experimental determination of critical cooling rate ( $R_c$ ), i.e. the rate at which  $\leq 2$  area% of crystals solidify. To experimentally model the GFA, we used six melts (basalt, basaltic andesite, poor evolved andesite, evolved andesite, dacite and rhyolite) with compositions shifting systematically from basalt (B) to rhyolite (R) (B<sub>100</sub>, B<sub>80</sub>R<sub>20</sub>, B<sub>60</sub>R<sub>40</sub>, B<sub>40</sub>R<sub>60</sub>, B<sub>20</sub>R<sub>80</sub> and R<sub>100</sub>; the numbers refer to proportions of B and R). The starting glasses were cooled from superliquidus temperature of 1300 °C down to 800 °C (quenching temperature) with six cooling rates of 9000, 1800, 180, 60, 7 and 1 °C/h.

The proportion of phases in each of the 51 run-products was determined from about 300 BS-SEM images at different magnifications. Identified phases are glass, clinopyroxene (cpx), spinel (sp), plagioclase (plg) and rarely a very low amount ( $< 1$  area%) of olivine, orthopyroxene and melilite. In general the amount of crystals continuously decreases as the cooling rate increases. However, solidification behaviour does not invariably follow this trend as observed for one composition (B<sub>80</sub>R<sub>20</sub>). High cooling rates also promotes the formation of dendritic crystals. For a given composition, the first phase which nucleates and grows is Sp (high cooling rates), followed by cpx and ultimately plg (low cooling rates). Sp is the most ubiquitous crystalline phase albeit its amount is few unit of area%; cpx always occurs with sp and is abundant (up to 60 area%) at intermediate cooling rates and in more basaltic compositions; plg crystallizes only in the most mafic compositions.

The  $R_c$  values span 5 order of magnitude being  $< 0.001$ , 0.114, 17, 68, 145 and 150 °C/min for R<sub>100</sub>, B<sub>20</sub>R<sub>80</sub>, B<sub>40</sub>R<sub>60</sub>, B<sub>60</sub>R<sub>40</sub> and B<sub>80</sub>R<sub>20</sub> and B<sub>100</sub>, respectively; the variation of  $R_c$  can be modelled *via* the NBO/T (non bridging oxygen per tetrahedron) parameter by the following master sigmoidal equation:  $R_c = a / (1 + e^{-(NBO/T - x_0)/b})$ , where  $a$ ,  $b$  and  $x_0$  are fitting parameters equal to 165(5), 0.047(5) and 0.283(6). Similar to other glass-forming systems (network, metallic and molecular systems), the  $R_c$  trend of natural sub-alkaline silicate melts can also be predicted by the classical reduced glass transition parameter  $Trg$  ( $Trg = Tg/T_m$ , where  $Tg$  is the temperature at  $10^{12}$  Pas\*s and  $T_m$  the temperature of melting) *via* the equation  $R_c = 4.939 \cdot 9 \cdot Trg^{-41.69}$ .

The results can be straightforward applied to retrieve solidification conditions of aphyric, degassed and oxidised lavas. In addition, the intricate relations between crystal content and kinetic conditions induced by cooling suggest that the solidification path at volcanic conditions can be also highly complex and strongly non-linear. Our equations can also be used to design glass-ceramics based on very abundant and low cost starting materials.

## Quality control of a recrystallized Proterozoic limestone used for the industrial production of quicklime in a Twin Shaft Regenerative (TSR) kiln: a South African case study

Vola G.\*<sup>1</sup>, Sarandrea L.<sup>1</sup>, Cavallo A.<sup>2</sup>, Della Porta G.<sup>3</sup> & Jadoul F.<sup>3</sup>

1. Laboratory and Process Unit, Cimprogetti Spa, Dalmine (BG). 2. Dipartimento di Scienze Geologiche e Geotecnologie, Università Milano-Bicocca. 3. Dipartimento di Scienze della Terra "A. Desio", Università degli Studi di Milano.

Corresponding email: [g.vola@cimprogetti.com](mailto:g.vola@cimprogetti.com)

Keywords: South African Proterozoic limestone, quicklime production, quality control, lime reactivity.

The dark grey bedded limestone from the Ouplaas Mine in Daniëlskuil, South Africa, is currently used to feed both the new 560 tpd Twin Shaft Regenerative (TSR) kilns, recently installed at the local manufacturing lime plant by Cimprogetti Spa. In order to support the client for setting up the quality control of the lime, compositional and microstructural analyses of the limestone, coupled with the technological characterization of limes burnt in laboratory at different temperatures, have been performed (Vola & Sarandrea, 2014). Especially, samples from two different quarry benches (A & B) have been studied to evaluate their burning attitude, and quicklime reactivity. This limestone belongs to the Kogelbeen Fm. of the Campbellrand-Malmani Carbonate Platform, Transvaal Supergroup, which is approximately 2500 Myrs old. It presents characteristic microbial stromatolite laminations, composed of prevalent planar, small scale domal, multi-layered sheets of problematic microorganisms, mainly microbes, originally deposited in a marine shallow subtidal environment. The most of the microfacies are strongly recrystallized. Micro and pseudosparites, with ghosts of peloids and mud intraclasts, are dominant with also abundant late diagenetic poikilotopic calcite cement, generally associated with burial diagenesis, mechanical compaction, and pressure solution that produced swarms of thick black stylolites rich of pyrite and graphite (kerogen). The quantitative phase analysis (XRD-QPA) permitted to identify the impurity content, which is mainly ascribed to clay minerals, i.e. illite and chlorite, microcrystalline quartz (chert), and, locally, fabric dolomite.

This limestone generally shows a sensitive burning attitude, and an overburning tendency at high temperature, so that the average slaking reactivity (EN 459-2) on limes burnt at 1050°C is very high ( $t_{60}$ = 1.3 min. and  $T_{max}$ = 72°C), but rapidly decreases at 1150°C ( $t_{60}$ = 7.5 min. and  $T_{max}$ = 68°C). Just two different layers of the quarry present significant exceptions, and one of them maintains an high reactivity also at 1150°C ( $t_{60}$ = 2.3 min.  $T_{max}$ = 67°C). The colour of the lime is mainly brown, due to the high content of manganese within the parental limestone. Light brown colour corresponds to soft-burnt limes, dark brown colour to medium-burnt limes, and dark-grey or black colours to hard-burnt limes. This information has been useful to control and setting up important kiln parameters, such as the heat distribution and the burning temperature of the plant. Considering the stratigraphic quarry log, and the reactivity of each layer, it was possible to calculate the average reactivity of each bench, and, subsequently, the expected reactivity of different mixtures feeding the kiln. The following scenarios have been reported: 1) A (100%):  $t_{60}$ = 6.5 min.; 2) A (50%) + B (50%):  $t_{60}$ = 7.3 min.; 3) B (100%):  $t_{60}$ = 8.3 min.

This study confirms that specific characteristics of the limestone, such as texture, degree of cementation, presence of dolomite, opaques, and clayey impurities, can significantly impact on quicklime reactivity, as well as, thermodynamic conditions of the process. Moreover, stratigraphic data, associated with laboratory tests, can be successfully adopted to select the best raw mix, reducing the impact of materials of a lesser quality.

Vola G. & Sarandrea L. 2014. Lime reactivity study. *World Cement*, 45, 6, June 2014, 6 p., in press.

## Improving cement sustainability by using nano-materials in clinker production

Zucchini A. \*, Comodi P., Di Michele A., Gentili S. & Rizzo G.

Dipartimento di Fisica e Geologia, Università degli Studi di Perugia.

Corresponding email: [azzurra.zucchini@gmail.com](mailto:azzurra.zucchini@gmail.com)

Keywords: Clinker, nano-materials, CO<sub>2</sub> emission, belite.

During the last few years, particular attention was given to reduce CO<sub>2</sub> emission from industrial processes. Cement industry is one of the most exposed CO<sub>2</sub> producers with more than 5-8% of the total antropogenic production of CO<sub>2</sub>. Carbon dioxide originates (i) from the decarbonation of calcite (CaCO<sub>3</sub>) during firing process and (ii) from energy consumption of rotary kilns during clinker burning. Many works recently dealt with belite-rich clinkers (Sui et al. 2004; Kacimi et al. 2009) since their low clinkering temperature which reflects in a reduction of CO<sub>2</sub> emissions, in high late strength, in high flow ability and in a low heat of hydration. The present work wants to analyse techniques to further decrease the environmental cost of belite-rich clinkers production by adding nano-materials and by-products (blast furnace slags) to the raw mixture. Nano-CaO was synthesized by a precipitation method with the aid of ultrasonic irradiation using CaCl<sub>2</sub> as source (that is a by-product of industrial processes) and NaOH as precipitator. The Ca(OH)<sub>2</sub> nanoparticles were then converted in nano-CaO by calcination process. Four different burning temperatures were chosen for clinker production (1450°C, 1350°C, 1250°C and 1100°C). Clinkers after cooling were analysed by means of Field-Emission Scanning Electron Microscopy (FE-SEM) and X-ray Powder Diffraction (XRPD). The *Rietveld* refinement of collected data was performed by means of TOPAS Academic software (Cheary and Coelho 1992; Cheary et al. 2004). Results showed that  $T = 1100^{\circ}\text{C}$  is the temperature limit for the firing process being the sample after cooling still dusting and not massive. Belite (C2S) is the most representative mineral phase in the clinkers being  $\beta$ -C2S in the range 20-50 wt%; whereas  $\gamma$ -C2S is absent from all the samples. Moreover,  $\beta$ -C2S increases as nano-CaO is added to the raw mixture at the expense of the second generation products, such as Fe-gehlenite (C2AS). Concluding, the optimum production process for belite-rich clinkers starts from nano-CaO enriched raw mixtures fired at approximately 1200°C. The result is a set of clinkers with  $\beta$ -C2S  $\sim$  35 wt%, C3S  $<$  3 wt%, Fe-C2AS  $\sim$  0 wt%. The study of the effects of different nanomaterials, such as SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>, added to different clinker typologies, including standard Portland clinkers, is in progress.

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## **SESSIONE S11**

### **Archaeometry and Cultural Heritage: the contribution of Geosciences**

#### *CONVENORS*

*G. Barone (Univ. Catania)*

*M. Benvenuti (Univ. Firenze)*

*L. Maritan (Univ. Padova)*

## Nanostructured coating and innovative organic-inorganic consolidant: efficiency tests on a calcarenite from Sabucina (Sicily)

Alfieri I.<sup>1</sup>, Barone G.<sup>2</sup>, Bergamonti L.<sup>1</sup>, Lorenzi A.<sup>1</sup>, Lottici P. P.<sup>3</sup>, Mazzoleni P.<sup>2</sup>, Predieri G.<sup>1</sup> & Raneri S.\*<sup>2</sup>

1. University of Parma, Department of Chemistry. 2. University of Catania, Department of Biological, Geological and Environmental Sciences. 3. University of Parma, Department of Physics and Earth Sciences.

Corresponding email: [pmazzol@unict.it](mailto:pmazzol@unict.it)

Keywords: TiO<sub>2</sub> coating, consolidant, Sabucina Stone.

Natural stones used in historical buildings often suffer the effects of weathering and degradation processes. In order to preserve and conserve natural building stones, in recent years suitable synthesized products have been deeply investigated. In the frame of the synthesis of innovative, cheap, eco-friendly, reversible, compatible and high activity products, nanostructured materials represent a cutting edge technology. In particular, TiO<sub>2</sub> nanoparticles are an efficient coating product in view of its self-cleaning photocatalytic action, as testified by the successfully results on Sicilian calcarenite (Bergamonti et al., 2013). However, surface coating could not be a complete solution for conservation purposes, especially when the structural, textural and porosimetric features of the stones require an integrated preservation and conservation effect both in terms of surface protection and of structural strengthening. Consolidant products are widely used in order to improve durability of building stones and the current researches are focused to test innovative products with high compatibility and low impact.

In this work we present the results obtained on the Sabucina stone, a calcarenite outcropping in Central Sicily and widely used as building and replacing stone, by applying coatings based on TiO<sub>2</sub> nanoparticles and hybrid organic-inorganic consolidant products also associated with hydrophobic coating.

Referring to TiO<sub>2</sub> nanostructured coating, we tested self-cleaning photocatalytic coatings obtained by sol-gel process at different pH values. Photocatalytic activity of the TiO<sub>2</sub> coatings on Sabucina stone was assessed under daylight and ultraviolet irradiation, monitoring methyl orange (MeO) and methylene blue (MB) dyes degradation as a function of time. To evaluate the effect of the treatment, colorimetric and water absorption tests were performed. Moreover, in order to verify the efficiency of coating in inhibiting degradation processes, aging tests have been carried out by evaluating stone resistance to salt crystallization.

In addition, a network based on aluminum and silicon oxides with epoxidic functional groups has been tested as consolidant product. In order to evaluate its effectiveness, colorimetric, water adsorption, compressive strength, aging tests and mercury porosimetry measurements have been performed.

Finally, the performance of an hydrophobic coating applied in association with the consolidant has been verified by colorimetric and water adsorption tests.

In conclusion, the obtained results show good photodegradation rates for titania nanosols and good protection properties, especially using the basic preparation. Referring to hybrid organic-inorganic strengthen product and hydrophobic coating, preliminary tests highlight promising applications to the preservation of calcarenites.

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## **An updated isotopic and petrographic reference database for white crystalline marbles used in antiquity**

Antonelli F.\* & Lazzarini L.

Laboratorio di Analisi dei Materiali Antichi (LAMA) – University Iuav of Venice.

Corresponding email: [fabrizio.antonelli@iuav.it](mailto:fabrizio.antonelli@iuav.it)

Keywords: Ancient marbles, Petroarchaeometry, Isotopic composition, Reference Database, Provenance.

The identification of the quarry of provenance of ancient marble artefacts is, on one hand, of the utmost interest to archaeologists and art historians, on other hand, one of the most debated problem of petroarchaeometry. Scholars of different disciplines (mineralogists, petrographers, geochemists, physicists) have been trying for more than a century such an identification by means of a unique or multiple laboratory analysis without totally positive results. To-date the best probability of success are obtained by combining together at least two analytical methodologies and jointly processing all the data obtained. In particular, the detailed mineralo-petrographic examination of a thin section and the determination of the C & O stable isotopic ratios on the same sample is currently the most widely used combination. Such a combination takes advantage of the best existing databases for the main Mediterranean marbles very commonly used in Classical antiquity. On the basis of a detailed scrutiny of the recent literature data published from 2002 to 2012, we propose here an upgrade and a chronological reorganization on a geographic base of the petrographic and isotopic databank based on hundreds of analyses relative to the marbles from the major and some minor quarries active in Greek and Roman times. These new data, never considered before all together and implemented with unpublished results, let us both to increase the statistical significance of the whole database and draw new global reference isotopic diagrams related to the main petrographic features (i.e. maximum grain size - MGS, texture/fabric and grain boundary shapes) of the different lithotypes which are useful to better establish the provenance of a given archaeological objects.

## Application of micro-Raman Spectroscopy for the characterization of rubies

Bersani D.\*<sup>1</sup>, Barone G.<sup>2</sup>, Lottici P.P.<sup>1</sup>, Mazzoleni P.<sup>2</sup>, Raneri S.<sup>2</sup> & Longobardo U.<sup>3</sup>

1. University of Parma, Physics and Earth Science Department. 2. University of Catania, Department of Biological, Geological and Environmental Sciences. 3. Jeweller – Catania.

Corresponding email: [daniло.bersani@fis.unipr.it](mailto:daniло.bersani@fis.unipr.it)

Keywords: Raman spectroscopy, gems, rubies.

The use of gems for manufacturing jewels and to adorn precious artefacts, such as royal insignia or liturgical objects, represents a well know practice since ancient times. Considering their value and the fact that they are often preserved in Museums, the use of non-destructive and non-invasive techniques for the characterization is required. Furthermore, the study of gems, and in particular the possibility to obtain information on their nature and provenance, represents a relevant procedure for archaeometric issues.

In this framework, Raman spectroscopy represents a useful tool being a quick, completely non-invasive and contactless technique which does not require any sample preparation.

Among the major commercial gems, ruby is considered one of the most precious gemstones, together with sapphire, emerald and diamond. Ruby is the red transparent gem variety of corundum; the colors are intense red to pink due to traces of Cr<sup>3+</sup> ions.

In this context, this work is focused on the spectroscopic characterization of different kinds of rubies, by using micro-Raman instrumentations equipped with different laser excitation sources in order to furnish gemological identification and to acquire information about the provenance of the gems. In detail, Raman spectra have been collected on seventeen samples of red loose gems by means a confocal JobinYvon Horiba Labram, with 473.1 nm excitation line from a diode pumped Nd:YAG laser and a micro-Raman Jasco NRS-3100 apparatus, equipped with laser excitation source at 785 nm.

The obtained results allow not only to discriminate rubies from simulant and fakes but also achieve useful information on inclusions and treatments.

Therefore, the main aim of this work is to test the potentiality of micro-Raman spectroscopy in rubies identification, establishing the basis for the characterization of rubies with portable Raman spectrometers directly in museums, on gems mounted in precious and unmovable artworks. In this perspective, this should be considered as a first step of a campaign of portable Raman measurements we are carrying out on ancient jewelry collections preserved in Sicilian Museum.

## The stones of the Egyptian Museum of Turin: geological, mineralogical and petrographic characterization

Borghi A.\*<sup>1</sup>, Angelici D.<sup>1</sup>, Borla M.<sup>2</sup>, Castelli D.<sup>1</sup>, d'Atri A.<sup>1</sup>, Gariani G.<sup>3</sup>, Lo Giudice A.<sup>3</sup>, Martire L.<sup>1</sup>,  
Re A.<sup>3</sup> & Vaggelli G.<sup>4</sup>

1. Dipartimento di Scienze della Terra, Università di Torino. 2. Soprintendenza per i Beni Archeologici del Piemonte e del Museo delle Antichità Egizie. 3. Dipartimento di Fisica, Università di Torino. 4. Istituto Geoscienze e Georisorse, C.N.R. Torino.

Corresponding email: [alessandro.borghi@unito.it](mailto:alessandro.borghi@unito.it)

Keywords: Applied Petrography, Cultural Heritage, Archaeometry, Egypt.

The Egyptian stones are of primary importance among all the natural stones used in various historical epochs, both for the wide use of the Ancient Egyptians and for the following use in Roman times. Rocks with different geological history and different chemic-mineralogical compositions represent, therefore, an unique artistic and cultural heritage.

A collaboration between the Egyptian Museum and the University of Turin started from 2005 with the aim to study the stones of Egyptian finds by a geological and minero-petrographical viewpoint in order to enhance the value of this artistic heritage and to set the base for its best conservation.

Magmatic, sedimentary and metamorphic rocks were recognised in decreasing order of abundance. The magmatic rocks of intrusive origin are the most represented and include the following varieties: - The "Red and Pink Assuan Granite": sieno-granite with porphyritic texture with pink to red K-feldspars. Macroscopically the rock is holocrystalline with a large grain size (millimetric to centimetric). The minerals are represented by pink-to-red K-feldspar, white plagioclase, glassy quartz and dark femic minerals.

- The "Black granite": granodiorite, quartzodiorite and tonalite varieties belong to this type of rock whose colour ranges from grey to almost black. The grain size is from medium to large. Peculiar is the presence of large white or pink feldspar porphyrocrystals, sometimes in aggregates, as well as the presence of lighter aplitic veins and darker mafic xenolites.

These magmatic rocks belong to the Arabo-Nubian shield outcropping in the southeastern sector along and parallel to the Red Sea coastline as well as in the southern sector of Sinai peninsula. The historical quarries are located near Assuan.

The sedimentary rocks are represented by Tertiary white limestones and the Nubian sandstone. The sandstone is dark yellow, has a medium grain size and locally shows alteration spots in darker colour. Pink sandstone finds were also recognised.

The limestone finds show a granular, porous and not very solid aspect with the exception of Tut Ankh Amon statue which is made up by a solid and micritic white limestone characterised by the presence of stilolitic joints and veins of sparry calcite.

Among the metamorphic rocks it is worth noting the occurrence of the so-called Becken Stone, which was used to carve three sarcophagi of the Late Period. The Bekhen Stone (Lithos Basanites for Greeks and Lapis Basanites for Romans) is the name attributed to a green-black meta-greywacke belonging to the Hammamat series of late-Precambrian age and outcropping in the North and Central sector of the Eastern Desert.

Another objective of the project is to characterize a selection of amulets made of lapis lazuli, in order to verify the presence / absence of the archaeometric parameters so far identified to discriminate the different backgrounds and provide indications about the origin of the raw material.

The available set of samples will allow to increase the number of scanned objects belonging to the Egyptian culture and, consequently, the results of the investigations will enable to confirm or not the existence, starting from the II-I millennium BC, of trades between the Egyptian civilization and the near East, where there are major deposits of lapis lazuli exploited in Antiquity. The survey will be expanded to other Egyptian collections.

## A new methodological approach for study pietra ollare artifacts

Cantù M.\*<sup>1</sup>, Conz E.<sup>2</sup>, Rebay G.<sup>1</sup> & Riccardi M.P.<sup>1</sup>

1. Dipartimento di Scienze della Terra e dell'Ambiente, Università degli Studi di Pavia. 2. Dipartimento di Scienze economiche e aziendali, Università degli Studi di Pavia.

Corresponding email: [michela.cantu01@ateneopv.it](mailto:michela.cantu01@ateneopv.it)

Keywords: pietra ollare, ophiolites, petrographic study.

The Italian term 'pietra ollare' indicates soft rocks, mostly basic and ultrabasic metamorphic rocks, that have been used, since the early times, for the production of pots, vessels and food containers. These rocks are characterized by good workability, fire resistant and refractory properties.

Quarries attested by historical sources as pietra ollare production centers are widespread in the Western and Central Alps and one of the goals of archaeometric studies is to find the extraction sites of the materials used to produce such artifacts.

In the last decades petrochemical studies of archeological findings of pietra ollare were carried out but these data do not allow to univocally associate shards to quarries, considering the diffusion of lithologies corresponding to pietra ollare throughout the Alps. These studies have also shown that the geochemical bulk analyses are not sufficient to discriminate artifacts of different geographical origin. We suggest a new archaeometric approach to characterize pietra ollare archeological findings, correlating archeological data, hand sample analysis and petrochemical analyses. This method hasn't the claim to establish the quarry from which the artifacts come but it can define a macro-area of provenance, with examples from the Alps.

The innovative methodology of this work concerns the petrographic study of the archaeological sample not only as an instrument for the identification of the mineralogical phases but also as the principal tool to reconstruct the blastesis-deformation history. Once the relative chronology of successive parageneses recorded by the rock is reconstructed, it is possible, for example, to distinguish among crystals of the same mineralogical phase that grew in different times of the rock history.

According to the petrographic study, geochemical analyses can be carried out on specific microstructural sites and the results can be compared to those obtained with the same approach on artifacts and samples extracted from quarries assumed to be the extraction sites. The strength of this approach is that the geochemical comparison must be made among crystals of the same mineralogical phase that presumably grew in the same time of the history of the rock, thus reducing the dimension of the provenance area, if the metamorphic evolution of different areas is known in detail.

## **Earthen mortars in historical buildings of Cremona: a multianalytical approach**

Cantù M., Gasparini E., Giacometti F., Rebay G., Riccardi M.P.\* & Tarantino S.C.

Dipartimento di Scienze della Terra e dell'Ambiente, Università degli Studi di Pavia.

Corresponding email: [mariapia.riccardi@unipv.it](mailto:mariapia.riccardi@unipv.it)

Keywords: earthen mortars, archaeometry, multianalytical approach.

The use of earthen mortars is widespread all over the Po plain and it is possible to attribute these materials to a long time span, ranging from the Roman Age to the Nineteenth Century. Considering the availability of good quality lime from the neighboring Piacenza area, the use of earthen mortars in the town of Cremona still needs to find a plausible explanation.

An accurate study of ancient architectural treatises was performed to better define the productive technologies of these materials and understand why they were used instead of the traditional lime-based ones. According to Sonsis (1807), a very good quality mortar could be obtained by mixing a red soil outcropping at Cava Tigozzi (a small town near Cremona) with a small amount of lime. To better understand the ancient productive technologies and define the raw materials utilized for the production of earthen mortars, a multidisciplinary mineralogical, geochemical and petrographical study was performed.

Samples of both earthen plasters and mortars with a structural function were collected in historical buildings of the XV-XVIII centuries. Fragments of mortars mounted in epoxy resin and thin sections were investigated with optical and electronic microscopy (SEM) to provide a textural and mineralo-chemical characterization of the materials. XRD and FT-IR studies better defined the mineralogical composition of the mixtures.

Furthermore, samples of soils were collected at Cava Tigozzi. XRD and FT-IR analyses were done in order to characterize these raw materials and compare them with the mixtures recognized in mortars.

## **From Roman to Romanesque, a mix of architectural styles and geomaterials in San Saturnino Basilica (Cagliari, Italy): petrophysical characterization, static-structural analysis and 3D laser-scan relief**

Cazzani A.M.<sup>1</sup>, Columbu S.<sup>2</sup>, Ruggieri A.\*<sup>3</sup>, Sitzia F.<sup>2</sup> & Verdiani G.<sup>4</sup>

1. Dipartimento DICAAR, University of Cagliari. 2. Dipartimento di Scienze Chimiche e Geologiche, University of Cagliari. 3. Soprintendenza per i Beni Architettonici, Paesaggistici, Storici, Artistici ed Etnoantropologici di Cagliari e Oristano (Contractor). 4. Dipartimento di Architettura, University of Firenze.

Corresponding email: [columbus@unica.it](mailto:columbus@unica.it)

Keywords: Petrophysical, Static-structural analysis, Ancient marbles.

The Basilica of St. Saturnino rises over a sacred site since the origins of the town of Cagliari. The Roman Empire recognized the importance of such place implementing the original sepulchral function consolidating the function of the area. The *martyrium* of St. Saturnino (beginning of the IV Century A.D.) signed its passage from pagan to Christian cemetery. In this period the original chapel was built starting a long evolution of the building across half a millennium, until its Romanesque evolution and its later abandon and partial destruction at the beginning of the XIV Century. Its further story continued across time, bringing to our age a rich and interesting monument, articulated around its original structure mixing parts from the Imperial Roman, Byzantine and Romanesque phases together with clumsy attempt of modern restorations. The Byzantine phase has left us a large cubic structure, with robust arches and vaults testifying the evolution of construction techniques in Medieval Sardinia. The formal technical reading of the elevations is complicated by the frequent reuse of Roman artifacts, often of exquisite workmanship. The presence of diachronic source materials, together the technical problems of attribution, often make it difficult to study the building. The analysis of materials has led to a thorough investigation of the macroscopic number of lithologies, some of which are in an advanced state of alteration. To start a clear reading of this complex system a multidisciplinary approach was chosen, combining historical reading, analysis of the stones and digital survey solutions. The most significant materials in the church were sampled, taking precise reference to the various construction phases of each historical context and interventions of structural changes occurring in the various centuries and numerous restorations mirror of philological different cultures. The whole building and its surrounding area were surveyed with the following methods: photography, 3D Laser Scanner for the whole interior and exterior parts, 3D photogrammetry of a selected set of stone surface samples.

Were sampled and geochemical and petrographic analyzed several architectural stone elements (shafts of columns, capitals, etc.) used as building materials, characteristic of the Roman period, made in various kinds of marbles, currently distributed between the inside and outside of the monumental structure. Were also analyzed carbonate rocks ("pietra cantone", "pietra forte" of the Cagliari formation), used to make the most of the perimeter walls. To a lesser extent, there are ashlar of Oligo-Miocenic volcanics of Sardinia, and the occasional presence of other stone materials coming not from the island. A complex system of traces in need of contemporary and well organized digital and scientific approach in order to enhance the knowledge about this monument. The contribution proposed here will present the progress state of this research and its results.

## Medieval Cu-Pb-(Zn)Ag smelting at Montieri and Cugnano, Colline Metallifere district (southern Tuscany)

Chiarantini L.\*<sup>1-2</sup>, Calossi V.<sup>1</sup>, Domnori M.<sup>1</sup>, Fratangelo V.<sup>1</sup>, Silvestri G.<sup>1</sup>, Bruttini J.<sup>3</sup>, Bianchi G.<sup>3</sup> & Benvenuti M.<sup>1</sup>

1. Dipartimento Scienze della Terra, Università di Firenze. 2. IGG-CNR Pisa. 3. Dipartimento di Scienze Storiche e dei Beni Culturali, Università di Siena.

Corresponding email: [laura.chiarantini@gmail.com](mailto:laura.chiarantini@gmail.com)

Keywords: Cu-Pb-Ag smelting, slag, Colline Metallifere, Medieval.

The Colline Metallifere district (southern Tuscany) hosts a number of Cu-Pb-Zn(Ag) vein deposits which fed a long-living mining and metallurgical industry, starting in the Chalcolithic period up to the 70s of past century. According to archaeological and historical documents, during the Medieval period (11<sup>th</sup>-14<sup>th</sup> cent. AD) metal production (copper and silver) in the district was mainly used for coinage. Recent archaeological excavations at the sites of Montieri (S. Niccolò Rectory) and Cugnano, uncovered several heaps of metallurgical wastes (mainly slag), whose detailed analysis revealed an extremely complex picture of metallurgical activities carried out in this area in the Middle Ages.

The considerable variability of slag's mineralogical/chemical composition partly reflects different metallurgical processes (and/or different steps of the same metallurgical process). In the lifetime of the S. Niccolò Rectory, at Montieri, the otherwise low amounts of metallurgical waste (slags) may be referred to preliminary steps of Pb (and Ag?) extraction from galena-rich ores, associated with Cu-Fe-Zn-Ag sulphides and sulfosalts. Slags contain variable amounts of (Cu-Fe-S) matte, As-Sb(Ag) speiss and metallic Pb. Interestingly, slags with low matte contents include abundant agglomerates of a phase (probable c-Al<sub>2</sub>O<sub>3</sub>), which could be the product of transformation at high temperatures of Al-rich phases (like alunite) either present in the ore gangue and/or in intentionally added fluxes and/or in the furnace walls. Also in the proximity to the S. Niccolò Rectory, within stratigraphic levels belonging to the 11<sup>th</sup> cent. AD, bell pits and high tin bronze fragments have been recently found which are a clear evidence of bell founding.

Neither at the Rectory nor in the partially excavated "Foundries" within the old Montieri village, clear evidence has been found of silver extraction (such as "cupels", crucibles or other metal fragments), suggesting that the refinement processes were conducted elsewhere.

A much larger metallurgical waste deposit (around 450 tons of slag) has been found during excavations at the Cugnano castle. Slags are tapped and have relatively low viscosity; compositional features (prevalence of wüstite over magnetite; high content of S, As, Sb; presence of "speiss" with Pb+Ag; low diffusion of lead in the glassy matrix) suggest that they refer to the first steps of lead smelting from Cu-Pb-Ag sulphidic (galena, tetrahedrite) ores of local provenance, maybe preliminary to silver extraction.

## Characterization of natural and artificial stone materials from S. Niccolò archaeological complex in Montieri (Tuscany, Italy)

Chiarelli N.\*<sup>1</sup>, Miriello D.<sup>2</sup>, Scala A.<sup>1</sup>, Bianchi G.<sup>3</sup>, Bruttini J.<sup>3</sup>, Fichera G.<sup>3</sup>, Giamello M.<sup>1</sup> & Memmi Turbanti I.<sup>1</sup>

1. Dipartimento di Scienze fisiche, della Terra e dell'ambiente, Università di Siena. 2. Dipartimento di Biologia, Ecologia e Scienze della Terra, Università della Calabria. 3. Dipartimento di Scienze storiche e dei beni culturali, Università di Siena.

Corresponding email: [nicoletta.chiarelli@unifi.it](mailto:nicoletta.chiarelli@unifi.it)

Keywords: Archaeometry, Mortars, Plasters, Bricks.

S. Niccolò archaeological site is situated on the north-east side of Montieri Hill (Southern Tuscany), in an ancient mining district. Ruins of the medieval ecclesiastical complex were discovered during recent excavations and consist of: a peculiar church, characterized by six apses; an annexe to the church; a productive area; a central place, interpreted as porticoed cloister; a great number of tombs. This archaeometric study is aimed to deepen the knowledge of the historical site through the characterization of natural and artificial building material rests (mortars, plasters and bricks). The petrographic analysis was performed on the thin sections by polarized light Optical Microscopy. Mineralogical and chemical composition was determined by XRPD and XRF, respectively. Textural and chemical micro-analysis were carried out by SEM-EDS. Preliminary petrographic study indicates that quartziferous-feldspathic-micaceous sandstone was utilized for the foundation walls of the complex, while the outer walls are mainly constituted by marly limestone and calcareous tufa ashlar. A petrographic, mineralogical and chemical study allowed us to distinguish various typologies of mortars, characterized by different aggregate and binder as well as by variable aggregate/binder ratios. The aggregate is constituted of minerals and lithic fragments. The most common minerals found were quartz, plagioclase, muscovite and calcite; sandstone, limestone, shale, quartzite, and phyllite were the most widespread lithic fragments. Shards of glasses, coal, metallurgic slags and crushed ceramic fragments (*cocciopesto*) were also identified. In the majority of the samples the binder is weakly hydraulic and it shows a moderate hydraulicity in the samples containing slags or *cocciopesto*. The archaeological and archaeometric data suggest a development of the site in different successive phases. The church was built during the most ancient one. The mortars sampled from all the six apses of the church belong to a unique typology, so that it can be ascribed to a single building phase. The fragments of metallurgic slags were observed in the mortar's aggregate of the annexe, of the productive area and in the complex's entrances, but they are lacking in the church. The use of slags as constituent of mortar's aggregate could be due to an evolution of building technology, with respect to the church, when probably the metallurgic activity have not yet started. These preliminary results represent the starting point for the future provenance study of the raw materials, in order to plan compatible products for restoration of the archaeological site.

## Characterization of the ancient mortars and 3D laser scanner survey to define the construction phases of the *Heliocaminus* Baths in the Hadrian's Villa (Tivoli, Italy)

Columbu S.<sup>1</sup>, Sitzia F.\*<sup>1</sup> & Verdiani G.<sup>2</sup>

1. Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari. 2. Dipartimento di Architettura, Università di Firenze.

Corresponding email: [columbus@unica.it](mailto:columbus@unica.it)

Keywords: Mortar characterization, 3D Laser-Scanner, Roman Architecture.

Inside the Hadrian's Villa in Tivoli, it is possible to see the ruins of special and unique buildings, aimed at their time to create spectacular places, to give appropriate spaces to the court and to the people living in this architecture masterpiece. The reading of these structures sometimes is not easy, so the main idea in this project is to start from the small evidences in the single buildings, find rules and solutions to combine them into a global digital survey based on a 3D digital model and then start using this model for hypothesis formulation. This kind of approach should only be multidisciplinary combining the knowledge about petrographic, mineralogical and chemical characterization with the techniques of the digital survey (using 3D Laser Scanner based solutions) and the reading of the architectural aspects. The research presented here will propose this methodological approach as the tool to interpret the different construction phases of the *Heliocaminus* baths (II Century A.D.): the first personal spa of Emperor Hadrian.

Using mineralogic-petrographic (by optical microscopy and XRD) and physical analysis a set of samples were investigated for their compositional aspects of the aggregate and of the pozzolanic binder of mortars, and their physical characteristics (real and apparent densities, open and closed porosity, water absorption kinetic, mechanical strength, etc.). These parameters, together with the analysis of the aggregate particle size and morphology, and a proper analysis of the relationships binder/aggregate, have shown a clear relationship between the physical-compositional characteristics of mortars and their function within the structure of the baths. Then, through the differential thermal analysis (TGA, DSC) it has been studied the hydraulic degree of mortars, which is also linked to the kind of aggregate and pozzolanic materials used.

All this has allowed us to detect some compositional discrepancies between the different mortars used in this building, even within the same room, highlighting how the *Heliocaminus* baths was carried out in several stages, with interruption of the construction works and with an evident change in the workers operating in its courtyard. All the gathered data, linked to the pointcloud 3D model of the *Heliocaminus* baths allowed an accurate location of all the meaningful traces of the story of this structure giving confirmations to the high architectural value of specific and innovative solution of that age. The contribution of the scientific analysis of the samples puts in evidence the importance of correct and innovative solutions in cultural heritage approach with proper technologies.

## The stones used for building the apse of the Pisa's Cathedral (Italy)

Coppola F.\* & Lezzerini M.

Dipartimento di Scienze della Terra, Università di Pisa.

Corresponding email: [francesca.coppola@hotmail.it](mailto:francesca.coppola@hotmail.it)

Keywords: stone, marble, building material.

A detailed knowledge of the building materials and of their main characteristics is a fundamental pre-requisite for a good stonework's restoration project. Nowadays Computer Aided Design (CAD) can be considered as an interesting tool for the achievement of stonework mapping and, more generally, to the management of a full restoration project.

This paper presents the mapping of the building stones used in the apse of the Pisa's Cathedral (XI century), with the scope of highlighting the potential of photogrammetry and CAD techniques in the field of restoration and conservation of stonework.

Once the survey of the apse masonry had been realized and the main geometry of each ashlar was detected, the building materials have been mostly identified by stone-to-stone visual inspection. For the recognition of the stones used for building the apse of the Pisa's Cathedral, the macroscopic characteristics widely described in several papers on the stones of medieval buildings in Pisa (Franzini & Lezzerini, 2003 and references therein) were exploited, while for marbles analysis traditional methods, such as textural features, accessory minerals and C-O stable isotope data (Moens et al., 1992; Gorgoni et al., 2002; Capedri et al., 2004) were applied.

Based on collected data, the Apse of Pisa's Cathedral was mostly made up of Mt. Pisano and Apuan marbles and black limestones quarried at some kilometres northwest from Pisa in the Monti d'Oltre Serchio area. Re-used marbles from quarries located in Eastern Mediterranean area (Turkey and Egypt) characterise the first construction phase of this monument. The lithotypes identified in intarsia of the apse are serpentinites of unknown origin, used as decorative stones for their marble-like qualities, and small elements of red limestone probably belonging to the Scaglia Rossa Formation of the Tuscan sequence.

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## **A crash test for Michelangelo's David: results from small-scale centrifuge modeling**

Costagliola P.<sup>1</sup>, Corti G.<sup>2</sup>, Benvenuti M.\*<sup>1</sup>, Bonini M.<sup>2</sup>, Landucci F.<sup>1</sup>, Pecchioni E.<sup>1</sup> & Vaiani A.<sup>1</sup>

1. Dipartimento di Scienze della Terra- Università di Firenze. 2. Istituto di Geoscienze e Georisorse, CNR Pisa.

Corresponding email: [m.benvenuti@unifi.it](mailto:m.benvenuti@unifi.it)

Keywords: Michelangelo's David, crash test, analogue modeling.

It has been noted since the mid 1800s that the Michelangelo's David, the standing marble male nude representing a masterpiece of the Italian Renaissance, is affected by small cracks on both legs that threaten its stability. Understanding the characteristics and the conditions under which these lesions developed is thus critical for the preservation of this universal masterpiece.

In this study, we use an analogue modeling approach to test the conditions that led to the development of fractures in the David's legs and to get insights into its stability. The experiments were performed by using the centrifuge apparatus at the Tectonic Modeling Laboratory of the Institute of Geosciences and Earth Resources (CNR-IGG) settled at the Earth Sciences Department of the University of Florence. Small-scale (10 cm-high) gypsum replicas of the statue were deformed in a centrifuge, where the models were affected by a body force stronger than gravity but otherwise playing the same role. Analysis of the model results suggests that both the stability and the resulting deformation of the statue are highly sensitive to its attitude. A forward inclination promotes destabilization: the higher the angle of inclination ( $\alpha$ ), the more unstable the statue becomes under its own weight, confirming existing finite element modeling (FEM). In a vertical position, rupture of the statue typically occurs in the lower portions of the legs, while ruptures tend to develop progressively higher along the legs as forward inclination increases. Comparison of these results with the lesions detected on the actual David suggests that a long-lasting, small forward inclination (likely close to  $\sim 5^\circ$ ) of the statue may have represented a critical driving factor for the development of the observed damages.

These simple, preliminary models are characterised by many important simplifications, and can be thus improved in the near future. However, our results support the applicability of small-scale centrifuge modeling to problems of conservation of Cultural Heritage. At least in principle, through the analogue model approach, any feature of the original work of art, including anisotropies, aging, restoration etc., could be simulated by a suited model. Analogue modeling may thus represent a powerful technique to analyze the stability and deformation of other masterpieces, providing complementary information to the more classical FEM approach.

## **Non-destructive investigation on the pigments from the earliest painted ware in the Neolithic Age of Sicily**

Cultraro M.<sup>1</sup>, Caruso F.\*<sup>2</sup>, Chillura Martino D.F.<sup>2</sup> & Caponetti E.<sup>2</sup>

1. Istituto per i Beni Archeologici e Monumentali del Consiglio Nazionale delle Ricerche (IBAM – CNR), Catania. 2. Dipartimento di Chimica “S. Cannizzaro” dell’Università degli Studi di Palermo.

Corresponding email: [massimo.cultraro@cnr.it](mailto:massimo.cultraro@cnr.it)

Keywords: XRF; XRD; Neolithic Painted Pottery, Neolithic Sicily; Pigments; Manganese.

This paper examines the painted red and black painted pottery named in the archaeological literature as “Bichrome” and “Trichrome” ware, assigned to the late 5<sup>th</sup> millennium BC (calibrated date). The analyzed artifacts come from different sites of Central and East Sicily (district between the Mount Etna and Dittaino river, Enna), and the most important of them is the Neolithic settlement at Trefontane, Paternò, explored in the early 20th century by I. Cafici (1914).

X-Ray Fluorescence and X-Ray Diffraction analyses are presented, focusing on the red and black pigments used to decorate such two- and three-colors ceramics. We successfully obtained technological information about the employed raw materials and the surface decorations of these samples. The main results is to demonstrate the use of manganese in black pigments and indicate, for the first time, an occurrence of this element in the earliest painted pottery of the Neolithic Age of Sicily.

## **Micro-chemical and -structural study of pyro-metallurgical materials found in different archaeological sites of Sardinia (Italy)**

De Caro T.\*, Riccucci C. & Faraldi F.

ISMN-CNR Montelibretti, Roma.

Corresponding email: [tilde.decaro@ismn.cnr.it](mailto:tilde.decaro@ismn.cnr.it)

Keywords: smelting, slags, tuyeres, ancient metallurgy, refractory tools.

A large amount of pyro-metallurgical materials such as slags, tuyeres and refractory tools pertaining to metal extractive and smelting processes related to the Punic and Roman periods (IV-III BC) have been found in different sites of Sardinia (Italy).

Micro-chemical, micro-structural and mineralogical investigations have been carried out by means of the combined use of different analytical technique such as optical microscopy (OM), scanning electron microscopy (SEM) with energy dispersive X-ray microanalysis (EDS), X-ray diffraction (XRD) in order to identify pyrometallurgical processes and the technological parameters and to determine the technological level of competence reached by the ancient metallurgists.

The results reveal that the findings can be associated at Tharros (north-western Sardinia) with an iron ore smelting processes while in the Montevecchio mine basin with smelting and extractive processes carried out close to the metal ore deposit for the argentiferous lead production and for the silver recovery via cupellation process.

## **Microchemical study of the corrosion products on archaeological bronze artefacts by means of micro-Raman spectroscopy**

De Caro T.\*

ISMN-CNR Montelibretti, Roma.

Corresponding email: [tilde.decaro@ismn.cnr.it](mailto:tilde.decaro@ismn.cnr.it)

Keywords: corrosion; bronze; archaeological artefacts, patina, micro-Raman.

A large number of Roman and Punic bronze artefacts have been found during archaeological excavations carried out in different Italian sites characterised by different soil features and degrading agents thus giving rise to the formation of different corrosion products whose chemical nature has been investigated via micro-Raman spectroscopy.

The results reveal that the main corrosion agents is chlorine that is both present as copper oxy-chloride polymorphs (in the form of atacamite and clinoatacamite,  $\text{Cu}_2\text{Cl}(\text{OH})_3$ ) showing the occurrence of the most aggressive form of bronze corrosion called "bronze disease" and more rarely also as a stable and uncommon chlorine compound such as a lead chlorophosphate (pyromorphite  $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$ ). Furthermore, micro-Raman investigation reveals the presence of other corrosion products such as copper oxide, carbonates, silicates, phosphates, and copper-iron sulphide whose presence demonstrates the close relationship between the soil constituents (Cl, P, Si, S, Fe, Ca) and corrosion products. The results demonstrate the fruitful use of the non-destructive micro-Raman spectroscopy to study corrosion phenomena and to discriminate between different polymorphs with high spatial resolution thus extending the applicability of the surface analysis methods.

## Mortars and plasters from the Forum of Pollentia (Mallorca, Balearic Islands, Spain): an archaeometric study

De Luca R.\*<sup>1</sup>, Cau Ontiveros M.A.<sup>2-3</sup>, Pecci A.<sup>1</sup>, Crisci G.M.<sup>1</sup>, Le Pera E.<sup>1</sup>, Bloise A.<sup>1</sup> & Miriello D.<sup>1</sup>

1. Department of Biology, Ecology and Earth Sciences, University of Calabria, Rende (CS).

2. Institució Catalana de Recerca i Estudis Avançats (ICREA), Spain. 3. Equip de Recerca Arqueològica i Arqueomètrica, Universitat de Barcelona (ERAAUB), Departament de Prehistòria, Història Antiga i Arqueologia, Spain

Corresponding email: [raffaella.deluca@unical.it](mailto:raffaella.deluca@unical.it)

Keywords: Pollentia, Balearic Islands, mortars, plasters, Roman production technology, constructive phases.

This work shows the result of the archaeometric study carried out on 27 samples of mortars and plasters coming from the *Forum of Pollentia*, an ancient Roman and Late Antique city located in the north-east coast of Mallorca (Balearic Islands, Spain).

The samples were taken from different buildings, in particular from some rooms of the so-called *Insula of tabernae*, the *Templete I*, the *Templete II*, the *East Building* (probably identified as a *Basilica*) and several other remains from the *East Sector*, where a *macellum* (market) could have been located (Orfila & Cau, 2004; Munar et al., 2009).

The petrographic, mineralogical and chemical characterization of the samples was carried out through the application of different analytical techniques: optical microscopy (OM), X-ray Powder Diffractometry (XRPD), X-ray Fluorescence (XRF), Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDS) and Image Analysis by the “JMicro Vision” software. The compositional data was also processed by the Aitchison’s method regarding compositional data (Aitchison, 1982; 1983; 1986) and subsequently subjected to multivariate Cluster Analysis.

The results obtained from these analyses allowed to determine the raw materials used. As previously shown by the study of the mortars and plasters from *Sa Portella* (the residential area of *Pollentia*) (De Luca et al., 2013), also in the *Forum*, the samples show principally two different typologies of aggregate: one constituted almost entirely of bioclasts and fragments of sedimentary rocks and the other composed principally by quartz and rock fragments of different nature. These two typologies of aggregate constitute two clear different sources of raw materials, compatible with the geology of the area (De Luca et al., 2013).

The study of the samples had also provided useful information about the building techniques and the production technology of mortars and plasters.

Through this study it was also possible to identify three different groups of samples, that were attributed to three different constructive phases, in accord with those proposed by archaeologists. Two of these groups are composed of samples with the same raw materials (mainly bioclasts and sedimentary rocks): one of these concerns samples coming from the rooms of the *Insula of tabernae* and the remains from the *East Sector*, that are dated to the Republican period (1<sup>st</sup> century BC). The other group is formed of samples belonging to the *Templete I*, the *Templete II* and the *East Building*, that date back to the high imperial period (1<sup>st</sup> century AD). Instead, the third group includes samples composed of quartz and rock fragments of different nature. Some of these samples come from the *Templete I*, one sample comes from the *East Sector* and another one from the *Insula of tabernae*. Because of the presence of different raw materials, it is probable that these samples belong to a different constructive phase. However, we cannot exclude that they belong to a later restoration work.

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## The provenance of volcanic millstones from archaeological sites of Messina

Di Bella M.\*<sup>1</sup>, Mazzoleni P.<sup>2</sup>, Tigano G.<sup>3</sup>, Russo S.<sup>1</sup>, Sabatino G.<sup>1</sup> & Tripodo A.<sup>4</sup>

1. Dipartimento di Fisica e Scienze della Terra, Università di Messina. 2. Dipartimento Sezione Scienze della Terra Scienze Biologiche Geologiche e Ambientali, Università di Catania. 3. Soprintendenza BB.CC.AA., Sezione per i beni archeologici Messina. 4. Dipartimento di Matematica e Informatica, Università di Messina.

Corresponding email: [mdibella@unime.it](mailto:mdibella@unime.it)

Keywords: archaeometric analysis, volcanic rocks, millstones.

Archaeometric study of volcanic millstones from various archaeological sites of the Messina city and province was conducted. The archaeometric analysis included the petrochemical characterization of the lithologies used for their construction and the provenance attribution of the raw materials. The studied samples were divided into two groups characterized by different age. The former includes the Bronze Age samples and the latter the Roman age samples. They represent different building style, from rudimentary prehistoric grindstones to the most advanced rotary mills drawn by animals used in Roman Times. Most of these artefacts were obtained from scoriaceous volcanic rocks, selected for their peculiar textural and physical characteristics, such as high strength, hardness and good porosity. The two groups of grindstone samples were firstly characterized from the petrographic, micro-analytical and geochemical - geodynamic point of view. Afterwards, to define the probable provenance area, trace elements variation diagrams opportunely constructed and other diagrams used in literature to classify similar lithic objects, have been used. Finally all the data, in particular the geochemical ones were compared with literature data of rocks from the volcanic sites identified like before said, to verify the real comparability. The results of this work provide an important contribution to the establishment of trade routes in the Mediterranean area, confirming the presence of commercial and cultural relations already existing in the Bronze Age, as demonstrated the origin of samples studied for the prehistoric series. The presence of grindstones from many different volcanic sites in the prehistoric sites, such as Etna, Aeolian Islands and Santorini testify the resourcefulness of the primitive man that to survive and to improve their condition of life, even went ever further. In particular, the finding of the sample (pestle) that appears to come from the Aegean area, confirms that the exchanges between the Tyrrhenian and the Aegean populations in the prehistoric times, were already widespread. Furthermore, characterization of the Roman Times millstones, has instead allowed to increase the knowledge regarding the diffusion of mills in the Mediterranean area and to confirm the utilization of some volcanic sites such as Mount Etna, Linosa, Pantelleria and the Euganean Hills as quarries of raw material for the building of objects to grinding the cereals.

## **Archeometric characterization through geochemical data of Proto-Byzantine glassware from Roman Amphitheatre of Catania (Italy)**

Di Bella M.<sup>1</sup>, Sabatino G.<sup>1</sup>, Quartieri S.\*<sup>1</sup>, Giacobbe C.<sup>2</sup> & Spigo U.<sup>3</sup>

1. Dipartimento di Fisica e Scienze della Terra, Università di Messina. 2. Dipartimento di Scienza e Alta Tecnologia, Università dell'Insubria, Como.  
3. Parco Archeologico delle Isole Eolie.

Corresponding email: [squartieri@unime.it](mailto:squartieri@unime.it)

Keywords: Proto-Byzantine ancient glass, glassware, Catania Roman Amphitheatre, chemical analyses, EMPA, SEM-E.

Twenty-five glass samples, including fragments of objects, glass drops and glass scoria coming from a Proto-Byzantine glassware of the Catania Roman Amphitheatre, were analysed for major, minor and trace elements. Two main groups of natron-based silica-lime glasses were identified. The majority of the samples (21) are High Iron, Manganese and Titanium (HIMT) glasses. Specifically, most of them (19) can be classified as HIMT1, while two as HIMT2 glasses, in agreement with the latest classification proposed in literature to classify this glass category. Three other samples belong to the Levantine I type.

Concerning the geochemical signatures of HIMT raw materials, the high abundance of HREE relative to LREE and of HFS elements (Zr, Nb, Ta, Ti, Hf, Th), suggests the use of impure sand, particularly enriched in heavy minerals and/or in mafic phases. Furthermore, the noticeable different contents of all the HFSE showed by the two main sample sub-groups - the enriched HIMT and the depleted Levantine I - allow us to propose these elements as discriminating factors between the two glass categories. This assumption is also confirmed by the analysis of literature data relative to coeval similar glass typologies, showing analogous HFSE distribution differences.

## **Hyperspectral monitoring of marble in buildings: a case study of the Santa Maria del Fiore (Firenze, Italy) facades**

Di Benedetto F.\*<sup>1</sup>, Suzuki A.<sup>1</sup>, Gao X.<sup>1</sup>, Vettori S.<sup>2</sup>, Costagliola P.<sup>1</sup>, Benvenuti M.<sup>1</sup>, Rimondi V.<sup>1</sup>, Camaiti M.<sup>3</sup>,  
Pecchioni E.<sup>1</sup>, Carretti E.<sup>4</sup> & Moretti S.<sup>1</sup>

1. Dipartimento di Scienze della Terra, Università di Firenze. 2. CNR-ICVBC. 3. CNR-IGG. 4. Dipartimento di Chimica & CSGI,  
Università di Firenze.

Corresponding email: [francesco.dibenedetto@unifi.it](mailto:francesco.dibenedetto@unifi.it)

Keywords: Hyperspectral technology, calcite alteration, spectral decomposition.

Hyperspectral instruments, discriminating materials on the basis of their different patterns of wavelength-specific absorption, might be employed in the characterization of the components in exposed stone surfaces, and therefore contribute to understand their conservation state. A portable radiometer (ASD-FieldSpec Pro spectroradiometer), which continuously and rapidly acquires punctual reflectance spectra in the 350-2500 nm spectral range, has the potentialities to be used for monitoring the state of conservation of stone surfaces through the evaluation of the relative abundance of some components considered precursor symptoms of decay. Major advantages of this technique include its non-destructive and non invasive nature.

In this study, gypsum is considered as a damage symptom in ancient building facades realized in marble. A method to unravel qualitative and semiquantitative information about the degree of alteration of the calcite to gypsum is proposed. This method is based on the spectral decomposition in individual spectral components assigned to calcite and gypsum, during the analysis of spectra of synthetic mixtures of microcrystalline calcite and gypsum. Advantages, perspectives and limits of the method are discussed. Furthermore, a case study is considered. The analysis of 24 areas of the white Carrara marble stones, was carried out on the facades of the Santa Maria del Fiore church (Firenze, Italy), cathedral of Florence belonging to the UNESCO world heritage monuments. The preliminary analysis of the data are presented and discussed.

## Volcanic activity and human settlements in the past 10 ka in the city of Naples (Italy)

Di Vito M.A.<sup>\*1</sup>, Boenzi G.<sup>2</sup>, de Vita S.<sup>1</sup> & Talamo P.<sup>2</sup>

1. Istituto Nazionale di Geofisica e Vulcanologia, sezione di Napoli Osservatorio Vesuviano. 2. MIBACT - Soprintendenza Archeologica di Napoli.

Corresponding email: [mauro.divito@ingv.it](mailto:mauro.divito@ingv.it)

Keywords: Geoarchaeology, Naples, Explosive eruptions.

The Naples area (Italy) is located near and within the active volcanoes of Vesuvius, Campi Flegrei and Ischia. The area, variably affected by deposition of products of eruption of these volcanoes, has been continuously inhabited from Neolithic to Present. Remains of different archaeological cultures are interbedded with pyroclastic deposits of explosive eruptions of variable intensity.

We present joint archaeological and volcanological studies of excavations conducted in the city of Naples, between the eastern border of the Campi Flegrei caldera and the western slopes of Vesuvius. The area has been investigated mainly thanks to the excavations works for the construction of Lines 1 and 6 of the Naples Underground. The excavations have yielded many traces of settlements and land use, intercalated with volcanic products dated between 10 ka and the Late Middle Age. Gently sloping hills and coastal plains characterized the investigated area, which is very close to the first Greek settlement in Naples.

At least 15 deposits of explosive eruptions of the Campi Flegrei, Ischia and Vesuvius volcanoes have been recognized in the defined time span. These deposits are intercalated with reworked deposits and paleosols containing traces of human activities, such as ancient agricultural practices. The volcanic deposits consist of pyroclastic layers with variable grain-size (ash-to-lapilli) that are correlatable on stratigraphic, lithological and petrological bases. Pyroclastic fallout and density current sediments deposited by known eruptions and partially reworked in continental and transitional environments have been recognized.

The exceptional alternation of archaeological and volcanological sequences makes it possible: i) to date exactly prehistoric and historical volcanic eruptions, ii) to determine the influence of volcanic activity on human life, iii) to study the effect of the deposition of volcanic products on the territory, and iv) to use the volcanic deposits as marker levels for dating and correlating unknown archaeological sequences. Furthermore our reconstruction reveals the high-level hazard posed to Naples by Phlegraean and Vesuvian high-to-low intensity explosive eruptions.

## **The Quaternary succession of the Bulè Valley (Po Valley, Piedmont) as possible supply for prehistoric jade axes**

Forno M.G.\*, Avondetto S., Groppo C. T. & Rolfo F.

Dipartimento di Scienze della Terra, Università degli studi di Torino.

Corresponding email: [gabriella.forno@unito.it](mailto:gabriella.forno@unito.it)

Keywords: Monviso, prehistoric jade axes, glacial deposits.

This contribution presents a detailed geological mapping and preliminary data on the Quaternary succession of the Bulè and low Alpetto tributary valleys (Po Valley, Piedmont). The investigated area, in the altitude range between 3016 and 1487 meters, is located in the Monviso Massif Ophiolitic Complex and in the adjacent carbonatic units of the Dora-Maira Massif.

The Quaternary sequence consists mainly of glacial and landslide deposits with local lacustrine, fluvial, debris and colluvial bodies. The detailed investigation of the petrographic composition of the glacial deposits allowed to recognize the occasional occurrence of jadeitite boulders, exploited during the Neolithic age for axe heads production. Four main jadeitite blocks have been found, with sizes up to 1 m<sup>3</sup>, some of them already reported by previous geological literature (Compagnoni et al., 2007) and other found during the present fieldwork (Avondetto, 2014). In detail, a Neolithic site of jade polishing has been discovered and referred to the middle of V millennium B.C. (Allisio, 2012) in the high Bulè Valley at 2880 meters. The jadeitite blocks have been mainly found in the glacial deposits. The petrographic characterization of the new jadeitite samples is in progress, and might potentially shed light on the still controversial genesis of these peculiar rocks.

The distribution of moraines (between 2450 and 1250 meters) and glacial diffuence saddles have led to the reconstruction of the glacial expansion episodes, reported in four major glacial steps. An ancient step (1), probably related to the Last Glacial Maximum, implies a confluence between the Alpetto Glacier and a left lobe of the Bulè Glacier. The subsequent step (2), related to the start of the glacial withdrawal, defines three progressive phases of glacial diffuence of the Bulè Glacier left lobe in the Alpetto Valley. The further step (3) suggests a right lobe diffuence of the Alpetto Glacier in the Vallone Bulè. Finally, the last step (4) is due to the drastic retreat of glacier fronts towards the valleys head. At the end of the last glacial period, some rock falls and sliding gravitational phenomena occurred, partly covering the glacial record. Small deep-seated gravitational slope deformations also developed, resulting in a loose or disjointed substrate and some morphological features, as doubled ridges, minor scarps and trenches.

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## Portoro, the black and gold Italian “marble”

Fratini F.<sup>1</sup>, Pecchioni E.\*<sup>2</sup>, Cantisani E.<sup>1</sup>, Antonelli F.<sup>3</sup>, Giamello M.<sup>4</sup> & Lezzerini M.<sup>5</sup>

1. CNR-ICVBC Firenze. 2. Dipartimento di Scienze della Terra, Università di Firenze  
3. IUAV- University of Venezia. 4. DSFTA, University of Siena. 5. Dipartimento di Scienze della Terra, Università di Pisa.

Corresponding email: [elena.pecchioni@unifi.it](mailto:elena.pecchioni@unifi.it)

Keywords: Portoro, "marble", chromatic alteration.

The “Portoro”, called also “*Mischio giallo e nero*”, “*Portovenere marble*”, “*Black and Gold*”, is one of the most famous and expansive “black marbles” for its characteristics yellow gold veins on a black background. It is a limestone of Rhaetian-Hettangian age belonging to the Tuscan Nappe.

It was used since Roman times, particularly in the city of Luni. Since the Middle Ages its use is widespread in Genoa, for the construction of monuments, cathedral, villas. At the end of the XIX century its use has spread abroad, especially in England, where it was used for fireplaces, coverings, plinths and panels for furniture. It was extracted in several quarries located near la Spezia, precisely on the promontory of Portovenere, in Palmaria Island and Tino Island but at present only one quarry is active. The low volume production of this “marble” is now challenged by similar commercial marbles, cheaper and with huge production, from abroad. This material, exposed to the weathering, tends to fade with time losing the look of his golden streaks and spots that determine all the aesthetic appeal. In the paper, this chromatic alteration will be investigated in order to define the guidelines for the most suitable use of this stone and for eventual restoration works of recent as well as historical monuments. Moreover the knowledge and awareness of the characteristics of this precious stone material may help in recognizing and maintaining the value of Italian Portoro.

## Common Ware from the environs of Vesuvius (Pollena Trocchia, Naples): new insights into the production technology of late Roman pottery

Germinario C.\*<sup>1</sup>, Cappelletti P.<sup>2</sup>, De Simone G. F.<sup>3</sup>, Langella A.<sup>1</sup>, Martucci C.<sup>4</sup>, Mercurio M.<sup>1</sup>, Morra V.<sup>2</sup>,  
Nodari L.<sup>5</sup> & Grifa C.<sup>1</sup>

1. Dipartimento di Scienze e Tecnologie, Università degli Studi del Sannio, Benevento. 2. Dipartimento Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli Federico II. 3. University of Oxford, Institute of Archaeology, 36 Beaumont Street, Oxford OX1 2PG, United Kingdom. 4. Dipartimento di Lettere e Beni Culturali, Seconda Università di Napoli, Santa Maria Capua Vetere (CE). 5. ICIS, Istituto di Chimica Inorganica e delle Superfici, CNR, Padova.

Corresponding email: [chiara.germinario@unisannio.it](mailto:chiara.germinario@unisannio.it)

Keywords: Late Roman pottery, quantitative analyses, Campania region.

The social and economical setting of Campania region, and in particular of the Vesuvian area, during the Late Roman period is almost unknown and is matter of hard debating among the researchers.

Recent studies brought evidence of a re-occupation of the Vesuvian area after the Pompeian catastrophe of the 79 AD and of a dense settlement pattern until the AD 472 eruption.

The archaeological sites in the environs of Vesuvius covered by the volcanoclastic deposits of the AD 472 eruption provide a clear *terminus ante quem* for the chronology and a snapshot of goods' circulation for a very narrow timeframe.

The 5<sup>th</sup> century AD represents, indeed, a moment of important transformation in the patterns of production and trade in the Mediterranean basin because while the African productions still played a prominent role, new regional workshops arose. At first these regional workshops imitated the African shapes, then evolved into independent productions which kept the traditional Roman skills in manufacture, but were scattered in several workshops in the region.

This study examines the ceramic fragments from the most prominent site (Pollena Trocchia) in the environs of Vesuvius as part of a broader study, which aims at the characterization of main productive units in Campania during the Late Roman period.

Twenty-five samples were selected among thousand of fragments; quantitative mineralogical and petrographical analyses (OM, IA, XRF, Quantitative X-Ray Powder Diffraction Method by using Rietveld approach, Mossbauer spectroscopy) were carried out in order to recognize the technological features of the pottery.

The tablewares, grouped in Slipped and Painted wares on the basis of the different coatings, are constituted by high-CaO samples (CaO=7.7-17.3wt%), with skeleton particles composed by quartz, feldspar, micas and traces of carbonates. A variable content of additive (from 5 to 13%) made of quartz, sanidine, plagioclase, clinopyroxene, scoriae, lithic fragments and rare garnet and chamotte, were mixed to the base clay. The occurrence of newly formed diopside (4-16%), gehlenite (1-4%) and hematite (1-3%), along with the high quantity of amorphous phases (32-57%) inferred high firing temperatures (850-950°C).

The cooking wares, showing a "sandwich structure" of the matrix, were made with low-CaO base clay (1.6-5.5wt%). In the coarser paste higher percentages of skeleton particles (3-15%) and volcanic and/or siliciclastic additive (8-21%) were found.

The amount of hematite suggests low firing temperature (800-850°C). The Mossbauer Spectroscopy also inferred a not-well controlled firing atmosphere showing relevant differences in the amount of Fe(II). Cores with a higher Fe(II)/Fe(total) ratio, accounts for the presence of a local non-oxidant environment during the firing, conversely, rims also show the presence of Fe(III) oxide.

## Production and provenance of Apulian Red Figured Ceramic from Taranto

Giannossa L.C.<sup>1</sup>, Giannelli G.<sup>1</sup>, Mastrorocco F.<sup>1</sup>, Muntoni I.M.<sup>2</sup>, Pallara M.<sup>3</sup>, Mangone A.<sup>1</sup> & Laviano R.\*<sup>3</sup>

1. Department of Chemistry, Università of Bari. 2. Superintendence for Archaeological Heritage of Puglia, Foggia. 3. Department of Earth Science and Geoenvironmental, Università di Bari "Aldo Moro".

Corresponding email: [rocco.laviano@uniba.it](mailto:rocco.laviano@uniba.it)

Keywords: SEM-EDS, ICP-MS, Apulian red figured pottery, statistical treatment.

A consistent physical-chemical and morpho-mineralogical research –started some years ago and still in progress– has been performed on Apulian red figured items (Mangone et al., 2008; Mangone et al., 2009; Mangone et al. 2013), dating back to the 5<sup>th</sup> and 4<sup>th</sup> cent. BC and coming from sites among the most relevant in Apulia (Southern Italy). The motive that fosters our project is the almost complete lack of information on technological production of this class of pottery, as well as the awareness that a systematic study on samples coming from representative sites of the entire production area can be a resource not only local.

We introduced here the study about the site of Taranto. The samples analyzed were found during archaeological excavations carried out in the last century in the Military Arsenal area and are stored in the National Archaeological Museum of Taranto (MARTA).

We examined ceramic bodies, red decorated areas, black gloss coatings and decorations by Scanning Electron Microscopy, X-Ray Diffraction and Ion Coupled Plasma Mass Spectrometry. Lastly, the compositional data matrix were processed with multivariate statistical analysis to identify groups of items with similar composition.

Our first aim was to discriminate the Apulian production from the Attic one by specific features in manufacturing processes.

The analytical results distinguished at least two unlike production technologies of Apulian red figured vases in Taranto during the 4<sup>th</sup> century BC: one characterized by a fine texture of the ceramic body, red figures saved from the ceramic paste and black gloss painted directly on the ceramic body, as traditional Attic production; the other one by a ceramic body with a coarser texture and a layer of *ingobbio rosso* to obtain red decorations, with a black gloss painted on it.

The *ingobbio rosso* technology, already highlighted in others sites of Apulia and never pointed out in Attic pottery– seems to represent a distinctive characteristic of Late Apulian production.

Also, data from Taranto show some clues about the beginning of this production during the second half of IV cent. BC, while the comparison with two clay slabs –coming from a tarantine workshop of black gloss and *acroma* pottery dated back to V-IV cent BC– supported the local provenance of the samples grouped in clusters, where all pottery attributed to Truro painter's, considered one of the most representative ceramist of tarantine production, is located together.

## **Archaeometric study of the more ancient painted wall found in Sicily (Apaforte – Licata)**

Ingoglia C.\*<sup>1</sup>, Barone G.<sup>2</sup>, Mazzoleni P.<sup>2</sup>, Raneri S.<sup>2</sup> & Aquilia E.<sup>2</sup>

1. University of Messina, Department of Ancient and Modern Civilization, Polo Annunziata – Messina. 2. University of Catania, Department of Biological, Geological and Environmental Sciences.

Corresponding email: [caterina.ingoglia@unime.it](mailto:caterina.ingoglia@unime.it)

Keywords: plasters, production, Licata.

In the present work, an analytical study of painted plaster samples coming from an ancient tomb, dated back to 4th – 3rd cent B.C. and located in Licata (Sicily, Southern Italy), has been carried out. This tomb situated in the street called “c.da Apaforte” is an interesting hypogeum composed of a single room made of stone blocks. The importance of this tomb is represented by the presence of the most ancient painted wall recovered in Sicilian hypogea structures.

In order to identify the pigmenting agents, the preparation layers and the deterioration processes we carried out non-destructive micro-Raman spectroscopy and micro-destructive analyses through SEM-EDS. Preliminary characterization of samples was done by optical microscopy (OM) with the aim at characterizing plaster features and degradation processes.

The micro-Raman measurements have been performed in order to investigate the molecular nature of the used materials and to obtain the characterization of the decorated surfaces. The quantitative analysis of the chemical composition of the different layers (pigments, preparation layers, deteriorated parts) has been obtained by SEM-EDS.

In order to establish the production technique used by the craftsmen, the results were compared with our recent data on Hellenistic plasters coming from an ancient buildings located in Licata and dated back 2<sup>nd</sup>cent B.C (Aquila E. et al., 2012).

Aquila E. et al., 2012. Caratterizzazione delle superfici decorate: il caso delle pitture ellenistiche in Sicilia. Atti del VI Congresso Nazionale di Archeometria. Scienza e Beni Culturali. Pavia 15-18 febbraio 2010. Bologna, 1-5.

## Mortars, plasters and mosaic floors from Ancient Stabiae: the art of building in Roman times (89 B.C.-79 A.D.)

Izzo F.\*<sup>1</sup>, Arizzi A.<sup>2</sup>, Cappelletti P.<sup>3</sup>, Cultrone G.<sup>2</sup>, D'Albora M.P.<sup>3</sup>, Germinario C.<sup>1</sup>, Grifa C.<sup>1</sup>, Guarino V.<sup>3</sup>, Mercurio M.<sup>1</sup>, Morra V.<sup>3</sup>, Sossio Graziano F.<sup>3</sup> & Langella A.<sup>1</sup>

1. Dipartimento di Scienze e Tecnologie, Università degli Studi del Sannio, Benevento. 2. Dipartimento di Mineralogia e Petrologia, Università di Granada, Spagna. 3. Dipartimento Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli Federico II.

Corresponding email: [izzofrancesco84@yahoo.it](mailto:izzofrancesco84@yahoo.it)

Keywords: Stabiae, roman mortars, ancient technologies.

Ancient *Stabiae* (Castellammare di Stabia, Naples) is the archaeological site with the largest number of roman seaside villas of the Mediterranean area. Among them, Villa San Marco is one of the most important examples of roman *otium villae*. During the last years, *Stabiae* has been subject of a restoration and development program driven by RAS Foundation (*Restoring Ancient Stabiae*) and involving several international and national academic and public stakeholders. The present research focuses on the archaeometric analysis of 10 plasters, 8 mortars and 2 mosaic floors from Villa San Marco, with the final aim to recognise the technology used by the ancient skilled workers.

Several analytical techniques were used for the study of plasters, mortars and mosaics (Digital videomicroscopy, Colorimetry, OM, XRD, SEM/EDS, DIA). A multi-layer study of the plasters was adopted to differentiate and characterise these materials.

We found out that the *rinzafo* layer (rendering mortar) was a hydraulic lime mortar made with pozzolanic lightweight aggregate (pumices) and cocchiopesto (1:1arriccio layer (scratch coat), lime mortars with volcanic sand and minor pozzolana and/or cocchiopesto (1:1rinzafo). The *intonachino* layer (B/A=2:1) was the removable support of the frescos and provided a lighter colour for the preparation layer of the frescos. This last thin layer, composed of lime mortars made with a carbonatic aggregate (B/A=1:1), is characterised by a low porosity in order to hinder the pigment adsorption. Encaustic painting technique was used for the fresco.

The structural mortars of the building were made with hydraulic lime and lightweight aggregate (pozzolana) and cocchiopesto (1:1opus reticulatum).

The preparation layers (*rudera* and *nuclei*) of the mosaics were built with volcanic sand and abundant cocchiopesto mixed to the hydraulic lime (B/A=1:1), providing a more resistant surface for the application of the *tesserae*, which were fixed only with lime. The white and black colours of the mosaics were yielded by limestone and tephritic lava.

These findings demonstrate a high level of specialisation own by the workers and artists involved in the construction of Villa San Marco and the other maritime villas of *Stabiae*. Moreover, the collected data highlight the wide potentiality of material supplying of the peri-vesuvian area.

The present research contributes to the knowledge of the technical, artistic and architectural skills achieved during Roman times and represent a valuable reference for future restoration interventions in Villa San Marco and in the other Roman villas in which similar materials were used.

## Majolica from Sassari: first evidence of a production center in Sardinia

Mameli P.\*<sup>1</sup>, Masala L.<sup>1</sup> & Rovina D.<sup>2</sup>

1. Dipartimento di Scienze della Natura e del Territorio- Università di Sassari.  
2. Soprintendenza ai Beni Archeologici delle Province di Sassari e Nuoro.

Corresponding email: [mamelip@uniss.it](mailto:mamelip@uniss.it)

Keywords: Majolica, Sardinia, XVI-XVII century.

Archaeological excavations begun in the city center of Sassari (Sardinia, Italy) in 1999, for the renewal of roads and underground utilities, have brought to light a significant amount of ceramic findings. These are mainly waste materials including spacers, incomplete ceramic products and polychrome majolica, whose abundances suggest the presence of a production center in the area. The possible local pottery was stratigraphically associated with monochrome and polychrome Ligurian, Tuscan (Montelupo), Latium and Spanish pottery, dating from the sixteenth and seventeenth century (Biccone et al., 2009).

The aim of this work is the preliminary textural, mineralogical and chemical characterization of the ceramic body and glaze of the unknown majolica, to provide information about the provenance of the raw materials and to get some data on the manufacture.

Twenty-one samples, containing 7 spacers, 11 painted open shapes (5 of uncertain production, 1 from Montelupo and 1 from Liguria) and 3 uncoated open form, have been selected for the analyses. Observations on thin sections through optical microscopy (OM) have been carried out in order to characterize the microstructure and the morphology of the pastes and the glazes, while chemical composition of the glazes were determined with a scanning electron microscopy equipped with an energy dispersion spectrometer (SEM-EDS). The crystalline phases of the paste have also been analyzed by means of X-ray diffraction (XRD).

The fragments of uncertain production show small variations in composition and texture. They are characterized by a very fine and isotropic marly groundmass with coarse inclusions of quartz, feldspars, oxides and fossils, mainly globigerinae.

Coatings consist of an opaque glaze layer on recto and on both recto and verso surfaces, characterized by lead and tin oxides, whose average thickness is ~300 µm.

Despite the paucity of clues for a pottery work, which are limited to good number of spacers, the archaeometric data point to a local production of majolica in Sardinia. Particularly, the provenance of the clay is referable to the local marls of Langhian age widely cropping around the town, which contain a sandy component coming from the dismantling of the Variscan metamorphic basement.

The study attest for the first time a production center for majolica in Sardinia.

Biccone L., Mameli P., Rovina D., Sanna L. 2009. La produzione di maioliche a Sassari tra XVI e XVII secolo: primi dati archeologici e archeometrici. Atti XLII Convegno Internazionale della Ceramica Albisola, 297-310.

## Archaeometric study of ceramic materials from archaeological excavations at the Roman iron-working site of San Giovanni (Portoferraio, Elba Island)

Manca R.<sup>1</sup>, Pecchioni E.<sup>1</sup>, Benvenuti M.\*<sup>1</sup>, Cambi F.<sup>2</sup>, Chiarantini L.<sup>1-3</sup>, Corretti A.<sup>4</sup>,  
Costagliola P.<sup>1</sup> & Pagliantini L.<sup>2</sup>

1. Dipartimento di Scienze della Terra, Università di Firenze. 2. Dipartimento di Scienze Storiche e dei Beni Culturali, Università di Siena. 3. IGG-CNR, Pisa. 4. Laboratorio Scienze dell'Antichità, Scuola Normale di Pisa.

Corresponding email: [m.benvenuti@unifi.it](mailto:m.benvenuti@unifi.it)

Keywords: San Giovanni (Elba Island), Roman ironworking centre, ceramics.

In the framework of the AITHALE project, which promotes systematic research on Elba island through a cooperation among various Institutions (Soprintendenza ai Beni Archeologici della Toscana, Universities of Firenze and Siena, Scuola Normale di Pisa, IGG-CNR, Musei Archeologici elbani), archaeological excavations were carried out in 2012-13 at San Giovanni, in the eastern end of the Portoferraio Bay. The site, known as one of the main ironworking centres during the Roman period (3<sup>rd</sup> -1<sup>st</sup> cent. BC.), but possibly even earlier, occurs at the foot of the promontory on which the Roman "Villa delle Grotte" was built in the 1<sup>st</sup> cent. BC.

Abundant waste heaps of metallurgical production occur on the site, mainly including slag, pieces of ore charge and fragments of furnaces. Previous (2009-11) geophysical prospecting on the site revealed subsurface structures, which after recent excavations appeared to be walls and other remains of a Roman farm devoted to wine production, possibly the *pars rustica* of the neighboring Villa delle Grotte. Samples of different kinds of "ceramics" (bricks, *dolia*, metallurgical furnaces) were taken both from the farm and a trench dug through the earlier (underlying) metallurgical debris.

Archaeometric analysis provided us with interesting information on production technologies and the origin of the raw materials used at San Giovanni in Roman (and pre-Roman?) times.

Broken pieces of refractory ceramics, partly slagged and vitrified, commonly occur in the metallurgical heaps. They are constituted by clay tempered with abundant quartz and lithic fragments in order to augment its refractoriness; rare fragments of tuyeres and channels for slag tapping have been found as well. Apparently, iron smelting furnaces at San Giovanni, unlike those found in the Etruscan site of Baratti-Populonia in the mainland, were not (or only partly) armored with refractory stones.

Mud clay bricks from the Roman farm, in accordance with recipes reported by Latin authors (Vitruvius, Pliny the Elder), are made with clay, sand, and organic materials (straw, etc.). The composition of temper used for roof tiles shows significant variations, indicating either imports from different production centres or re-use of old roof tiles. Finally, we analyzed fragments of *dolia*, the large ceramic containers used for the storage and fermentation of wine. The employment of lithic fragments of basaltic to trachytic composition as *dolia*'s temper may point to a production area in the medium Tiber Valley, which hosted - in the 1<sup>st</sup> cent. B.C. - at least one famous *figlina* (pottery workshop) specialized in the production of *opus doliare*.

## Development of an ultra-miniaturised XRD/XRF instrument for the in situ mineralogical and chemical analysis of planetary soils and rocks and implication for Archeometry

Marinangeli L.\*<sup>1</sup>, Pompilio L.<sup>1</sup>, Baliva A.<sup>1</sup>, Bonanno G.<sup>2</sup>, Domeneghetti M.C.<sup>3</sup>, Fioretti A.M.<sup>4</sup>, Nestola F.<sup>5</sup>, Piluso E.<sup>6</sup>, Pondrelli M.<sup>7</sup>, Tateo F.<sup>3</sup> & the XMAP team

1. TeleLab-DiSPUTer, Università G. d'Annunzio. 2. INAF-Osservatorio Astronomico di Catania  
3. Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia. 4. CNR - Institute of Geosciences and Earth Resources, Padova. 5. Dipartimento di Geoscienze, Università di Padova. 6. Università della Calabria Dipartimento di Biologia, Ecologia e Scienze della Terra (DIBEST). 7. IRSPS, Università G. d'Annunzio, Pescara.

Corresponding email: [lucia.marinangeli@unich.it](mailto:lucia.marinangeli@unich.it)

Keywords: XRD, XRF, portable instrument.

The knowledge of the surface composition is crucial for the identification of potential resources and for the understanding of the surface/crustal evolution. An ultra-miniaturised (mass 1.5 kg; volume ~22x6x12 cm<sup>3</sup>) combined XRD/XRF instrument has been developed for the mineralogical and chemical characterization of Martian soils/rocks and was included in the ExoMars-Pasteur payload (Marinangeli et al. 2007, 2011). The simultaneous acquisition of in-situ chemical and mineralogical information would give significant improvement to any robotic missions and may unravel many doubtful points regarding the mantle composition, crustal evolution and resource potential. The instrument is based on an innovative and advanced concept which gathers the experience achieved in Europe for the design miniaturisation in the space industries.

The instrument prototype built with ESA funding in 2006, consists of a radioisotope (<sup>55</sup>Fe) as source of X-rays, a collimator and a CCD-based detection system. The instrument follows a fixed reflection geometry to fulfill the diffraction principle. The instrument takes advantage of the use of a radioactive source to reduce the power consumption compared to an X-ray tube, a critical parameter for in situ power resources. However, given the status of the art for cold-cathode X-ray carbon nanotube, this option may be also investigated in the future.

A complete measurement cycle consists in the acquisition and integration of data for several hours. XRF and XRD data are acquired simultaneously and the separation of the two types of information is achieved via software. The instrument is able to analyze samples as fine powders or pristine surface with a clean and smooth cut. The latter option is applicable to analyze paintings or ceramics without sample preparation.

A number of measurements have been acquired on soils/rocks and compared with measurements acquired using commercial instruments in order to define the instrument detection limits and accuracy. Further tests on pottery as well as a field demo are planned in the next future.

Marinangeli L., Hutchinson I., Baliva A., Stevoli A., Ambrosi R., Critani F., Delhez R., Scandelli L., Holland A., Nelms N., MARS-XRD Team. 2007. Lunar and Planetary Science XXXVIII, Abstract #1322.  
Marinangeli et al. 2011. *EPSC-DPS*, Abstract #1232.

## Traceability of iron from Elba Island: new data from experimental Archaeometallurgy

Mazzotta C.\*<sup>1</sup>, Lazzeri L.<sup>1</sup>, Benvenuti M.<sup>1-6</sup>, Borrini D., Corretti A.<sup>2-6</sup>, Dini A.<sup>3-6</sup>, D'Orazio M.<sup>4-6</sup>, Giannola A.<sup>5</sup>, Orlando A.<sup>7</sup>, Cambi F.<sup>5-6</sup>, Chiarantini L.<sup>1-3-6</sup>, Costagliola P.<sup>1</sup>, Pari L.<sup>6</sup> & Saredo N.<sup>6</sup>

1. Dipartimento di Scienze della Terra, Univ. di Firenze. 2. Laboratorio Scienze dell'Antichità, Scuola Normale di Pisa  
3. IGG-CNR, Pisa. 4. Dipartimento di Scienze della Terra, Univ. di Pisa. 5. Dipartimento di Scienze Storiche e dei Beni Culturali, Università di Siena.  
6. Aithale Research Team. 7. IGG-CNR, Firenze.

Corresponding email: [caterina85.m@gmail.com](mailto:caterina85.m@gmail.com)

Keywords: Ancient iron, Elba Island, traceability.

Iron deposits from Elba Island (Tuscan Archipelago) were extensively exploited since the 1<sup>st</sup> millennium BC: both raw iron ore and smelted blooms were extensively traded throughout the Mediterranean region. However, archaeological evidence of Roman and pre-Roman (Etruscan) ore exploitation and extractive metallurgy on Elba Island is extremely scarce mostly due to the past century's slag recovery for re-use in modern blast furnaces. Recent studies of hematite-rich ores from Elba showed a prominent and apparently unique (at an European scale) co-enrichment in W and Sn that may represent a provenance marker not only for the ore itself (remains of which are commonly found at many ancient smelting/smithing sites) but, possibly, also for iron blooms and metallurgical slag. Within the frame of the multidisciplinary research Project "AITHALE" (from the Greek name of Elba Island), we have performed a series of archaeometallurgical experiments primarily to investigate the extent of Sn and W partitioning during the various steps of the chaîne opératoire of bloomery iron production. On March 2013 at the Bacino stope, Rio Marina mine (Elba Island) a furnace was prepared entirely made of local clay; forced draught was provided by an air compressor connected through a clay tuyere with the furnace. After 1h preheating, about 45 kg of pre-roasted hematite-rich ore (taken from the nearby Bacino stope) and charcoal were regularly added to the top of the furnace in roughly a 1:1 ratio. A total of some 30 kg of fayalite-rich slag were tapped from the furnace in five separate steps. At the end of the experiment about 5 kg of iron bloom were obtained. The hematite-rich ores, analyzed by ICP-MS, have bulk contents of Sn and W of, respectively, 75 and 656 ppm; EMPA analyses showed that W is present both in solid solution in hematite and as micrometric crystals of scheelite (CaWO<sub>4</sub>). The W/Sn ratio of the slag's silicate melt ( $\approx 20$ ) is much higher than that of the bloom ( $\approx 3$ ), indicating that under the operating conditions of this experimental process W preferentially partitions into the slag. Smelting experiments of Sn/W-rich hematite from Terranera mine (Elba Island, to the south of Rio Marina district) were also carried out in a Deltech DT-31VT-OS2 vertical quench furnace (at the Petrology Laboratory of the Dip.to Scienze della Terra, Firenze) under controlled redox and temperature conditions and variable ore:charcoal: (siliceous) flux ratios. In one experiment, we obtained metallic iron with appreciable amounts of dissolved Sn (0.2-0.3 wt%, EPMA analysis), but with W still below the instrumental detection limit (0.05 wt%). This confirms the preferential partitioning of W into the silicate slag. In both types of experiments the slags resemble in their mineralogical and textural features to analogue materials found at ancient ironworking sites, as for instance Baratti-Popolonia, the most important site in ancient Italy for iron production during the Etruscan and Roman periods.

## Archaeometric analysis of vitreous material ornaments from the Villa di Villa Sanctuary (TV, Italy)

Olmeda G.\*<sup>1</sup>, Angelini I.<sup>2</sup>, Molin G.<sup>1</sup> & Leonardi G.<sup>1</sup>

1. Department of Cultural Heritage, Università di Padova. 2. Department of Geosciences, Università di Padova.

Corresponding email: [giulia.olmeda@studenti.unipd.it](mailto:giulia.olmeda@studenti.unipd.it)

Keywords: Protohistoric glasses, archaeometric analysis, Northern Italy.

In the site of Villa di Villa (Treviso, north-eastern Italy) is located a Sanctuary that has been excavated since 1976. The vitreous material ornaments unearthed during the excavations are particularly interesting because have different typologies: two annular beads, one globular bead, one melon bead, three bracelet fragments and one semicircular rod fragment. The age of the finds cover a wide chronological range, from the Final Bronze to the Late Roman Age. Therefore the study of composition, texture and morphological characteristics of the ornaments enables to shed light on the different types of raw materials used and to relate the evolution of the glass production techniques within the period of the Sanctuary activity. Eleven micro-samples from the bodies and the decorations of eight vitreous material objects were sampled and analyzed by Scanning Electron Microscopy combined with EDS and Electron Probe Microanalysis (EPMA), whereas non – invasive X-Ray Diffraction was performed on the ornaments. Only one blue annular bead is an LMHK glass produced with mixed alkali plant ashes as flux, suggesting that the sample may be dated to the Final Bronze Age. The other vitreous materials are LMG glasses obtained using natron as flux, although some samples have a particular intermediate composition. A few specimens show relatively low content of Na<sub>2</sub>O (12,15-14,23 wt%) but they are characterized by the presence of high amounts of Pb (about 10 wt%) or Sb (about 8 wt%) in the glass matrix. All the glasses have an elevated contents of Al<sub>2</sub>O<sub>3</sub> (1,78-3,29 wt%) that testify the use of an impure sand as source of silica. The percentage of all the other elements are mainly linked to the colour and the opacity of the glasses. The dark blue arm rings and beads are Co coloured, while only the pale blue melon bead *faiänce* is coloured by Cu. The identified trace elements related to Co are not the same in all the samples suggesting the use of Co-colourant with different origins. White and yellow glasses are opacified respectively by Ca<sub>2</sub>Sb<sub>2</sub>O<sub>7</sub>-CaSb<sub>2</sub>O<sub>6</sub> (CaO in the glass phase about 8 wt%) and Pb<sub>2</sub>Sb<sub>2</sub>O<sub>7</sub> (PbO in the glass phase=10,71wt%); moreover they present a significant level of Sb<sub>2</sub>O<sub>3</sub> in the glass matrix up to 8 wt%. All but one of the Villa di Villa samples have traces of Mn (0,32-0,79 wt%). In the site both glasses and *faiänce* are present. The chemical composition and the morphology observed reflect the variability of the materials in colour and age. Even if opacifiers are not present in some glasses, the heterogeneous texture observed is related to the presence of metal inclusions, unreacted raw materials and/or newly formed crystals. The results of the archaeometric study of the Villa di Villa ornaments allow the identification of the raw materials used and permit also to estimate the age of the finds. The relationship between the Villa di Villa ornaments and coeval European and Mediterranean vitreous materials will be discussed according to the specific object typologies.

## The monumental submerged punic harbor of Malfatano and associated Piscinni quarries, Archaeometric and Geoarchaeological approach

Orrù P.E.\*<sup>1</sup>, Solinas E.<sup>2</sup>, Columbu S.<sup>1</sup>, Deiana G.<sup>1</sup>, M.T. Melis<sup>1</sup>, Piras G.<sup>3</sup> & Serrao P.<sup>4</sup>

1. Dipartimento di Scienze della Terra, Università di Cagliari. 2. AIA Sub – Associazione Italiana Archeologi Subacquei – Roma. 3. S.G.A – Studio Geologico Associato – Cagliari. 4. G.H.T. Engineering S.r.l.s. – Cagliari.

Corresponding email: [orru@unica.it](mailto:orru@unica.it)

Keywords: Archaeometry, Punic harbor, Sea level change.

The Ria of Malfatano is the site of the most important maritime structures from the Punic-Roman times in the Mediterranean, whereby the bay's two opposing monumental structures have been preserved between - 7 and - 2 meters due to the rising sea levels. Piscinni quarries have recently been recognized together with other archaeological finds belonging to the Punic and Late Antiquity ages (Orrù et al., 2014), these were built with littoral sandstones of the Last Interglacial (MIS 5,5) (Lecca and Carboni 2007). Piscinni's quarries because of the proximity of coastline to the basement didn't have access from land, thus it is likely that the placement of the material was done by means of floats, as for the loading of materials from the quarry. However, we may assign the date of the structure to the Carthaginian age (Mastino et al., 2005). Considering the military strategy adopted by Carthage from their second treatise with Rome in the middle of IV century B.C., it is eminently possible to envisage a military function of this port basin (V-III century B.C.; 2400±100 ky BP). Piscinni quarries provided an extremely selective quality of construction material, sandstones and microconglomerates with strong carbonatic cementation, a lithotype that can easily and quickly be worked and which has good geomechanical characteristics both in terms of breaking loads and resistance to alteration. Using a high resolution terrain model has been possible to estimate the total extracted volume of about 120,000 m<sup>3</sup>, for coastal quarries and about 30.000 m<sup>3</sup> for submerged quarries area; only a small proportion, estimated at 25,000 m<sup>3</sup> was used for the realization of the crowning work of the breakwater at the entrance of Capo Malfatano bay. There is also an extensive use of sandstone in the Bithia settlement, where, from the Phoenician tombs in the necropolis to the buildings found in the acropolis area in Torre di Chia to the Punic sanctuary of Bes, (Bassoli et al., 2013). Rocks analysis and high detail measures have involved both submerged reefs, harbor and quarries using a HR side scan sonar (800 kHz), while for the quarries coastal areas aerophotogrammetric surveys were performed using a automatic navigation drone.

## **Micropaleontological contribution to the archaeometric study of ceramics from Caltagirone (Sicily)**

Privitera A., Mastandrea A., Rao A., Guido A.\* & Russo F.

Department of Biology, Ecology and Earth Sciences, University of Calabria, Cosenza.

Corresponding email: [aguido@unical.it](mailto:aguido@unical.it)

Keywords: ceramic of caltagirone, microfossils, heating temperature.

This research deal with the role of microfossils for the ceramic paste characterization. This approach, so far rarely investigated in archaeometry, allowed to confirm the biostratigraphic position of the Monte San Giorgio clay, which was widely used in the past for the production of the Caltagirone (CT) ceramics. The micro and nanomorphological modifications and the geochemical changes of foraminifera tests engulfed in ceramics enabled to assess the firing temperatures. The research was developed in two phases. A systematic and biostratigraphic study on the planktonic foraminifera and nannofossils has been performed in the first phase, which permitted to recognize the age of the clayey sediment used as raw material. The second phase was focused on micromorphological and geochemical analyses performed on the experimental ceramic made with the clay of Monte San Giorgio. Different known firing conditions, according to the ancient techniques, were adopted to made the experimental samples. They were compared with the ceramic fragments, furnished by the Ceramics Regional Museum “Antonino Ragona” of Caltagirone, in order to validate our approach on unknown archaeological material. The micropaleontological study for archaeometric analyses seems to be useful in the evaluation of firing processes and sometimes decisive in distinguishing the typical features of the clay used in a given production.

## Mortars from the Roman villa of the Vetti (Tuscany): preliminary data

Ramacciotti M.\*<sup>1</sup>, Cantini F.<sup>1</sup>, Donati F.<sup>1</sup> & Lezzerini M.<sup>2</sup>

1. Dipartimento di Civiltà e Forme del Sapere, Università di Pisa. 2. Dipartimento di Scienze della Terra, Università di Pisa.

Corresponding email: [mirco.ramacciotti@gmail.com](mailto:mirco.ramacciotti@gmail.com)

Keywords: plaster, pigment, building material.

Since the end of the III century A.D. the Roman Empire lived a period of relative stability and the following decades knew a sort of villas renaissance, especially in the peripheral areas.

The Roman villa of the Vetti (middle IV century), built in the town of Limite sull'Arno (Florence), is one of the most interesting late ancient aristocratic mansion discovered in the present Tuscany, comparable to other examples like those of San Vincenzino (Livorno) and Torraccia di Chiusi (Siena). The archaeological excavations have revealed a portion of the *pars urbana* and in particular an apsidal room and its mosaic floor in which a hunting scene is pictured (Alderighi *et al.*, 2011). This work is focused on plasters and mortars found in this sector of the building during the campaigns of 2010 and 2011.

From the macroscopic point of view (number of layers, aggregate/binder ratio, colour of binder) four different types of plaster mortars have been identified; a fifth group comprehends the mortars from joints between masonry units and from the mosaic pavement. Mineralogical and petrographic data obtained by optical observation and XRPD, TG/DSC analyses as suggested by Riccardi *et al.* (2007) indicate the presence into mortars of hydraulic binders and river sand as aggregate fraction.

Some plaster fragments are characterized by the presence of decorative painting; petrographic features, XRPD and SEM data suggest the use of lime milk (white), ochers (red, yellow, brown and orange), carbons (black) and the typical egyptian blue pigment.

Alderighi L., Cantini F., Fatighenti B, Gallerini G. & Mastrofrancesco A. 2011. Capraia e Limite (FI). La villa dei Vetti: nuove e vecchie indagini archeologiche in una grande villa tardoantica del medio Valdarno. Notiziario della Soprintendenza per Beni Archeologici della Toscana, 6, 47-81.

Riccardi M.P., Lezzerini M., Carò F., Franzini M. & Messiga B. 2007. Microtextural and microchemical studies of hydraulic ancient mortars: two analytical approaches to understand pre-industrial technology processes. Journal of Cultural Heritage, 8, 350-360.

## **Analysis of building stone materials used in Flavian Amphitheatre in Pozzuoli (Italy): types and provenance**

Rispoli C.\*<sup>1</sup>, Stanislao C.<sup>1</sup>, Esposito R.<sup>2</sup>, Cappelletti P.<sup>1</sup>, Morra V.<sup>1</sup>, Fedele L.<sup>1</sup> & Gialanella C.<sup>3</sup>

1. DiSTAR, Federico II University, Naples. 2. Dipartimento Scienze Umanistiche, Federico II University, Napoli. 3. Special Superintendence of Archeological Heritage of Naples and Pompei.

Corresponding email: [tinarisp@hotmail.it](mailto:tinarisp@hotmail.it)

Keywords: Flavian Amphitheater, Campi Flegrei lavas, mineralogical-petrographical analysis, archeological site.

This work is the result of the interaction between archeological and geological investigations on the Flavian Amphitheatre, one of the most important archeological sites in Campania region, situated in an area of great geological and archeological interest: the Campi Flegrei.

The first aim of this research was to analyze stone material whenever employed for structural use, focusing on the type of materials and their provenance.

After several surveys and photographic campaigns, considering the overall complexity of the monument and the presence of different geomaterials, our work has been focused on subterranean corbels and on pillars of external arches that show an severe state of decay. Thanks to the permission allowed by Special Superintendence of Archeological Heritage of Naples and Pompeii it has been possibile to take out small non-invasive, but representative, samples of geomaterials in order to reach our characterization scopes and to provide useful information on probable future restoration activities.

Mineralogical-petrographic characterization of samples taken by corbels and pillars have been performed mainly by X-ray powder diffraction (XRPD) and polarizing microscope analysis on thin sections (OM, optical microscopy).

The macroscopic analysis suggested, as regards materials used for the abovementioned structures, an interleaving of *Piperno* (eutaxitic texture characterized by long dark grey lenses – *fiamme* – and alveolization, a peculiar alteration style of this specific rock) and lavas from the Campi Flegrei district (porphyritic texture, along with spalling and fracturing as weathering pathologies). This alternation was also confirmed by historical literature data (Maiuri A., 1955). On the contrary, detailed OM investigation on thin sections revealed mineralogical and textural characteristics typical just of Phlegrean lavas.

From a comparison with available geo-petrographical literature data (Melluso et al., 2012), samples taken from pillars revealed a similarity with lavas from the Monte Olibano dome, due to the presence of plagioclase and olivine xenocrysts, glomeroporphyritic clusters of clinopyroxene-plagioclase, or plagioclase and sanidine.

On the other hand, the weakly porphyritic texture, and the presence of sodalite and sanidine phenocrysts in the samples from corbels suggested their provenance from one of the other rare lava outcrop in the Campi Flegrei: the Punta Marmolite dome.

These findings (mineralogical and petrographic analysis vs. archeological descriptions) are clearly an example of what could be the results of a complementary study performed by different expertise, that could lead to more correct inputs in the framework of future restoration intervention, whenever any of these expertise provide their essential contribution in the field of diagnostics and conservation.

Maiuri A. 1955. Studi e ricerche sull'anfiteatro Flavio puteolano, Memorie dell'accademia archeologia, lettere e belle arti- serie 3, Napoli.

Melluso L., de Gennaro R., Fedele L, Franciosi L. Morra V. 2012. Evidence of crystallization in residual, Cl-F-rich, agpaitic trachyphonolitic magmas and primitive Mg-rich basalt-trachyphonolite interaction in the lava domes of the Phlegrean Fields (Italy); Geo. Mag 149, 532-550.

## **Petrochemical characterization of Bronze Age pottery from the settlement of Mt. San Paolillo (Catania, Italy)**

Rodríguez-Ruiz de Almodóvar C.<sup>1</sup>, Bermúdez Coronel-Prats R.<sup>2-3</sup>, Barone G.<sup>2</sup>, Cultrone G.\*<sup>3</sup>,  
Mazzoleni P.<sup>2</sup> & Tanasi D.<sup>4</sup>

1. Department of Geology, University of Huelva, Huelva, Spain. 2. Department of Biological, Geological and Environmental Sciences, University of Catania. 3. Department of Mineralogy and Petrology, University of Granada, Spain. 4. Arcadia University, The College of Global Studies, Arcadia Sicily Center, Siracusa.

Corresponding email: [cultrone@ugr.es](mailto:cultrone@ugr.es)

Keywords: Middle-Late Bronze Age, ceramics, Mount San Paolillo (Catania).

The excavations carried out in 1997 by the Superintendence of Cultural Heritage of Catania at the Mount San Paolillo, in the northern suburb of the city, brought to the discovery of a Prehistoric settlement that still represents the most important evidence for the Middle and Late Bronze Age in this area. During the explorations, a hut, a storage jars deposit and a pottery workshop have been located, all providing a high quantity of heterogeneous ceramics with apparent typological parallels in other cultural districts, such as the territories of Siracusa, Augusta and Messina. Due to the lack of data about Etruscan Middle and Late Bronze Age pottery production, it has been decided to sample a large quantity of specimens, in order to include all the 15 fabrics visually identified and all the main typological classes, comprising tableware, cooking vessels, coarse ware, storage jars but also baking plates, kiln spacer and clay renders. 32 statistically representative samples have been studied through a palimpsest of petrographic and chemical analyses.

The archaeometric results show that the considered pottery is strongly heterogeneous and permit the identification of 5 petrographic fabrics. Those ceramics better studied are characterised by abundant temper consisting by volcanic rock fragments and rarely by grog. Only few samples present a fine grain and common quartz. The groundmass ranges from non micaceous to very micaceous, in some cases is also evident a mixing of clays.

The chemistry of ceramics has revealed the existence of two groups with low and high CaO contents. The chemical and petrographic differences suggest the use of different raw materials. Another distinctive geochemical character is the high Fe<sub>2</sub>O<sub>3</sub> abundance (more than 8.7 wt.%) which is imputed to the use as temper of altered pyroclastic rocks cropping out nearby the archaeological site.

In addition, further data confirming a local provenance result from the analysis of the mineral phases carried out through SEM+ EDX.

The data provided by the archaeometric analyses gave a very significant contribute for the study of the Middle and Late Bronze Age pottery of the Catania territory, clarifying methods, productive strategies and technical levels of the prehistoric artisans. In particular, the most striking data has been represented by the operation of mixing clays with different composition in order to obtain a fabric with peculiar features. Furthermore, this work demonstrates some typological features are not connected with "imported products" but just simple local copy of other native ceramics of different cultural districts.

## Strategies for the building stone and damage mapping applied to the historical center of Catania

Salemi A.<sup>1</sup>, Sanfilippo G.<sup>1</sup>, Aquilia E.\*<sup>2</sup>, Barone G.<sup>2</sup>, Mazzoleni P.<sup>2</sup>

1. Catania University, Department Civil Engineering and Architecture. 2. Catania University, Department of Biological, Geological and Environmental Sciences.

Corresponding email: [e.aquilia@hotmail.it](mailto:e.aquilia@hotmail.it)

Keywords: degradation, stone material, conservation.

The problem of conservation and restoration of the historical centers request a knowledge of the effective state of deterioration with the definition of, not only the typology of damage, but also the intensity of degradation and its development. The degradation's maps are the first step for identifying macroscopic pathological manifestations. These are classified on the basis of Italian *UNI 11182* of 2006 but does not give sufficient information since it is purely qualitative and descriptive.

In the last decade of XX sec. the scientific group of Fitzner (Fitzner et al., 2002) developed a method for the complete definition of the degradation on monuments that was rarely used in Italian context. Moreover, the analysis of the interactions between micro-climate, material, shape, construction techniques and technological system are needed to understand the phenomena that, during time, have generated the degradation.

So, in this work we resume a sophisticated instrumental analysis implementing it with geometric, technical-constructive and modern digital survey.

With the aim to highlight the potentiality of the proposed method we report the study of the Villa Cerami portal, in which the degradation forms are mapped at decimetric scale and another example of baroque architecture belonging to the Catania post-earthquake reconstruction at large (architectonic) scale of observations to evidence the different damage in the façade. In both cases the method permitted to give a complete picture of the damage and to esteem the different degradation index. This preliminary report is encouraging and may be extended to the main monuments of historical centers with the aim to plan the correct restoration projects, and give the priority of interventions.

Fitzner B., Heinrichs K. & La Bouchardiere D. 2002. Damage index for stone monuments. In: Galan, E. & Zezza, F. (ed.): Protection and Conservation of the Cultural Heritage of the Mediterranean Cities, Proceedings of the 5th International Symposium on the Conservation of Monuments in the Mediterranean Basin, Sevilla, Spain. 315-326, Swets&Zeitlinger, Lisse, The Netherlands.

## LA-ICP-MS analyses on clinopyroxenes for the provenance determination of the Pompeii cooking ware

Scarpelli R.\*<sup>1</sup>, De Francesco A.M.<sup>1</sup>, Gaeta M.<sup>2</sup> & Cottica D.<sup>3</sup>

1. Dipartimento di Biologia, Ecologia e Scienze della Terra, Università della Calabria. 2. Dipartimento di Scienze della Terra, Università degli Studi di Roma Sapienza. 3. Dipartimento di Studi Umanistici, Università Cà Foscari, Venezia.

Corresponding email: [roberta.scarpelli@unical.it](mailto:roberta.scarpelli@unical.it)

Keywords: LA-ICP-MS, ceramics, provenance, clinopyroxenes.

The cooking ware, is the most attested ceramic production found at Pompeii during the I.E. (= Impianto Elettrico) excavations in 1980-1981. The great variability of ceramic shapes and fabrics, have suggested a wide diffusion in Roman town, of products, not only of local provenance.

The analysed wares are dated from 1st century BC to 1st century AD and belong to different typologies of pottery: the pots with “*orlo a tesa*” and jar with “*orlo a mandorla*”. The pots with “*orlo a tesa*” were distributed widely from the 1st century BC around the western Mediterranean basin, along the coasts of *Hispania Terraconensis*, Gaul, Tuscany and Carthage.

The jars with “*orlo a mandorla*”, were produced between the 2nd century BC and the Augustan age in the western Mediterranean and exported principally from the Tyrrhenian coast.

The following archaeometric study, aimed to identify the production area of some ceramic samples and to verify the archeological assumptions.

Petrographic and mineralogical analysis distinguished two groups characterized by a volcanic temper. Plagioclase, sanidine, clinopyroxene, amphibole, biotite crystals and a great amount of volcanic rock fragments were observed in both sets of ceramics. The differences are related to higher content of sialic minerals - i.e. plagioclase, sanidine and quartz- in a group and on the contrary of mafic minerals (in particular of clinopyroxenes) in the other one.

This mineralogical assemblage is common to several scoriaceous pyroclastic-flow and pyroclastic-fall deposits of the Campanian volcanoes, Vesuvius, Campi Flegrei and Roccamonfina as well as Roman province including the Vulcini, Vico and Monti Sabatini volcanic districts (Peccerillo & Turco, 2004; Marra & D'Ambrosio, 2013). It excludes the Alban Hills, whose products lack plagioclase and K-feldspar phenocrysts (Gaeta *et al.*, 2006).

In order to characterize in a quantitative way the mineralogical assemblage, LA-ICP-MS coupled with SEM/EDS analysis were performed on clinopyroxene crystals, occurring in the volcanic rock fragments of the ceramics and in the juvenile products of Latium and Campania volcanic districts.

The statistical approach distinguished the two investigate magmatic Provinces, corroborating the Vesuvian production for a group and the Latium provenance for the other one.

Gaeta M., Freda C., Christensen J. N., Dallai L., Marra F., Karner D. B. & Scarlato P. 2006. Time-dependent geochemistry of clinopyroxene from the Alban Hills (central Italy): clues to the source and evolution of ultrapotassic magmas. *Lithos*, 86, 330-46.

Marra F. & D'Ambrosio E. 2013. Trace Element Classification Diagrams of Pyroclastic Rocks from the Volcanic Districts of Central Italy: the Case Study of the Ancient Roman Ships of Pisa. *Archaeometry*, 55, 993-1019.

Peccerillo A. & Turco E. 2004. Petrological and geochemical variations of Plio-Quaternary volcanism in the Tyrrhenian Sea area: regional distribution of magma types, petrogenesis and geodynamic implications. *Periodico di mineralogia*, 73, 231-251.

## Implemented, *in situ*, water absorption test by contact sponge

Scrivano S.\* & Gaggero L.

Dipartimento di Scienze della Terra dell'Ambiente e della Vita, Università di Genova.

Corresponding email: [simona-scrivano@libero.it](mailto:simona-scrivano@libero.it)

Keywords: Ornamental stones, contact sponge method, non-invasive *in situ* analysis.

Water absorption in heritage materials is a key parameter for which the UNI Normal normative deserved a specific protocol. In fact, difficulties arise in operating on test samples or on materials with porosity varied for decay, compared with fresh or reference rock or mortar.

The UNI Normal procedure requires to use a sponge with known density, soaked in water, weighed, placed on the material for 1 minute (UNI 11432, 2011; Pardini & Tiano, 2004), then weighed again.

While carrying on this test we noticed that fluctuation in the values of the environmental parameters during the single test were negligible, but not the pressure applied to the surface, that induced the release of different water amounts towards the material.

For this reason we designed a metal piece of the same diameter of the plate carrying the sponge to be screwed at the tip of a pocket penetrometer. With this instrument the sponge was put in contact with the surface for 1 minute applying two different loads, at first pushed with  $0.3 \text{ kg/cm}^2$  in order to press the sponge, but not its holder, against the surface. A second load ( $1.1 \text{ kg/cm}^2$ ) was chosen to apply a relevant pressure, still avoiding deviating the load to the sponge holder.

We applied both the current and the implemented method to determine the water absorption by contact sponge on 5 fresh rock types (Fine - and Coarse grained Pietra di Vicenza, Rosso Verona, Breccia Aurora, Arenaria Macigno).

The results show that the current methodology imply manual skill and experience to produce a coherent set of data; the variable involved are in fact not only the imposed pressure but also the compression mechanics. The adoption of pressure parameterization allowed reproducible measurements. Moreover the use of a thicker sponge enables to apply the method even on rougher surfaces, as the device holding the sponge avoids the contact with the tested object.

Finally, the implemented measurements gave the possibility of a direct comparison with the capillary water absorption method.

Pardini C. & Tiano P. 2004. Valutazione *in situ* dei trattamenti protettivi per il materiale lapideo, proposta di una nuova semplice metodologia. ARKOS, 5, 30-36.

UNI 11432. 2011. Beni culturali Materiali lapidei naturali ed artificiali - Misura della capacità di assorbimento di acqua mediante spugna di contatto. Pagg 6.

## New insights on production technologies of Late-Antique glass mosaic tesserae with calcium phosphate as opacifier

Silvestri A.\*<sup>1</sup>, Nestola F.<sup>1</sup> & Peruzzo L.<sup>2</sup>

1. Dipartimento di Geoscienze, Università di Padova. 2. Istituto di Geoscienze e Georisorse, CNR, Padova.

Corresponding email: [alberta.silvestri@unipd.it](mailto:alberta.silvestri@unipd.it)

Keywords: Glass mosaic, opacifier, calcium phosphate.

Glass mosaics are heterogeneous materials, composed of glassy matrix and crystalline phases, and produced by complex pyrotechnological processes from selected raw materials (generally minerals) with various functions (formers, fluxes, stabilisers, colourants, decolourants and opacifiers). In particular, this study focuses on opacifiers composed of calcium phosphate and identified into some Late-Antique glass tesserae, green or blue in colour, from Padova (Italy) (Silvestri et al., 2012) and Tyana (Turkey) (Serra et al., 2009). It is generally accepted that calcium phosphate is a primary opacifier, probably obtained by the intentional addition of bone powder to a transparent glass (Verità, 2000), but no specific crystallographic-mineralogical studies have been carried out on this opacifier until now. In tesserae from both sites, analyses, performed by scanning electron microscopy (SEM) and X-ray powder diffraction (XRPD), show that calcium phosphate grains, probably hydroxyapatite, have a reaction rim, enriched in sodium, which comes from the surrounding glass and replaces the calcium of the opacifier. The above replacement process between opacifier and glassy matrix is also confirmed by the presence of newly formed crystals composed of calcium silicate (wollastonite), found in the proximity of calcium phosphate grains (Silvestri et al., 2012). The same micro-texture was found in all the tesserae, suggesting similar production technologies in both sites and that production technologies may be highly standardised. Investigations on the calcium phosphate, on its reaction rim and on interactions with surrounding soda-lime-silica glass are in progress by means of X-ray diffraction (XRD), electron backscattered diffraction (EBSD), electron microprobe (EMPA), and micro-Raman spectroscopy in order to clarify the nature of these inclusions and to make inferences on the production technologies of such kind of glass tesserae.

Serra C.L., Silvestri A. & Molin G. 2009. Archaeometric characterization, Appendix of Lachin M.T. "Vitreous Mosaic from Tyana (Cappadocia)". In: Lafli E. Ed., Late Antique/Early Byzantine Glass in the Eastern Mediterranean, Colloquia Anatolica Et Aegaea –Acta Congressus Communis Omnium Gentium Smyrnae II, Izmir, Turkey, 175-183.

Silvestri A., Tonietto S., Molin G. & Guerriero P. 2012. The palaeo-Christian glass mosaic of St. Prodocimus (Padova, Italy): archaeometric characterisation of tesserae with antimony- or phosphorous-based opacifiers. *J. Archaeol. Sci.*, 39, 2177-2190.

Verità M. 2000. Tecniche di fabbricazione dei materiali musivi vitrei: indagini chimiche e mineralogiche. In: Borsook, E., Gioffredi-Superbi, F., Pagliarulo, G. Eds., Medieval mosaics: light, color, materials, 47-64, Silvana Editoriale, Milano.

## Characterization of pigments and microclimate monitoring for the preservation of a rare medieval parchment

Tempesta G.\*, Porfido C. & Monno A.

Dipartimento di Scienze della Terra e Geoambientali, Università di Bari.

Corresponding email: [gioacchino.tempesta@uniba.it](mailto:gioacchino.tempesta@uniba.it)

Keywords: parchment, spectrophotometry, pigments.

A rare medieval parchment called Exultet I preserved in the Diocesan museum of Metropolitan Capitolo of Bari has been studied. The Exultet was sung after a procession with the Paschal Candle before the beginning of the Liturgy of the Word in the XI century and it is certainly one of the highest literary and artistic expressions that Bari produced. Eight sheets with text, music lines and numerous beautiful miniatures painted upside-down respect to the liturgical text compose the parchment roll. The opening of the theca that preserves the unwrapped roll gave us the opportunity to perform diagnostic measurement on the pigments of the illuminated areas and to locate a wireless weather station for monitoring the microclimate. For these analyses a mobile laboratory has been set up in the museum. The techniques used for a non-invasive and in situ analysis of miniature paintings has been microscopic observation with digital microscope, UV-VIS-NiR spectrophotometry in reflectance mode with optic fibres (FORS), X-Ray fluorescence spectrometry (XRF) and finally  $\mu$ -Rman spectroscopy. The use of several techniques is able to give us all information without causing any stress to the parchment especially if the measures are fast, as in our case (Aceto et al., 2012). The pigments have been identified mainly with FORS with comparison with standards and they are: red ochre and red lead used as red, lapis lazuli and azurite as blue, green earth and copper resinate as green, yellow ochre and orpiment as yellow. In the most important miniatures in some areas of the background, several traces of a residual gold leaf have been identified by XRF. The presence of rare and precious pigments as gold leaf and lapis lazuli underline the importance of the parchment. The preparation of the figures made by using a lead stylus has been also identified. The presence on all the roll of humpbacks formed in the last years well fit with the data collected that shows a continuity of condition between the showcase and the museum room. These means that the presence of visitors leads to changes in temperature, humidity and CO<sub>2</sub>, resulting much higher than those suggested for parchments. Finally the hypothesis of a repainting, formulated on the basis of the conservation status of the colours of the illuminated areas and from the comparison of similar hues, has been confirmed by the characterization of the colour palette. In some points the analysis returned the blue pigment as azurite and the red ones as minium, these results are in contrast with those of blue and red, respectively used, in all other illustrations of the roll were lapis lazuli and red ochre are plentiful.

Aceto M., Agostino A., Fenoglio G., Gulmini M., Bianco V., Pellizzi E. 2012. Non invasive analysis of miniature paintings: Proposal for an analytical protocol. *Spectrochim. Acta, Part A: Mol. Biomol. Spectrosc.*, 91, 352-359.

## **Ancient extractive metallurgy of copper in the Aosta Valley (Western Alps, Italy): new evidence from pre-Roman slags from the Misérègne site**

Toffolo L.\*<sup>1</sup>, Martin S.<sup>1</sup>, Nimis P.<sup>1</sup> & Rottoli M.<sup>2</sup>

1. Dipartimento di Geoscienze, Università degli Studi di Padova. 2. ARCO Cooperativa di Ricerche Archeobiologiche, Como.

Corresponding email: [luca.toffolo@studenti.unipd.it](mailto:luca.toffolo@studenti.unipd.it)

Keywords: slag, ancient copper extractive metallurgy, Aosta Valley.

Many metallurgical sites are scattered across the Aosta Valley territory (e.g. Tumiatì *et al.*, 2005). The age of some of them is unknown and often the slag heaps are the sole vestiges of metallurgical activities. Such is the case of Misérègne (Fénis), where the village is built on an enormous slag deposit.

We performed radiocarbon dating on charcoal fragments included in the slags and obtained ages comprised between the 4<sup>th</sup> and 1<sup>st</sup> century BC. So far, these are the most ancient ages for early mining activity in the Aosta Valley, probably carried out by the local population of the Salassi.

We studied the slags following a petrologic approach. The occurrence of matte inclusions in the slags indicates that the processed raw minerals were Cu-Fe sulfides. Relying on morphologic and micro-textural features, we classified the slags into three categories, i.e., coarse, massive and flat, as suggested by Addis (2013). In all the slag classes the most abundant phase is olivine. Other common phases are spinel group minerals and sulfides, mainly pyrrhotite and bornite solid solutions. The olivine crystal shapes allowed us to qualitatively estimate the degree of undercooling ( $\Delta T$ ) and the rate of cooling of the slags: the coarse slags show a high  $\Delta T$ ; the massive slags seem to record an initial, long-lasting low- $\Delta T$  stage, followed by an increase in the cooling rate; the flat slags underwent a brief low- $\Delta T$  stage, followed by a sudden marked increase in  $\Delta T$ . Combining this information with the slag bulk chemistry, the sulfide compositions, the slag morphology and the presence of inclusions of charcoal, quartz and other slag fragments, we hypothesize that the massive and coarse slags come from the lower and, respectively, the upper portion of the same slag contained in the furnace, while the flat ones were tapped slags. Minimum furnace working temperatures estimated by means of olivine-spinel geothermometry are in the ranges 932-964°C, 968-1037°C, 1202-1239°C for the coarse, massive and flat slags, respectively. According to the above observations, the flat slags should record conditions that are the closest to the actual furnace working temperature.

Addis A. 2013. Late Bronze Age metallurgy in the Italian Eastern Alps: copper smelting slags and mine exploitation. Tesi di dottorato, Dipartimento di Geoscienze, Università degli Studi di Padova.

Tumiatì S., Casartelli P., Mambretti A., Martin S. 2005. The ancient mine of Servette (Saint-Marcel, Val d'Aosta, Western Italian Alps): a mineralogical, metallurgical and charcoal analysis of furnace slags, *Archaeometry*, 47, 317-340.

## Looking for the Garamantian emeralds. An archaeometric approach to reconstruct the trading of amazonite stone beads in the ancient Sahara

Zerboni A.\*<sup>1</sup>, Vignola P.<sup>2</sup>, Risplendente A.<sup>1</sup>, Ducale E.<sup>1</sup>, Gatto M.C.<sup>3</sup> & Mori L.<sup>4</sup>

1. Dipartimento di Scienze della Terra "A. Desio", Università di Milano. 2. C.N.R.-I.D.P.A., Milano. 3. Department of Near Eastern Languages and Civilizations, Yale University, New Haven, USA. 4. Dipartimento di Scienze dell'Antichità, Università di Roma 'La Sapienza'.

Corresponding email: [andrea.zerboni@unimi.it](mailto:andrea.zerboni@unimi.it)

Keywords: Amazonite stone beads, Microprobe, Garamantes.

We discuss the results of the archaeometric study carried out on green-coloured stone beads found during the excavation of an historical site at Fewet (SW Libya, central Sahara). Therein, a compound, dated between the 2<sup>nd</sup> century BC and the 1<sup>st</sup> century AD and occupied by the Garamantes of the Fezzan, was one of the villages located along one of the most important trans-Saharan caravan route (Mori, 2013). In the current literature, Saharan green stone beads dating to historical times are generally identified with the term *émeraude garamantique*. Previous investigations in the region have generally attributed the green stone beads and pendants found in Garamantian archaeological contexts to amazonite and have identified the mining site with the pegmatite dike at Eghei Zuma (northern Tibesti, southern Libya), accepting the hypothesis initially proposed by T. Monod (1974). To confirm this observation we submit several samples of green stone beads from Fewet and several comparison samples, including samples of raw material from Eghei Zuma, to microprobe analyses. Geochemical results highlight that our green-coloured stone beads consist of different lithotypes (serpentinite and amazonite) and the source of this amazonite could not be the pegmatite outcrop at Eghei Zuma. Finally, we try to identify a list of potential sources of amazonite in the Sahara and surrounding regions and discuss the archaeological implication of our results, which concerns the main direction of ancient trade routes for elite goods and the movement of amazonite beads in the Sahara in Garamantian times (Zerboni and Vignola, 2013).

Monod T. 1974. Le mythe de «l'Émeraude des Garamantes». *Antiquités africaines*, 8, 51-66.

Mori L. 2013. Life and death of a rural village in Garamantian Times. *Archaeological investigations in the Fewet oasis (Libyan Sahara)*. Arid Zone Archaeology Monographs, 6, Edizioni all'Insegna del Giglio, Firenze.

Zerboni A. & Vignola P. 2013. Green stone beads from the excavation in Fewet. In: Mori L. Eds., *Life and death of a rural village in Garamantian Times. Archaeological investigations in the Fewet oasis (Libyan Sahara)*. Arid Zone Archaeology Monographs, 6, 157–167. Edizioni all'Insegna del Giglio, Firenze.

## SESSIONE S12

### **Looking inside the planet Earth: Experimental and Computational Methods in Mineralogy and Geochemistry**

#### *CONVENORS*

*D. Belmonte (Univ. Genova)*

*F. Nestola (Univ. Padova)*

*M. Prencipe (Univ. Torino)*

## A comparison between *Ab Initio* calculated and measured vibrational frequencies of the triclinic Albite

Aliatis I.\*<sup>1</sup>, Lambruschi E.<sup>1</sup>, Mantovani L.<sup>1</sup>, Bersani D.<sup>1</sup>, Andò S.<sup>3</sup>, Gatta G. D.<sup>2</sup>, Gentile P.<sup>3</sup>, Salvioli-Mariani E.<sup>1</sup>, Prencipe M.<sup>4</sup>, Tribaudino M.<sup>1</sup> & Lottici P.P.<sup>1</sup>

1. Dipartimento di Fisica e Scienze della Terra, Università di Parma. 2. Dipartimento di Scienze della Terra, Università di Milano. 3. Dipartimento di Scienze dell'Ambiente e del Territorio e di Scienze della Terra, Università di Milano Bicocca. 4. Dipartimento di Scienze della Terra, Università di Torino.

Corresponding email: [irene.aliatis@difest.unipr.it](mailto:irene.aliatis@difest.unipr.it)

Keywords: Ab initio calculation, Raman Spectroscopy, albite.

Feldspar-group minerals are among the most common rock-forming minerals of planetary crusts. On Earth, they occur in igneous, metamorphic and sedimentary rocks. On the Moon, plagioclase is the most abundant mineral and feldspars are one of the main minerals in Martian meteorites. Feldspars show subtle variations in crystal structure that allow petrologists to gain information about the chemical and physical conditions prevailing during rock formation. The whole spectrum of their possible structural states can be found in rocks with different cooling histories, providing an opportunity to study the way a structure responds to a slowly changing geological environment.

Albite, NaAlSi<sub>3</sub>O<sub>8</sub>, is the sodic end-member of high temperature plagioclase and alkali feldspar solid solutions. The analysis of its vibrational frequencies and their assignments to the fundamental normal modes are the aim of this study.

The Raman spectrum of albite has been calculated by using the CRYSTAL14 program (Dovesi et al., 2014). Calculations were made at the hybrid Hartree-Fock/Density Functional level (HF/DFT): the WC1LYP Hamiltonian, which provides excellent agreement between calculated and experimentally measured vibrational frequencies (see e.g. Prencipe et al., 2012), was employed.

The comparison between the frequencies measured by Raman spectroscopy on an ordered natural albite, var. Cleavelandite from Minas Gerais (Brasil), with those calculated by HF/DFT is discussed. All the expected 39 A<sub>g</sub> modes have been identified in the Raman spectra and their frequencies well correspond to the calculated ones (the average absolute discrepancy ( $\langle|\Delta| \rangle$ ) is  $\sim 3$  cm<sup>-1</sup>; the maximum discrepancy ( $|\Delta|_{\max}$ ) is  $\sim 10$  cm<sup>-1</sup>). The good quality of the WC1LYP results allowed for reliable assignments to specific patterns of atomic vibrational motion (normal modes).

Dovesi R., Saunders V. R., Roetti C., Orlando R., Zicovich-Wilson C. M., Pascale F., Civalleri B., Doll K., Harrison N. M., Bush I. J., D'Arco P., Llunell M., Causà M. & Noël Y. 2014. CRYSTAL14 User's Manual. University of Torino.  
Prencipe M., Mantovani L., Tribaudino M., Bersani D. & Lottici P. P. 2012. The Raman spectrum of diopside: a comparison between ab initio calculated and experimentally measured frequencies. Eur. J. Mineral., 24, 457-464.

## Effect of Transition Metal Ions (*TMI*) on the compressibility of orthorhombic perovskites

Ardit M.\*<sup>1</sup>, Dondi M.<sup>2</sup> & Cruciani G.<sup>1</sup>

1. Dipartimento di Fisica e Scienze della Terra, Università di Ferrara. 2. ISTEC-CNR Faenza.

Corresponding email: [rdmttt@unife.it](mailto:rdmttt@unife.it).

Keywords: Orthorhombic perovskite, high-pressure, transition metal ions.

Variations in the chemical nature of *A* and *B* cations, as well as changes in *P* and *T*, are accommodated in the framework structure of perovskite (general formula  $^{[XII]}A^{[VI]}BO_3$ ) by octahedral tilting and more distorted polyhedra. The structural answer to these internal and external stresses is a decreasing of the symmetry (Mitchell, 2002). From the cubic archetype, perovskites often become orthorhombic. This class of perovskites received considerable attention in Earth Sciences since it was discovered that the major minerals of the upper mantle (i.e. olivine, pyroxene, and garnet) transform into the denser (Mg,Fe)SiO<sub>3</sub> perovskite-structured mineral, at *P-T* conditions of the upper/lower mantle interface (Navrotsky & Weidner, 1989). Considered as the dominant component of the lower mantle, this orthorhombic compound remarked on the importance to understand the relationship between external condition, structural properties, and chemistry of perovskite phases. For these reasons, perovskites are the subject of many studies devoted to establish their *HP* behaviour. Part of these studies (Andraut & Poirier, 1991; Thomas, 1998; Zhao et al., 2004) attempt to predict the evolution of these compounds under *HP* regime by means of semiempirical and theoretical models. As a common generalization, the structural evolution of orthorhombic perovskites with *P* can be rationalized in terms of relative compressibilities of the two polyhedra (*AO*<sub>12</sub> and *BO*<sub>6</sub>): when the *AO*<sub>12</sub> site is more compressible than the *BO*<sub>6</sub> octahedron, the volume reduction will lead to an increasing of the octahedral tilting; conversely, when the *AO*<sub>12</sub> site is less compressible than the *BO*<sub>6</sub> octahedron, the structure will evolve by decreasing the octahedral tilting raising its symmetry towards the cubic archetype. The model proposed by Zhao et al. (2004) predicts that the polyhedral compressibility ratio can be devised as the ratio of the estimated variation of bond valence in the *A* and *B* polyhedral sites due to the change of the average metal-oxygen bond distance. In this contribution the structural evolution of perovskites upon pressure will be modeled through a new polyhedral bond valence approach. The obtained results will be compared with those derived from previous models, and it will be shown as transition metal ions at the B site act as an incompressibility factor.

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## Ultrafast growth of quasicrystals in shock-produced melts and its implications for the early solar nebula

Bindi L.\*

Dipartimento di Scienze della Terra, Università di Firenze.

Corresponding email: [luca.bindi@unifi.it](mailto:luca.bindi@unifi.it)

Keywords: solar system, Earths core, quasicrystals.

The first natural quasicrystal (Bindi et al., 2009, 2011, 2012), icosahedrite ( $\text{Al}_{63}\text{Cu}_{24}\text{Fe}_{13}$ ), was discovered in the Khatyrka meteorite (Macpherson et al., 2013), a CV3 carbonaceous chondrite (CV3 CC) that formed 4.5 billion years ago. The initial reports, based on a museum sample, revealed icosahedrite in a complex assemblage of unusual metallic crystal phases [khatyrkite ( $\text{CuAl}_2$ ), cupalite ( $\text{CuAl}$ ), and  $\beta$ -phase ( $\text{AlCuFe}$ )], and conventional chondritic minerals [diopside, forsterite, spinel ( $\text{MgAl}_2\text{O}_4$ ), nepheline]. Understanding how this mineral assemblage formed has been a deep mystery. An expedition to the Koryak Mountains in far eastern Russia in 2011 recovered more samples (Steinhardt and Bindi, 2012). Here we present results from those samples that distinguish Khatyrka from previous CV3 CCs and strongly indicate a resolution of the mystery. Two new minerals are identified ( $\text{Fe}_{3-x}\text{Si}_x\text{O}_4$  spinelloid with  $x = 0.4$ , and an  $\text{AlNiFe}$  phase); these are associated with Al-Cu-bearing taenite, Al- and Cu-bearing iron sulfide and an eutectic texture of khatyrkite and nearly pure Al. The presence of ahrensite (Fe-rich ringwoodite), spinelloid and stishovite show that the meteorite underwent the strongest shock ever observed in a CV3 CC (local pressures 5-10 GPa). Ahrensite-silica lamellar eutectic textures, the metal eutectic pattern, and the range of oxidation states all point to shock melts locally produced at about 1200 °C, followed by very rapid cooling and solidification down to temperatures.

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## The energy and crystal morphology of diamond inclusions to explain their genesis

Bruno M.\*

Dipartimento di Scienze della Terra, Università degli Studi di Torino.

Corresponding email: [marco.bruno@unito.it](mailto:marco.bruno@unito.it)

Keywords: diamond, surface, olivine.

Inclusions in diamond (Dis) are among the deepest materials originating from Earth's interior reaching the planet's surface. Diamonds are billions of years old and remain unaltered over time, preserving the pristine conditions of Earth. Therefore, their study plays a key role in understanding and interpreting the geodynamics, geophysics, petrology, geochemistry, and mineralogy of Earth's mantle from the lithosphere to the lowermost part.

Diamond inclusions (DIs) are divided into three groups: protogenetic, syngenetic, and epigenetic (Meyer, 1987). DIs are classified as protogenetic when they form before encapsulation by the host diamond, whereas they are considered syngenetic when the inclusion and its host diamond form at the same time and by the same genetic processes. Both groups play a key role in the study of diamond formation processes, contrary to epigenetic phases, which are secondary minerals, usually associated with crustal processes, and are atypical with respect to the primary minerals in mantle xenoliths.

Such a distinction is important, because, in the case of syngenesi, any geological information extracted from the inclusion (e.g., pressure and temperature of formation, geochemical environment, age) would also unequivocally apply to its host diamond. On the other hand, a protogenetic inclusion would record conditions that existed before its encapsulation.

Distinguishing between syngenesi and protogenesis is as crucial as it is extremely difficult and controversial. The most common observation used to deduce syngenesi is the imposition of the host diamond morphology on the DI (Harris, 1968). Another significant contribution to the syngenesi-versus-protogenesis debate derives from the observation that some Dis occur in a specific orientational relationship with respect to diamond, which can be considered as evidence in favor of epitaxial growth of the DI above the diamond or vice versa and, hence, of syngenesi (Meyer, 1987).

Here, we discuss the peculiar crystal morphology of olivine included in diamond (DI). First, we show that the observed cuboctahedral shape of olivine in diamond is actually a combination of an orthorhombic bipyramid (i.e., {495}) and pinacoids. This implies that the shape of olivine can be equivalent to that of diamond, even if the forms making up the two crystals are completely different. Second, we demonstrate that the morphology of the DI cannot be considered as evidence of syngenesi. In particular, if the crystal morphology is modified but the DI does not show a preferential orientation with respect to the diamond, the bulk of the DI is protogenetic, whereas its shape is syngenetic.

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## Reconstruction of rocks petrophysical properties as input data for analytical and numerical modeling

Cantucci B.\*<sup>1</sup>, Montegrossi G.<sup>2</sup>, Lucci F.<sup>3</sup> & Quattrocchi F.<sup>1</sup>

1. Istituto Nazionale di Geofisica e Vulcanologia, Roma. 2. CNR, IGG Firenze. 3. Dipartimento di Scienze della Terra, Università degli Studi Roma TRE.

Corresponding email: [barbara.cantucci@ingv.it](mailto:barbara.cantucci@ingv.it)

Keywords: Thermo-physical properties, closed deep wells, numerical modeling, porosity-permeability profiles.

The worldwide increasing energy demand has favored several studies devoted to evaluate the underground energy potential also in areas previously discharged or neglected. Nowadays technologies such as geological storage of gas (CO<sub>2</sub> and/or CH<sub>4</sub>), renewable energies, geothermal energy (from low to high enthalpy) and nuclear waste are considered strategic in terms of low carbon energy development.

For a safe and worthwhile use of these technologies, an accurate characterization of the substratum in terms of geology, hydrogeology, geochemistry and geomechanics is a pre-requisite. This includes knowledge of essential parameters such as texture, porosity, permeability, mineralogy and thermo-physical properties of rocks necessary to characterize the reservoir and consequently to model heat and fluid transport.

These parameters are strictly related to the tectonic history and the evolution of a specific area and should be measured directly on rock samples. Unfortunately, during the pre-feasibility study stage, available direct measures of target reservoirs are limited, moreover the reopening of closed deep wells, often, may be very expensive.

This work propose a methodology for the reconstruction of thermo-physical properties of rock formations, combining well-log information, measured temperatures and petro-mineralogical analyses.

As case study we used a deep structure (about 1900 m b.s.l.), located in the medium Tyrrhenian sea (i.e. Northern Latium off-shore), already identified as potential target for geological storage of fluids (Procesi et al., 2013). Local stratigraphy is constrained by well-log data of a deep well (Matilde 1, more than 3000 m deep) drilled in the 1975 for hydrocarbon exploration and closed soon after because unproductive.

The presented approach assumes that thermal properties of rock minerals contribute to total capacity and conductivity of the rock proportionally to their abundance. On the basis of thermal properties of rocks, relationship among thermal capacity, conductivity, porosity and permeability were established so that porosity was the only independent variable. Finally, with a trial and error procedure the vertical profile of porosity and permeability was reconstructed by numerical modeling of heat transport using the measured temperatures and the Italian heat flow maps as boundary conditions.

This method can represent an useful tool for reservoir engineering and geochemical modelers to estimate, in a first step, thermo-physical input data for analytical and numerical modeling without the reopening of a well.

Procesi M., Cantucci B., Buttinelli M., Armezzani G., Quattrocchi F., Boschi E. 2013. Strategic use of the underground in an energy mix plan: Synergies among CO<sub>2</sub>, CH<sub>4</sub> geological storage and geothermal energy. Latium Region case study (Central Italy). Applied Energy 110, 104-131.

## High pressure behavior of natural fluorapatite and carbonate-fluorapatite

Curetti N.\*<sup>1-2</sup>, Cámara Artigas F.<sup>1-2</sup>, Benna P.<sup>1-2</sup> & Ferraris C.<sup>3</sup>

1. Dipartimento di Scienze della Terra, Università di Torino. 2. CrisDi Interdepartmental Center for Crystallography, Torino. 3. Muséum National d'Histoire Naturelle, Paris, France.

Corresponding email: [nadia.curetti@unito.it](mailto:nadia.curetti@unito.it)

Keywords: apatite, single-crystal XRD, bulk modulus.

Knowledge of the mineral-physics of apatite helps to assess the geological implications of its actual stability field, but also its mechanical properties - useful for its technological applications. Changes in its chemical and physical properties are observed when carbonate is incorporated into the apatite structure. The entry of CO<sub>3</sub> can occur by substitution of both channel anion (type A) and phosphate ion (type B); the first process causes an increase in *a* and a decrease in *c*, vice versa the second one a decrease in *a* and an increase in *c*.

Several *in situ* HP experiments have been already carried out on synthetic samples of fluor-, hydroxyl-, and chlor-apatite. A study of natural fluorapatite was performed by Matsukage et al. (2004), who found a  $K_T$  lower than previous works (BM2:  $K_T = 91.6(1.0)$  GPa vs  $97.9(1.9)$  GPa in Brunet et al., 1999 and  $97.8(1.0)$  GPa in Comodi et al., 2001). Recently Liu et al. (2011) have studied the effects of carbonate substitution on the compressibility of hydroxylapatite: the presence of carbonate (type-A and -B) lowers the value of  $K_T$ . However, it is difficult to assess if the softening is due to type-A or -B or both.

We have performed a X-ray study on natural single crystals of both fluorapatite [FOW;  $a=9.3549(9)\text{Å}$ ,  $c=6.874(1)\text{Å}$ ,  $V=521.0(1)\text{Å}^3$ ] and type-B carbonate fluorapatite [FRA;  $a=9.330(1)\text{Å}$ ,  $c=6.898(1)\text{Å}$ ,  $V=520.0(2)\text{Å}^3$ ] The two crystals were mounted concurrently in a ETH-type DAC, with a single crystal of quartz as internal P calibrant and a 16:3:1 mixture of methanol:ethanol:water as P-transmitting medium. We used SINGLE program (Angel & Finger, 2011) on a Siemens P4 four-circle diffractometer and EosFit7c (Angel et al., 2014) to collect and fit the data, respectively.

Our data [28 P points up to 7.05(4)GPa; *V* values fitted with a BM3-EoS] confirm that type-B CO<sub>3</sub>-substitution decreases the bulk modulus from  $K_T=89.4(1.3)$ GPa [ $K_T'=5.1(4)$ ] to  $K_T=86.3(1.2)$ GPa [ $K_T'=5.0(4)$ ]. This preliminary result well agrees with those ones previously found for fluorapatite.

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## Water effect on clinopyroxene compositions: insights from high pressure experiments on hawaiitic magmas

De Cristofaro S.P.<sup>1</sup>, Perinelli C.\*<sup>1</sup>, Gaeta M.<sup>1</sup>, Palladino D.M.<sup>1</sup> & Armienti P.<sup>2</sup>

1. Dipartimento di Scienze della Terra, Sapienza Università di Roma. 2. Dipartimento di Scienze della Terra, Università di Pisa.

Corresponding email: [cristina.perinelli@uniroma1.it](mailto:cristina.perinelli@uniroma1.it)

Keywords: Phase equilibria, clinopyroxene, geohygrometer.

Water is a critical component to magma genesis and evolution: its content affects liquidus temperatures, crystal fractionation trends, melt rheology and, in turn, the dynamics of magma ascent and eruption. Hence, it is of broad interest to determine the initial concentration of water in magmas and its variation during magma ascent and differentiation. Analysis of melt inclusions and experimental studies allowed to define the qualitative effects of water on magmatic processes; however, approaches for the quantitative estimation of water content in magmas are still scarce. Clinopyroxene (Cpx) is among the earliest and most abundant phases in basaltic rocks, being potentially the most complete tracer of magmatic crystallization. In addition, since the Cpx abundances and compositions are controlled by magma water solubility, this phase has been used as empirical hygrometer for magmas of Mt. Etna (Armienti et al., 2011). Available experimental data on hydrous liquids representative of Mt. Etna volcanics, used to calibrate the empirical method, cover a wide range of pressure ( $0.2 \leq P \leq 0.8$  GPa). However, very few runs were performed at high pressure ( $P \geq 0.5$  GPa) up to now. Here we report new HP experimental data on Etnean hawaiites, relevant for the implementation of the Cpx hygrometer. Experiments were carried out in a piston-cylinder apparatus at a pressure of 0.8 GPa in the presence of 2-10 wt% of H<sub>2</sub>O, in a range of temperature from 1050 °C to 1175 °C. As expected, the results indicate that the increase of water content (up to 6 wt%) decreases the liquidus temperature of about 100 °C. Cpx and plagioclase are the liquidus phases at all hydrate conditions, followed by oxide and olivine for water contents lower than 4 wt %. Higher H<sub>2</sub>O concentrations strongly reduce the stability field of oxides, which disappear at H<sub>2</sub>O > 4 wt%. In terms of Cpx end-members, it appears that, at a given temperature (e.g. 1125 °C), the main effect of an increasing water content is to increase the DiHd, EnFs and Jd components, coupled with a decrease of Ca-Ts end-member. These results confirm that Cpx composition is an effective tool to estimate H<sub>2</sub>O contents in mafic magmas.

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## Elastic Properties of Minerals from Ab initio Simulations: The case of Silicate Garnets

Erba A.\*, Mahmoud A. & Dovesi R.

Dipartimento di Chimica and Centre of Excellence NIS, Università di Torino.

Corresponding email: [alessandro.erba@unito.it](mailto:alessandro.erba@unito.it)

Keywords: Elastic constants, ab initio simulations, silicate garnets.

Standard ab initio quantum-chemical methods based on the Density Functional Theory (DFT) represent a powerful tool for the accurate determination of a variety of properties of materials, such as structural, electronic, spectroscopic, optical, elastic, magnetic, etc. (Dronskowski, 2005). The increasing efficiency of the algorithms and the growing parallel computing resources are rapidly widening the range of applicability of such schemes that can now be routinely used for studying minerals of geophysical interest. We have recently developed and implemented in the CRYSTAL14 public program (Dovesi et al., 2014) a fully-automated, general-purpose, computationally-efficient algorithm for the calculation of the elastic tensor of crystals (Erba et al. 2014b). Related quantities such as bulk, shear and Young moduli, Poisson's ratio and directional seismic wave velocities can now be computed. The effect of pressure on elastic response properties can be computed as well (Erba et al. 2014a). A family of silicate garnets (namely, pyrope, almandine, spessartine, uvarovite, grossular and andradite) has been considered which are major rock-forming minerals of the Earth's mantle. They are cubic crystals of space group Ia-3d, with 80 atoms in the primitive cell; their size represents a challenge for the ab initio description of their elastic properties at geophysical conditions. Calculations performed with the popular hybrid B3LYP functional provide an excellent description of the elastic properties of such garnets at ambient conditions as well as at high pressure, up to 60 GPa (Erba et al. 2014a; Erba et al. 2014b). The evolution of the elastic anisotropy under increasing pressure has been evaluated. Recently developed techniques for the study of solid solutions have been applied to the investigation of compositional effects on the bulk modulus of the grandite (grossular-andradite) solid solution series: while heterogeneous experiments were suggesting a strong deviation from linearity, our simulations reveal an almost linear behavior thus contributing to define a clear picture according to which the bulk modulus-composition trend is linear for all silicate garnets solid solutions.

Dovesi R., Orlando R., Erba A., Zicovich-Wilson C.M., Civalieri B., Casassa S., Maschio L., Ferrabone M., De La Pierre M., D'Arco Ph., Noel Y., Causà M., Rérat M. & Kirtman B. 2014. CRYSTAL14: A program for the *ab initio* investigation of crystalline solids. Int. J. Quantum Chem. DOI: 10.1002/qua.24658.

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## Modeling of Ca, Si and Al structural environments in glasses of the CAS system

Giuli G.<sup>1</sup>, Paris E.\*<sup>1</sup> & Romano C.<sup>2</sup>

1. Scuola di Scienze e Tecnologie, Università di Camerino. 2. Dipartimento di Scienze, Università di Roma Tre.

Corresponding email: [eleonora.paris@unicam.it](mailto:eleonora.paris@unicam.it)

Keywords: CAS glasses, structure, XANES modeling.

Alkaline-earth aluminosilicate glasses are an important type of materials, both for the many technical application in materials science and also because glasses of this composition can be used as analogues of basaltic melts. The understanding of the structural behavior of the cations in the glasses can provide more detailed data on the relationship between chemistry, structure and physical properties. In Earth Sciences, these information are the key for the comprehension of igneous processes as well as for the modeling of physical properties for these industrially-relevant materials.

In this work, X-ray absorption near-edge structure spectroscopy (XANES) has been applied to determine the structure of Ca, Al and Si in glasses in the CAS system (Wu et al., 1999). Experimental XANES spectra have been collected for a series of samples of peralkaline composition along the joints  $\text{SiO}_2\text{-Ca}_3\text{Al}_2\text{O}_6$  and  $\text{SiO}_2\text{-CaAl}_2\text{O}_4$  with variable contents of  $\text{SiO}_2$ ,  $\text{CaO}$  and  $\text{Al}_2\text{O}_3$ . First, the glass spectra have been compared with those obtained on minerals with well-known structure and chosen to represent a variety of coordination numbers and cation polyhedral geometries and distortions. The geometrical information obtained by this comparison have been used to build model structures surrounding each cation to approximate the glass structure. Using the clusters as starting tridimensional networks, theoretical XANES modelling has been carried out by means of the MXAN code which makes use of Full Multiple Scattering calculations and, by fitting the experimental spectra, allows to iteratively modifying the cluster structure (bond distances, coordination numbers, bond angles).

The results obtained are very promising to be used to:

- a) unravel the geometrical environment around each cation, even with low atomic number,
- b) interpret even subtle modifications of the spectra observed in the experimental spectra with the chemistry,
- c) acquire structural information also beyond the first coordination shell.

## Cancrinite-group minerals at non-ambient conditions: a model of the thermo-elastic and structure behavior

Lotti P.\*<sup>1</sup>, Gatta G.D.<sup>1 2</sup>, Merlini M.<sup>1</sup>, Cámara F.<sup>3 4</sup>, Rotiroli N.<sup>1</sup>, Comboni D.<sup>5</sup> & Alvaro M.<sup>6</sup>

1. Dipartimento di Scienze della Terra - Università degli Studi di Milano. 2. CNR - Istituto di Cristallografia - Sede di Bari. 3. Dipartimento di Scienze della Terra - Università degli Studi di Torino. 4. CrisDi - Interdepartmental Centre for the Research and Development of Crystallography - Torino. 5. Dipartimento di Scienze della Terra e dell'Ambiente - Università di Pavia. 6. Dipartimento di Geoscienze - Università degli Studi di Padova.

Corresponding email: [paolo.lotti@unimi.it](mailto:paolo.lotti@unimi.it)

Keywords: cancrinite, high pressure, comparative elastic behavior.

The cancrinite-group of minerals comprises more than ten species sharing the [CAN]-topology of the tetrahedral framework. Their microporous structure has wide 12-ring channels, bound by columns of cages (*can* units). Besides the aluminosilicate composition of the framework (with the only exception of tiptopite, having instead Be and P), the minerals of the cancrinite group show a remarkable chemical variability concerning the extraframework population. Two subgroups can be identified according to the content of the *can* units: the first with Na-H<sub>2</sub>O (cancrinite and vishnevite) and the second with Ca-Cl chains (balliranoite and davyne). The channels are stuffed by cations, anions and molecules. In Nature, cancrinite-group minerals occur in the late/hydrothermal stages of alkaline (SiO<sub>2</sub>)-undersaturated magmatism and in related effusive or contact rocks. On the technological front, cancrinite-group compounds have been proposed as stable storage form for alkaline waste solutions, of which are common precipitation products.

We aimed to model the thermo-elastic behavior and the mechanisms of (*P,T*)-induced structure evolution of cancrinite-group minerals, focusing to the role played by the extraframework population. The study was restricted to the following (CO<sub>3</sub>)-rich and (SO<sub>4</sub>)-rich end-members: cancrinite  $\{[(\text{Na,Ca})_6(\text{CO}_3)_{1.2-1.7}][\text{Na}_2(\text{H}_2\text{O})_2][\text{Al}_6\text{Si}_6\text{O}_{24}]\}$ , vishnevite  $\{[(\text{Na,Ca,K})_6(\text{SO}_4)][\text{Na}_2(\text{H}_2\text{O})_2][\text{Al}_6\text{Si}_6\text{O}_{24}]\}$ , balliranoite  $\{[(\text{Na,Ca})_6(\text{CO}_3)_{1.2-1.7}][\text{Ca}_2\text{Cl}_2][\text{Al}_6\text{Si}_6\text{O}_{24}]\}$  and davyne  $\{[(\text{Na,Ca,K})_6((\text{SO}_4),\text{Cl})][\text{Ca}_2\text{Cl}_2][\text{Al}_6\text{Si}_6\text{O}_{24}]\}$ . Their high-*P* and low-*T* (*T* < 293 K) behavior was investigated by *in situ* single crystal X-ray diffraction, using diamond-anvil cells and (N<sub>2</sub>)-cryo-devices, respectively.

Though sharing a similar volume compressibility [i.e.,  $\sim 0.021 \text{ GPa}^{-1}$ ,  $K_{T0} \sim 47 \text{ GPa}$ ] and thermal expansivity [i.e.,  $\sim 4.0-4.5 \cdot 10^{-5} \text{ K}^{-1}$ ], these minerals show a different anisotropic pattern, more pronounced in cancrinite and vishnevite. This behavior is governed by different deformation mechanisms, which reflect the different coordination environments of the cage population between the minerals of the two subgroups. In vishnevite, a *P*-induced re-organization of the channel population took place at *P*  $\geq 3.5 \text{ GPa}$ , suggesting that also the channel-constituents (and not only the cage one) can play an active role on the structure response at non-ambient conditions.

In addition, the high-*T* behavior of cancrinite was studied up to 823 K, by *in situ* single-crystal X-ray diffraction. At 748 K, a slow dehydration process takes place towards a (quasi)-anhydrous structure.

These are the first experimental findings aimed to provide a comparative thermo-elastic analysis of the CAN-group compounds, expanding the knowledge about the *P/T*-behavior of isotypic materials with open-framework structures.

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## Ab-initio investigation of the thermodynamic stability of the magnesio-wüstite solid solution under Earth's lower mantle conditions

Merli M.<sup>1</sup>, Sciascia\* L.<sup>1</sup>, Pavese A.<sup>2-3</sup> & Diella V.<sup>3</sup>

1. Dipartimento di Scienze della Terra e del Mare- Università degli Studi di Palermo. 2. Consiglio Nazionale delle Ricerche, CNR-IDPA, Sezione di Milano. 3. Dipartimento Scienze della Terra "A. Desio", Università degli Studi di Milano.

Corresponding email: [luciana.sciascia@unipa.it](mailto:luciana.sciascia@unipa.it)

Keywords: solid solution, Mg-wüstite, quantum mechanical.

Mg-wüstite, (Mg,Fe)O, is the second most abundant phase in the Earth's lower mantle. A profound understanding of the thermodynamic stability of this phase under deep mantle conditions is thus crucial for developing accurate models of the Earth's interior and the importance of drawing a complete picture of the stability fields of the Mg-wüstite solid solution, especially at high pressure/temperature regimes, is straightforward.

In the light of the above considerations, the present work has been undertaken where the thermo-chemical properties of the (Mg,Fe)O solid solution, over a wide PT range, have been modelled using mixing Helmholtz energy,  $\Delta F(T, x)_{mixing}$ . Calculations have been performed by means of cluster expansion, quantum mechanical and semi-empirical techniques.

Both high-spin (HS) and low-spin (LS) configurations of iron have been explored as a function of composition ( $x$ : molar fraction of FeO) over the MgO-FeO binary. Only the HS-model provides physically sound results at room pressure, yielding a correct trend of cell edge versus composition, whereas LS's issues are at variance with observations. Mixing Helmholtz energy has been parametrized by the following relationship  $\Delta F(T, x)_{mixing} = x \times y \times [(U(T)_0 + U(T)_1 \times (x - y) + U(T)_2 \pm (x - y)^2]$ , where  $y = 1 - x$  and  $U_j(T)$  are polynomials in T of the third order.  $\Delta F(T, x)_{mixing}$  exhibits a quasi-symmetric behaviour and allows one to build the T-X phase relations diagram over the MgO-FeO join. On the basis of the HS-model including vibrational contribution to Helmholtz energy, a solid solution's critical temperature of some 950 K has been predicted, remarkably lower than olivine's and Mg-Fe-garnet's. All this points to a more difficult Mg-Fe mixing in periclase-like structure than olivine and garnet, which, in turn, provide more degrees of freedom for atomic relaxation. From  $\Delta F(T, x)_{mixing}$ , the values of  $\Delta H(T, x)_{mixing}$  and  $\Delta S(T, x)_{mixing}$  have been derived, both exhibiting so modest a dependence on T as to be negligible.  $\Delta H(T, x)_{mixing}$  and  $\Delta S(T, x)_{mixing}$  exhibit quasi-regularity; either has been parametrized as  $W \times x \times (1 - x)$ , obtaining  $W_{H, Mg-Fe}$  and  $W_{S, Mg-Fe}$  of 17.7 kJ/mol and 26.8 J/mol/K, respectively.  $\Delta S(T, x)_{excess}$  has been estimated to be smaller than 0.5 J/mol/K in absolute. Moreover, it has been observed that the HS-configuration is stable and promote Mg-Fe solid solution up to  $\gg 15$  GPa better than LS does. At higher pressures, the LS-model becomes favourite and increasingly stabilizes (Mg,Fe)O upon rising P, whereas HS predicts ex-solving into the end members above  $\gg 40$  GPa.

## New iron-carbonates and iron-oxides at core/mantle boundary conditions

Merlini M.\*

Università degli Studi di Milano.

Corresponding email: [marco.merlini@unimi.it](mailto:marco.merlini@unimi.it)

Keywords: crystal structure, lowermost mantle, carbonate.

The recent improvements at synchrotron beamlines, currently allow single crystal diffraction experiments at extreme pressures and temperatures (Merlini et al., 2013; Dubrovinsky et al., 2010) on very small single crystal domains. We successfully applied such technique to determine the crystal structure adopted by carbonates at lower mantle pressures. The knowledge of carbon-bearing phases is in fact fundamental for any quantitative modelling of global carbon cycle. The major technical difficulty arises after first order transitions or decomposition reactions, since original crystal (apx.  $10 \times 10 \times 5 \mu\text{m}^3$ ) is transformed in much smaller crystalline domains often with random orientation. The use of 3D reciprocal space visualization software and the improved resolution of new generation flat panel detectors, however, allow both identification and integration of each single crystal domain, with suitable accuracy for ab-initio structure solution, performed with direct and charge-flipping methods and successive structure refinements. At higher pressure, towards Mbar (lowermost mantle and D'' region) in agreement with theoretical calculations (Arapan et al, 1997; Oganov et al., 2008) and other experimental results (Boulard et al., 2011), carbon coordination transform into 4-fold CO<sub>4</sub> units, with different polymerization in the structure depending on carbonate composition. The second important crystal chemistry feature detected is related to Fe<sup>2+</sup> in Fe-bearing magnesite, which spontaneously oxidizes at HP/HT, forming Fe<sup>3+</sup> carbonates, Fe<sup>3+</sup> oxides and reduced carbon (diamonds). Single crystal diffraction approach allowed full structure determination of these phases, yielding to the discovery of few unpredicted structures, such as Mg<sub>2</sub>Fe<sub>2</sub>C<sub>4</sub>O<sub>13</sub> and Fe<sub>13</sub>O<sub>19</sub>, which can be well reproduced in different experiments. Mg<sub>2</sub>Fe<sub>2</sub>C<sub>4</sub>O<sub>13</sub> carbonate present truncated chain C<sub>4</sub>O<sub>13</sub> groups, and Fe<sub>13</sub>O<sub>19</sub> oxide, whose stoichiometry is intermediate between magnetite and hematite, is a one-layer structure, with features encountered in magnetic materials. The results fully support the ideas of unexpected complexities in the mineralogy of the lowermost mantle, and single crystal technique, once properly optimized in ad-hoc synchrotron beamlines, is fundamental for extracting accurate structural information, otherwise rarely accessible with other experimental techniques.

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## **Diamond-garnet geobarometry using isomekes: the role of garnet compressibility and thermal expansion**

Milani S.\*, Alvaro M. & Nestola F.

Dipartimento di Geoscienze - Università di Padova.

Corresponding email: [sula.milani@studenti.unipd.it](mailto:sula.milani@studenti.unipd.it)

Keywords: garnet, diamond, isomekes.

Some of the diamonds formed in the sub-cratonic lithospheric mantle contain mineral, fluid and melt inclusions which have been trapped during diamond formation. These inclusions represent therefore a direct window on the Earth's upper mantle which is otherwise inaccessible to direct observations. Study of inclusions in diamonds, therefore, is important for better constraining the chemical and physical conditions which determine the processes of diamond formation.

The pressure and temperature at which the diamond-inclusion pairs grown are usually calculated applying classical geothermobarometric methods based on the chemical exchange between minerals. However, these geothermobarometers can be applied only when the appropriate set of mineral assemblages is present in the same inclusion. Recently, a method based on the pressure exerted by the diamond on the mineral inclusions and on the stresses in the surrounding diamond has been applied to obtain the pressure of the diamond source for olivine inclusions. The method can be applied to any single mineral inclusion. However, it requires accurate knowledge of the thermoelastic parameters (e.g. bulk modulus, thermal expansion) for both diamond and inclusion. While the thermoelastic parameters of the diamond have been already determined to a precision that yields insignificant uncertainties in calculated entrapment pressures ( $P_e$ ), this is not true for what concern the so far published data for garnets, that show a wide scatter. The uncertainties that arise from the comparison of these published data may indeed propagate in considerable uncertainties to the pressure calculated by the method described above.

In order to avoid inconsistency issues arising from the use of different datasets, we have measured the  $P$ - $V$  equations of state (EoS) and  $T$ - $V$  equations of state for different garnet compositions (i.e. pyrope,  $\text{Py}_{60}\text{Al}_{40}$ , almandine, uvarovite, grossular) by single-crystal X-ray diffraction using one single experimental setting (i.e. instrument, method, etc.). The set of elastic coefficients obtained are therefore intrinsically-internally consistent one to another and can provide a fundamental reference to estimate the compositional effect on the elastic properties. These data can be used to calculate the compositional effect on the positions of garnet-diamond isomekes and thus the entrapment pressures for garnet inclusions found trapped in diamonds.

## The Moving CMAS: Thermodynamics of Silicate Melts at High Pressure and Temperature

Ottonello G.\*<sup>1</sup>, Attene M.<sup>2</sup> & Vetuschi Zuccolini M.<sup>1</sup>

1. DISTAV - Università di Genova. 2. IMATI-CNR Genova.

Corresponding email: [giotto@dipteris.unige.it](mailto:giotto@dipteris.unige.it)

Keywords: CMAS liquid, Polymer chemistry, Thermodynamics.

The CMAS system (CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>) is a reasonable proxy to the complex chemistry of natural melts. Though this compositional reduction may appear excessive at first glance, it is justified by the heterogeneity of the system and the complexity of the thermodynamic interactions which determine the aggregation state in a wide P-T regime. In fact, though the energy transfer involved in the crystal-liquid and liquid-glass state transitions of prototypical glass-forming oxides (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>) may be precisely assessed through quantum mechanical computations of the translational ( $Q_{tra}$ ), rotational ( $Q_{rot}$ ) and vibrational ( $Q_{vib}$ ) components of the partition function, the complex interplay between the  $Q_{rot} + Q_{tra}$  and  $Q_{vib}$  components controls the amount of heat internally released through partial solidification of the crystal mush that partly counterbalances the loss of heat toward the exterior along a P-T trajectory. The chemical interaction among components at the liquid state may be resolved by quantifying electrostatically the interaction between Network Formers (NF) and Network Modifiers (NM) in terms of delta of donor-pressure. A polymer chemistry application, widely known as “Toop-Samis” approach, is able to “count” the contacts among structural units in the liquid and, coupled with a Toop’s asymmetric deconvolution that reduces all binary interactions basically to two sublattice (NF-NM) interaction terms (i.e. the HPA model and its developments), allows us to quantify the Gibbs free energy of mixing of the liquid independently of its chemical complexity. The mathematical handling of the hyper-surfaces representing the equipotential loci which delimit the stability fields at liquidus may be carried out through segmented Delaunay triangulations and efficient convex hull techniques. For a simplex of rank 3 (i.e. a four-component system like the CMAS) we may only “see” the primary phase volumes in a distorted tetrahedral representation. However, to depict the lines of descent (i.e. the chemical path of the liquid in the tetrahedron, induced by loss of heat), we must precisely know the primary phase volumes at all P conditions and the composition of the precipitating solids. This task is computationally very demanding. Adopting for instance a  $5 \times 10^{-2}$  compositional step and a 5 K T-discretization, each isobaric outcome in the 3000-1000 K T-range implies the generation of  $8 \times 10^8$  Gibbs free energy points, which, when coupled with the corresponding values computed for all the crystalline, gaseous and glassy phases nucleating in the system and constrained to obey the principle of minimization of Gibbs free energy at equilibrium, must be handled by the convex-hull routine to generate the equipotential loci hyper-surface.

## A Bader's topological approach for the investigation of the high pressure stability field of the Mg-perovskite phase

Parisi F.<sup>1,2</sup>, Sciascia L.\*<sup>3</sup>, Merli M.<sup>3</sup> & Princivalle F.<sup>2</sup>

1. Dipartimento di Fisica e Chimica, Università degli Studi di Palermo. 2. Dipartimento di Matematica e Geoscienze, Università degli Studi di Trieste.  
3. Dipartimento di Scienze della Terra e del Mare, Università degli Studi di Palermo.

Corresponding email: [luciana.sciascia@unipa.it](mailto:luciana.sciascia@unipa.it)

Keywords: Bader, electron density, phase transition.

The stability field of the Mg-perovskite phase, has been investigated by characterizing the evolution of the electron arrangement in the crystal.

The interest in the structural stability of this phase comes from the consideration that the Mg-perovskite is assumed to be the dominant component of the Earth's lower mantle (Oganov and Price, 2005) and the transition to the so-called post-perovskite phase can explain the discontinuity in seismic velocities observed above the core–mantle boundary (the D'' discontinuity).

Although quite a large amount of data on the perovskite so far exists, its behavior at the extreme conditions of the Earth mantle is still lacking information. This is mainly due to the technical difficulties related to the experimental setup. At extreme conditions, where the experiments lose accuracy, computational approach can be very helpful in complementing these studies.

In the present work, *ab initio* calculations of the perovskite structures in the range 0-180 Gpa have been performed at the HF/DFT exchange–correlation terms level, using Hamiltonians based on a WC1LYP hybrid scheme. The electron densities, calculated throughout the *ab initio* wave functions, have been analyzed by means of the Bader's theory, coupled with Thom's catastrophe theory.

The topological results show the occurrence of two topological anomalies. The first, i.e. the appearance of a cage critical point coalescent with a ring critical point, occurs at ~20 GPa and is a clear indication of the stabilization of the perovskite phase. The inverse process, observed at ~110 GPa, i.e. the vanishing of a cage-ring critical points couple, indicates the destabilization of this phase, and can be interpreted in the light of the perovskite to post-perovskite phase transition, which seems to be responsible of the discontinuity in seismic velocities observed above the core–mantle boundary (the D'' discontinuity).

It is worth to underline the important geophysical implication of these results. The stability field of perovskite explains several observed puzzling properties of the D'' layer: its seismic anisotropy, the strongly undulating shear-wave discontinuity at its top and possibly the anticorrelation between shear and bulk sound velocities.

The proposed approach is addressed to depict a phase transition from a novel viewpoint, particularly useful in predicting the stability of a compound at extreme conditions, at which laboratory experiments are extremely difficult.

## Thermal expansion behavior of orthopyroxenes: the role of the Fe-Mn substitution

Scandolo L.\*<sup>1</sup>, Mazzucchelli M.L.<sup>1</sup>, Domeneghetti M.C.<sup>1</sup>, Alvaro M.<sup>2</sup>, Nestola F.<sup>2</sup> & Pandolfo F.<sup>1</sup>

1. Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia. 2. Dipartimento di Geoscienze, Università di Padova.

Corresponding email: [lorenzo.scandolo01@ateneopy.it](mailto:lorenzo.scandolo01@ateneopy.it)

Keywords: Orthopyroxene, high temperature, thermal expansion, single-crystal X-ray diffraction.

Two Pbc orthopyroxene samples, donpeacorite and bronzite with chemical formula  $\text{Mn}_{0.54}\text{Ca}_{0.03}\text{Mg}_{1.43}\text{Si}_2\text{O}_6$  ( $X_{\text{Mn}}=0.27$ ) and  $\text{Fe}_{0.54}\text{Ca}_{0.03}\text{Mg}_{1.43}\text{Si}_2\text{O}_6$  ( $X_{\text{Fe}}=0.27$ ) respectively were investigated by single crystal X-ray diffraction (SC-XRD) at high-temperature conditions (see Pandolfo, 2014 for further details). The nearly identical  $X_{\text{Fe}}$  and  $X_{\text{Mn}}$  make the two samples the perfect candidates to investigate the effect of the compositional change at the M2 site (i.e. Fe-Mn substitution) on the thermal expansion behavior of orthopyroxenes.

The unit cell parameters thermal expansion behaviour of both samples have been investigated at 17 different temperatures between room- $T$  and 1073 K. In the entire temperature range no evidences for phase transitions have been found. In order to avoid any effect of the ordering-disordering process during the high-temperature in situ experiment both samples have been previously disordered with an ex situ annealing at about 1273K (following the protocol given in Alvaro et al., 2011).

The unit-cell parameters and volume thermal expansion, collected on the disordered samples have been fit to a Fei-type and Berman-type Equation of State (EoS) using EoSFit7c program (Angel, 2014). As a consequence of the compositional change while the thermal expansion along  $b$ -direction is nearly identical for both samples, slight differences have been found along  $a$  and  $c$  lattice. However, the differences in thermal expansion along  $a$  lattice are counterbalanced by the differences along  $c$  lattice. Therefore, as results of the different behavior along  $a$  and  $c$ , the unit cell volume thermal expansion for both samples is identical within standard deviations.

At room temperature the relative magnitudes of unit-cell thermal expansion coefficient for our sample are in clear agreement with the literature available data for Fe-Mg orthopyroxene, while at high-temperature thermal expansion coefficients show different behavior for the two sample mainly because of the changes of the expansion mechanism. Therefore it seems that the Fe-Mn substitution controls the unit-cell volume-expansion with temperature only by affecting  $V_0$  unit cell volume at room- $T$ .

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## Effect of alkali on the structure and viscosity of iron-bearing silicate glasses

Stabile P.<sup>1</sup>, Giuli G.\*<sup>1</sup>, Cicconi M.R.<sup>1</sup>, Paris E.<sup>1</sup>, Behrens H.<sup>2</sup>, Knipping J.-L.<sup>2</sup> & Webb S.<sup>3</sup>

1. School of Science and Technology, Geology Division, University of Camerino. 2. Institute of Mineralogy, Leibniz University of Hannover, Germany. 3. Mineralogy Department, GZG, Georg-August-University of Göttingen, Germany.

Corresponding email: [gabriele.giuli@unicam.it](mailto:gabriele.giuli@unicam.it)

Keywords: silicate glasses, structure, viscosity, alkali.

In the frame of a larger work aimed at studying the Fe-S interaction in silicate magmas and its effect on S solubility, the purpose of this project is to synthesise and study a series of rhyolitic glasses, with 5 wt% of FeO and different Na/(Na+K) ratios, equilibrated in air under controlled oxygen fugacity conditions. Together with composition, temperature and pressure, oxygen fugacity ( $fO_2$ ) plays an important role on physical and chemical properties in glasses and melts. Due to different  $fO_2$ , in fact, transition elements such as iron can exist in glasses in different oxidation states ( $Fe^0$ ,  $Fe^{2+}$  and  $Fe^{3+}$ ), which also influence the glass properties.

Alkali content is known to affect strongly the Fe oxidation state in silicate glasses (Moretti and Ottonello, 2003) but it is still controversial to which extent alkali can modify Fe structural role in glasses/melts. In this work the iron speciation ratio of each sample was determined by colorimetric wet chemistry and by XAS to study how  $Fe^{2+}/Fe_{tot}$  vary as a function of oxygen fugacity. X-Ray Absorption Spectroscopy (XAS) has been also employed to unravel Fe local geometry in the glasses:  $Fe^{3+}$  is in 4-fold coordination (tetrahedral) whereas  $Fe^{2+}$  coordination number is intermediate between 4 and 5.

Viscosity of the glasses has been measured by micropenetration method: the rate at which a 2 mm diameter single crystal sphere of  $Al_2O_3$  is forced into the melt is measured, and viscosity (in Pa s) is calculated by knowing the applied force (F), the time (t), the radius of the sphere (R) and the indentation depth (L) (Pocklington, 1940). Preliminary results show that viscosity of Fe-bearing melts strongly increase with decreasing Na/(Na+K) ratio in the oxidized samples.

These results have important implications for the effect of alkali ratio on the Fe speciation and on the solubility of sulphide in pantelleritic magmas, and will be essential for the improvement of comprehensive thermodynamic models able to predict S solubility variations in a wide range of silicate compositions.

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## Understanding pyroxene vibrational properties: *ab initio* calculated and experimental Raman spectra of spodumene (LiAlSi<sub>2</sub>O<sub>6</sub>)

Stangarone C.\*<sup>1</sup>, Prencipe M.<sup>2</sup>, Mantovani L.<sup>1</sup>, Bersani D.<sup>1</sup>, Tribaudino M.<sup>1</sup> & Lottici P.P.<sup>1</sup>

1. Dipartimento di Fisica e Scienze della Terra, Università di Parma. 2. Dipartimento di Scienze della Terra, Università di Torino.

Corresponding email: [claudia.stangarone@studenti.unipr.it](mailto:claudia.stangarone@studenti.unipr.it)

Keywords: *Ab initio* method, Raman Spectroscopy, Pyroxenes.

Mantle dynamics and its mineral properties are an active research field. Minerals of pyroxene group are one of the most abundant rock-forming minerals on Earth's crust and mantle (Deer et al., 1966). Studying the vibrational properties of pyroxenes under different environmental conditions would lead to understand the propagation of seismic waves in the mantle and consequently its constitution and dynamics. Depth, mantle temperature and pressure conditions preclude the application of a fully experimental scientific approach and force to create theoretical models mostly based on simulation.

Currently *ab initio* methods are used in simulations and predictions of properties of minerals with excellent agreement with experimental data. In addition, Raman scattering methods probe the lattice vibrations of a material. The applications of these techniques to the study of rock-forming minerals and therefore to the Earth's interior, enable us to describe their crystal lattice dynamics and to calculate thermodynamic parameters (Huang et al., 2000). The aim of this study is to improve the interpretation of Raman experimental spectra of spodumene, a Li and Al monoclinic chain silicate belonging to *C2/c* space group at ambient condition, by exploiting the accuracy of the quantum mechanical calculations.

An *ab initio* HF/DFT study of Raman spectra of spodumene has been performed with the program CRYSTAL14 (Dovesi et al., 2013) which employs localized, gaussian-type basis sets. The chosen Hamiltonian WC1LYP is based on the Wu-Cohen exchange functional (Wu & Cohen 2006), corrected by a fraction (16%) of *non-local exact* Hartree-Fock exchange, and Lee-Young-Parr correlation functional (Lee et al., 1988).

The simulated data have been compared with experimental data on a natural sample of spodumene, that was already characterized by single crystal X-Ray diffraction (Tribaudino et al., 2003). All the 30 expected Raman active vibrational modes (14 A<sub>g</sub> and 16 B<sub>g</sub>) have been recognized by the polarized spectra. The calculation provides an excellent agreement with the experimental results: the average absolute difference between calculated and experimental Raman frequencies is about 4.8 cm<sup>-1</sup>. The predicted Raman intensities are also in good agreement with the experimental data.

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## ***Ab Initio* calculated and experimental Raman spectra of Ca-Mg germanate (CaMgGe<sub>2</sub>O<sub>6</sub>): studying phase transitions of the Earth mantle**

Stangarone C.\*<sup>1</sup>, Lambruschi E.<sup>1</sup>, Aliatis I.<sup>1</sup>, Prencipe M.<sup>2</sup>, Bersani D.<sup>1</sup>, Mantovani L.<sup>1</sup>, Tribaudino M.<sup>1</sup>, Lottici P.P.<sup>1</sup> & Redhammer G.<sup>3</sup>

1. Dipartimento di Fisica e Scienze della Terra - Università di Parma. 2. Dipartimento di Scienze della Terra - Università di Torino. 3. Department of Materials Science & Physics, Division of Mineralogy, University of Salzburg.

Corresponding email: [claudia.stangarone@studenti.unipr.it](mailto:claudia.stangarone@studenti.unipr.it)

Keywords: *Ab initio* methods, Raman Spectroscopy, Germanates.

Pyroxenes are chain silicate minerals, widespread constituents of the Earth crust and of the upper mantle, as well as of rocky planets and meteorites. Crystal chemical relationships between germanates and silicates have acquired a lot of interest since the beginning of speculations on phase transitions and constitution of the mantle, because germanates behave as high-pressure models for high pressure transformations of the corresponding silicates (Ringwood et al., 1963; Ringwood, 1968).

In this study we highlight the importance to create theoretical models based on simulation to predict mineral properties. We have performed an *ab initio* HF/DFT calculation of the Raman spectrum of CaMgGe<sub>2</sub>O<sub>6</sub> at ambient conditions to study the vibrational properties of Ge-pyroxenes. CaMgGe<sub>2</sub>O<sub>6</sub> is a monoclinic pyroxene belonging to *C2/c* space group. The simulation has been performed with the CRYSTAL14 (Dovesi et al., 2013) software which employs localized, gaussian-type basis sets. The chosen Hamiltonian WC1LYP is based on the Wu-Cohen exchange functional (Wu & Cohen, 2006), corrected by a fraction (16%) of non-local exact Hartree-Fock exchange, and Lee-Young-Parr correlation functional (Lee et al., 1998).

The simulated data have been compared with experimental micro-Raman spectroscopy measurements on a synthetic sample of CaMgGe<sub>2</sub>O<sub>6</sub>, obtained from a ceramic solid-state sintering route at  $T = 1573$  K of a mixture of CaCO<sub>3</sub>, GeO<sub>2</sub> and MgO in the desired stoichiometry. The cell parameters for CaMgGe<sub>2</sub>O<sub>6</sub> are:  $a = 10.0987(9)$  Å,  $b = 8.9777(8)$  Å and  $c = 5.4214(5)$  Å with  $\beta = 105.3729(9)^\circ$  and  $V = 473.93(7)$  Å<sup>3</sup>. The satisfactory agreement between calculated and measured Raman spectra (frequencies and relative intensities) enables the attribution of specific vibrational normal modes to the observed features.

Dovesi R., Saunders V. R., Roetti C., Orlando R., Zicovich-Wilson C. M., Pascale F., Civalleri B., Doll K., Harrison N. M., Bush I. J., D'Arco P., Llunell M., Causà M. & Noël Y. 2014. CRYSTAL14 User's Manual. University of Torino.

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## Dolomite behaviour at high-pressure and phase transition to Dolomite-II. a couple of theory and experiment

Zucchini A.\*<sup>1</sup>, Prencipe M.<sup>2</sup>, Comodi P.<sup>1</sup> & Nazzareni S.<sup>1</sup>

1. Dipartimento di Fisica e Geologia, Università di Perugia. 2. Dipartimento di Scienze della Terra, Università di Torino.

Corresponding email: [azzurra.zucchini@gmail.com](mailto:azzurra.zucchini@gmail.com)

Keywords: dolomite, synchrotron X-ray diffraction, ab-initio calculations.

Carbonates are found to be stable up to lower mantle conditions. Thus, they are considered as possible carbon carrier minerals into the deep upper mantle by subduction processes. This work is aimed to study dolomite compressibility as a function of disordering and temperature. Moreover, time was devoted to analyse how ordered and disordered dolomite crystal structures behave as the phase transition to dolomite-II (Merlini et al. 2012) is approached. Both experimental and theoretical approaches were used. The high pressure–high temperature (HP-HT) experiments were carried out at ID09A beamline at the European Synchrotron Radiation Facility ESRF, Grenoble, France. Data were collected up to 20 GPa. *Ab-initio* calculations were carried out by means of CRYSTAL09 program (Dovesi et al. 2005). Ordered and disordered geometries (Zucchini et al. 2012) were optimised at different pressures up to approximately 26 GPa. Dolomite *P-V* data were fitted by a third order Birch-Murnaghan Equation-of-State. Results of both theory and experiments show that ordered and disordered dolomites have approximately the same bulk compressibility; whereas *T* has a significant effect in increasing dolomite compressibility. Ambient temperature experimental data were also used for crystal structure refinements. Results show that octahedra in the ordered sample are almost equally compressible; whereas CaO<sub>6</sub> in the disordered sample is less compressible than MgO<sub>6</sub>. That is, the partial replacement of Ca by Mg increases CaO<sub>6</sub> and decrease MgO<sub>6</sub> bonds strength, thus making stiffer CaO<sub>6</sub> and more relaxed MgO<sub>6</sub>. Moreover, structural refinements and calculated geometries show that octahedra are distorted. A decrease of distortion with *P* is observed as both O-Ca-O and O-Mg-O angles approach 90° as *P* increases, approaching regularity. Cation polyhedra in the ordered dolomite became almost regular at approximately 14–15 GPa. Both experiments and calculations allow to conclude that dolomite-I/II transformation is approached at ~14–15 GPa in the ordered dolomite and at ~17GPa in the ordered dolomite at HT. As regards the disordered crystal structure, there are no strong evidences of the phase transition. Two main hypothesis arises: either (i) disordered dolomite is stable at higher pressure than the ordered one, that is, disordering stabilizes dolomite-I or (ii) disordered dolomite does not undergo phase transition to dolomite-II.

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## **SESSIONE S13**

### **New Minerals: The role played by the Italian Community - A tribute to Carlo Maria Gramaccioli**

#### *CONVENORS*

*M.E. Ciriotti (AMI)*

*F. Demartin (Univ. Milano)*

*M. Pasero (Univ. Pisa)*

## New fumarolic minerals from Mt. Hekla volcano, Iceland: $\text{FeF}_3(\text{H}_2\text{O})_3$

Balić-Žunić T.<sup>1</sup>, Mitolo D.<sup>2</sup>, Garavelli A.\*<sup>2</sup>, Jakobsson S.P.<sup>3</sup> & Leonardsen E.<sup>4</sup>

<sup>1</sup> Natural History Museum of Denmark, University of Copenhagen, Denmark. <sup>2</sup> Dipartimento di Scienze della Terra e Geoambientali, Università degli Studi "A. Moro" di Bari. <sup>3</sup> Icelandic Institute of Natural History, Gardabaer, Iceland. <sup>4</sup> St. Karlsmindevej 46, Hundested, Denmark.

Corresponding email: [anna.garavelli@uniba.it](mailto:anna.garavelli@uniba.it)

Keywords: Hekla sublimates, iron fluoride, new minerals.

Mt. Hekla is located west of Iceland SE volcanic rift-zone and represents the Iceland's most famous and historically most active volcano. A systematic sublimates and incrustations collection and analyses has been performed subsequently to the 1991 eruption and it conducted to the discovery of a number of new mineral phases: eldfellite (Balić-Žunić et al., 2009), heklaite (Garavelli et al., 2010), jakobssonite (Balić-Žunić et al., 2012), leonardsenite (Mitolo et al., 2013), oskarssonite (Jacobsen et al., 2014). Natural Fe-fluoride hydrate, with ideal formula  $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ , was found in the Hekla fumaroles both in the tetragonal and rhombohedral forms. The rhombohedral polymorph is still under investigation. Natural, tetragonal  $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$  is the new phase here described and corresponds to the synthetic  $\beta\text{-FeF}_3(\text{H}_2\text{O})_3$  (Teufer, 1964). It occurs as micrometer-sized quadratic crystals, or aggregates inside up to 3 mm thick yellow to brown crust on altered scoria together with hematite, opal, malladrite, heklaite and ralstonite. X-ray powder diffraction data indicate tetragonal symmetry, space group  $P4/n$ , with unit-cell parameters  $a$  7.8383(4),  $c$  3.8718(2) Å,  $V$  237.88(3) Å<sup>3</sup> and  $Z = 2$ . The average chemical composition is (wt.%) : Fe 38.52, F 38.23, Cl 1.03, O 21.10, total 98.88. The empirical formula (based on Fe = 1) is  $\text{Fe}(\text{F}_{2.94}\text{Cl}_{0.04})_{\Sigma 2.98}(\text{H}_2\text{O})_{1.94}$  corresponding to the ideal formula  $\text{FeF}_3(\text{H}_2\text{O})_3$ . Fe-fluoride hydrate is isostructural with rosenbergite,  $\text{AlF}_3(\text{H}_2\text{O})_3$  (Olmi et al., 1993). The crystal structure consists of infinite straight chains of  $[\text{FeF}_3(\text{H}_2\text{O})_3]$  octahedra extending along [001] (Teufer, 1964). The adjacent octahedra share apical F atoms, whereas the four unshared, equatorially coordinated atoms, are represented by disordered arrangement of two F and two O atoms (from water molecules). The additional water molecules occupy the spaces between chains and are tetrahedrally coordinated by four (F, H<sub>2</sub>O) from four different chains. The new mineral will be submitted for approval to the IMA-CNMNC.

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Teufer, G. (1964). The crystal structure of  $\beta$ -iron(III) trifluoride trihydrate,  $\beta\text{-FeF}_3 \cdot 3\text{H}_2\text{O}$ . Acta Cryst., 17, 1480.

## Mambertiite (IMA 2013-098), a new bismuth-molybdenum oxide from Su Seinargiu, Sardinia

Biagioni C.\*<sup>1</sup>, Campostrini I.<sup>2</sup>, Demartin F.<sup>2</sup>, Orlandi P.<sup>1</sup> & Pasero M.<sup>1</sup>

1. Dipartimento di Scienze della Terra, Università di Pisa. 2. Dipartimento di Chimica, Università degli Studi di Milano.

Corresponding email: [biagioni@dst.unipi.it](mailto:biagioni@dst.unipi.it)

Keywords: mambertiite, new mineral, bismuth, molybdenum, Su Seinargiu, Sardinia.

The Mo-Bi mineralization of Su Seinargiu, Sarroch, Cagliari, Sardinia, Italy, is hosted in granitic rocks of Hercynian age (Caboi et al., 1978; Ghezzi et al., 1981). The alteration of the primary Mo and Bi minerals has originated a series of secondary minerals, among which six new minerals: sardignaites, gelosaites, tancaite-(Ce) (Orlandi et al., 2013), and the recently approved phases ichnusaite, nuragheite, and mambertiite.

Mambertiite has been identified in small vugs of quartz veins, as pale yellow {100} tabular crystals, up to 1 mm in length and few microns thick, with adamantine luster. The mineral is brittle, with a conchoidal fracture.

Electron microprobe analysis gave (wt% - mean of 12 spot analyses): Mo<sub>2</sub>O<sub>5</sub> 59.59, Bi<sub>2</sub>O<sub>3</sub> 36.96, WO<sub>3</sub> 2.03, H<sub>2</sub>O 1.44, sum 100.02. On the basis of 9 O atoms per formula unit, the empirical formula is Bi<sub>0.99</sub>(Mo<sup>5+</sup><sub>2.74</sub>W<sub>0.05</sub>)<sub>Σ2.79</sub>O<sub>8</sub>(OH).

The crystal structure of mambertiite is composed by eight-fold coordinated Bi-centered polyhedra and five independent Mo-centered octahedra. Among the latter, two of them are completely filled by molybdenum, whereas the remaining three have a partial occupancy. Two kinds of (1-10) layers occur in mambertiite, alternating along [1-10]\*: one is composed by Bi-centered polyhedra and the two partially occupied Mo4 and Mo5 sites, the other is composed by the zigzag chains, running along *c*, formed by the fully-occupied Mo1 and Mo2 sites, and the partially occupied Mo3 site.

Mambertiite, whose name honors the mineral collector Marzio Mamberti (b. 1959) for his contribution to the knowledge of the Sardinian mineralogy, is the fourth mineral species having Bi and Mo as essential components, the other three being koechlinite, Bi<sub>2</sub>MoO<sub>6</sub>, sardignaites, BiMo<sub>2</sub>O<sub>7</sub>(OH)·2H<sub>2</sub>O, and gelosaites, BiMo<sup>6+</sup><sub>(2-5x)</sub>Mo<sup>5+</sup><sub>6x</sub>O<sub>7</sub>(OH)·H<sub>2</sub>O (0 ≤ *x* ≤ 0.4). Mambertiite is structurally related to gelosaites. With respect to gelosaites, mambertiite has a greater Mo content (interpreted as Mo<sup>5+</sup>) and this probably is responsible for the lowering of the space group symmetry from *P*2<sub>1</sub>/*n* in gelosaites (Orlandi et al., 2011) to *P*-1 in mambertiite. Hence, mambertiite and gelosaites could be two members of a series of compounds having different Mo<sup>6+</sup>:Mo<sup>5+</sup> atomic ratios.

The mineral and its name have been approved by the IMA-CNMNC (IMA 2013-098).

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Orlandi P., Demartin F., Pasero M., Leverett P., Williams P.A. & Hibbs D.E. 2011. Gelosaites, BiMo<sup>6+</sup><sub>(2-5x)</sub>Mo<sup>5+</sup><sub>6x</sub>O<sub>7</sub>(OH)·H<sub>2</sub>O (0 ≤ *x* ≤ 0.4), a new mineral from Su Seinargiu (CA), Sardinia, Italy, and a second occurrence from Kingsgate, New England, Australia. Am. Mineral., 96, 268–273.

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## Apuan Alps: a reference ore district for the study of sulfosalt crystal-chemistry

Biagioni C.\*<sup>1</sup>, Moëlo Y.<sup>2</sup> & Orlandi P.<sup>1</sup>

1. Dipartimento di Scienze della Terra, Università di Pisa. 2. Institut des Matériaux Jean Rouxel, Université de Nantes, France.

Corresponding email: [biagioni@dst.unipi.it](mailto:biagioni@dst.unipi.it)

Keywords: lead, antimony, arsenic, thallium, mercury, sulfosalts.

Since the description of meneghinite from the Bottino mine by Bechi (1852), the Apuan Alps have become a reference ore district for the sampling and the study of sulfosalts. Up to now, 55 different sulfosalt species have been identified; among them, 17 have their type-locality in this area. This richness is related to the occurrence of small polymetallic hydrothermal ore bodies whose present mineralogy and parageneses are related to the Tertiary Alpine tectono-metamorphic events.

The majority of the new sulfosalt species have been described in the last twenty years. In particular, the most prolific kind of ore deposit is represented by the baryte ± pyrite ± iron oxides ores exploited at the Buca della Vena, Monte Arsiccio, and Pollone mines up to the end of 1980s. A common feature of these occurrences is the presence of oxysulfosalts, i.e. sulfosalts in which oxygen plays a structural role. Scainiite, pillaitite, pellouxite, and rouxelite have Buca della Vena as their type locality. Recently rouxelite was identified also from the Monte Arsiccio mine, associated with chovanite, another oxysulfosalt first found in Slovakia (Topa *et al.*, 2012). A new occurrence of this latter mineral from the Pollone mine allowed the solution of its real 8 Å structure. Pollone mine is type locality for meerschautite, an Ag-Pb/Sb-As oxysulfosalt characterized by the lowest O:S atomic ratio described so far. In addition to meerschautite, other complex Ag-Pb/Sb-As sulfosalts like sterryite and the new minerals parasterryite and carducciite have been found at this locality.

Recently, Tl-Hg-Pb-As-Sb-(Ag,Cu) sulfosalt assemblages have been identified at the Monte Arsiccio mine (e.g., Biagioni *et al.*, 2014), with the description of three new minerals, i.e. boscardinite, protochabournéite, and arsiccioite. These phases are associated with other very rare compounds (aktashite, laffittite, routhierite, and a Cu-Hg derivative of quatrandorite).

Finally, particular physicochemical conditions promoting the crystallization of persulfides, i.e. compounds characterized by S-S bonds, were present in the cavities of the Liassic marbles, as testified by the crystallization of two new mineral species, moëloite and disulfodasonite.

Consequently, the hydrothermal veins of the Apuan Alps represent an extraordinary natural laboratory for the study of the crystal-chemistry of sulfosalts in metamorphic settings.

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## Two As-bearing new mineral species from Valletta mine: grandaite and braccoite

Bittarello E.<sup>1</sup>, Ciriotti M.E.\*<sup>2</sup> & Cámara F.<sup>3</sup>

1. Dipartimento di Scienze della Terra, Università degli Studi di Torino. 2. CrisDi, Interdepartmental Centre for the Research and Development of Crystallography, Torino. 3. Associazione Micromineralogica Italiana, Devesi-Cirié, Torino.

Corresponding email: [m.ciriotti@tin.it](mailto:m.ciriotti@tin.it)

Keywords: Valletta mine, grandaite, braccoite.

The Valletta Mine (Canosio, Maira Valley, Piedmont, Italy) is a small iron deposit with subordinate manganese. A systematic study of the mineral phases in the quartzites with quartz veins revealed that those contain a large variety of mineral phases rich in arsenic, vanadium, barium and strontium. Among those, two mineral species have been found and approved by IMA-CNMMC: braccoite, ideally  $\text{NaMn}^{2+}_5[\text{Si}_5\text{AsO}_{17}(\text{OH})](\text{OH})$ , and grandaite, ideally  $\text{Sr}_2\text{Al}(\text{AsO}_4)_2(\text{OH})$ .

Braccoite (IMA 2013-093) occurs as subhedral crystals in brown-red colour thin masses, with pale yellow streak and vitreous to resinous luster, and is associated with tiragalloite, gamagarite, hematite, manganberzeliite, palenzonaite, quartz, saneroite, tokyoite, unidentified Mn oxides, organic compounds, and Mn arsenates and silicates under study. Its crystal structure has been solved and refined. Braccoite is triclinic, space group  $\text{P}\bar{1}$  with  $a$  9.7354(4),  $b$  9.9572(3),  $c$  9.0657(3) Å,  $\alpha$  92.691(2)°,  $\beta$  117.057(4)°,  $\gamma$  105.323(3)°,  $V$  740.37(4) Å<sup>3</sup> and  $Z$  2. Chemical analyses by WDS electron microprobe gave the empirical formula calculated on the basis of  $\Sigma$  cations-(Na,K) = 11 p.f.u.  $\text{Na}_{1.06}(\text{Mn}^{2+}_{4.46}\text{Mn}^{3+}_{0.32}\text{Mg}_{0.19}\text{V}^{3+}_{0.01}\text{Al}_{0.01}\text{Ca}_{0.01})[\text{Si}_5(\text{As}_{0.48}\text{Si}_{0.37}\text{V}^{5+}_{0.15})\text{O}_{17}(\text{OH})](\text{OH}_{0.98}\text{F}_{0.02})$ . Braccoite is isostructural with saneroite, but has dominance of As over V. Braccoite is named in honour of Roberto Bracco, a systematic collector with a special interest in manganese minerals.

Grandaite (IMA 2013-059) occurs in quartz veins as thin masses of bright orange to salmon to brown colour, or infrequently as fan-like aggregates of small (< 1 mm) crystals, with reddish brown streak and waxy to vitreous lustre. Grandaite is associated with aegirine, baryte, braunite, hematite, tilasite, quartz, unidentified Mn-oxides, and Mn-silicates under study. Its crystal structure has been solved and refined. Grandaite is monoclinic, space group  $P2_1/m$ , with  $a$  7.5764(5),  $b$  5.9507(4),  $c$  8.8050(6) Å,  $\beta$  112.551(2)°,  $V$  366.62(4) Å<sup>3</sup>.

Chemical analyses by electron microprobe gave the empirical formula calculated on the basis of 9 O a.p.f.u.,  $(\text{Sr}_{1.41}\text{Ca}_{0.64}\text{Ba}_{0.05}\text{Pb}_{0.01})_{\Sigma=2.11}(\text{Al}_{0.68}\text{Fe}^{3+}_{0.14}\text{Mn}^{3+}_{0.12}\text{Mg}_{0.13})_{\Sigma=1.07}[(\text{As}_{0.96}\text{V}_{0.01})_{\Sigma=0.97}\text{O}_4]_2(\text{OH})$ . Grandaite is isostructural with brackebuschite and is named after the informal appellation of the province in which the type locality is located.

## The Italian contribution to the tourmaline systematics

Bosi F.\*

Dipartimento di Scienze della Terra, Sapienza Università di Roma. Department of Geosciences, Swedish Museum of Natural History, Stockholm, Sweden.

Corresponding email: [ferdinando.bosi@uniroma1.it](mailto:ferdinando.bosi@uniroma1.it)

Keywords: Tourmaline, new mineral, systematic.

The contribution of the Italian Community to discovery of new minerals and their classification is certainly important as shown by the tourmaline case.

Tourmalines are complex borosilicates described by the general formula:  $XY_3Z_6T_6O_{18}(BO_3)_3V_3W$ , where  $^{[9]}X = Na^+, K^+, Ca^{2+}$ , (=vacancy);  $^{[6]}Y = Al^{3+}, Fe^{3+}, Cr^{3+}, V^{3+}, Mg^{2+}, Fe^{2+}, Mn^{2+}, Li^+$ ;  $^{[6]}Z = Al^{3+}, Fe^{3+}, Cr^{3+}, V^{3+}, Mg^{2+}, Fe^{2+}$ ;  $^{[4]}T = Si^{4+}, Al^{3+}, B^{3+}$ ;  $^{[3]}B = B^{3+}$ ;  $^{[3]}V = OH^{1-}, O^{2-}$ ;  $^{[3]}W = OH^{1-}, F^{1-}, O^{2-}$ . The dominance of these ions at one or more sites of the structure gives rise to a range of distinct mineral species. Tourmaline is a supergroup currently consisting in twenty-eight species approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association.

Fourteen tourmaline species were approved after the publication of the recent tourmaline classification (Henry et al., 2011), and nine of them were found by Italian mineralogists (e.g. Bosi et al., 2012; 2013). Of these nine, six define a new compositional field characterized by  $(Cr,Al,V)^{3+}$  over the Y and Z sites and  $O^{2-}$  at the W position of the general formula. Furthermore, two of these nine (tsilaisite and fluor-tsilaisite) come from Italy (Elba Island) and were found in the same zoned crystal.

The impact of these new minerals on the systematic and crystal chemistry of tourmaline is relevant. For example, the ternary diagram in terms of Al-V-Cr at Y and Z shows a full solid solution among oxy-dravite – oxy-chromium-dravite – oxy-vanadium-dravite along with the following site preferences:  $V^{3+} > Cr^{3+} > Al^{3+}$  for the Y site and  $Al^{3+} > Cr^{3+} > V^{3+}$  for the Z site. Such site preferences determine the existence of three end-members between the apices of the triangular compositional diagram: Al and Cr (chromo-alumino-povondraite), Cr and V (vanadio-oxy-chromium-dravite), V and Al (vanadio-oxy-dravite). With regards to the tourmalines from Elba Island, fluor-tsilaisite shows a solid solution with the tsilaisite (by  $F \leftrightarrow OH$ ) as well as with the fluor-elbaite (by  $2Mn^{2+} \leftrightarrow Al + Li$ ). Although fluor-tsilaisite may ideally be linked to the elbaite through the substitution  $2Mn^{2+} + F \leftrightarrow (Al + Li) + (OH)$ , the occurrence of such a substitution is unlikely because of the observed inverse correlation between F and  $Mn^{2+}$ . In the above mentioned zoned crystal, tsilaisite and fluor-elbaite are linked through fluor-tsilaisite, which appears to be a stepwise intermediate composition from the tsilaisitic core to the fluor-elbaitic rim.

Bosi F., Skogby H., Agrosi G. & Scandale E. 2012. Tsilaisite,  $NaMn_3Al_6(Si_6O_{18})(BO_3)_3(OH)_3OH$ , a new mineral species of the tourmaline supergroup from Grotta d'Oggi, San Pietro in Campo, island of Elba, Italy. *Am. Mineral.*, 97, 989-994.

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Henry D.J., Novák M., Hawthorne F.C., Ertl A., Dutrow B., Uher P. & Pezzotta F. 2011. Nomenclature of the tourmaline supergroup minerals. *Am. Mineral.*, 96, 895-913.

## A new natural ammonium decaborate from La Fossa crater, Vulcano Island, Italy

Campostrini I.\* & Demartin F.

Dipartimento di Chimica, Università degli Studi di Milano.

Corresponding email: [italo.campostrini@unimi.it](mailto:italo.campostrini@unimi.it)

Keywords: diammonium tetrahydroxydecaborate monohydrate, La Fossa crater, Vulcano Island, Italy.

Boron is a widespread element in the fumaroles of La Fossa crater at Vulcano Island and forms a number of different minerals such as the particularly abundant boric acid sassolite,  $H_3BO_3$ , metaborite,  $HBO_2$ , clinometaborite,  $HBO_2$ , some borates such as santite,  $K[B_5O_6(OH)_4] \cdot 2H_2O$  and larderellite,  $NH_4[B_5O_7(OH)_2] \cdot H_2O$  and a number of fluoroborates such as barberiite,  $NH_4BF_4$ , knasibfite,  $K_3Na_4[SiF_6]_3[BF_4]$  and avogadrite,  $KBF_4$  (Campostrini et al., 2011). Ammonium is also particularly abundant in the intracrater fumarolic system and in the last few years, due to a decreasing of temperature and magmatic fluids flow, the mineral assemblage of the fumaroles has changed leading to the formation of ammonium bearing sulfates and sulphate-chlorides minerals.

In Spring 2013, a new ammonium borate mineral was found in the FA fumarole (temperature about 250° C) as white crystals up to 0.2 mm, together with sassolite, adranosite and alunite: it corresponds to the synthetic compound diammonium tetrahydroxydecaborate monohydrate,  $(NH_4)_2[B_{10}O_{14}(OH)_4] \cdot H_2O$  (Li et al., 2003). The mineral crystallizes in the triclinic space group P-1 with  $a = 7.638(2)$ ,  $b = 9.253(2)$ ,  $c = 11.959(3)$  Å,  $\alpha = 99.44(1)$ ,  $\beta = 105.92(1)$ ,  $\gamma = 91.51(1)^\circ$ . Its structure contains infinite chains of composition  $[B_{10}O_{14}(OH)_4]_n^{2n-}$  linked by hydrogen bonds to form borate sheets. Water molecules and ammonium ions are located between these sheets and connect adjacent sheets via hydrogen bonds. The basic structural unit contained is a double ring formed by one  $BO_4$  tetrahedron and four  $BO_3$  triangles, an unit already observed in santite as an isolated ion (Zachariasen, 1937; Merlino & Sartori, 1970) or linked to form infinite chains in larderellite (Merlino & Sartori, 1969).

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## A new ammonium arsenite chloride from the Solfatara di Pozzuoli, Napoli, Italy

Campostrini I.\*, Demartin F. & Russo M.

Dipartimento di Chimica, Università degli Studi di Milano.

Corresponding email: [italo.campostrini@unimi.it](mailto:italo.campostrini@unimi.it)

Keywords: ammonium arsenite chloride hydrated, Solfatara di Pozzuoli.

The Solfatara di Pozzuoli is one of about 40 volcanoes in the Campi Flegrei area and is located three kilometers from the center of the town of Pozzuoli. Solfatara formed during the third Flegrean eruptive period and dates to about 3700-3900 years ago. Inside the Solfatara some active fumaroles are present, the most important of which is called "Bocca Grande" and has a temperature of about 160 °C.

During a research campaign carried out in 2011 we could collect at "Bocca Grande" fumarole some samples with small yellow or colorless hexagonal tabular crystals. The mineral is associated with realgar, dimorphite, alacranite, salammoniac, mascagnite and an amorphous arsenic sulfide. Its powder pattern corresponds to that of the synthetic compound  $\text{NH}_4\text{ClAs}_2\text{O}_3(\text{H}_2\text{O})_{0.5}$  (PDF2 entry 00-076-1366) and the hexagonal unit-cell parameters obtained using the unit-cell software (Holland & Redfern, 1997) are:  $a = 5.259(2)$ ;  $c = 12.590(5)$ . Due to the small size of the crystals was not possible to obtain structural data from single-crystal diffraction.

The mineral has probably some structural relationships with lucabindiite,  $(\text{K},\text{NH}_4)\text{As}_4\text{O}_6(\text{Cl},\text{Br})$ , a complex arsenite chloride found for the first time at La Fossa crater, Vulcano Island, Sicily and described by Garavelli et al. (2013).

The chemical analysis carried out in EDS mode using a JEOL JSM 5500LV scanning electron microscope equipped with a iXRF EDS microprobe gave a composition very close to that of lucabindiite, but with an ammonium content significantly greater than that of potassium and a lower bromine content.

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## A monoclinic K-Li-Cu-Mg silicate from the Cerchiara mine: a dimorph of lavinskyite?

Carbone C.<sup>1</sup>, Kolitsch U.<sup>2-3</sup>, Belmonte D.<sup>1</sup>, Cabella R.<sup>1</sup>, Lucchetti G.<sup>1</sup> & Ciriotti M.<sup>4</sup>

1. DISTAV, Università di Genova. 2. Mineralogisch-Petrographische Abt., Naturhistorisches Museum, Wien, Austria. 3. Institut für Mineralogie und Kristallographie, Geozentrum, Universität Wien, Austria. 4. AMI, Devesi-Cirié, Torino.

Corresponding email: [carbone@dipteris.unige.it](mailto:carbone@dipteris.unige.it)

Keywords: Lavinskyite, monoclinic dimorph, Cerchiara mine.

A possibly new K-Li-Cu-Mg silicate occurs at the Cerchiara mine (Liguria, Italy) as blue, micaceous aggregates embedded in calcite-filled microfractures and veinlets related to re-equilibration of the ophiolitic sequence during tectonometamorphic overprinting under prehnite-pumpellyite facies conditions (Lucchetti et al., 1988). The associated minerals include calcite, quartz, norrishite and “schefferite” (a Mn-bearing variety of diopside). Micro-Raman, and chemical analyses by SEM-EDS and LA-ICP-MS confirm the compositional analogy of this K-Li-Cu-Mg silicate with lavinskyite. The crystal structure has been solved using single-crystal X-ray diffractometer data ( $R_{\text{int}} = 5.2\%$ ) from a tiny crystal fragment (0.015 x 0.05 x 0.10 mm) by direct methods and refined in space group  $P2_1/c$  (no. 14) to  $R1 = 5.1\%$  and  $wR2_{\text{all}} = 13.2\%$  [1942 'observed' reflections with  $F_o > 4 s(F_o)$ , 200 parameters]. Refined unit-cell parameters are:  $a = 10.224(2)$ ,  $b = 19.085(4)$ ,  $c = 5.252(1)$  Å,  $\beta = 92.23(3)^\circ$ ,  $V = 1024.0(4)$  Å<sup>3</sup> ( $Z = 2$ ). The atomic arrangement is best described as a sheet structure consisting of corrugated brucite-like  $(\text{CuO}_2)_n$  layers with amphibole-type  $(\text{SiO}_3)_n$  chains joined to both their upper and lower surfaces. Adjacent complex sheets are linked by (Li,Cu,Na,Mg) atoms in square coordination (nearly planar) and interlayer K atoms. The K site is fully occupied by K, whereas the Li site [M(4) site] is occupied by major Li and more or less minor Cu, Na and Mg. This silicate has basically the same topology as orthorhombic lavinskyite  $[\text{K}(\text{LiCu})\text{Cu}_6(\text{Si}_4\text{O}_{11})_2(\text{OH})_4]$ , Pcnb (Yang et al., 2014)], which is isostructural with plancheite (Evans & Mrose, 1977). The monoclinic silicate and lavinskyite also have nearly the same empirical formula:  $(\text{K}_{1.08}\Sigma_{1.08}(\text{Li}_{0.89}\text{Mg}_{0.36}\text{Cu}_{0.33}\text{Na}_{0.22}\text{Mn}^{2+}_{0.04})\Sigma_{1.85}\text{Cu}_{6.00}\text{Si}_{8.08}\text{O}_{22}(\text{OH})_{4.02}$  and  $(\text{K}_{0.99}\text{Ba}_{0.01})\Sigma_{1.00}(\text{Li}_{1.04}\text{Cu}_{0.93}\text{Na}_{0.10})\Sigma_{2.07}(\text{Cu}_{5.57}\text{Mg}_{0.43}\text{Mn}_{0.01})\Sigma_{6.01}(\text{Si}_{4.00}\text{O}_{11})_2(\text{OH})_4$ , respectively. The most important difference between the two apparent dimorphs is the fact that the M(4) site in lavinskyite is distinctly split, unlike the corresponding site in the silicate. The occupancy of the split site is  $M(4a) = 0.5\text{Cu}$ ,  $M(4b) = 0.5\text{Li}$  (Yang et al., 2014), whereas the non-split M(4) site in the silicate shows a mixed occupancy by Li and Cu (and possibly minor Na and Mg), based on the chemical analysis and the structure refinement. In conclusion, it appears that a complex and delicate interplay between the Li:Cu and Cu:Mg ratios, along with an additional influence of impurity cations such as Na, results in a slightly distorted atomic arrangement for the silicate from Cerchiara and a different space group ( $P2_1/c$ , a subgroup of lavinskyite's Pcnb) and unit cell.

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## “Mesitine” and its relationship with other carbonates from Traversella Mine

Costa E.\*, Benna P., Bittarello E., Cámara Artigas F., Dino G., Rossetti P., Rubbo M. & Verneti A.

Dipartimento di Scienze della Terra, Università degli Studi di Torino.

Corresponding email: [emanuele.costa@unito.it](mailto:emanuele.costa@unito.it)

Keywords: Traversella, carbonate, mesitine.

*Mesitine*, sometimes also written *mesitite*, is an old name, not I.M.A. approved, used for the identification of iron-rich magnesite with different iron percentage (Dana, 1911; Bayliss, 2011). Between the most famous samples collected in the mineralogical museum of Europe, *mesitine* of Traversella are amongst the most representative and beautiful, but sometimes the identification of the mineral specie was inferred mainly through provenience of the specimen, visual appearance and minerals association rather than with analytical determination.

During a survey of some samples of the Regional Museum of Science in Turin, in a frame of valorization of the mineralogical collection coming from the localities of Brosso and Traversella (Torino, Piemonte, North West Italy) some old samples of this second locality (collected around 1850-70) were analyzed together with some freshly obtained samples (2010-2012) from the still open galleries existing in the Traversella mining complex, kindly provided by the Gruppo Mineralogico Traversella. Analysis were performed by mean of SEM-EDS and ICP-OES facilities in the Department of Earth Science at the Turin University.

Results shows that only part of the samples previously identified as *mesitine* are really iron-rich magnesite, whereas a substantial amount of samples was actually dolomite; these carbonates coexist in the Traversella complex with calcite, siderite and sporadic ankerite.

In the paper the authors will examine the presence of these carbonates in the mineralogical samples from Traversella, the role of the term *mesitine* in the mineralogical community and the complexity to achieve a secure identification on some carbonate samples coming from site with high geochemical complexity and mineralogical variability.

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## Chemical, Mössbauer and structural data on a potentially new mineral from Harrow Peaks (Antarctica) in the oxo-amphibole group (amphibole supergroup)

Gentili S.\*<sup>1</sup>, Biagioni C.<sup>2</sup>, Comodi P.<sup>1</sup>, Pasero M.<sup>2</sup>, McCammon C.<sup>3</sup> & Bonadiman C.<sup>4</sup>

1. Dipartimento di Fisica e Geologia, Università di Perugia. 2. Dipartimento di Scienze della Terra, Università di Pisa  
3. Bayerisches Geoinstitut, Universität Bayreuth, Germany. 4. Dipartimento di Fisica e Scienze della Terra, Università di Ferrara.

Corresponding email: [silvia.gentili@studenti.unipg.it](mailto:silvia.gentili@studenti.unipg.it)

Keywords: amphibole supergroup, oxo-amphibole group, new mineral, Antarctica.

Among the 89 minerals currently recognized as valid species within the amphibole supergroup, only six belong to the oxo-amphibole group: ferri-obertiite, ferro-ferri-obertiite, kaersutite, mangani-dellaventurait, mangano-mangani-ungarettiite, and oxo-magnesio-hastingsite. According to the newly approved report of the amphibole subcommittee (Hawthorne et al., 2012), minerals of the oxo-amphibole group must have  ${}^W\text{O}^{2-} > (\text{OH}+\text{F}+\text{Cl})^-$ .

We collected chemical (electron and ion microprobe), micromössbauer and single-crystal X-ray diffraction data on a potentially new mineral in the oxo-amphibole group. Its end-member formula is  $\text{NaCa}_2(\text{Mg}_3\text{Fe}^{3+}\text{Ti})(\text{Si}_6\text{Al}_2)\text{O}_{22}\text{O}_2$ , and it would represent the  $\text{Fe}^{3+}$ -dominant analogue of kaersutite. The mineral occurs in mantle spinel-bearing lherzolite from Harrow Peaks, Victoria Land, Antarctica.

The chemical composition was determined by ion microprobe (hydrogen, fluorine and chlorine) and electron microprobe (all other major elements) analyses. The  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  ratio was collected at room temperature by micromössbauer technique. The result shows a  $\text{Fe}^{3+}:\text{Fe}^{2+}$  atomic ratio of 59:41. Analytical data (wt%) gave:  $\text{SiO}_2$  41.69,  $\text{TiO}_2$  5.30,  $\text{Al}_2\text{O}_3$  13.65,  $\text{Cr}_2\text{O}_3$  0.09,  $\text{Fe}_2\text{O}_3$  4.52,  $\text{MgO}$  15.54,  $\text{CaO}$  11.03,  $\text{MnO}$  0.11,  $\text{FeO}$  2.83,  $\text{Na}_2\text{O}$  2.88,  $\text{K}_2\text{O}$  0.96,  $\text{H}_2\text{O}$  0.70,  $\text{F}$  0.24,  $\text{Cl}$  0.08,  $\text{O}=(\text{F},\text{Cl})$  -0.12, sum 99.50. The empirical formula, based on 24 total anions is:  ${}^A(\text{Na}_{0.82}\text{K}_{0.18})$   ${}^B(\text{Ca}_{1.73}\text{Fe}^{2+}_{0.26}\text{Mn}_{0.01})$   ${}^C(\text{Mg}_{3.38}\text{Fe}^{2+}_{0.09}\text{Fe}^{3+}_{0.50}\text{Al}_{0.44}\text{Cr}_{0.01}\text{Ti}_{0.58})$   ${}^T(\text{Si}_{6.09}\text{Al}_{1.91})$   $\text{O}_{22}$   ${}^W[\text{O}_{1.19}(\text{OH})_{0.68}\text{F}_{0.11}\text{Cl}_{0.02}]$ .

The mineral is monoclinic, space group  $C2/m$ ,  $a$  9.8378(8),  $b$  18.0562(9),  $c$  5.3027(6) Å,  $\beta$  105.199(9)°. The crystal structure was refined to  $R_1 = 0.040$  for 1783 observed [ $F_o > 4\sigma(F_o)$ ] reflections. The partition of cations among the various sites was carried out so as to match the chemical data and minimize the differences between theoretical and experimental site scatterings. The refined site scattering at M4 site showed no substantial  $\text{Fe}^{2+}$ , whereas the comparison of theoretical and experimental site scatterings from M1, M2, M3 and A sites shows a fairly good agreement. This suggests that the crystal used for the structural study has a slight  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  ratio higher than the crystal used for the Mössbauer analysis, and this would place it closer to the end-member composition.

A proposal for the approval of the new mineral and its name will be submitted soon to the IMA-CNMNC.

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## First occurrence of octahedral $V^{5+}$ in micas: the case of the new mineral balestraite, $KLi_2VSi_4O_{10}O_2$

Lepore G.O.\*<sup>1</sup>, Bindi L.<sup>1</sup>, Zanetti A.<sup>2</sup>, Ciriotti M.E.<sup>3</sup>, Medenbach O.<sup>4</sup> & Bonazzi P.<sup>1</sup>

1. Dipartimento di Scienze della Terra, Università di Firenze. 2. Istituto di Geoscienze e Georisorse, CNR, UOS di Pavia. 3. Associazione Micromineralogica Italiana, Devesi-Ciriè. 4. Institut für Geologie, Mineralogie und Geophysik, Ruhr-Universität Bochum, Germany.

Corresponding email: [giovanniorazio.lepore@unifi.it](mailto:giovanniorazio.lepore@unifi.it)

Keywords: balestraite, new mineral, Li-mica, V-mica, Cerchiara mine, pentavalent vanadium.

A mica-supergroup mineral characterized by a very high V content and completely free of Al was found at the boundary between carbonate secondary veins and hematite bands occurring in the manganeseiferous ores associated to the metacherts of the ophiolitic sequences at the Cerchiara mine, Eastern Liguria (Italy). Chemical (EPMA and LA-ICP-MS), as well as structural (SX-XRD) characterization, supported by Raman data, led to the definition of a new mineral species belonging to the mica supergroup which was named balestraite after Corrado Balestra, a prominent Italian amateur mineralogist. Balestraite, ideally  $KLi_2V^{5+}Si_4O_{10}O_2$ , is a 1M trioctahedral mica crystallizing in the C2 space group, with  $a = 5.2024(5)$  Å,  $b = 8.9782(7)$  Å,  $c = 9.997(2)$  Å,  $\beta = 100.40(2)^\circ$ ,  $V = 459.3(1)$  Å<sup>3</sup>,  $Z = 2$ . The reduction of symmetry from the "ideal" space group  $C2/m$  is due to the ordering of V at only one (M2) of the two pseudo-symmetric octahedral sites, while Li almost fully occupies the other two sites. This ordering scheme is made evident by both the site scattering (22.4 e<sup>-</sup> in M2 vs. 3.0 and 3.2 e<sup>-</sup> in M1 and M3, respectively) and the geometrical features of the three octahedra. The Raman spectrum shows no peaks in the region of the O-H stretching band (3300-3800 cm<sup>-1</sup>) and therefore balestraite was considered as completely anhydrous. With this assumption, the charge balance of the formula requires all vanadium to be present at the pentavalent state. This requirement is fully confirmed by the geometrical features of the M2 octahedron exhibiting a [2+2+2] distribution characteristic of the valence state +5 (Schindler et al. 2000). The presence of octahedral  $V^{5+}$  is also supported by the occurrence of a high-wavenumber Raman band (973 cm<sup>-1</sup>), in keeping with what reported by Frost et al. (2005) for symmetric vibrational modes from  $V^{5+}O_6$  units in decavanadate minerals. The peculiar composition of the octahedral sheet together with the tetrasilicic character of the tetrahedral sheet and its anhydrous character lead to unusual geometrical features for this mica.

The occurrence of  $V^{5+}$  together with the virtually complete  $O^{2-} \rightarrow OH^-$  substitution at the O4 site indicate strongly oxidizing conditions of crystallization which are supported by the occurrence of balestraite at the boundary of hematite bands.

The mineral and its name have been approved by the Commission on New Minerals, Nomenclature and Classification, IMA (2013-080).

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## “La Fossa” crater at Vulcano, Aeolian Islands (Italy): A treasure trove of minerals important for material science

Pinto D.\*<sup>1</sup>, Garavelli A.<sup>1</sup>, Mitolo D.<sup>1</sup> & Bindi L.<sup>2</sup>

1. Dipartimento di Scienze della Terra e Geoambientali - Università degli Studi di Bari "A. Moro"

2. Dipartimento di Scienze della Terra - Università degli Studi di Firenze.

Corresponding email: [daniela.pinto@uniba.it](mailto:daniela.pinto@uniba.it)

Keywords: Bi-oxysulfate, sublimate, Vulcano fumarols.

Bismuth oxide sulfates meet with interest in chemistry and material sciences as high ionic-conducting materials (Smirnov *et al.*, 2003; Crumpton & Greaves, 2004). The occurrence of these compounds in Nature is very rare, although more than 10 synthetic bismuth oxysulfates have been described in the literature (Aurivillius, 1987, 1988; Francesconi *et al.*, 1998; Smirnov *et al.*, 2003; Crumpton & Greaves, 2004). To date, only two hydrated phases, cannonite,  $\text{Bi}_2(\text{SO}_4)\text{O}(\text{OH})_2$  (Stanley *et al.*, 1992; Capitani *et al.*, 2013) and riomarinaite,  $\text{Bi}(\text{SO}_4)(\text{OH})\cdot\text{H}_2\text{O}$  (Rögner, 2005), and the two recently approved anhydrous oxysulfates, baličžuničite,  $\text{Bi}_2\text{O}(\text{SO}_4)_2$  (Pinto *et al.* 2013) and leguernite,  $\text{Bi}_{12.67}\text{O}_{14}(\text{SO}_4)_5$  (Garavelli *et al.* 2013), are known as minerals. Baličžunicite and leguernite were found in a sublimate assemblage collected in 1990 from high temperature fumaroles of the La Fossa crater of Vulcano (Aeolian Islands, Italy). In the same sublimate assemblage, strictly associated to them, a third Bi-oxysulfate phase was found. It represents a potential new mineral corresponding to the synthetic phase  $\text{Bi}_{28}\text{O}_{32}(\text{SO}_4)_{10}$  described by Aurivillius (1987). This new natural Bi-oxysulfate from Vulcano occurs as needle-like crystals up to 0.4 mm long and 0.01 mm across. Single-crystal X-ray diffraction data indicate monoclinic symmetry, space group  $C2$ , with unit-cell parameters  $a$  21.659(4),  $b$  5.6648(9),  $c$  15.092(3) Å,  $\beta$  119.43(1)°,  $V = 1612.7(5)$  Å<sup>3</sup> and  $Z = 4$ . The crystal structure is built up of blocks of Bi and O atoms extending in the  $b$  direction, but separated from each other in the  $a$  and  $c$  directions, and of pleated layers of  $\text{SO}_4^{2-}$  tetrahedral roughly parallel to (100). The Bi, O blocks of composition  $[\text{Bi}_{14}\text{O}_{16}]^{10+}$  have a fluorite-like structure and contain 6 rows of  $(\text{OBi}_4)$  tetrahedral chains. The structure of this new phase shows strong similarities with that of leguernite, in which similar fluorite-like Bi-O blocks of composition  $[\text{Bi}_{12}\text{O}_{14}]^{8+}$  extend along [010].

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## Fumarolic minerals after the 1944 Vesuvius eruption

Russo M.\*<sup>1</sup>, Campostrini I.<sup>2</sup> & Demartin F.<sup>2</sup>

1. Istituto Nazionale di Geofisica e Vulcanologia, sezione di Napoli - Osservatorio Vesuviano  
2. Dipartimento di Chimica, Università degli Studi di Milano.

Corresponding email: [m.ciriotti@tin.it](mailto:m.ciriotti@tin.it)

Keywords: Vesuvius, 1944 eruption.

The 1944 eruption of Vesuvius was the last eruption of this volcano and marked the transition from an open conduit to a closed conduit state. The eruption took place during wartime so that nobody was interested to sample fumarolic minerals before and after the eruption. The only mineralogical studies were made by A. Parascandola (1951) who indicated the presence in the fumaroles of twelve mineral species. As a part of a joint project concerning the study of fumarolic minerals of the Italian volcanoes, a systematic investigation was undertaken by us.

A number of species never found before at this locality have been characterized: ammineite (Russo & Campostrini, 2011), artroeite (Campostrini & Gramaccioli, 2005), brochantite, caledonite, cerussite, connellite, coussellite, garksutite, hydrocerussite, linarite, matlockite, mimetite, parascandolaite (Demartin et al, 2014), phoenicochroite and sellaitite. Many of these species such as phoenicochroite, coussellite and caledonite have never been found in fumarolic environment and their occurrence is particularly interesting.

Parascandolaite,  $\text{KMgF}_3$  is a new perovskite-type fluoride and the presence of matlockite was confirmed after the doubtful report by Zambonini (1910).

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## The structure of cyanotrichite: a combined analysis of Automated Electron Diffraction Tomography and Synchrotron Powder X-ray Diffraction

Ventrucci G.\*<sup>1</sup>, Mugnaioli E.<sup>2</sup>, Capitani G.C.<sup>3</sup>, Scordari F.<sup>1</sup>, Pinto D.<sup>1</sup>, Lausi A.<sup>4</sup> & Pario G.<sup>1</sup>

1. Dipartimento di Scienze della Terra e Geoambientali, Università degli Studi di Bari. 2. Dipartimento di Scienze Fisiche, della Terra e dell'Ambiente, Università degli Studi di Siena. 3. Dipartimento di Scienze dell'Ambiente e del Territorio e di Scienze della Terra, Università degli Studi di Milano-Bicocca 4. ELETTRA Sincrotrone Trieste.

Corresponding email: [gennaro.ventrucci@uniba.it](mailto:gennaro.ventrucci@uniba.it)

Keywords: Electron crystallography, automatic diffraction tomography, powder X-ray diffraction.

The hydrated copper-aluminium sulphate cyanotrichite, ideally  $\text{Cu}_4\text{Al}_2(\text{SO}_4)(\text{OH})_{12}\text{H}_2\text{O}$ , often occurs in sky blue clumps or aggregates of sub-millimeter sized fibrous crystals. The problem of indistinguishable admixing of variable amounts of carbonate-cyanotrichite with cyanotrichite, the close association with other copper sulphates (chalcoalumite, brochantite) and the very small size of the acicular crystals hampered to date an *ab initio* structure determination from conventional X-ray diffraction. In light of these difficulties, we have taken advantage of the recent development of precessed automated electron diffraction tomography (ADT) combined with synchrotron powder X-ray diffraction to investigate the crystal structure of cyanotrichite. Through ADT investigation, two similar monoclinic cell were determined, corresponding to cyanotrichite ( $a = 10.16, b = 2.90, c = 12.64 \text{ \AA}$  and  $\beta = 92.4^\circ$ ) and carbonate-cyanotrichite ( $a = 10.16, b = 2.91, c = 12.42 \text{ \AA}$  and  $\beta = 98.4^\circ$ ). A structure model was obtained *ab initio* by direct methods in space group  $C2$  from electron diffraction data and tested with the Rietveld method against X-ray powder diffraction profiles. All reflections in the powder pattern were indexed with the two cyanotrichite-like phases, according to electron diffraction data. The Rietveld analysis, consistently with electron diffraction investigations, indicates that the refined structural model has based on  $\text{Al}(\text{OH})_6$  octahedra interconnected through common edges to build infinite columns running along **b**. Each Al-columns is coupled by sharing the remaining edges to two Cu-columns based on Cu distorted octahedra giving rise to ribbons along **b**. These ribbons are linked by  $\text{SO}_4$  tetrahedra to form corrugated layers.

## **SESSIONE S14**

### **Human activities and natural environment: News from Environmental Mineralogy and Geochemistry**

*CONVENORS*

*P. Costagliola (Univ. Firenze)*

*F. Frau (Univ. Cagliari)*

## Antimony removal from aqueous solutions by the use of Zn-Al sulphate layered double hydroxide (LDH)

Arda C.\*, Pusceddu I. & Frau F.

Department of Chemical and Geological Sciences, University of Cagliari.

Corresponding email: [carla.ardau@tiscali.it](mailto:carla.ardau@tiscali.it)

Keywords: Zn–Al sulphate layered double hydroxide, Sb(V) contamination, wastewater treatment.

Antimony represents an element of increasing environmental concern for its toxicity. It is listed as a priority pollutant by the World Health Organization, which established a guideline value of 20 µg/L for drinking water. Due to its various industrial uses, its global fluxes have increased at least ten-fold in the last decades, resulting in an increase of environmental Sb contamination. There are not many developed methods for the removal of Sb from contaminated waters. In oxic conditions  $\text{Sb}(\text{OH})_6^-$  is the dominant Sb(V) form over a wide pH range. This study focuses on the efficiency of a specific LDH in removing Sb(V) from aqueous solutions. LDHs are a group of compounds with a layered structure, hosting anions in the interlayer, which can exchange with anions present in solution, making LDHs potentially suitable for the removal of contaminants from aqueous solutions. Among the possible LDHs compositions, in this study we examined the removal of aqueous Sb(V) by Zn–Al sulphate LDH (Arda et al 2013 and references therein). The removal of Sb(V) from solution was carried out in a batch system by using variable Sb(V) concentrations and LDH amounts. Dosages were chosen assuming that the main Sb(V) removal mechanism is an interlayer anion exchange, and that for maintaining the electroneutrality of the LDH, the entrance of 1 mole of  $\text{Sb}(\text{OH})_6^-$  should be compensated by the exit of 0.5 mole of  $\text{SO}_4^{2-}$  present in the interlayer. Effectively, the removing of Sb(V) from aqueous solution is accompanied by a concomitant release of sulphate from LDH to solution. Sulphate release increases vs time proportionally to the Sb(V) removal. The  $\text{Sb}(\text{V})_{\text{removed}}/\text{S}_{\text{released}}$  molar ratio results close to 2. XRD analyses showed a complex LDH structural rearrangement during the exchange processes. Such rearrangement possibly entails for an initially rapid Sb(V) removal, slowing down as the availability of “exchange sites” diminishes. The efficacy of Zn–Al sulphate LDH in removing Sb(V) from solution can rapidly reach ~100%, providing that in starting conditions  $\text{Sb}(\text{OH})_6^-$  solution/ $\text{SO}_4^{2-}$  solid  $4^{2-}$  substitution cannot be obtained, and the final product will always contain a certain amount of residual  $\text{SO}_4^{2-}$ . All above granted, the study confirms the huge capacity of Zn-Al sulphate LDH to adapt the original structure in order to host different-sized/charged anions, supporting their potential key role in the water treatment. For Sb(V), the optimal operational conditions will be a compromise between the time wished for its removal and the cost of LDH dose.

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Arda C., Frau F. & Lattanzi P. 2013. New data on arsenic sorption properties of Zn–Al sulphate layered double hydroxides: Influence of competition with other anions. *Appl Clay Sci*, 80–81, 1–9.

## New data on composition, leaching behaviour and cytotoxicity of urban PM<sub>2.5</sub> from Rome city, in the year 2013

Armiento G.<sup>1</sup>, Carnevale M.<sup>2</sup>, Inglessis M.<sup>3</sup>, Montekali M.R.<sup>1</sup>, Nardi E.<sup>1</sup>, Palleschi S.<sup>4</sup>, Rossi B.<sup>4</sup>, Rossi T.<sup>2</sup>, Sacco F.<sup>5</sup>, Silvestroni L.<sup>6</sup> & Gianfagna A.\*<sup>2</sup>

1. ENEA - UTPRA GEOC - Laboratorio di Biogeochimica Ambientale, Roma. 2. Dipartimento di Scienze della Terra, Sapienza Università di Roma. 3. Dipartimento Ambiente e Connessa Prevenzione Primaria - Istituto Superiore di Sanità, Roma. 4. Dipartimento Ematologia, Oncologia e Medicina Molecolare - Istituto Superiore di Sanità, Roma. 5. ARPA LAZIO - Sez. Prov.le di Roma - Servizio ARIA, Roma. 6. Dipartimento di Medicina Sperimentale - Sapienza Università di Roma.

Corresponding email: [antonio.gianfagna@uniroma1.it](mailto:antonio.gianfagna@uniroma1.it)

Keywords: Urban PM<sub>2.5</sub>, leaching test, cytotoxicity.

Previous investigations on PM<sub>2.5</sub> from the city of Rome provided information about the inorganic fraction, constituted by abundant sulphates, oxides and other mineral phases. Moreover, preliminary data from leaching tests of heavy metals, referred to 2011 and 2012 samples, were also reported in previous works (Mazziotti Tagliani et al., 2012; Armiento et al., 2013). Bulk chemical composition evidenced the presence of heavy metals, in particular As, Cd, Cu, Cr, Fe, Ni, Pb and Zn, and their potential mobility was evaluated by a batch kinetic leaching test, using a physiological solution (mimicking the pulmonary environment, pH 7.4, 37 °C). According to standard procedures (2008/50/CE), both PTFE and quartz filters were utilized.

In 2013, two new PM<sub>2.5</sub> seasonal samplings, in three different urban sites, were carried out, during winter and summer.

Interestingly, the total metal concentrations measured show, for some elements and in some urban stations, substantial differences between the winter and summer samples. Regarding the leaching behaviour, Cd resulted always as the most mobile heavy metal, whereas no Fe release was observed so far. In winter, only Cd and Pb were detected in leaching solutions, with lower mobility respect to the summer samples, which present higher elements leaching also for Cu, Ni, and Zn.

Different heavy metal concentrations originate from various and different sources, and are influenced by different climate conditions, e.g. during winter, cold and rain inhibit air particles dispersion, which is much more abundant in summer. Leaching tests seem to confirm this inference, suggesting that the elements are present in different mineralogical phases.

The toxicity of the leached material was evaluated in an array of *in-vitro* experiments by using two different, physiologically relevant cell models: a human alveolar epithelial cell line, A549, and human polymorphonuclear leucocytes freshly purified from peripheral blood. Cell homeostasis and responsiveness to primary functional stimuli were significantly affected by the compounds leached from PM<sub>2.5</sub> without impairment of cell vitality, with the compounds leached from winter PM being generally more effective than those from summer PM. Further experiments are in progress to evaluate whether either soluble compounds or nanoparticles play a role in the effects observed.

Mazziotti Tagliani S., Nardi E., Pacifico R., Inglessis M., Sacco F., Piga L., Palleschi S., Silvestroni L. & Gianfagna A. (2012). Mineralogical characterization and environmental-health implications of urban PM<sub>2.5</sub> from Rome (Italy). EMC2012 – 2-6 September, Frankfurt, Germany.

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## Removal of metals from mine-waste drainages (Iglesias, Italy) by Al-induced precipitation of LDH

Atzori R.\*, Ardaù C., Podda F. & Frau F.

Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari.

Corresponding email: [roberta.atzori@unica.it](mailto:roberta.atzori@unica.it)

Keywords: mine drainages, metal contamination, waste-water treatment.

The removal of toxic metals from waste waters is one of the most important problems in mining environments. A number of technologies to reduce the release of toxic metals to the environment have been developed. Layered double hydroxides (LDH) are a series of lamellar compounds with the general formula  $[M^{2+}_{1-x} M^{3+}_x (OH)_2] (A^n)_{x/n} \cdot mH_2O$ , widely studied for the removal of anionic pollutants from water thanks to their large specific surface area and their high anion exchange capacity. Starting point of our study was the finding of LDH (i.e., glaucocerinite and zinco-wardite) spontaneously formed in mining environments and their efficacy in the attenuation of As content in drainage water (Ardaù et al., 2011). Synthetic LDH of Zn-Al were prepared in laboratory and tested for sorption of As, Mo and Sb (Ardaù et al., 2012; Ardaù et al., 2013 and this issue). Our idea was to use mine-waste drainages of the Monteponi mine area (Iglesias, Italy) as a reagent for the precipitation of LDH and the consequent removal of metals. The mine-waste drainage used in the first experiments is characterised by neutral pH and high levels of  $SO_4$  (~ 4000 mg/L), Mg (~ 600 mg/L), Zn (~ 200 mg/L) and other metals such as Pb, Mn and Cd, but very low concentration of Al. The experiment was carried out by adding to water an adequate amount of a salt of Al in order to induce the LDH precipitation. NaOH was added to solution before the beginning of the experiment to maintain a neutral pH. White precipitate was obtained and successively analysed by XRD and, prior acid digestion, by ICP-OES. Chemical analysis was also carried out on the water before the experiment and after filtration to separate the solid phase. First results showed that the mineralogical nature of the compound is a pure LDH, without the apparent co-precipitation of other phases, in which the chemical composition showed a molar  $[Zn^{2+}]/[Al^{3+}]$  ratio equal to 2.4. Aluminium was not detected in the water at the end of the experiment, which indicates a complete precipitation of Al added to the mine-waste drainage. These preliminary results encourage further investigations on the removal of divalent metals (e.g. Zn, Mn, Cd, Ni, etc.) from M(III)-poor mine waters by inducing LDH precipitation.

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Ardaù C., Frau F., & Lattanzi P. 2013. New data on arsenic sorption properties of Zn-Al sulphate layered double hydroxides: Influence of competition with other anions. *Appl. Clay Science*, 80–81, 1–9.

## Chromium adsorption and desorption on naked Surface Active Maghemite Nanoparticles (SAMNs): possible environmental implications

Baratella D.<sup>1</sup>, Salviulo G.\*<sup>1</sup>, Magro M.<sup>2</sup> & Vianello F.<sup>2</sup>

1. Dipartimento di Geoscienze, Università di Padova. 2. Dipartimento di Biomedicina Comparata e Alimentazione, Università di Padova.

Corresponding email: [gabriella.salviulo@unipd.it](mailto:gabriella.salviulo@unipd.it)

Keywords: water remediation, Cr(VI), magnetic nanoparticles.

The importance of the interface between geosphere and biosphere is known and represents one of the most fascinating frontiers of minerals science, especially if explored at nanoscale. Heavy metal release, transport and dispersion into the biosphere have a direct impact on the environment and on human health. Therefore, there has been an increasing development of applications for water and soils remediation, among which magnetic nanoparticles stand out. Environmental applications and risk assessment of manufactured nanoparticles greatly depend on the understanding of their interactions with water and soils. Novel superparamagnetic nanoparticles (SAMNs), constituted of stoichiometric maghemite, characterized by specific surface chemical behavior without any coating or superficial modification, are stable in water for months as colloidal suspensions, present a high average magnetic moment and can be easily derivatized to immobilize specific molecules. Various studies were recently carried out exploiting these peculiar properties (Magro et al., 2012a; Magro et al., 2012b). The applicability of SAMNs as adsorbent for chromium(VI) in water and soil remediation is under study. Chromate adsorption on the nanomaterial was attributed to the presence of under-coordinated iron(III) sites on nanoparticle surface, which allow the binding of Cr(VI) via dative bonds. The interaction of Cr(VI) with SAMN surface caused a red shift (140 nm) of SAMN@Cr(VI) spectrum compared to bare SAMNs. Chromate binding on SAMNs was studied according to the Langmuir isotherm model and Langmuir isotherm constants, K and  $\Gamma_{\max}$  were found to be  $2.5 \text{ L} \times \text{g}^{-1}$  and  $44.0 \text{ mg} \times \text{g}^{-1}$ , respectively. This last value is higher than those reported for various compounds commonly used as adsorbents. Recovery of the SAMN-chromate composite can be accomplished using magnetic properties of the material and chromate can be desorbed by increasing solution pH. By this way, SAMNs can be utilized for subsequent cycles of remediation without reducing their efficiency. This is one of the very few studies that have, to date, examined chromium removal by naked maghemite nanoparticles. The maintenance of adsorption capacity coupled with the easy removal make these nanoparticles an attractive material for large scale water purification applications. Future experiments using this strategy with SAMNs are planned.

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## **A time- and cost-saving method for the quantitative determination of inorganic soil conditioners: a case of study on zeolite in clay soils**

Brigatti M.F.\*, Laurora A. & Malferrari D.

Dipartimento Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia.

Corresponding email: [brigatti@unimore.it](mailto:brigatti@unimore.it)

Keywords: zeolite, polyphasic, clay-soil.

Zeolites are natural rocks with peculiar physical chemical characteristics, which make them capable of controlled cations exchange mechanism when mixed to soils, with evident advantages for a sustainable development of agricultural practices. A new method is presented to quantitatively determine the amount of zeolite added to soils during field tests conducted within the European LIFE +2010 project “ZeoLIFE - Water pollution reduction and water saving using a natural zeolite cycle” (project code: LIFE +10 ENV/IT/000321), in order to assess the effectiveness of zeolites as soil conditioners, partly replacing chemical fertilizers.

Standard samples were prepared by mixing known amounts of zeolite and an “averaged soil sample” obtained by carefully quartering, grinding and mixing soil samples randomly taken from different points of the selected experimental field. In detail, 1, 2, 3, 4, 5, 7, and 10 wt% zeolite coming from a selected quarry were added to the averaged soil; 10 wt% corundum NIST SRM 674a was also introduced in each standard sample in order to estimate intensity variations due to sample preparation and instrumental biases.

Soil sample taken from different parcels (5, 7 and 15 tons/ha zeolite) in which the experimental field was divided were manually crushed and dried under the same ambient conditions used for the preparation of the standards. After quartering and grinding, each sample was added with 10 wt% NIST certified standard, and XRPD patterns were collected, at the same experimental conditions used for standards.

Measurements on soil samples demonstrate a good agreement between calculated and measured values, even if almost all replicas underestimate the calculated values. Slight variations with respect to calculated values can be attributed to inaccuracy during zeolite spreading on the experimental plot, as well as to inhomogeneity due to imperfect plowing. In addition, assuming that spreading and plowing were homogeneous, and that the samples collected were representative, in our opinion underestimation can be attributed only to an overestimation of the apparent density of the soil.

Despite the fact that the discussed method is specifically suited for the ZeoLIFE project purposes, it could be conveniently generalized to all the applications that require the quantitative determination of mono or polyphasic crystalline materials within complex mixtures.

## The wild rat as sentinel animal to detect potential risk for human environmental exposure to asbestos: seeking latent sources in Casale Monferrato (NW Italy)

Capella S.\*<sup>1-2</sup>, Ardizzone M.<sup>3</sup>, Vizio C.<sup>4</sup>, Ingravalle F.<sup>5</sup>, Ru G.<sup>5</sup>, Bozzetta E.<sup>6</sup>, Dondo A.<sup>7</sup>, Seghesio A.<sup>8</sup>,  
Mirabelli D.<sup>9</sup>, Vigliaturo R.<sup>1</sup> & Belluso E.<sup>1-2-10</sup>

1. Department of Earth Sciences, University of Torino. 2. Interdepartmental Centre for Studies on Asbestos and other Toxic Particulates "G. Scansetti", University of Torino. 3. Via Bligny 4, 15033, Casale Monferrato (AL). 4. Regione Bocca 16/A, 15034, Cellamonte (AL). 5. Biostatistics Epidemiology and Risk Analysis Unit, Veterinary Medical Research Institute for Piemonte, Liguria and Valle D'Aosta (IZSPLVA), Torino. 6. Histopathology Laboratory, Veterinary Medical Research Institute for Piemonte, Liguria and Valle D'Aosta (IZSPLVA), Torino. 7. Animal Diagnostic Department, Veterinary Medical Research Institute for Piemonte, Liguria and Valle D'Aosta (IZSPLVA), Torino. 8. Local Health Authority of Alessandria and Asti. 9. Cancer Epidemiology Unit, CPO Piemonte, Torino. 10. Institute of Geosciences and Earth Resources, CNR, Unit of Torino.

Corresponding email: [silvana.capella@unito.it](mailto:silvana.capella@unito.it)

Keywords: Asbestos, Sentinel animals, SEM-EDS, Hidden sources.

Asbestos have been incorporated into many different products since its discovery, centuries ago. Countless applications of asbestos result from their many unique characteristics. It has long been recognized the link between their breathing and the pulmonary related diseases (asbestosis, malignant mesothelioma and lung cancer) in occupational exposed workers. For this reason asbestos have been banned in many countries, including Italy (L.257/92). Also a particular kind of exposure, specifically anthropogenic environmental exposure, shown his dangerousness, e.g. in the areas where asbestos industries were active.

At present, the dose-response relationship has no a threshold and the relationship between exposure to environmental sources of asbestos and health effects still represents an open issue. In Casale Monferrato city (Piemonte Region, NW Italy), the biggest Italian plant of Eternit® (a mixture of cement-asbestos) was active from 1907 to 1986 but sources of exposure may still exist in the environment and they can represent a potential of human exposure. The idea was to identify the possible presence of previously unrecognized asbestos sources, by measuring the asbestos fibre content in the lungs of wild rats (used as sentinel animals). Measurement of the lung fiber burden in wild rats has proved feasible. Previously we carried out a pilot study that demonstrated that it was possible not only to detect, but also to characterize asbestos fibers both qualitatively and quantitatively. Casale Monferrato district has been divided in a grid with 61 cells (200 x 200 m). Neighborhood with different degree of priority have been identified, based on technological processes and asbestos transports, historically reported within the city. We established to capture a minimum of 5 wild rats in each cell with a multi-capture device and for each pool constituted by 5 lungs, SEM-EDS investigation will be carried out. Until now, 18 wild rats have been captured in five different cells but only in one of them, the completed pool has been collected. The SEM-EDS investigation of this pool showed 40800 fibers per gram of dry weight (ff/gdw) of asbestos tremolite and 5100 ff/gdw of asbestos grunerite, i.e. a burden of asbestos both from natural and anthropic source. In April this project titled "Sentinel animals for asbestos", was introduced to the citizenry and authority of Casale Monferrato with the aim to make the inhabitants aware of our research, and to involve them to obtain directly indication about the sites where rats are present to increase their capture. A Facebook page for this aim has been opened and promoted.

## Geosphere-biosphere interactions in soil-plant systems, Iglesias mining district, Sardinia

Concas S.\*<sup>1</sup>, Bacchetta G.<sup>2</sup>, Barbaferri M.<sup>3</sup>, Di Bonito M.<sup>4</sup>, Lattanzi P.<sup>1</sup>, Pinto V.<sup>5</sup>, Rosellini I.<sup>3</sup> & Vacca A.<sup>1</sup>

1. Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari. 2. Dipartimento di Scienze della vita e dell'ambiente, Università di Cagliari. 3. ISE-CNR, Pisa. 4. Nottingham Trent University, UK. 5. ENEA, La Casaccia (Roma).

Corresponding email: [saraconcas@yahoo.it](mailto:saraconcas@yahoo.it)

Keywords: heavy metals, soil, plant.

The Iglesias area (southwestern Sardinia) is characterized by a geochemical anomaly of heavy metals such as Zn, Pb, and Hg, and is affected by environmental pollution associated with several centuries of mining activity.

In this study, we investigated the mobility of heavy metals in the interactive environmental system soil - soil pore water- plant, with specific reference to *Pistacia lentiscus* L., a spontaneous vegetal species that may be useful for phytostabilization of mine waste piles (Bacchetta et al., 2012).

The soil bulk contents of several heavy metals (Zn, Pb, As, Cd, and Hg) exceed Italian law limits (D.Lgs 152/2006) for 'industrial' soils. These high contents are partly the expression of a natural anomaly; however, in mining affected sites contents are higher than the local background, demonstrating the anthropic contribution. The mobility of metals was estimated through two different single extraction chemical methods: with DTPA solution, followed by analysis of the extracted metals by ICP-OES; and with sodium citrate/hydroxylamine hydrochloride/TEA followed by colorimetric titration with Dithizone (DZ) solution (Pinto et al., 2010). The two methods show a good correlation, although the DZ method gives higher estimates of 'mobile' metals.

An innovative aspect of this study was the sampling and analysis of soil pore waters as a direct measure of metal mobility and bioavailability (Tye et al., 2003; Di Bonito et al., 2008). Among trace metals, Zn is usually the most abundant (up to 8 mg/L), except for two sites where very high Ba contents (up to 73 mg/L) were measured. Geochemical modelisation shows in general an approach to equilibrium of the solutions with the minerals present in soils.

With respect to transfer to the biosphere, the metal concentrations (Zn, Pb and Hg) in *P. lentiscus* are much lower than, but roughly proportional to, contents in soil ( $BAC \ll 1$ ), and decrease in the order roots>stems>leaves, with the partial exception of Hg, for which there is locally an enrichment in leaves. The *P. lentiscus* seems then to behave as a tolerant species with strategies of exclusion, and with character of 'indicator'.

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## Colloidal precipitates related to AMD settings: a combined HT-XRD and bulk leaching test approach

Consani S.\*<sup>1</sup>, Carbone C.<sup>1</sup>, Salviulo G.<sup>2</sup>, Dinelli E.<sup>3</sup> & Lucchetti G.<sup>1</sup>

1. DISTAV, Università di Genova. 2. Dipartimento di Geoscienze, Università di Padova. 3. Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Bologna.

Corresponding email: [sirio.consani@edu.unige.it](mailto:sirio.consani@edu.unige.it)

Keywords: Colloidal precipitates, Libiola mine, PTE.

The AMD (Acid Mine Drainage) alteration processes influence deeply the dispersion of chemical elements around abandoned mine sites. Previous works highlighted the fact that near abandoned Fe-Cu mine where AMD takes place low-crystallinity and/or amorphous precipitates play a major role in controlling the fate of pollutants in the surrounding environment. While it is well known that Fe-rich precipitates tend to transform to more stable crystalline phases little is known on the phase transition of Cu-Al rich amorphous phases. The colloidal precipitates object of this study were distinguished on the basis of their crystallinity. The aim of this work was to a) induce a possible phase transition through HT-XRD analyses and b) evaluate the capacity of the transformation product to release PTE (Potential Toxic Elements) using bulk leaching tests. The four samples are representative of 1) Fe-rich amorphous phases deposited by waters with pH= 7,62 and Eh=265 mV; 2) Al-amorphous phases originated by water with pH= 4,95 and Eh= 298,5 mV 3) Cu-Al low crystallinity precipitates composed by (hydro)woodwardite  $[(\text{Cu}_{1-x}\text{Al}_x)(\text{OH})_2(\text{SO}_4)_{x/2} \cdot n\text{H}_2\text{O}]$ , allophane  $[\text{Al}_2\text{O}_3(\text{SiO}_2)_{1.3-2} \cdot 2.5-3\text{H}_2\text{O}]$  (pH= 7,8 and Eh=230,5 mV) and 4) Fe-rich crystalline phases (pH= 6,8 and Eh= 179,6 mV) composed by goethite (FeOOH), jarosite  $[\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6]$  and an unidentified amorphous phase. Bulk chemical analyses were carried out to study the chemical composition of the samples, and showed sharp differences between the chemistry of Fe-rich precipitates and the others. The major element in these samples is by far Fe, followed by Cu, S, and Al with minor amounts of Ni and Zn. The major elements of Al rich and Cu-Al rich precipitates are Si, Al, Cu, Zn, S, Fe with minor amounts of Ni. In particular, in the Cu-Al rich samples were found high amounts of REE, which show an average concentration of 137 ppm, with a maximum of more than 600 ppm for Y. In order to monitor the possible transition to crystalline phases, in situ HT-XRD coupled with TG-DTA analyses were carried out. These experiments highlighted that the transition to more crystalline phases can occur in two different ways a) a direct transition to product with higher crystallinity b) an indirect transition with the occurrence of an intermediate amorphous phase precursor to the high crystallinity phases. To investigate the possibility that these low crystallinity or amorphous phases release into the environment PTE during their transformation into crystalline phases, bulk leaching tests were performed on the untreated samples and on the heated ones. The results testify that the elements show different behaviour due to their different affinity with the reaction product and to their chemical behaviour; in particular, the high amount of the PTE is not released during the phase transition process and is still retained by the solids.

## Antimony removal from aqueous solution by Layered Double Hydroxides

Dore E.\*<sup>1</sup>, Lefèvre G.<sup>2</sup> & Frau F.<sup>1</sup>

1. Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari. 2. Institut de Recherche de Chimie Paris, CNRS, Chimie ParisTech, France.

Corresponding email: [elisabettadore@yahoo.it](mailto:elisabettadore@yahoo.it)

Keywords: Antimony, Layered Double Hydroxides, polluted water treatment.

Antimony (Sb) is a toxic trace element widely present in environmental compartments through both natural and anthropogenic sources. The World Health Organization and the Italian Legislation set safe drinking water levels for Sb at 20  $\mu\text{g L}^{-1}$  and 5  $\mu\text{g L}^{-1}$ , respectively (WHO, 2011; GURI, 2006). Typical concentrations of Sb in natural unpolluted waters are very low, less than 1  $\mu\text{g L}^{-1}$ , but increase up to few tenths of  $\text{mg L}^{-1}$  as a consequence of anthropogenic activities, especially in areas near mining sites and smelter activities (Cidu et al., 2013). In oxygenated waters Sb(V) is the predominant species in solution as the oxyanion  $\text{Sb}(\text{OH})_6^-$ .

Possible solutions for pollutants abatement from water comprise the use of sorption technologies. Layered Double Hydroxides (LDHs) are a group of natural and synthetic compounds, widely used in remediation studies. LDHs have general formula  $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2]^{x+} [(\text{A}^{n-})_{x/n}]^{x-} \cdot m\text{H}_2\text{O}$ , with large compositional variability (e.g.  $\text{M}^{2+} = \text{Mg}, \text{Zn}, \text{Ca}$ ;  $\text{M}^{3+} = \text{Al}, \text{Fe}$ ;  $\text{A}^{n-} = \text{Cl}^-, \text{NO}_3^-, \text{CO}_3^{2-}, \text{SO}_4^{2-}$ ); their structure consists of brucite-like sheet, positively charged, stacked along the *c* axis with (oxy)anion and water molecules in the interlayer. LDHs have high anion exchange capacity and are able to remove environmental pollutants present in neutral and slightly alkaline waters as (oxy)anions. Also  $\text{M}^{2+}\text{M}^{3+}$  oxides derived from LDHs calcination can be used to remove toxic (oxy)anions from water, because are able to reconstruct the layered structure through rehydration and sorption of (oxy)anions (Goh et al., 2008). Batch sorption experiments were carried out to test the ability of LDHs in  $\text{Sb}(\text{OH})_6^-$  removal from aqueous solutions. Experiments were performed with synthetic  $\text{NO}_3$ -LDHs and calcined LDHs, with different cationic composition (Mg/Al,Fe-LDHs and Zn/Al-LDHs) in order to identify the most effective composition. First results show that both calcined and uncalcined LDHs have good potential use as  $\text{Sb}(\text{OH})_6^-$  removers. XRD and Attenuated Total Reflection (ATR) IR data suggest that  $\text{Sb}(\text{OH})_6^-$  can be efficiently removed from solutions through different processes in function of different cationic composition, and encourage further investigation.

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## Chrysotile within calcite veins from Northern Apennines

Giordani M.\*, Mattioli M. & Valentini L.

Dipartimento di Scienze della Terra, della Vita e dell'Ambiente, Università di Urbino

Corresponding email: [matteo.giordani@uniurb.it](mailto:matteo.giordani@uniurb.it)

Keywords: Chrysotile, calcite veins, Northern Apennines.

In the Northern Apennines several olistoliths made up of serpentinites, calcionelle limestones and ophiolitic breccias have been recognized within the Porcellara Complex, Monte Cassio Unit. These olistoliths are frequently crossed by a dense network of centimeter to decimeter veins generally filled by carbonate minerals (e.g. La Costa, Berceto, PR). Morphological and compositional data (SEM-EDS and XRPD) have revealed that these carbonate minerals consist mainly of well-formed, white to milky calcite crystals, strictly associated with chrysotile. This mineral is found as white thin fibers (< 1 micron), grew up in intimate association with calcite crystals. These fibers may be very rare and randomly scattered within the crystals of calcite, or can be grouped into bundles of millimeter to centimeter size. At times, the chrysotile can get to completely fill the vein. Chrysotile fibers are well-formed and euhedral at all scales from hand specimen to electron microscope images. In some cases, individual fibers of chrysotile are not visible in hand specimen or under the petrographic microscope; however, SEM images show the characteristic elongate crystal morphology. The fibers are also characteristically curved at the millimeter scale. It is important to note that the fibers of chrysotile appear, frequently, as a physical extension of calcite crystals, without any evident morphological discontinuity in the transition from a massive (calcite) to a fibrous (chrysotile) appearance. The results of detailed SEM-EDS elemental analyses carried out in various segments of the contact areas between calcite and chrysotile crystals seem to show a gradual transition in chemical composition from pure calcite to pure chrysotile phases, passing through various intermediate arrangements.

## Employment of zeolites in open field experiments: characterization and monitoring of the cation exchange mechanisms in relation to the crop cycle progress

Malferrari D.\*<sup>1</sup>, Laurora A.<sup>1</sup>, Passaglia E.<sup>1</sup>, Faccini B.<sup>2</sup>, Di Giuseppe D.<sup>2</sup>, Coltorti M.<sup>2</sup>,  
Abbondanzi F.<sup>3</sup> & Campisi T.<sup>3</sup>

1. Dipartimento Scienze Chimiche e Geologiche, Università di Modena e Reggio E. 2. Dipartimento di Fisica e Scienze della Terra, Università di Ferrara. 3. Centro Ricerche e Servizi Ambientali (C.R.S.A.) MED INGEGNERIA S.R.L.

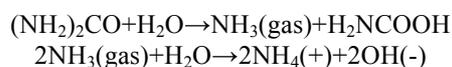
Corresponding email: [daniele.malferrari@unimore.it](mailto:daniele.malferrari@unimore.it)

Keywords: zeolite, ammonium, CEC.

The project “ZEOLIFE - Water pollution reduction and water saving using a natural zeolite cycle” (LIFE+10 ENV/IT/000321) has been conceived to test an innovative integrated zeolite application having the aim to experience the employment of natural and ammonium exchanged zeolite (NH<sub>4</sub>-zeolite hereafter) in a two-years open field test ([www.zeolife.it](http://www.zeolife.it) for more details).

This summary describes some of the results relating to the characterization of zeolite samples collected in the experimental field during different stages of the crop cycle (i.e., after the application of synthetic fertilizers but before the development of the plants, and at end of cultivation cycle after harvest). In fact, during the first crop year, the experimental field was subdivided in six plots of about one hectare each: one plot was amended with 7Kg/m<sup>2</sup> of NH<sub>4</sub>-zeolite prepared by the prototype, two plots with 5 and 15 Kg/m<sup>2</sup> of natural zeolite, and three plots were not amended and used as control. The NH<sub>4</sub>-zeolite plot was amended with 50% chemical fertilizers comparing to the quantity used in the control plot, while 5 and 15Kg/m<sup>2</sup> natural zeolite plots with 70% chemical fertilizer. All plots were sown with grain sorghum.

Fertilization was done with urea and diammonium phosphate using 5.561 Kmoli/ha and 0.1945 Kmoli/ha (relative to the control plot), respectively, according to the production disciplinary. Since the conversion of urea to ammonium occurs according to the following reactions:



it follows that for each mole of urea can be formed, as a maximum, two moles of NH<sub>4</sub> (diammonium phosphate has the same conversion ratio). Therefore, in the control plots may be formed, as a maximum, 11.557 Kmoli/ha of NH<sub>4</sub> (5.578, 8.090 Kmoli/ha in the plots in which the reduction of synthetic fertilizers compared to control were 50 and 30%, respectively).

The laboratory tests indicated that the maximum operational C.E.C. of the selected zeolite for ammonium is 0.389 moles/Kg; it is likely to assume an “in-situ (on field) C.E.C.” not higher 50% of the operational C.E.C. It follows that in the two plots amended with natural zeolite, all the ammonium that may be formed from synthetic fertilizers can potentially be absorbed by zeolite itself. On the other hand, this should not occur in the plot amended with NH<sub>4</sub>-zeolite that should be completely ammonium saturated.

Experimental measurements (chemical analysis of major elements, exchangeable ammonium and total nitrogen) on soil-zeolite samples collected in the experimental field, show that there is a net change in the chemistry of zeolite after the cultivation cycle. In particular, at the end of the first one:

1) in NH<sub>4</sub>-zeolite there is almost no residue of exchangeable ammonium (0.248mmol/Kg, equivalent to 17.3 moles/ha referred to the parcel amended with 7Kg/m<sup>2</sup>);

2) in the natural zeolite (i.e., parcels amended with 5 and 15Kg/m<sup>2</sup> of natural zeolite) remains a modest amount of exchangeable ammonium (0.638 and 0.428 mmol/kg, equal to 31.9 and 64.1 moles/ha);

3) in the zeolites of all plots the content of Ca and Mg increases, whereas Na and K decreases, both with respect to NH<sub>4</sub>- and natural zeolite at the beginning of the experiment.

## Morphological and compositional data of erionite from Lessini Mounts, NE Italy

Mattioli M.\*<sup>1</sup>, Giordani M.<sup>1</sup>, Dogan M.<sup>2</sup> & Dogan A.U.<sup>3</sup>

1. Department of Earth, Life and Environmental Sciences, University of Urbino, PU. 2. Geological Engineering Department, Hacettepe University, Beytepe, Ankara, Turkey. 3. Department of Chemical and Biochemical Engineering & Center for Global and Regional Environmental Research, University of Iowa, Iowa City, IA, USA.

Corresponding email: [michele.mattioli@uniurb.it](mailto:michele.mattioli@uniurb.it)

Keywords: Lessini, zeolites, erionite.

In the Lessini Mounts a volcanic activity developed from the late Paleocene to the late Oligocene (De Vecchi & Sedeà, 1995) with the emplacement of submarine and subaerial lava flows and tuffs. These rocks (basanites, alkali-basalts, transitional basalts to tholeiites) are often deeply weathered, with vesicles and fractures filled by secondary minerals. These are mainly represented by zeolites such as phillipsite, harmotome, chabazite, analcime, gmelinite, natrolite, offretite and erionite. Recently, erionite has been carefully investigated because of its link to malignant mesothelioma (Dogan et al., 2006; Bertino et al., 2007). As a consequence, erionite has been classified as a Group I Human-Carcinogen by the International Agency for Research on Cancer and this makes it the most carcinogenic naturally occurring fibrous mineral known. In this work, we present morphological and compositional data on erionite crystals recently discovered in the Lessini Mts. (Mattioli et al., 2008).

From a morphological point of view the studied samples show two different types of erionite. (1) Prismatic to acicular crystals ended by short hexagonal prisms of about 15  $\mu\text{m}$  in diameter, whereas the main body of the crystals is extremely thin (diameter is 5  $\mu\text{m}$ ), is characterized by an excellent, prismatic cleavage and devoid of any geometry. (2) Fibrous crystals with diameter <1  $\mu\text{m}$  and a length up to about 50  $\mu\text{m}$ ; these fibers are flexible and tend to intimately aggregate in parallel bundles of up to 10  $\mu\text{m}$  in diameter. Erionite of both types show a great tendency to break down into fibers, which are potentially extremely pathogenic upon inhalation. In the type (1) the majority of the measured fibers is in the range 2-30  $\mu\text{m}$  in length and 0.1-0.4  $\mu\text{m}$  in diameter, whereas in the type (2) almost all of the measured fibres are 50 to 60  $\mu\text{m}$  in length and <0.1  $\mu\text{m}$  in diameter. The EDS spectra acquired on the bundles of fibers revealed the occurrence of Ca, Mg, Na, and K as extra-framework cations. In addition, a small amount of Fe was detected. Preliminary semi-quantitative analyses in the type (1) fibers pointed out that chemical composition differs depending on the analytical point, indicating a significant inhomogeneity of the sample.

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## Si, Al and Zn biomineralization processes in plant roots of *Euphorbia pithyusa*

Medas D.<sup>1</sup>, Casu. M.A.<sup>2</sup>, Iadecola A.<sup>3</sup>, Giannoncelli A.<sup>4</sup>, Meneghini C.<sup>5</sup>, Lattanzi P.<sup>1</sup> & De Giudici G.\*<sup>1</sup>

1. Dipartimento di Scienze Chimiche e Geologiche - Università di Cagliari. 2. Pharmacology - UOS of Cagliari - Scientific and Technological Park of Sardinia POLARIS, Pula. 3. ESRF - European Radiation Synchrotron Facility. 4. TwinMic beamline, ELETTRA synchrotron, Trieste. 5. Physics Department - University of Roma Tre- Rome.

Corresponding email: [gbiudic@unica.it](mailto:gbiudic@unica.it)

Keywords: biomineralization, soil minerals, phytoremediation.

In the abandoned mine of Ingurtosu (SW Sardinia, Italy) a field experimental trial was carried out in the frame of the UMBRELLA project (7FP EU). The idea of this project was to couple microorganisms with plants to favour metals accumulation in plants and reduce the effects of metal pollution in soils of heavy metals contaminated sites. *Euphorbia pithyusa* was selected as an endemic pioneer plant. About two years after the beginning of the experiment, exploration of the processes occurring at the soil-root interface was carried out by combining X-ray fluorescence mapping (S-XRF) and X-ray absorption spectrometry (XAS) to X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Transmission Electron Microscopy (TEM). We observed that Si and Al are mainly concentrated in the epidermis of the roots forming a rim that represent a physico-chemical barrier against organic and inorganic stresses. In addition, Si is able to bind Zn by forming an amorphous Zn-silicate in the epidermis zone. This process leads to the decrease of Zn concentration from the epidermis to the internal part of the root, where Zn is bonded to other Zn atoms. In the case of Fe, the Si-Al rim seems to be more efficient and, as observed in LEXRF maps, Fe is mainly concentrated in the external zone of the roots. EXAFS analysis reveals that the coordination environment of Fe is comparable to that of hematite. The exact cause of Fe precipitation around roots or in the epidermis zone is unknown, but the oxidizing activity of roots, together with the action of microorganisms, is thought to be involved. Si and Al particles of the rim can act as a nucleus for hematite precipitation (Batty et al., 2000) that, in turn, could act as a barrier against metals penetration.

Although Si and Al are not regarded as essential nutrients and the later is an important growth-limiting factor (Rout et al., 2001), obtained results suggest that these elements are fundamental for controlling metal migration through the roots, and their beneficial function for plant need to be reassessed. The addition of microorganisms to the soil at the Ingurtosu mine seems to have no effect on biominerals features, and on Zn and Fe speciation. Our results can be useful for environmental science because biomineralization in plants can lead to development of specific phytostabilization techniques, reducing the mobility of the contaminants and prevents their migration to the groundwater or air, thus decreasing bioavailability for entry into the food chain.

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## X-ray absorption spectroscopy study of the structural environment of iron in mineral fibers

Pollastri S.\*<sup>1</sup>, Gualtieri A.F.<sup>1</sup>, D'Acapito F.<sup>2</sup>, Trapananti A.<sup>2</sup> & Colantoni I.<sup>3</sup>

1. Dipartimento di scienze Chimiche e Geologiche, Università degli Studi di Modena e Reggio Emilia, Modena. 2. CNR-IOM-OGG c/o ESRF, GILDA CRG, Grenoble, France. 3. Dipartimento di Fisica, Università di Roma "Tor Vergata", Roma.

Corresponding email: [simone.pollastri@unimore.it](mailto:simone.pollastri@unimore.it)

Keywords: Mineral fibers, structural environment of iron, X-ray absorption spectroscopy.

The oxidation state and chemical environment of iron in mineral fibers are crucial factors to assess the bio-chemical activity induced by surface iron activity, which is known to be a primary cause of toxicity as it produces free radical release, mobilization by chelators and iron-catalyzed reactions (Hardy & Aust, 1995). It was observed that antioxidant enzymes and strong iron chelators decrease the toxicity of mineral fibers in cell cultures and experimental animals, strongly suggesting that a crucial role might be played by iron-generated active oxygen species (Fubini & Mollo, 1995). In this context, in order to understand the relationship between structural environment of iron and fibers' pathogenicity, XAFS spectra at the iron K-edge of eight mineral fibers of social and economic importance (chrysotiles, amphiboles and erionite, systematically investigated for the first time) were collected at the BM08 GILDA-CRG beamline (ESRF, Grenoble, France). Both the XANES and EXAFS region were investigated; for all experiments, energy calibration was achieved using iron foil as reference and the position of the first inflection point was taken at 7112 eV. The results show that there is no predominant oxidation state of the iron while the octahedral coordination seems to be prevalent chemical environment, in agreement with literature data (Morgan et al., 1971; Roque-Malherbe et al., 1990; Hardy & Aust, 1995). The present work is within the context of a systematic study of main mineral fibers, in order to get a better understanding of the processes that are the basis of cyto- and geno-toxicity of these compounds, with the final aim to get a conclusive comparison of the toxicity of chrysotile and amphibole asbestos and refute the "amphibole hypothesis" (only amphibole asbestos is hazardous to human health); by ruling out this "hypothesis" there is basically no scientific support to the use of chrysotile asbestos. Within this scenario, the results of this project should be of help to make aware the scientific communities worldwide of the actual toxicological potential of these minerals fibers, and especially that of chrysotile, in order to supply objective tools to the World Organizations to test the "amphibole hypothesis" and decide on the ban of asbestos worldwide.

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## The quality of sediments in the Mt. Amiata Hg district (southern Tuscany)

Rimondi V.\*<sup>1</sup>, Benvenuti M.<sup>1</sup>, Benvenuti M.M.<sup>1</sup>, Buccianti A.<sup>1</sup>, Costagliola P.<sup>1</sup>, Di Benedetto F.<sup>1</sup> & Lattanzi P.<sup>2</sup>

1. Dipartimento di Scienze della Terra, Università di Firenze. 2. Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari.

Corresponding email: [valentina.rimondi@unifi.it](mailto:valentina.rimondi@unifi.it)

Keywords: Mercury, Mt. Amiata, multivariate analysis, sediment quality.

The establishment of adequate Sediment Quality Guidelines (SQGs) is a crucial point of the recent debate among the EU member states. In most jurisdictions, there is an increase awareness that proper SQGs for contaminants should be site-specific, and should rely on background concentrations. Accordingly, a detailed characterization of background conditions is fundamental in mineralized areas, where background levels of contaminants may exceed the SQGs proposed for other (non-mineralized) locations.

The Mt. Amiata Hg district (southeastern Tuscany, Italy) hosts the fourth largest Hg producing region worldwide, which was active up to 1970s. In this region, anthropogenic contamination overlaps on the natural Hg (and associated As) anomaly. In the present work, sediments of different age (pre-mining, syn-mining and post-mining) were sampled in order to: (i) reconstruct the history of Hg(As) diffusion in this region; (ii) identify a geochemical marker for sediment quality; (iii) establish the Hg(As) background. The chemical dataset (major elements and Hg and As concentrations) was explored by multivariate analysis by taking into account the properties of compositional data. This analysis showed that pre- and post-mining sediments can be distinguished on the base of the  $Al_2O_3/CaO$  ratio. Accordingly, a progressive enrichment in CaO was shown as sediments become younger in age (up to  $Al_2O_3/CaO \approx 1$  for syn- and post-mining sediments). Furthermore, Hg in the Mt. Amiata sediment is not randomly distributed, but it is inversely correlated to CaO ( $R^2 = 0.87$  after that the terms of the subcomposition Hg- $Al_2O_3$ -CaO were transformed in two coordinates of the real space), increasing up to two orders of magnitude between pre- and syn-mining sediments. Common to most of Hg mines worldwide, final roasted wastes (calcines) at Mt. Amiata are enriched in: (i) CaO, due to the calcination process (lime addition), and (ii) Hg, due to the inefficiency of the Hg extraction process. Then, natural weathering of discarded materials caused CaO and Hg enrichment of post- and syn-mining sediments at Mt. Amiata. According to these results, CaO may act as a proxy for Hg in this area, representing a geochemical marker of calcine weathering and an easy way to evaluate sediment quality.

On the base of Hg contents in pre-mining sediments, a preliminary Hg regional background of 2-6  $\mu g/g$  is suggested, which largely exceeds the Hg established contamination level for soils in Italy (1  $\mu g/g$ ).

## **Background levels of potentially toxic elements in ultramafic soils from the Voltri Unit: a mineralogical and geochemical approach**

Solimano M.\*<sup>1</sup>, Marescotti P.<sup>1</sup>, Crispini L.<sup>1</sup>, Beccaris G.<sup>2</sup>, Scotti E.<sup>2</sup>, Fornasaro S.<sup>1</sup>, Orecchia M.<sup>1</sup> & Lucchetti G.<sup>1</sup>

1. Dipartimento di Scienze della Terra, dell'Ambiente e della Vita - Università di Genova. 2. Agenzia Regionale per la Protezione dell'Ambiente Ligure (ARPA-Liguria), Genova.

Corresponding email: [monica.solimano@unige.it](mailto:monica.solimano@unige.it)

Keywords: background values, ultramafic soils, ecotoxic metals.

Ultramafic soils are characterized by the presence of several potentially toxic elements (PTE's; such as Cr, Co, and Ni) that commonly exceed residential and industrial concentration limits according to Italian laws (D.M. 471/1999; D.Lgs 152/2006). Therefore, the determination of the background levels and baseline values of PTE's within serpentinitic and peridotitic soils is of paramount importance in order to evaluate the potential risk of contamination for ecosystems as well as to distinguish between lithogenic and anthropogenic inputs. With this work we investigated the mineralogy, the mineral chemistry, and the bulk chemistry of undisturbed soils and associated parent rocks from four selected sites occurring in the "Bric del Dente Serpentinite" and "Monte Tobbio Peridotite" Formations (Voltri Unit, Ligurian Alps). Selected metal and semimetal concentrations (V, Cr, Co, Ni, Cu, Zn, As, Cd, Sb, Pb) were assessed by ICP-OES at the ARPA-Liguria laboratories according to the EPA-3050B and EPA-6010 methods. The mineralogy and the mineral chemistry of soils and rocks have been determined by means of optical microscopy (transmitted- and reflected light) and electron microprobe analyses (WDS). The bulk chemistry analyses evidenced very high concentrations of Cr (up to 3020 ppm in rocks and 1269 ppm in soils), Ni (up to 1855 ppm in rocks and 1041 ppm in soils), Co (up to 85 ppm in rocks and 64 ppm in soils), and V (up to 199 ppm in rocks and 39 ppm in soils). The mineralogical results showed that most of the Cr is contained within primary Fe-oxides and spinels (mainly magnetite and chromite). Olivine and serpentine group minerals are the main Ni-bearing minerals though non-trascurable Ni concentration have been also detected in Fe-oxides and Ni-sulphides. Among the other identified primary minerals only chlorites are characterized by significant, though very variable, amounts of Co, V, Ni. In general, most of the detected metal-bearing mineral species resulted completely unaltered either in rocks and soils evidencing their resistance to weathering and their tendency to remain as stable residual minerals within soils. Secondary authigenic minerals in soils are mainly represented by Fe-oxides and -oxyhydroxides and clay minerals. In general they contain relative small amounts of PTE's if compared to primary minerals and cannot be considered as the main source for the bulk metal content of soils. These preliminary results evidenced that all the studied rocks and soils have a baseline values of Cr, Ni, Co, and V well above (up to one order of magnitude) concentration limits of the Italian laws for industrial and residential sites. These baseline values should be considered as the natural background levels of the studied soils since most of the metals are related to the residual mineral species derived from the parent rocks. Further studies are in progress, through leaching experiments, to determine the relative mobility and bioavailability of the studied metals.

## Asbestos fate in ACM and lungs: a comparative characterization

Vigliaturo R.<sup>\*1-2</sup>, Harries D.<sup>2</sup>, Pollok K.<sup>2</sup>, Langenhorst T.F.<sup>2</sup>, Capella S.<sup>1</sup> & Belluso E.<sup>1-3</sup>

1. Earth sciences department, University of Torino. 2. Department of Analytical Mineralogy of Micro- and Nanostructures, Friedrich-Schiller University of Jena, Germany. 3. CNR, Institute of Geosciences and Earth Resources, Torino.

Corresponding email: [vigliaturo\\_ruggero@libero.it](mailto:vigliaturo_ruggero@libero.it)

Keywords: Transmission electron microscopy, asbestos, mineral fibers.

In 2006 it has been proposed to introduce the term of “nanosafety”. Nowadays, developments in nanotechnology grow increasingly, with the intention of new useful discoveries and the concern of possible health consequences, some of them have been already experienced by mankind since more than 100 hundred years.

Among these health risks, asbestos cement was invented by Hatschek and patented under the name “Eternit” in 1900. Until now, this technologically exceptional material is used in many countries, however accepting the fatal health consequences created by the disease asbestos. It is evident that many protocols applied to the asbestos problem can be easily exploited to monitor these emerging technologies and new harmful mineral nanoparticle and fiber.

From this perspective, we will analyze the fibers contained in two different matrices: the first type artificial and the second type organic. We have purposely avoided to gather information on the source material, not to influence our judgment or to address the analytical process, as if it were performed on an unknown material. In order to characterize the target materials, we combined different analytical techniques: XRPD, SEM and TEM. Handling the three, depending on what samples gradually reveals.

A sample from an unknown fiber cement sheet roof was characterized, combining X-ray powder diffraction (XRPD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The same was performed on a lung of a eternit factory worker died of mesothelioma, using only TEM because of the sample nature (received already embedded in paraffin).

To the naked eye the ACM sample present two principal component: the cement matrix and the fibrous component. A first investigation through XRPD reveals the possible presence of typical cement phases in the matrix. No fibrous phases has been identified at this point. Having a thought on the production process, we could imagine that the fibers presence in an XRD support is really low in relation to other components. Historically, in asbestos sheet, was recognized a percentage of fibers variable from 10 to 16, randomly distributed in the whole matrix.

Moreover, the sample is heterogeneous powder, multiphase and randomly oriented, all factors that tend to hide the possibility to detect the fibrous component. SEM observation brings in evidence the presence of many fibers bundles distributed in the whole sample and in intimate contact with the matrix components. Going beyond with the TEM, it's possible to identify the fibrous phase combining high resolution (HRTEM) techniques, bright field (BF) imaging and selected area electron diffraction (SAED).

In a preliminary TEM investigation the specimen contained in the lung present partially and totally amorphized fibers, mainly of chrysotile and rare amphibole fibers. These fibers are more sensitive to the beam than the natural ones and seems to be covered by an amorphous shell that shows that the amorphization process starts from the surface and proceed through the core of the fiber.

## Isomorphic substitution in mica: implications on the weathering process

Zalaffi M.S., Brigatti M.F, Elmi C. & Malferrari D.\*

Dipartimento Scienze Chimiche e Geologiche, Università di Modena e Reggio E.

Corresponding email: [daniele.malferrari@unimore.it](mailto:daniele.malferrari@unimore.it)

Keywords: flogopite, alteration, surface.

*Aim of the work.* With this research we have studied the morphological changes, induced by the exposure to acid vapors at controlled temperature, on the surface of selected mica crystals. Specific consideration has been paid to the role of isomorphous substitutions in tetrahedral and/or octahedral sites by bi- and trivalent iron, being this element particularly susceptible to redox reactions.

*Materials and methods.* To model the surface alteration processes it is necessary to start from minerals that, in addition to being well characterized from the crystal chemical point of view, present a large surface and that, at the same time, have a structure comparable to that of other smaller minerals. For this reason, were selected crystals of phlogopite, a trioctahedral mica, with formula  $\text{KMg}_3(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$ , that forms a solid solution with the member annite. In particular were selected crystals that present: i)  $\text{Fe}^{3+}$  replacing the aluminum in tetrahedral coordination (label FLO); ii)  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  only in octahedral coordination (label CZA2d). Natural and acid vapor exposed crystals were characterized by atomic force microscopy (AFM) and scanning electron microscopy (SEM) coupled with Energy Dispersive X-ray Spectroscopy (EDS); it should be pointed out that the measurements were performed on the same face before and after treatment.

*Exposure to oxidising vapors.* The treatment in an oxidising atmosphere was done by exposure to sulfuric acid vapors. In particular the samples, glued on coverslips, were placed inside a desiccator containing 20mL of sulfuric acid, and then was left in an oven at  $75^\circ\text{C}$  for one week. At this temperature value,  $\text{H}_2\text{SO}_4$  partially vaporizes generating also  $\text{SO}_3$  and  $\text{SO}_2$ , rendering the atmosphere strongly oxidizing. It is expected that the oxidation interaction takes place for the most part with hydroxyl groups by tearing them a proton. Secondly, it is possible that occurs a redox between  $\text{Fe}^{2+}$  and the anion  $(\text{SO}_4)^{2-}$ . The divalent iron may oxidize to  $\text{Fe}^{3+}$  donating electrons to the sulfur that could be reduced to sulfide.

*AFM results.*

1) Sample FLO. Natural sample presents on the surface patterns, with almost constant profile, that are no longer recognizable in the sample exposed to acid vapors, where also occurs the appearance of well-defined alteration structures of polyhedral shape.

2) Sample CZA2d. Natural sample presents an irregular surface with a larger number of flaking and cleavage structures compared to the sample FLO. The surface exposed to the acid vapors shows alteration structures, with pseudo-parallel trend, that suggest the presence of cavities that are formed along preferential directions; the depth of these cavities is approximately 1nm and is therefore compatible with the removal of an entire coordination polyhedron (tetrahedron-octahedron-tetrahedron).

The profiles obtained from AFM measurements on sample CZA2d, show that polyhedra formed by the union of rings of six tetrahedra are no longer recognizable on the surface of the exposed sample, unlike what happened in sample FLO subjected to the same oxidizing treatment. This evidence suggests that the process of alteration, locally, may have acted more in depth, thus being more incisive in this type of structure or, conversely, that substitutions in octahedra favor surface alteration processes.

## **SESSIONE S15**

### **Gemstones: from Nature to marketing**

*CONVENORS*

*E. Scandale (Univ. Bari)*

*L. Prospero (IGI – Milano)*

## Val Malenco, Central Alps, Italy: a source of gem materials

Adamo I.<sup>\*1-2</sup>, Bocchio R.<sup>1</sup> & Diella V.<sup>3</sup>

1. Dipartimento di Scienze della Terra, Università degli Studi di Milano. 2. Istituto Gemmologico Italiano, Milano. 3. CNR - Istituto per la Dinamica dei Processi Ambientali, Milano.

Corresponding email: [ilaria.adamo@unimi.it](mailto:ilaria.adamo@unimi.it)

Keywords: Val Malenco, green andradite, nephrite jade, rhodonite, serpentine, clinozoisite.

A distinguish feature of Val Malenco, Central Alps, Italy, is the remarkable number of recovered minerals (more than 250 species), which have attracted the interest of mineralogists since the end of 18<sup>th</sup> century, making the valley renowned at international level. Among the various minerals, some have a significant gemological interest and are used in jewelry as gems or ornamental carvings.

The most notable and one of the best Italian gem material is the green andradite garnet ( $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$ ), known with the varietal name “demantoid” (Adamo et al., 2009). Attractive gemstones have been produced from crystal recovered in asbestos mines hosted by serpentinites and located in a small area, where the most famous localities are: Cengiàsc (including the Sferlùn quarry), Dossi di Francia, Coston d’Acquanegra, Valbrutta, and Al Ross (Bedogné et al., 1993). These asbestos deposits, now closed for safety reasons, are sited at ~1800–2200 m above sea level. The gemological properties, including the characteristic “horse-tail” inclusions (fibrous chrysotile), and the chemical composition (Adr  $\geq 98$  mol%) are typical of serpentinites-related demantoid. Trace of chromium, together with major iron, are responsible for the green color of this gem.

Another interesting gem material is the nephrite jade, discovered at Alpe Mastabia and hosted in a talc-tremolitic orebody, associated with dolomitic marbles (Adamo & Bocchio, 2013). The jade, occurring as intergrowth of fine fibers, is mainly composed of pure tremolite,  $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ , and contains a low concentration of iron, which causes its typical pale green color. The occurrence of other constituents, including calcite, molybdenite and galena, influences the color of the jade.

Gem-quality rhodonite ( $\text{Mn}_3\text{Si}_5\text{O}_{15}$ ) from Val Malenco occurs in the Mn-mineralization at Monte del Forno. Rhodonite has typically a massive aspect, with an attractive pink color (due to Mn). It is always associated with tephroite, spessartine, pyroxmangite, biotite, magnetite, calcite, quartz, and Mn-oxides and hydroxides.

“Noble” serpentine, green and yellowish green in color, composed mainly of lizardite and antigorite (with various amount of calcite, dolomite, brucite, and chlorite) was found at Pizzo Tremogge included in forsterite-bearing marbles. In the same area, precious Mn-rich clinozoisite (clinohulite variety) has also mined for its fine pink color.

Other interesting gem materials from Val Malenco include diopside (green or, more rarely, blue) and Cr-bearing green grossular.

Adamo I. & Bocchio R. 2013. Nephrite jade from Val Malenco, Italy: review and update. *Gems Gemol.*, 49, 98-106.

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Bedogné F., Montrasio A. & Sciesa E. 1993. I minerali della provincia di Sondrio. Valmalenco. Bettini, Sondrio.

## “Noble” serpentine: a case study from Val Malenco, Central Alps, Italy

Adamo I.\*<sup>1-2</sup>, Diella V.<sup>3</sup>, Bocchio R.<sup>1</sup>, Marinoni N.<sup>1</sup>, Mainardi M.<sup>1</sup>, Fontana E.<sup>1</sup> & Rinaudo C.<sup>4</sup>

1. Dipartimento di Scienze della Terra, Università degli Studi di Milano. 2. Istituto Gemmologico Italiano, Milano. 3. CNR-Istituto per la Dinamica dei Processi Ambientali, Milano. 4. Dipartimento di Scienze e Innovazione Tecnologica, Università degli Studi del Piemonte Orientale, Alessandria.

Corresponding email: [ilaria.adamo@unimi.it](mailto:ilaria.adamo@unimi.it)

Keywords: serpentine, lizardite, antigorite, Val Malenco.

Serpentine-group minerals (chrysotile, lizardite and antigorite) are common rock-forming hydrous magnesium phyllosilicates, with ideal chemical formula  $Mg_3Si_2O_5(OH)_4$ . They form under a wide range of temperatures, including Earth surface conditions and hot hydrothermal temperatures (Evans et al., 2013). When characterized by a compact microstructure and fine and uniform colors (generally green), they are used in gemology for ornamental carvings and gems, often referred as “noble” or “precious” serpentine (O’Donoghue, 2006).

In Italy, gem-quality serpentine occurs in various deposits in the Alps and the Apennines. This study aims to provide a gemological and mineralogical characterization of serpentine from Pizzo Tremogge, Val Malenco, Central Alps, which is one of the most known Italian source for “noble” serpentine (Bedogné et al., 1993). At Pizzo Tremogge serpentine minerals are included in forsterite-bearing marbles Paleozoic in age.

The suite of rough and cut gem-quality samples from this locality, kindly provided by Mr. P. Nana (Sondrio, Italy), were investigated by means of gemological analyses, X-Ray Powder Diffraction, EMP chemical analyses, and Raman spectroscopy.

The gemological properties of serpentine from Val Malenco are in the range of typical gem-quality serpentine. In particular, the specimens have all a massive and opaque aspect, with a color ranging from green to yellowish green, sometimes with white veins and black spots. The refractive index, measured by the distant vision method, is about 1.55, whereas the specific gravity ranges from 2.49-2.67, with variations related to the occurrence of other phases. The samples are inert to UV (254 and 366 nm) radiations and have a Mohs hardness of ~4. Four different samples have been analyzed by X-ray powder diffraction and Raman spectroscopy, which are considered the more efficient methods for identifying different species of serpentine. The identified phases are: lizardite, antigorite, calcite, dolomite, brucite and chlorite. In addition EMP analyses allowed us to evidence chemical differences between lizardite and antigorite that mainly arise from the extent of cationic substitution: lizardite is always Al and Fe -enriched (0.10-0.18 and 0.11-0.16 a.p.f.u., calculated on the basis of seven anhydrous oxygens respectively) in respect to antigorite (0.02-0.08 and 0.04-0.08 a.p.f.u, respectively). Minor amounts of Ti (0.001-0.008 a.p.f.u.) and trace amounts of Ca, Cr, Ni, and Zn have been also detected.

The compact and fine-grained microstructure and the typical green color confer to the serpentine from Pizzo Tremogge an agreeable aspect and make it noteworthy as gemological material.

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Bedogné F., Montrasio A. & Sciesa E. 1993. I minerali della provincia di Sondrio. Valmalenco. Bettini, Sondrio.

O’Donoghue M. 2006. *Gems*. 6<sup>th</sup> ed. Butterworth-Heinemann, Oxford, UK.

## Berillium diffusion in treated corundum: analysis and identification

Adamo I.<sup>1-2</sup>, Gatta G.D.\*<sup>1</sup>, Caucia F.<sup>3</sup>, Ntolia V.<sup>1</sup> & Prospero L.<sup>2</sup>

1. Dipartimento di Scienze della Terra, Università degli Studi di Milano. 2. Istituto Gemmologico Italiano, Milano. 3. Dipartimento di Scienze della Terra, Università degli Studi di Pavia.

Corresponding email: [diego.gatta@unimi.it](mailto:diego.gatta@unimi.it)

Keywords: Be-treated corundum, LA-ICP-MS, Single-crystal X-ray diffraction and polarized Raman spectroscopy.

At the end of 2001, unprecedented amounts of saturated orange and orangy pink (the so-called “padparadscha”) corundums became widely available to the worldwide jewelry market. Many studies subsequently revealed that the light element beryllium (Be) had been diffused into a wide range of corundum gems in order to alter/produce their color. The Be diffusion process requires heating at high temperature (over 1750 - 1800°C) in oxidizing atmosphere, using beryllium-bearing additives (chrysoberyl or beryllium oxide). At the present, a full range of colors, including yellow, blue and red, have been produced or altered by Be treatment, sometimes used in combination with traditional heating. The beryllium diffusion process is surely the most broadly applicable treatment to induce coloration in corundum so far achieved, explaining the extraordinary effect on the market. Consequently, the analysis and identification of Be diffused corundum and its separation from untreated or traditionally heated counterpart has become a major issue in the gem trade.

The observation of Be-diffused corundum at optical microscope can result useful for identification. Diagnostic evidence is an anomalous color distribution, characterized by a layer of surface-conformal color induced by Be-diffusion, which however is not visible when the corundum was colored throughout. Other microscopic evidences indicative of an exposure to very high temperatures, as those typically used for Be-diffusion, are features of inclusions significantly altered, melted or internally recrystallized during the treatment (e.g., highly altered zircon inclusions with whitish crusts of baddeleyite). Spectroscopic techniques (e.g. UV-Vis-NIR, IR, Raman) have been employed to provide identification criteria, but they do not allow a separation from the natural or traditionally heated corundum. At the present, the only reliable identification of Be-diffused corundum is based on the detection of trace levels of beryllium, by means of advanced chemical analyses, such as secondary ion mass spectrometry (SIMS), laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS), and laser-induced breakdown spectroscopy (LIBS). The detection of Be amounts >1 wt ppm (generally 4-15 wt ppm, rarely up to 50 wt ppm) allows us to surely identify the stone as Be-diffused and the laboratory report should state that the gem shows “indication of heating and color induced by diffusion of a chemical element from an external source”. Single-crystal X-ray diffraction and polarized Raman spectroscopy were used to provide additional identification aids, but structural parameters (i.e., cell parameters, bond distance, thermal displacement parameters) and Raman spectra do not change significantly between Be-diffused and untreated specimens.

## Green andradite (demantoid variety) from Muslim Bagh, Zhob District, Balochistan, Pakistan: gemological and mineralogical characterization

Adamo I.<sup>1-2</sup>, Diella V.<sup>3</sup>, Bocchio R.\*<sup>1</sup>, Salvini S.<sup>1</sup> & Schmetzer K.<sup>4</sup>

1. Dipartimento di Scienze della Terra, Università degli Studi di Milano. 2. Istituto Gemmologico Italiano, Milano  
3. CNR-Istituto per la Dinamica dei Processi Ambientali, Milano. 4. Petershausen, Germany.

Corresponding email: [rosangela.bocchio@unimi.it](mailto:rosangela.bocchio@unimi.it)

Keywords: andradite, demantoid, Pakistan.

Andradite garnet (Ca<sub>3</sub>Fe<sub>2</sub>Si<sub>3</sub>O<sub>12</sub>) is a rock-forming mineral, typically found in metamorphic rocks, such as serpentinites and skarns. Green andradite, often described with the varietal name “demantoid”, represents one of the most appreciate and precious gemstones among the garnet group minerals, due to its color, brilliance, and rarity.

The traditional green andradite sources are Russia and Italy (Val Malenco, Central Alps), whereas recently new commercially important deposits were found in Madagascar, Iran, Pakistan (Kaghan Valley), and Namibia (Adamo et al., 2011).

Recently, gem-quality green andradite crystals indicated to come from Muslim Bagh, Balochistan (Pakistan) are occasionally available in the Peshawar gem market. The transparent and fine gem-quality dodecahedral crystals show an attractive fancy green color, although they are very small, rarely exceeding 1 ct in weight. The Muslim Bagh area shows a nearly complete ophiolite sequence, mainly composed by peridotites (harzburgite and dunite), partially to completely serpentinitized. Many outcrops of dunites contain podiform chromite deposits (Kakar et al., 2013).

A suite of gem-quality samples from this locality, provided by the collector S. Hanken (Germany), has been investigated by means of standard gemological methods, SEM-EDS, and EMP chemical analyses. All the samples (0.18-0.98 ct) are transparent, with a fancy medium green color. They are all single refractive with moderate to strong anomalous birefringence and refractive indices >1.79. The measured density ranges from 3.80 to 3.90 g/cm<sup>3</sup> and the gems are inert under ultraviolet radiation. These gemological properties are characteristic of andradite, demantoid variety. The samples contain “horse-tail” inclusions and opaque whitish crystals, chemically identified as chrysotile and antigorite, respectively. Opaque blackish crystalline inclusions of chromium-bearing magnetite are also present. The specimens show various growth structures and, in a few cases, dodecahedral twinning. The chemical composition of garnet results in almost pure andradite (Adr<sub>96</sub> mol%, generally ~98-99 mol%), with minor amounts of Mg, Al, Cr, Ti, V, and Mn. In particular, chromium ranges from below detection limit to maximum 0.92 wt% as Cr<sub>2</sub>O<sub>3</sub>, this latter measured near the Cr-rich magnetite inclusions. Chromium causes, along with the major constituent Fe<sup>3+</sup>, the bright green color of this andradite, such as typical for demantoid associated with serpentinites (Bocchio et al., 2010).

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## **Mogok: Mysteries and Secrets of the Legendary Valley of Rubies**

Barlocher F.\*

Minerals and gemstones dealer.

Corresponding email: [federico.barlocher@gmail.com](mailto:federico.barlocher@gmail.com)

Keywords: Mogok, gemstones, Myanmar.

This presentation will provide a comprehensive update about the most famous and mysterious colored gemstone gem mining district in the world. Videos and photographs that have never been released to the public will be shared with attendees so that a better understanding of the source, from a miner's perspective, will develop. This aspect of gemology, whilst not scientific in form will nevertheless be invaluable to those in attendance whilst a little humorous at times. Federico's tour of Myanmar's premier gem source, and certainly the world's foremost natural ruby source, is not to be missed!

## Identification of the cromophores in *Corallium rubrum* gem quality corals by HPLC/UV and <sup>1</sup>H NMR spectroscopy

Bracco S.<sup>1</sup>, Brajkovic A.\*<sup>2</sup>, Fumagalli P.<sup>2</sup>, Fusi P.<sup>3</sup> & Rolandi V.\*<sup>4</sup>

1. Dipartimento di Scienza dei Materiali, Università degli Studi di Milano-Bicocca, Milano. 2. Dipartimento di Scienze dell'Ambiente e del Territorio e di Scienze della Terra, Università degli Studi di Milano-Bicocca, Milano. 3. Dipartimento di Biotecnologie e Bioscienze, Università degli Studi di Milano-Bicocca, Milano. 4. Collegio Italiano Gemmologi, Milano.

Corresponding email: [anna.brajkovic@unimib.it](mailto:anna.brajkovic@unimib.it)

Keywords: *Corallium rubrum*, HPLC/UV, NMR.

Gem corals are technically non-vertebrate biomaterials. They derive from the branched skeletons of the colonies of marine invertebrates (polyps) belonging to the classes Hydrozoa and Anthozoa of the phylum Cnidaria. According to the main taxonomical characteristics, the Anthozoans have been subdivided into two subclasses: Octocorallia (or Alcyonaria) and Hexacorallia (or Zoantharia) (Bayer, 1956). From a compositional point of view, corals are biocomposites with key components of minerals (calcite or/and aragonite) and organic macromolecules. Structural characterization of the chromophore pigments was carried out by means of HPLC combined with UV and MS (Cvejic et al., 2007) and by Raman spectroscopy (Merlin et al., 1986; Rolandi et al., 2005; Fritsch et al., 2008; Brambilla et al., 2012). Nevertheless, the nature of the cromophores in *Corallium rubrum* is still under discussion. *Corallium rubrum* corals live in the Mediterranean Sea and belong to Anthozoa class, subclass: Octocorallia. Their colour varies from dark red to red, orange-pink, bright rosé, pale fresh pink, and sometimes white. The first attempt to determine the chemical composition of the cromophores in the red corals from Marseille revealed the presence of the canthaxanthin carotenoid (Cvejic et al., 2007). Using Raman spectroscopy Fritsch et al. (2008) explained that pigments in *Corallium rubrum* and in other corals are due to unsubstituted polyenes, characterized by the lack of methyl groups in the carbon chain, as already indicated by Merlin et al. (1986). More recently, Brambilla et al. (2012), by means of the ECC theory in Raman spectroscopy, stated that the Raman spectrum of *Corallium rubrum* turns out to be an interesting puzzle because it lies in between the spectra of carotenoids and psyttafulvines (fully de-methylated). Therefore such pigment does not belong to the class of unsubstituted polyenes nor to carotenoids, but it could have a composition with a partially methylated polyenic chain. To confirm and complete such theoretical results, the Authors tested a group of rough specimens of colony skeletons of *Corallium rubrum*. The cromophore pigments were extracted by incubating ground corals in chloroform for 5 days at 4°C, under agitation. By exploiting <sup>1</sup>H NMR spectroscopy the composition of several specimens was investigated. With the purpose to obtain resolved and diagnostic signals, the specimens were further purified by means of HPLC, using a C18 column eluted with acetonitrile/methanol. On the separated pure fractions <sup>1</sup>H NMR spectroscopy was again performed. Results are still under investigation.

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## Colouring mechanisms in natural spinels

D'Ippolito V.\*<sup>1</sup>, Andreozzi G.B.<sup>1</sup> & Hålenius U.<sup>2</sup>

1. Dipartimento di Scienze della Terra- Sapienza Università di Roma. 2. Department of Geosciences- Swedish Museum of Natural History, Stockholm, Sweden.

Corresponding email: [veronica.dippolito@uniroma1.it](mailto:veronica.dippolito@uniroma1.it)

Keywords: Spinel, Colour, UV-VIS-NIR spectroscopy.

Natural minerals belonging to the spinel group are actively sought as gemstones because of their wide range of intense colours, high mechanical resistance and high thermal and chemical stability. Causes of colour in spinels may be different, most of them being related to transition metal ions, their valence and their coordination. However, more complex colouring mechanisms are difficult to characterize and often remain unexplained. A detailed study on the causes of colours in spinels is lacking in literature.

To shed light on the origin of colour in spinels, a large set of about thirty multi-colour natural samples was explored by Electron Microprobe Analysis and UV-VIS-NIR-MIR spectroscopy. On basis of chemical characterization, the analysed spinels exhibit a dominant spinel *s.s.* ( $\text{MgAl}_2\text{O}_4$ ) or gahnite ( $\text{ZnAl}_2\text{O}_4$ ) composition. The different colours do not depend on the end-member composition. In detail, samples having spinel *s.s.* composition show a wide range of colours, while those with gahnitic composition exhibit colours in blue hues. The various colours are caused by different combinations of two or more minor transition metal cations such as  $\text{Co}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$  and  $\text{V}^{3+}$ , occupying tetrahedrally (T) and/or octahedrally (M) coordinated sites in the spinel structure.

Optical spectra of natural spinels were recorded in the UV/VIS to NIR spectral range (32000–2000  $\text{cm}^{-1}$ ). Red, orange and magenta coloured spinels show similar absorption spectra with main absorption bands at  $\sim 25500 \text{ cm}^{-1}$  and  $\sim 18500 \text{ cm}^{-1}$  assigned to spin-allowed *d-d* transitions in  $\text{Cr}^{3+}$  and  $\text{V}^{3+}$  at the M site. When the contents of  $\text{Cr}^{3+}$  predominate over the contents of  $\text{V}^{3+}$ , the spinels appear as red, otherwise they are orange. Magenta spinels with appreciable Cr-contents and secondary amounts of Fe show a red shift of the band at  $\sim 18500 \text{ cm}^{-1}$ , with respect to the red coloured samples.

The pink, blue and dark green spinels, in spite of exhibiting very different colours, show similar absorption spectra characterized by a strong UV-edge absorption at energy  $\gg 30000 \text{ cm}^{-1}$  due to the  $\text{O}^{2-} \rightarrow \text{Fe}^{2+}$  and  $\text{O}^{2-} \rightarrow \text{Fe}^{3+}$  charge transfer transitions and a series of weak absorption bands in the visible range mainly related to spin-forbidden *d-d* transitions of  $\text{Fe}^{2+}$  at the T site. The peak of maximum absorption in the range 20000 and 10000  $\text{cm}^{-1}$  moves from  $\sim 18000 \text{ cm}^{-1}$  for the pink spinels to  $\sim 15500 \text{ cm}^{-1}$  for the green spinels (with the blue spinels showing an intermediate situation) depending on an increase in total iron content and thus also on  $\text{Fe}^{3+}$  content. In fact, the latter interacts with  $\text{Fe}^{2+}$  producing a  $\text{Fe}^{2+}$ - $\text{Fe}^{3+}$  intervalence charge transfer band at 15500  $\text{cm}^{-1}$  in the green samples. The optical absorption of the light blue and blue coloured spinels in the range 18000-15000  $\text{cm}^{-1}$  is strongly influenced by the presence of very low contents of  $\text{Co}^{2+}$  (up to 600 ppm) ordered at tetrahedrally coordinated sites.

## Natural vs. synthetic quartz: review and new data

Gagliardi V.\*<sup>1</sup>, Adamo I.<sup>2</sup>, Caucia F.<sup>3</sup> & Rotiroti N.<sup>2</sup>

1. Istituto Gemmologico Italiano. 2. Dipartimento di Scienze della Terra, Università degli studi di Milano. 3. Dipartimento di Scienze della Terra e dell'Ambiente, Università degli Studi di Pavia.

Corresponding email: [valegagliardi84@gmail.com](mailto:valegagliardi84@gmail.com)

Keywords: quarta, natural, synthetic.

Quartz, and its most important gem quality varieties (amethyst, citrine, smoky...), are widely produced in laboratory. The hydrothermal technique used for this purpose is known since 1905, when Giorgio Spezia, for the first time, was able to produce a lab-grown crystal of quartz.

Since 1970, when synthetic gem quality quartz became commercially available, gemologists had the problem of identifying the origin of the material.

At the present this problem still exists; therefore it is necessary to keep revising the diagnostic criteria for separation and enlarging the natural and synthetic sample database.

A multi-methodological study, resulting from the combination of conventional gemological analysis and other more sophisticated techniques (i.e. infrared spectroscopy, LA-ICP-MS chemical analysis, single-crystal X-ray diffraction), was made in order to provide a review of the methods commonly used for the distinction of natural and synthetic stones.

Some microscopic features, like various crystalline inclusions, polysynthetic lamellar twinning on the Brasil law, the “zebra-stripe” fluid inclusions, provide evidence of the natural origin.

Synthetic samples, instead, can be distinguished by the presence of seed-plate and “bread-crumbs” inclusions.

In the case of flawless stones, more advanced analytical techniques are helpful.

The presence of the infrared absorption band at  $3595\text{ cm}^{-1}$  is considered the most consistent feature of natural origin. The chemical analysis by LA-ICP-MS allow us to detect a gallium enrichment in natural quartz compared to its synthetic counterpart. Also a significant cobalt content ( $>30\text{ ppm}$ ) and high concentration of potassium ( $>1000\text{ ppm}$ ) are typical of synthetic citrine.

In addition some preliminary results from single-crystal X-ray diffraction show that there are slight, but systematic, difference between the unit-cell parameters of natural and lab-grown amethyst [average volume  $113.12(2)\text{ \AA}^3$  in natural vs.  $113.23(2)\text{ \AA}^3$  in synthetic] and citrine quartz [average volume  $113.03(2)\text{ \AA}^3$  in natural vs.  $113.16(2)\text{ \AA}^3$  in synthetic].

The separation of natural vs. synthetic quartz is possible in most of the cases using a combination of various analytical techniques.

We are currently increasing our database with chemical, crystallographic and spectroscopic features of natural and synthetic quartz in order to provide a protocol for a non-ambiguous identification.

## On the state of the art of synthesis processes of colored gems: An Overview

Gagliardi V.\*

Istituto Gemmologico Italiano.

Corresponding email: [valegagliardi84@gmail.com](mailto:valegagliardi84@gmail.com)

Keywords: synthetis, melt, solution.

In this contribute, we will present an overview on the state-of-the-art of the synthesis protocol of the main colored gems. Synthetic gem crystals have been manufactured since the late 1800's, and their production is often marked by a need for them in industrial applications outside of the jewelry industry. During the last century, researchers have developed a number of different ways to create synthetic gem materials in the laboratory. Most of these methods fall into two major categories: melt or solution. In melt processes, the chemical composition of melt is the same as the composition of the resulting crystal. In solution processes, the solution or melt has chemical composition than that of the resulting crystal. Constituents are dissolved in the solution or melt at high temperature, and the crystal forms initially on a seed crystal as the melt temperature is lowered. The three most important synthesis processes from melt are: 1) the flame fusion (Verneuil method), 2) the "pulling method" (Czochralsky method) and 3) the floating zone method. The flame fusion is the least expensive and most common way to make gems such as synthetic corundum and spinel. Gems synthesized by "pulling method" include e.g. corundum and alexandrite. The floating zone method makes possible to create synthetic corundum. The two most important synthesis processes from solution are: 1) the flux-growth and 2) the hydrothermal growth. Some synthetic gems, e.g. emerald, ruby, sapphire, alexandrite and spinel (red and blue) can be created through a flux-growth method. The hydrothermal growth process is slow and expensive, but it is one of the best method to create emerald, aquamarine, red and blue beryl, quartz, or colored corundum.

In the market, gemstones are often available without any gemological report, leaving open questions about their origin (i.e., natural, synthetic). As synthetics for jewelry applications can be "made to order", they are likely to be much less rare than natural gems of equal size, clarity and saturation of color. Only by an accurate gemological investigation is possible to distinguish natural and synthetic stones and, in addition, the synthesis protocols among those previously described.

## Natural and enhanced colours in natural and synthetic corundum. Is it always possible to detect them?

Greggio L.<sup>1</sup>, Musa M.\*<sup>1</sup>, D'Amico F.<sup>1</sup>, Gori L.<sup>1</sup>, Passera E.<sup>1</sup>, Tagliapietra R.<sup>2</sup>, R. Navone<sup>3</sup>, Croce A.<sup>4</sup> & Rinaudo C.<sup>4</sup>

1. GECI - Gemological Education Certification Institute. 2. Renishaw S.p.A. 3. R.A.G. di Raffaella Navone. 4. Dipartimento di Scienze ed Innovazione Tecnologica, Università degli Studi del Piemonte Orientale.

Corresponding email: [maya.musa@geci-web.com](mailto:maya.musa@geci-web.com)

Keywords: micro-Raman Spectroscopy, heat treatment, OH defects.

Corundum, especially rubies, are some of the most important gems in the nowadays gemstone trade.

Due to their high demand, frequently extracted stones that do not show the most appreciated characteristics, undergo to different treatments to improve color and clarity: heat treatment, lattice diffusion and Be-diffusion treatment, fractures Pb-glassy-filling. These treatments are common for corundum and well known in literature. Recently, Pb+Co glassy-filled treated blue sapphires have been submitted to several gemological laboratory, engendering many discussions at international level and especially about nomenclature problems, because the color is due to Cobalt.

One of the requests to the gemological laboratory, is to reveal the geographic origin (Bgasheva T.V., et al., 2012; Pattamalai K. & Hansawek R., 2007). However some of these treatments, like heat treatment or Be-diffusion, can significantly modify the spectroscopic information (i.e. Uv-Vis/NIR spectrum) and make the data collection difficult. Moreover both treatments can be quite difficult to be proved with standard gemological tests. For example, in some cases after heat-treatment we can observe an alteration in the intensity of OH-defect vibrational absorption band by FTIR spectroscopy (Beran & Rossman 2006), but the interpretation of the data is ambiguous, due to the fact that this alteration is closely related with the treatment environment (oxidative or reductive).

The aim of the present study is the opportunity to characterize, with non-destructive analytical methods, the colors of natural stones and treated corundum.

We analyzed several different stones: natural rubies, blue sapphires, yellow corundum and polychrome corundum, each and all untreated, with different geographic and geologic origin. We perform different tests and, particularly, we applied micro-Raman spectroscopy to evaluate the possibility of characterization of the natural chromophore group, responsible of the different colors of the analyzed stones. All data have been compared with those collected from heat treated and Be-treated corundum as well as from synthetic corundum, with different colors.

Moreover, to complete the spectroscopic set of data, FTIR spectroscopy was applied to the characterization OH-defect absorption, with the aim to compare untreated vs treated stones with the same geological origin.

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Bgasheva T.V., Ahmetshin E.A., Zharikov E.V. 2012. Heat treatment enhancement of natural orange-red sapphire, *Advances in materials science*, 12, No. 2 (32).

Pattamalai K. & Hansawek R. 2007. Heat treatment of sapphires from Ilkaka-sakaraha. GEOTHAI'07 International Conference on Geology of Thailand: Towards Sustainable Development and Sufficiency Economy.

## Characterization of the new gemstone Pezzottaite $\text{Cs}(\text{Be}_2\text{Li})\text{Al}_2\text{Si}_6\text{O}_{18}$

Lambruschi E.\*<sup>1</sup>, Gatta G.D.<sup>2-3</sup>, Adamo I.<sup>2</sup>, Bersani D.<sup>1</sup>, Salvioli-Mariani E.<sup>1</sup>, Lottici P.P.<sup>1</sup> & Pezzotta F.<sup>4</sup>

1. Dipartimento di Fisica e Scienze della Terra-Università di Parma. 2. Dipartimento di Scienze della Terra-Università di Milano. 3. CNR – Istituto di Cristallografia Bari. 4. Dipartimento di Mineralogia- Museo di Storia Naturale di Milano.

Corresponding email: [erica.lambruschi@difest.unipr.it](mailto:erica.lambruschi@difest.unipr.it)

Keywords: Pezzottaite, Cs-beryl, chemical analysis, single crystal X-ray diffraction.

Pezzottaite is a rare Cs-bearing mineral with ideal composition  $\text{Cs}(\text{Be}_2\text{Li})\text{Al}_2\text{Si}_6\text{O}_{18}$ , discovered in November 2002. It is considered as a member of the “beryl group”, along with beryl *sensu-stricto* ( $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ ), bazzite ( $\text{Be}_3\text{Sc}_2\text{Si}_6\text{O}_{18}$ ), stoppaniite ( $\text{Be}_3\text{Fe}_2\text{Si}_6\text{O}_{18}$ ) and indialite ( $\text{Mg}_2\text{Al}_3(\text{AlSi}_5\text{O}_{18})$ ).

We have performed a multi-methodological study of pezzottaite (sample from Ambatovita, central Madagascar), highlighting the main differences with Cs-rich beryl (sample from Monte Capanne, Isola d’Elba, Italy). The two samples have been characterized by electron microprobe analysis in wavelength dispersive mode (EMPA-WDS), single-crystal X-ray diffraction and Raman spectroscopy (Gatta et al., 2012; Lambruschi et al., 2014).

Chemical analysis showed an high amount of cesium ( $\text{Cs}_2\text{O}$  12.91 wt%) for pezzottaite with respect to Cs-beryl ( $\text{Cs}_2\text{O}$  1.27 wt%).

As regards the crystal structure, the pezzottaite has a trigonal symmetry (space group  $R3c$  with  $a\sim 15.9$  and  $c\sim 27.8$  Å), while beryl is hexagonal (space group  $P6/mcc$ , with  $a\sim 9.2$  and  $c\sim 9.2$  Å).

The Raman spectrum of pezzottaite over the extended region  $100\text{--}3650\text{ cm}^{-1}$  was collected for the first time, and compared with the spectrum of Cs-beryl. Cs-beryl shows only an intense peak at  $3604\text{ cm}^{-1}$ , ascribable to  $\text{H}_2\text{O}$  stretching vibrations. In the pezzottaite sample, two weak Raman bands at  $3590$  and  $3545\text{ cm}^{-1}$  are observed, which could be assigned to the fundamental  $\text{H}_2\text{O}$  or OH stretching vibrations respectively, despite the mineral should be nominally anhydrous. The Raman spectra are useful to distinguish the type of  $\text{H}_2\text{O}$  channel (i.e., type “I” or type “II”) and then to evaluate the presence of alkali in the channels. In addition, the Raman spectrum of pezzottaite shows two intense and characteristic bands at  $111\text{ cm}^{-1}$  and  $1100\text{ cm}^{-1}$ , which are not present in the beryl spectrum.

The use of a non-destructive technique like Raman spectroscopy provides a quick and inexpensive protocol to distinguish between beryl and pezzottaite.

Gatta G.D., Adamo I., Meven M. & Lambruschi E. 2012. A single-crystal neutron and X-ray diffraction study of pezzottaite,  $\text{Cs}(\text{Be}_2\text{Li})\text{Al}_2\text{Si}_6\text{O}_{18}$ . *Phys. Chem. Minerals*, 39, 829–840.

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## Collector gemstones: their evolution, their rarity

Macri M.\*

Dipartimento di Scienze della Terra - Sapienza università di Roma.

Corresponding email: [michele.macri@uniroma1.it](mailto:michele.macri@uniroma1.it)

Keywords: gemstones, collector.

We could spend hours talking about the crisis that has mined the gems and jewelry market, or about the difficulties in finding top quality untreated gemstones, or about the diffusion of new treatments and simulants that are compromising the confidence of gems consumers... but we prefer to talk about something else! We prefer to illustrate a brilliant and innovative gemstone approach, to show a new niche in the gemological field, to tell a beautiful story concerning original and natural gemstones, to report a way to survive in this chaotic gemological jungle.

A decade ago the 90% of gem and jewelry market belonged to the diamond, the 9% to ruby, sapphire, emerald and pearl, and the remaining part was shared by twenty other stones. There was also a very small niche of gem collectors interested in maybe other eighty faceted gems. Today, by attending international mineralogical and gemological exhibitions, surfing on internet and reading the major gemological magazines, it is possible to count more than 600 mineral species faceted as gemstones. To better understand this changing in gem market, we have to know why a mineral usually can't be faceted: 1) It is too ugly, 2) the existing rough material is too small to be faceted, 3) the cut is too difficult, 4) there is not a buyer for the gem.

The number 1) does not deserve any comment: if a mineral was not enough attractive ten years ago, then is also not attractive today, and it won't be cut; also point 2) is not responsible for the demographic explosion of new gems, it is true that new minerals have been discovered in the last 10 years, but the new minerals that could be used in gemology are less than ten. So we need to focus more carefully on the points 3) and 4). At the present the faceters improved the cutting techniques and are able to facet materials that couldn't cut few years ago: it is actually possible to see around amazing gems of sulphur, barite, apophyllite, cerussite, Celestine, halite and other minerals really uncommon as precious stones! But someone had to buy these unusual gemstones, that's the meaning of point number 4.

Many gem and jewels collectors already had in their collections all the most famous stones and were looking for something else. This, combined with the difficulty in finding amazing natural stones, untreated, convinced them and the sellers to place on the market different materials; so is actually possible to find in many jewelries earrings and pendants mounting trapiche emeralds or dinosaur bones!

Minerals as benitoite, hackmanite, vayrynenite, taaffeite, jeremejevite which were used only in endless conversations between systematic mineralogy addicted, will be the subject of a gemological presentation.

Believe it or not! During this gemological presentation, there will be also discussed minerals as calcite, barite, cerussite, celestine, halite and sulphur, minerals that have been recently faceted due to the improvements in cutting techniques. There will be also presented new gemstones with optical effects and rare inclusions, that appeared in the gem market to supply the growing demand of the gemstones collectors: color-change diaspore, 12 rays star corundum, reversed trapiche emeralds, quartz with amazing inclusions, rainbow garnet and many other unique gemstones.

## Gem production and gem-market in Madagascar in recent years

Pezzotta F.\*

Museo di Storia Naturale, Milano.

Corresponding email: [fpezzotta@yahoo.com](mailto:fpezzotta@yahoo.com)

Keywords: Madagascar, gem-mining, gem-market.

Madagascar experienced in recent years a period of political instability, consequent to a coup d'état in 2010, and the formation of a "transitional" government up to December 2013, when new democratic elections occurred. Because of such political troubles, the mining sector in Madagascar suffered administrative uncertainty, with the result that many gem-mining and gem-trading companies left the country and productions diminished. Security problems in the country, with armed groups of bandits, sometimes connected with the militaries, increase the risk of mining and trading gem in the field and outside towns. Nevertheless, the I.G.M (Gemological Institute of Madagascar), created in 2003 by a project financed by the world Bank, and directly connected with the Mining Ministry, remained active and it represents a reference point for gemology teaching and gem-testing in the island. Moreover, after the recent elections and the establishment of a government recognized by the international community, many Asian, European and African companies of the gem-trading sector returned back to Madagascar renewing their activity. Here is the information about gem-discoveries, mining and trading in Madagascar in the last years: - The production of sapphires of many different colors, including blue, pink, *geuda*, etc., and many associated gemstones, continued in the last years in the large Ilakaka deposit, in southern Madagascar. Most of the mechanized operations stopped and several tens of thousand miners, distributed over an area of several hundreds square kilometers, are still working with primitive and manual tools. Most of the production (if not all) leave Madagascar to be cut, heat treated, and traded in Bangkok. - Sapphires and ruby, even in rough stones of large size, were discovered at the beginning of 2011 at Ididy, in a remote area covered by rain-forest between Andilamena and Tamatave, in central-east Madagascar. - Much less production of corundum gem-varieties occurred in the last years in some classic or relatively new deposits such as Ambondromifehy (basaltic sapphires), Vatomandry, Maroloambo and Andilamena (ruby), Andranondambo and Ranotsara (sapphires). - New discoveries of high quality aquamarine occurred in the last years in: Fidirana (2010, west of Betafo); Ambatofotsy-Carolle (2011, north of Betafo); Vangaindrano (since 2012, typical blue-green color, heat-treated to produce a very nice blue color). - Very significant production (over 25 tons) of low grade multicolored tourmaline, suitable for the Indian market, occurred in 2011 and 2012 in Ikalamavony. Carving qualities mostly of red color were produced in Tsitondroina (2012-2013), Valozoro (2009-2010), Nanidhizana (2008), and Vohitrakanga (2010-2013). Very limited gem-tourmaline production occurred in the Ikalamavony area and in the Sahatany valley. - Demantoid production, after the huge production occurred after the discovery in 2009, diminished greatly up to rather no production in 2013. Future of the mining activity at the place is at present uncertain. - All the other classic gemstones of Madagascar (e.g. emerald, alexandrite, morganite, danburite, kunzite, scapolite, cornupine, moonstone, iolite, marolambo garnet, mandarin garnet, malaia garnet, tsavorite, green-blue apatite, opal, amethyst, etc.) are still produced through occasional finds and in small quantities.

## Structural and spectroscopic analysis of Baltic amber

Precisvalle N.\*<sup>1</sup>, Martucci A.<sup>1</sup>, Rodeghero E.<sup>1</sup>, Bianchini G.<sup>1</sup> & Braschi I.<sup>2</sup>

1. Dep. of Physics and Earth Sciences, University of Ferrara. 2. Dep. of Agricultural Sciences, University of Bologna.

Corresponding email: [nicola.precisvalle@student.unife.it](mailto:nicola.precisvalle@student.unife.it)

Keywords: succinite, succinic acid, IR spectroscopy, x-ray diffraction, thermal analysis.

Amber is a fossilized tree resin appreciated since antiquity for its unique aesthetic qualities in the production of small decorative objects. Its chemical composition is strongly related to the origin of the resin, but Baltic amber is synonymous with the chemical name butanedioic acid (C<sub>4</sub>H<sub>6</sub>O<sub>4</sub>), more commonly known as succinic acid (Beck, 1986). C<sub>4</sub>H<sub>6</sub>O<sub>4</sub> is also a natural constituent of plant and animal tissues which has been used in Europe as a natural antibiotic and general curative for centuries. It has been stated, for example, that succinic acid isolated from Baltic amber can stimulate human and plant organisms, and can contribute to an increase in the yield of some cultivated plants (Matuszewska and John, 2004). In the literature it was reported that not all Baltic ambers contain succinic acid (Matuszewska and John, 2004). The primary goal of this study was to characterize succinite, a Baltic amber characterized by levels of succinic acid ranging from 3 to 8%. The selected succinite samples - (Palmnicken, Baltic Coast, and Prussia amber) consisted of opaque pale brown to nearly dark red-brown rounded masses of this amber variety. For comparative purposes, our tests were also carried out on a number of reference materials, including amber from Danzig Region, Poland, and commercial specimens. Standard gemological methods were used to document the samples' colour, hardness, refractive indices, fluorescence to long and short-wave ultraviolet radiation, and inclusions. X-ray powder patterns were collected before and after adsorption on a Bruker D8 Advance diffractometer equipped with SOL-X detector. Thermal analyses (TG and DTA) were performed in air up to 900°C at 10°C min<sup>-1</sup>. According to Shashoua et al. (2006), IR techniques have been shown to identify the provenance of the amber beyond the basic Baltic/non-Baltic distinction. In this study, infrared spectra collected on a Thermo Electron Corporation FT Nicolet 5700 Spectrometer FTIR spectra revealed characteristic spectral differences that make it possible to positively identify Baltic amber.

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## **Ferropericlase included in diamond: lower or upper mantle origin?**

Schiazza M.\*<sup>1</sup>, Nestola F.<sup>1</sup>, Nimis P.<sup>1</sup>, Angel R.J.<sup>1</sup>, Reali R.<sup>1</sup> & Hutchison M.<sup>2</sup>

1. Dipartimento di Geoscienze - Università di Padova. 2. Trigon GeoServices Ltd, Las Vegas (USA).

Corresponding email: [fabrizio.nestola@unipd.it](mailto:fabrizio.nestola@unipd.it)

Keywords: Ferropericlase, diamond, lower mantle, geobarometry.

Ferropericlase [(Mg,Fe)O] is a common oxide found as inclusions in diamonds considered to be of lower mantle origin (i.e. from below 660 km depth). Indeed, ferropericlase is often associated with low-Ni enstatite and such enstatite could be the inversion product of MgSiO<sub>3</sub> perovskite. Nonetheless, ferropericlase is stable over the entire mantle P-T range and its relative abundance as inclusions in diamonds with respect to possible inverted MgSiO<sub>3</sub> is much higher than expected based on high-PT experiments. In order to provide new and stronger evidence of lower mantle origin for ferropericlase inclusions, we are investigating four diamonds from Juina (Brazil). By measuring the residual stress on the inclusions, and combining it with knowledge of the EoS of the diamond and the inclusion, it is possible to determine the isomeke that defines possible minimum P and T of entrapment (Angel et al., 2014). This elastic measurement could thus contribute to resolve the question as to whether ferropericlase inclusions in diamond originate entirely in the lower mantle, whether or not enstatite inclusions are also present.

Angel R.J., Mazzucchelli M.L., Alvaro M., Nimis P., Nestola F. 2014. Geobarometry from host-inclusion systems: the role of elastic relaxation. Submitted as Letter to American Mineralogist.

## Micro-Raman mapping: a powerful method to investigate gemological mysteries

Tagliapietra R.\*<sup>1</sup>, Greggio L.<sup>2</sup>, Musa M.<sup>2</sup>, D'Amico F.<sup>2</sup>, Gori L.<sup>2</sup>, Passera E.<sup>2</sup>, R. Navone<sup>3</sup>, Croce A.<sup>4</sup> & Rinaudo C.<sup>4</sup>

1. Renishaw S.p.A.. 2. GECEI - Gemological Education Certification Institute. 3. R.A.G. di Raffaella Navone. 4. Dipartimento di Scienze ed Innovazione Tecnologica, Università del Piemonte Orientale.

Corresponding email: [riccardo.tagliapietra@renishaw.com](mailto:riccardo.tagliapietra@renishaw.com)

Keywords: micro-Raman Spectroscopy, Sapphire, Mineral phase, Heat-treatments.

Micro-Raman Spectroscopy is an analytical technique with a lot of applications in many scientific and industrial fields. Amongst its main features there are: fast analysis, no sample preparation and non-destructive test.

All these characteristics make Raman spectroscopy a very powerful analytical tool to study gems and related materials. Raman spectroscopy, in fact, characterizes different mineralogical phases on the basis of the vibrational modes of the chemical group.

Thanks to the recent innovations in advanced optics, electronics and mechanics, the last generation of Raman spectroscope is able to generate Raman images, on the basis of the scattering vibrational modes of the samples.

In this research work, we present some of the first results obtained by the application of these innovative technique, applied on the study of corundum inclusions and their relatively crystallinity after heat-treatments.

In fact, the heat-treatment in Corundum is used to enhance the color and to modify the clarity, and it is commonly accepted by the gem trade. Undesirable dark color shades in rubies can significantly reduce their value, and, on the other hand, a combination of light tone and low saturation can make the difference between a ruby and a pink sapphire (Bgasheva et al., 2012; Pattamalai & Hansawek, 2007). To detect heat treatment in Corundum sometime, when the standard gemological tests are not decisive, it is necessary to analyze the stones applying advanced analytical techniques. In some cases the heat-treatment is responsible for the modification of the spectroscopic response. In these cases it is necessary to know, or hypothesize, the original color of the stone.

For this study we have used ultra fast and high spatial resolution Raman Imaging techniques, allowing also 3D characterization with ULWD microscope objectives.

We have characterized several untreated corundums, analyzing, not only the inclusions, but also the hypothetic chromophore group, responsible for the stone color. For this purpose, we analyzed several untreated gems quality corundums from North Madagascar (basaltic origin – courtesy of Mr. Drera B.) and all the data were compared with treated corundum from GECEI collection.

Bgasheva T.V., Ahmetshin E.A., Zharikov E.V. 2012. Heat treatment enhancement of natural orange-red sapphire, *Advances in materials science*, 12, No. 2 (32).

Pattamalai K. & Hansawek R. 2007. Heat treatment of sapphires from Ilkaka-sakaraha, GEOTHAI'07 International Conference on Geology of Thailand: Towards Sustainable Development and Sufficiency Economy.

## **Application of Laser Induced Breakdown Spectroscopy on gem quality minerals: some cases of study**

Tempesta G.\*, Agrosi G. & Scandale E.

Dipartimento di Scienze della Terra e Geoambientali, Università di Bari.

Corresponding email: [gioacchino.tempesta@uniba.it](mailto:gioacchino.tempesta@uniba.it)

Keywords: Gemstone, LIBS, Chemical Zoning.

The application of the Laser Induced Breakdown Spectroscopy (LIBS) to gemmological materials is well known for the gemstone treatment detection but LIBS can also provide a useful contribution in mineralogical studies in which the chemical analyses is essential, playing a key role in the studies on the origin of minerals (Agrosi et al., 2014). The possibility to detect simultaneously all elements, including also light elements such as boron, lithium, and beryllium in a fast way and without sample preparation its clearly a great advantage of the LIBS. Moreover this technique is able to detect chromophorous elements even if they are in very low concentration. Nevertheless the main problems affecting LIBS are the difficulties to perform quantitative analyses and the partial destructivity of the method. Recently, with the development of the technique and in particular with the development of a new softwares there is also the possibilities to perform quantitative analyses with or without calibration. The last examples are the standard Calibration-Free LIBS and the One Point Calibration LIBS, CF-LIBS and OPC-LIBS respectively (Cavalcanti et al., 2013). The improvement of the instrumentation performance and the possibility to focalize the laser beam with an optical lens of a microscope allow to obtain an high resolution and a low destructivity of the sample. Moreover, the use of a double-pulse laser produce a signal enhancement useful for the quantitative chemical analyses guaranteeing a minimal sample damage. In this way we may obtain a considerable improvement on the detection limit of the trace elements, whose determination is essential to define the origin of gemstones. In the mineralogical studies the  $\mu$ -LIBS appear very attractive because the possibility to select the smallest sampling areas ensures a better reconstruction of the chemical zoning and consequently allows to stimate the rock forming condition because the chemical zoning is sensitive to the changing of the physical and chemical parameters. Some cases of study have been performed on beryls and corundums with different objectives and the results will be discuss.

Cavalcanti G.H., Teixeira D.V., Legnaioli S., Lorenzetti G., Pardini L., Palleschi V. 2013. One-point calibration for calibration-free laser-induced breakdown spectroscopy quantitative analysis. *Spectrochim. Acta Part B*, 87, 51-56.

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## Reconfiguration of pre-existing defects in natural diamond lattice: spectroscopic evidence

Zullino A.\*

Istituto Gemmologico Italiano.

Corresponding email: [andreazullino88@gmail.com](mailto:andreazullino88@gmail.com)

Keywords: Diamond, defects, treatments.

Diamond is doubtless the most important gem in the jewellery industry due to its exceptional physical properties, luster and value. The world that revolves around the diamond, from mine to market, is really complex and fascinating at the same time. Nowadays diamond based materials are the target research of many specialized laboratory in the world, and their legitimacy allowed to reach great scientific results. From a gemmological point of view understanding the diamond on the atomic scale is becoming the only way to solve many problems that affect the gemstones market. Complex treatments and synthesis techniques, developed during the last decades, allow to obtain colourless or fancy diamonds very similar to the natural ones. The human eyes and the standard gemmological instruments are often not useful for discerning natural from synthetic or treated diamonds, usually advanced spectroscopic analysis are essential to achieve this goal. This work is a review of what is known regarding natural diamond lattice defects, and how they can be drastically changed by artificial treatments. It is well known that diamond structure consists in carbon atoms each of which is tetrahedrally bonded to four other carbon atoms with covalent bonds, forming a compact lattice belonging to the cubic system. However atomic impurities, vacancies and structural defects are present in crystal structure of diamond in the 99% of cases. The scientific classification of diamond is based on the individuation of nitrogen and boron atoms, and their configuration in diamond lattice (Breeding & Shigley, 2009). Starting from a poor colour quality I<sub>2a</sub> crystal (for example brown) it is possible to obtain colourless diamond through HPHT (*High Temperature High Pressure*) processes (Fisher et al., 2000). Another complex and diffused procedure is to irradiate with ionizing radiation and anneal type I diamonds, to obtain coloured diamonds very similar to the natural ones (Collins, 2007). The aforementioned treatments, performed in prohibitive experimental conditions, produce a reconfiguration of pre-existing defects, with the aim of creating or destroying particular colour centres in diamond lattice. Therefore the diamond colour can be definitively improved modifying the starting defects involving nitrogen atoms, and create new ones which optical properties are drastically different (Collins, 1992).

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## **SESSIONE S16**

### **Rock-forming minerals and their bearing to petrogenetic processes**

#### *CONVENORS*

*G. Andreozzi (Univ. Roma)*

*P. Fumagalli (Univ. Milano)*

*F. Scordari (Univ. Bari)*

## **X-ray topographic study of a diamond from Udachnaya: implications for the genetic nature of inclusions**

Agrosi G.\*<sup>1</sup>, Nestola F.<sup>2</sup>, Tempesta G.<sup>1</sup>, Bruno M.<sup>3</sup>, Scandale E.<sup>1</sup> & Harris J.W.<sup>4</sup>

1. Dipartimento di Scienze della Terra e Geoambientali, Università degli Studi di Bari Aldo Moro Bari. 2. Dipartimento di Geoscienze, Università di Padova. 3. Dipartimento di Scienze della Terra, Università di Torino. 4. School of Geographical and Earth Sciences, University of Glasgow, UK.

Corresponding email: [giovanna.agrosi@uniba.it](mailto:giovanna.agrosi@uniba.it)

Keywords: diamond, olivine inclusions, x-ray diffraction topography.

In recent years, several studies have focused on the growth conditions of the diamonds through the analysis of the mineral inclusions trapped in them. In these studies, it is crucial to distinguish between protogenetic, syngenetic and epigenetic inclusions. X-ray topography (XRDT) can be a helpful tool to verify the genetic nature of inclusions in diamond. This technique characterizes, in a non-destructive way, the extended defects within a mineral and reconstructs the growth history of the sample (Agrosi et al., 2013). With this aim a diamond from the Udachnaya kimberlite, Siberia, was investigated. The diamond crystal was the one previously studied by Nestola et al. (2011) who performed in-situ crystal structure refinement of the olivine inclusions to obtain data about the formation pressure. Optical observations revealed an anomalous birefringence in the adjacent diamond and the inclusions had typical “diamond-imposed cubo-octahedral” shape for the largest olivines. The diffraction contrast study shows that the diamond exhibits significant deformation fields related to plastic post growth deformation. Section topographs revealed that no dislocations nucleated from the olivine inclusions. Generally, when a solid inclusion has been incorporated in full-grown state in another growing crystal, the associated volume distortion needs of a number of dislocations to ensure a better connection between the inclusion and the host phase. In some cases, complex twinning can be developed (Agrosi et al., 2013). In our case, the olivine assumes the morphology imposed from the diamond and, consequently, it does not produce volume distortion and the nucleation of dislocations is not necessary. This process generally occur during the simultaneously growth of the two minerals, confirming what was already stated by Bulanova (1995). However, the syngenetic nature of inclusions generally implies epitaxial relationship between diamond and inclusions that in our sample can be ruled out because the orientations of these olivines are random (Bruno et al., 2014). Therefore, the specific and significant results that characterize this sample will be discussed in detail.

Agrosi G., Tempesta G., Scandale E., Harris J.W. 2013. Growth and post growth defects of a diamond from Finsch mine. *Eur. J. Mineral*, 25(4), 551-559.

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## X-ray diffraction topography of brown diamonds from Argyle and Udachnaya

Agrosi G.\*<sup>1</sup>, Tempesta G.<sup>1</sup>, Brajkovic A.<sup>2</sup> & Scandale E.<sup>1</sup>

1. Dipartimento di Scienze della Terra e Geoambientali, Università degli Studi di Bari Aldo Moro. 2. Dipartimento di Scienze dell'ambiente e del territorio di Scienze della Terra, Università degli studi di Milano Bicocca.

Corresponding email: [giovanna.agrosi@uniba.it](mailto:giovanna.agrosi@uniba.it)

Keywords: diamond, x-ray topography, micro-laminations.

Two crystals of brown diamonds, coming from Argyle and Udachnaya, were studied, in a non-destructive way, by means of X-Ray Diffraction Topography (XRDT) with the aim to elucidate the relationships between the structural defects and the growth history. The sample from Argyle mine, labelled Br11, was a light-brown diamond with an irregular tetrahedral morphology and free of inclusions. Br11 shows a complex intergrowth phenomenon: the analyses of the diffraction contrasts and the optical observations reveal that the sample is really formed by two individuals twinned by the well-known spinel law. These individuals, in turn, are formed by different sub-individuals with different orientation, piled up along the [111] direction. An aggregation of numerous and thick lamellae parallel to the triangular morphology of the (111) face characterizes each sub-individual. Moreover, the XRDT images show partial dissolution followed by a final overgrowth. The sample from Udachnaya, labelled Ud02, was a light-brown diamond with an octahedral morphology that exhibits several large inclusions and fractures partially healed by dark epigenetic microinclusions. The analyses of the diffraction contrasts of the Ud02 sample show extended deformation fields, growth bands parallel to the octahedral faces and, in addition, a micro-lamination parallel to (1-1-1) that across the whole sample irrespectively of the different growth sectors. These laminations represent a polysynthetic twinning commonly observed in diamonds, which have undergone plastic deformation and are considered post-growth defects (Agrosi et al., 2013). No dislocations nucleated from the inclusions were observed. The analysis of the structural defects allows a reconstruction of a complex growth history of these samples characterized by a sequence of alternating episodes of growth, dissolution and plastic deformation. Lastly, the common feature of the micro-laminations was related to the origin of brown colour.

Agrosi G., Tempesta G., Scandale E., Harris J.W. 2013. Growth and post growth defects of a diamond from Finsch mine. *Eur. J. Mineral*, 25(4), 551-559.

## Trace elements in olivine from Italy convergent margin and inferences on the mineralogy of the mantle wedge

Ammannati E.\*<sup>1</sup>, Jacob D.E.<sup>2</sup>, Avanzinelli R.<sup>1</sup>, Foley S.<sup>2</sup> & Conticelli S.<sup>1</sup>

1. Dipartimento di Scienze della Terra, Università degli Studi di Firenze. 2. ARC Centre of Excellence for Core to Crust Fluid Systems & Dept. of Earth and Planetary Sciences, Macquarie University, Sydney, Australia.

Corresponding email: [edoardo.ammannati@unifi.it](mailto:edoardo.ammannati@unifi.it)

Keywords: olivine, trace elements, subduction.

Major and trace elements in forsteritic olivine from mafic igneous rocks has proven a valuable tool to infer on metasomatic processes that affect the mantle-source of magmas prior to melting. The deviation of some compatible trace elements (e.g. Ni, Co, Cr) and their ratios to major elements (Fe, Mg), from the values of olivine from MORB, has been used to quantify the contribution of an olivine-free mantle source in the origin of some OIB. Despite the potential of this approach, very few studies exist on olivine from convergent settings, leaving a gap in our knowledge of magma genesis in the mantle wedge.

Here we present the first comprehensive set of major and trace elements analyses of high-Mg olivine crystals from the Plio-Quaternary magmatic rocks of the Italian Peninsula. The samples are among the most primitive members of the relevant petrographic series: from Ca-alkaline to strongly alkaline rocks ('ultrapotassic') with lamproitic and leucititic affinity. Olivine crystals were analyzed for major (EPMA) and a wide palette of trace elements (EPMA and LA ICP-MS).

The olivine crystals display a wide variety of Ni, Cr, Mn and Ca contents, which encompass the whole spectrum of magmatic olivines worldwide. Olivines from the lamproite family have remarkably high Ni (up to 5.000 ppm) and Cr, low Ca and Mn/Fe. These values are consistent with a contribution from a mantle source that had undergone depletion and then silica- and K-rich metasomatism prior to melting, leading to olivine-consumption in favour of orthopyroxene. Conversely, the olivine crystals from the rocks of the leucititic family have diametrically opposed trace elements contents. These olivines have variably high Ca (up to 4.000 ppm), Mn/Fe, and low Ni (less than 2,000 ppm) and Cr. This is compatible with a metasomatic reaction in the presence of excess Ca, that would stabilize olivine and clinopyroxene at the expenses of orthopyroxene.

Olivine crystals from both groups are characterized by remarkably high-Li contents (consistently above 5 ppm), pointing toward the involvement of crustal material that have been subducted and then recycled into the mantle wedge. Our results provide further evidence that two different types of sediments are responsible for the two metasomatic processes depicted above: silico-clastic sediments in the source of the rocks of the Lamproite group, carbonate-rich sediments in that of the rocks of the Leucitite group. This duality is strictly linked to the geodynamic of the subduction front beneath Italy and to its changes with time and space.

## Core-to-rim chemical zoning and compositional evolution of tourmaline in the granitic pegmatite of the Cruzeiro mine, Minas Gerais, Brazil

Andreozzi G.B.\*<sup>1</sup>, Bosi F.<sup>1-2</sup>, Halenius U.<sup>2</sup> & Gori C.<sup>3</sup>

1. Dipartimento di Scienze della Terra, Sapienza Università di Roma. 2. Department of Geosciences, Swedish Museum of Natural History, Stockholm, Sweden. 3. Dipartimento di Fisica e Scienze della Terra "Macedonio Melloni", Università di Parma.

Corresponding email: [gianni.andreozzi@uniroma1.it](mailto:gianni.andreozzi@uniroma1.it)

Keywords: Tourmaline, chemical zoning, granitic pegmatite.

Core-to-rim evolution of a large color-zoned tourmaline crystal from the Cruzeiro pegmatite has been accurately described in terms of site population at the Y site (Al, Fe, Li etc.) and at the O1 site (O, OH, F). Four crystals were extracted from the color-zoned tourmaline and investigated by an integrated multi-analytical approach (crystal-structure refinement, electron microprobe analysis, Mössbauer spectroscopy and optical absorption spectroscopy). Compositional evolution from schorl to fluor-elbaite, with minor contribution of fluor-schorl, oxy-schorl and elbaite, has been proved to occur from core to rim. Comparison with previous studies (Federico et al. 1998; Bosi et al. 2005, 2013) revealed that the observed evolution reflects tourmaline compositional variation across the Cruzeiro pegmatite. In particular, black schorl/fluor-schorl (in the Border and Wall zones) is followed by blue-green fluor-elbaite (which only crystallizes in the Intermediate zone) and may locally evolve into multi-color elbaite (in the miarolitic cavities, shaped by fluid phase ex-solution).

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## Equation of state of hercynite spinel, $\text{FeAl}_2\text{O}_4$ , and high-pressure systematics of Mg-Fe-Cr-Al spinels

Anzolini C.\*<sup>1</sup>, Nestola F.<sup>1</sup>, Periotto B.<sup>1</sup>, Andreozzi G.B.<sup>2</sup>, Lenaz D.<sup>3</sup> & Princivalle F.<sup>3</sup>

1. Dipartimento di Geoscienze, Università di Padova. 2. Dipartimento di Scienze della Terra, Sapienza Università di Roma. 3. Dipartimento di Matematica e Geoscienze, Università di Trieste.

Corresponding email: [chiara.anzolini@studenti.unipd.it](mailto:chiara.anzolini@studenti.unipd.it)

Keywords: hercynite, diffraction, pressure, diamond.

Due to their abundance in several geological environments, spinels cover a crucial role in geology. A high number of scientific papers have been published on their stability and behaviour and, more recently, several works focused on their elastic behaviour under extreme conditions of temperature and pressure, which can be used to retrieve the conditions at which spinels crystallize. In detail, spinels of high-pressure mantle origin represent one of the most common inclusions found in diamonds and therefore they can provide strong indications about the diamond formation environment. In this specific case, the most common spinels are represented by the Cr-spinels, mainly by solid solutions constituted by magnesiochromite,  $\text{MgCr}_2\text{O}_4$ , and chromite,  $\text{FeCr}_2\text{O}_4$ . However, the hercynite component,  $\text{FeAl}_2\text{O}_4$ , is not negligible at all in high-pressure spinels with percentage reaching 10-15%, whereas the spinel s.s.,  $\text{MgAl}_2\text{O}_4$ , only represents some unit percentage.

However, whereas the high-pressure behaviour of  $\text{MgCr}_2\text{O}_4$ ,  $\text{FeCr}_2\text{O}_4$  and  $\text{MgAl}_2\text{O}_4$  has been definitively investigated even very recently (i.e. Nestola et al., 2014; Nestola et al., 2007), the elastic behaviour of hercynite remains still to be studied and compared with that of the other end-members in order to understand which is the effect of the Al for Cr substitution under high-pressure conditions on the elasticity of Cr-rich spinels. In our knowledge the only datum on the bulk modulus of hercynite was published 42 years ago by Wang and Simmons (1972) by ultrasonic measurements. Wang and Simmons (1972) reported a  $K_s$  value of 210.3 GPa. Here we have investigated a synthetic single crystal of pure hercynite,  $\text{FeAl}_2\text{O}_4$ , by X-ray diffraction under high-pressure conditions and room temperature using a diamond-anvil cell up to about 7.5 GPa in order to verify if the very old data can be still valid. For purpose of comparison we used the same experimental approach used in Nestola et al. (2014) on  $\text{MgCr}_2\text{O}_4$  and  $\text{FeCr}_2\text{O}_4$  and Nestola et al. (2007) on  $\text{MgAl}_2\text{O}_4$ . Our results could be crucial in determining correct stability field calculations, which are based on thermodynamic properties, like the bulk modulus.

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## Diffusive fractionation of chemical elements during planetary differentiation processes

Beddini G.\* & Perugini D.

Dipartimento di Fisica e Geologia, Università degli Studi di Perugia.

Corresponding email: [giuliobeddini@gmail.com](mailto:giuliobeddini@gmail.com)

Keywords: Diffusive fractionation, Processes of differentiation, Glass inclusions.

Magmatic masses show strong compositional heterogeneity on many scales of observation. These are the result of the development in space and time of chaotic dynamics that, during their evolution, generate structures with scale invariance properties, e.g. fractals.

The development of this physical process, which is expressed through the mechanism of stretching and folding, involves an intimate contact between fluids and the genesis of a compositional gradient, which propagate at many length scales. This induces molecular diffusion generates a new process of differentiation due to the mixing between compositionally different melts which are formed during the evolution of the magma: the diffusive fractionation process.

This process can occur during any process of differentiation (two end-member mixing, fractional crystallization, partial melting, etc..) and can potentially mask their effects making the interpretation of the compositions of igneous rocks very problematic.

In this work a detailed analysis of all works in the literature reporting the concentrations of trace elements measured on glasses and glass inclusions hosted in mineral phases like Olivine or Quartz has been performed in order to assess the impact of this new process of differentiation on present knowledge of igneous systems. We considered only this two mineral phases because trace elements do not enter in their crystal lattice so their concentrations is not influenced by secondary processes.

With these data we have build element vs element plots, using La as reference for estimating the very variable correlation ( $R^2$ ) between pairs of chemical elements. Furthermore we have created graphics ( $R^2$  vs  $\Delta r_i$ ;  $r_i$  being the ionic radius of each element) which show a progressive loss of the linear correlation with increasing difference in the ionic radius.

The results showed that, for all collected data, both on terrestrial (igneous rocks with different evolution degree) and extraterrestrial (chondrites and Martian Shergottites) samples show a clear evidence of the presence of the diffusive fractionation process, highlighting that the petrogenetic interpretations advanced so far for the petrogenesis of these rocks may be subject to uncertainties and/or oversimplifications.

The results of this work shed new light on the processes responsible for the generation of compositional heterogeneities in igneous systems and provide a new dimension of knowledge that may have a decisive impact on knowledge of the processes of magma evolution and planetary differentiation.

## Thermodynamics, stability and liquidus phase relations of sapphirine at high pressure and temperature: a computational study

Belmonte D.\*, Ottonello G. & Vetuschi Zuccolini M.

DISTAV, Università di Genova.

Corresponding email: [donato.belmonte@unige.it](mailto:donato.belmonte@unige.it)

Keywords: Sapphirine, ab initio, thermodynamic properties.

Sapphirine is widely recognized as a key mineralogical phase in ultra-high temperature metamorphism of amphibolite to granulite facies rocks. Nevertheless, its stability extends over a wide range of P-T conditions and diverse bulk rock compositions as well. In spite of its geological and mineralogical significance, the thermodynamic and thermophysical properties of this mineral are poorly defined and largely unknown. In the last two decades a number of thermodynamic assessments appeared in the literature trying to give a quantitative appraisal of the stability relations of sapphirine-bearing assemblages in multicomponent systems (e.g. Jung et al., 2004). Although all these assessments are internally-consistent, the inferred thermodynamic properties are model-dependent and affected by evident drawbacks. In this contribution, we present a density functional theory (DFT) based ab initio computational study on the thermodynamic and equation of state parameters of sapphirine end-members in the join  $Mg_4Al_8Si_2O_{20}$ - $Mg_3Al_{10}SiO_{20}$  (Belmonte et al., 2014). The MgO- $Al_2O_3$ - $SiO_2$  (MAS) ternary system was taken as reference phase diagram to define the topology of the primary stability field of sapphirine up to pressures of about 20 kbar and model its liquidus phase relations and high-pressure crystallization processes. First principles calculations have been coupled with the Hybrid Polymeric Approach (HPA) for multicomponent liquids to compute and minimize the Gibbs free energy of liquid and solid phases through the convex-hull analysis of equipotential surfaces. According to our computational investigation, sapphirine turns out to have a small field of primary crystallization in the MAS ternary diagram at 1-bar pressure, which becomes larger due to pressure effects up to 10 kbar, then progressively shrinks and disappears above 21 kbar. The inferred liquidus phase relations allow to get new insights into the stability relations of sapphirine at high-pressure and temperature conditions. First of all, our study supports the evidence that less aluminous compositions are stabilized by increasing pressure. Furthermore, the survival of a noticeably large primary field of crystallization of sapphirine in MAS system up to relatively high-pressure conditions strengthens the hypothesis that sapphirine could be a primary liquidus phase in basaltic magmas at high pressure, as supported by few experimental works (Milholland & Presnall 1998; Liu & Presnall, 2000) and a recent natural finding of igneous sapphirine (Giovanardi et al., 2013).

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Liu T.-C. & Presnall D.C. 2000. Liquidus phase relations in the system CaO-MgO- $Al_2O_3$ - $SiO_2$  at 2.0 GPa: Applications to basalt fractionation, eclogites, and igneous sapphirine. *J. Petrol.*, 41, 3-20.

Milholland C.S. & Presnall D.C. 1998. Liquidus phase relations in the CaO-MgO- $Al_2O_3$ - $SiO_2$  system at 3.0 GPa: The aluminous pyroxene thermal divide and high pressure fractionation of picritic and komatiitic magmas. *J. Petrol.*, 39, 3-27.

## Effect of crystal chemistry on cleavage process in micas: petrogenetic implications

Brigatti M.F. \*, Elmi C., Laurora A. & Malferrari D.

Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia.

Corresponding email: [brigatti@unimore.it](mailto:brigatti@unimore.it)

Keywords: micas, cleavage, cluster.

Crystal chemistry and topology of the interlayer in micas were detailed by several authors and readily appeared not only to be sensitive to the composition, but to reflect also the topology of other sites occurring in the mica structure as well as crystallization conditions.

The aim of this work is to relate the crystal chemistry of the cleavage surface, mostly occurring at the interlayer, to cation ordering and genetic processes. In particular, cleavage can be related to the electrostatic potential of basal oxygen atoms that is the individual distance of the interlayer cation to a basal oxygen atom, where the influence of layer crystal chemistry is implicit in these distances.

A similar approach commonly leads to a remarkable overestimation of cleavage energy with respect to experimental observations. Better agreement can be obtained if considering cleavage as a consequence of stress values directed along the layer and normal to the layer.  $\gamma$  can thus be expressed as a function of virtual in plane displacements, thus directed along in plane directions, as defined by X and Y fractional coordinates along (100) and (010), respectively, thus allowing the identification of preferential cleavage directions and, along these latter, to the definition of local maxima and maxima points, surrounding the equilibrium configuration. The difference among maximum and minimum values, that represent the energy required to induce cleavage following a pure shearing mechanism, is significantly less than the potential at equilibrium configuration, which represents in turn the energy required to induce cleavage following a pure normal stress approach.

A better matching of experimental to theoretical data, for what concerns cleavage energy, may thus be explained by introducing a combined shear to normal stress cleavage process. The lower is the difference between maximum to minimum point, the more the crystal is unstable, from a mechanical viewpoint, since small energies, associated with in-plane stress and strains, can cause the crystal to cleave. If the difference between the point of minimum to the point of maximum is small, than the structure is expected to be very brittle, cleavage surface very well defined, since the smaller is the displacement to cause cleavage the less likely is the activation of structural defects eventually present in crystal structure.

All these values changes as a function of chemical composition and of crystal structural features. The relevance of these interdependences may be significant for explaining clustering of given elements at crystal surface, thus imparting a different chemical composition at crystal surface with respect to the bulk and to indicate mechanical stability fields for phyllosilicates with given crystal chemical and crystal structural features.

## Ca-Zn substitution in clinopyroxenes: anomalous solution behavior and implications for mantle petrology

Gori C.\*<sup>1</sup>, Tribaudino M.<sup>1</sup>, Mantovani L.<sup>1</sup>, Delmonte D.<sup>1-2</sup>, Mezzadri F.<sup>2-3</sup>, Gilioli E.<sup>2</sup> & Calestani G.<sup>2-3</sup>

1. Dipartimento di Fisica e Scienze della Terra "Macedonio Melloni"-Università degli Studi di Parma. 2. IMEM, Istituto dei Materiali per l'Elettronica e il Magnetismo-CNR. 3. Dipartimento di Chimica-Università degli Studi di Parma.

Corresponding email: [claudia.gori@studenti.unipr.it](mailto:claudia.gori@studenti.unipr.it)

Keywords: Ca-Zn pyroxenes, high pressure synthesis, crystal structure, Zn partitioning in clinopyroxenes.

Growing interest was recently paid in Zn substitution in clinopyroxenes. Although Zn is an element present in trace amount in silicates, Zn partitioning in clinopyroxenes, olivine and orthopyroxenes provides a clue to interpret the origin of mantle related differentiates. For instance it was found in peridotite xenoliths that Zn/Fe ratios are equally fractionated between olivine, orthopyroxene and melt, but strongly fractionated when garnet and clinopyroxene are considered (Le Roux et al., 2010). These differences can be explained by the crystal structure where these metal transition ions are hosted. In clinopyroxene Zn has a higher preference for the eight-fold-coordinated M2 site, involving a substitution of Zn for Ca, which can be studied in the  $\text{CaZnSi}_2\text{O}_6$ - $\text{Zn}_2\text{Si}_2\text{O}_6$  series; experimental data are however lacking. We have therefore synthesized a set of Ca/Zn pyroxenes along the series, and studied their crystal structure by single crystal X-ray diffraction. The pyroxenes were synthesized after three hours of solid state reaction at  $T = 1200^\circ\text{C}$  and  $P = 5 \text{ GPa}$ , by means of a multi anvil Walker-type press. A single phase clinopyroxene, together with a small amount of coesite, was invariably found; no evidence of a two pyroxene assemblage was observed, indicating that a solvus, if any, is present at lower temperature. Single crystal XRD and Rietveld analysis of powder patterns showed that the symmetry is  $C2/c$  for the whole series. No phase transition with composition is found. Changes in volume are linear and rather small, in spite of the remarkable difference in ionic radius between Ca and Zn (1.0 vs 0.74). Differently from Ca-Co, Mg and Fe pyroxenes the volume decreases much less than we would expect assuming that changes in volume are only due to differences in ionic radius (Mantovani et al., 2014). Single crystal XRD shows a strong M2-M2' splitting, with Ca and Zn splitted by 0.5 Å. The coordination of Zn in the M2 cavity is four-fold, even in Ca richer samples. The different behavior of Zn respect to Ca, Mg and Fe clinopyroxenes was related to the covalent character of Zn, most apparent in the M2 cavity. The different cation behavior in the M2 site respect to other metal transition elements explains then the different partitioning for Zn in garnets and clinopyroxenes respect to olivine and orthopyroxenes.

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Mantovani L., Tribaudino M., Bertoni G., Salviati G. & Bromiley, G. 2014. Solid solutions and phase transitions in  $(\text{Ca}, \text{M}^{2+})\text{M}^{2+}\text{Si}_2\text{O}_6$  pyroxenes ( $\text{M}^{2+} = \text{Co}, \text{Fe}, \text{Mg}$ ). *Am. Mineral.*, 99, 704-711.

## The cooling kinetics of plagioclase revealed by electron microprobe mapping

Iezzi G.<sup>\*1-2</sup>, Mollo S.<sup>2</sup>, Shahini E.<sup>1</sup>, Cavallo A.<sup>2</sup> & Scarlato P.<sup>2</sup>

<sup>1</sup> Dipartimento di Ingegneria & Geologia, Università G. d'Annunzio, Chieti, Italy <sup>2</sup> Istituto Nazionale di Geofisica e Vulcanologia, Roma, Italy.

Corresponding email: [g.iezzi@unich.it](mailto:g.iezzi@unich.it)

Keywords: andesite, plagioclase, EPMA map, cooling, crystallization, thermometer.

In this study we have used electron microprobe mapping to investigate plagioclase compositional evolution due to cooling kinetics. We re-analyzed five run-products from a prior study (Iezzi et al. 2011), crystallized by cooling a natural andesitic melt from 1300 to 800 °C at 25, 12.5, 3, 0.5 and 0.125 °C/min under atmospheric pressure and air redox state. As the cooling rate decreases, the texture of large plagioclases changes from skeletal to hollow to nearly equant. In this study, we use x-ray map data to obtain a database of 12275 quantitative chemical analyses. The frequency of An-rich plagioclases showing disequilibrium compositions substantially increases with increasing cooling rate. At 25 and 12.5 °C/min the distribution is single-mode and narrow, at 0.5 and 0.125 °C/min is single-mode but very broad, whereas at the intermediate cooling rate of 3 °C/min two distinct plagioclase populations are present. This intermediate cooling rate is fast enough to cause departure from equilibrium for the crystallization of the An-rich population but also sufficiently slow that An-poor plagioclases nucleate from the residual melt. We interpret our findings in the context of time-temperature-transformation (TTT) diagrams, and infer the crystallization kinetics of plagioclase in the experiments. Compositional trends and our inferences regarding TTT systematics are consistent with two discrete nucleation events that produced separate populations of plagioclase (i.e., An-rich and An-poor populations) at 3 °C/min. Using plagioclase-melt pairs as input data for the thermometric reaction between An and Ab components, we find that plagioclase mirrors very high (near-liquidus) crystallization temperatures with increasing cooling rate. These results have important implications for the estimate of post-eruptive solidification conditions. Lava flows and intrusive bodies from centimeters to a few meters thick are characterized by a short solidification time and a significant thermal diffusion. Under such circumstances, it is possible to crystallize plagioclases with variable and disequilibrium chemical compositions simply by cooling a homogeneous andesitic melt. X-ray element maps enrich the study of plagioclase compositional variations generated under conditions of rapid cooling.

Iezzi G., Mollo S., Shaini E., Cavallo A. & Scarlato P. 2014. The cooling kinetics of plagioclase revealed by electron microprobe mapping. *American Mineralogist*, in press.

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## Fluorophlogopite and F-rich phases in limestone clasts from the Campanian Ignimbrite quarried at Fiano (southern Italy): mineralogical, geochemical and volcanological insights

Lacalamita M.<sup>1</sup>, Balassone G.<sup>2</sup>, Schingaro E.\*<sup>1</sup>, Mesto E.<sup>1</sup>, Scordari F.<sup>1</sup>, Mormone A.<sup>3</sup>, Piochi M.<sup>3</sup> & Joachimski M.<sup>4</sup>

<sup>1</sup> Dipartimento di Scienze della Terra e Geoambientali, University of Bari. <sup>2</sup> Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, "Federico" University, Napoli. <sup>3</sup> Istituto Nazionale di Geofisica e Vulcanologia, Osservatorio Vesuviano, Napoli. <sup>4</sup> GeoZentrum Nordbayern, University of Erlangen-Nuremberg, Erlangen, Germany.

Corresponding email: [emanuela.schingaro@uniba.it](mailto:emanuela.schingaro@uniba.it)

Keywords: Campanian Ignimbrite, southern Italy, Fiano xenoliths, F(Mg)-rich minerals, crystal chemistry.

Fluorine-rich metamorphosed xenoliths associated to the distal Campanian Ignimbrite (CI) tephra (Campania region, southern Italy) have long attracted the interest of the mineralogical community (i.e. Scacchi, 1890; Zambonini, 1919; Masi & Turi, 1972; Balassone et al., 2002). These rocks derive from the Mesozoic carbonate lithotypes of the Campanian Apennine, embedded in the pyroclastic flow and presently resting at the bottom of the tuff formations. The sedimentary protoliths suffered from the action of hot, volatile-rich pyroclastic flow, and consequently were affected by thermal metamorphism to various degrees. Their peculiarity is the occurrence of F- and Mg-bearing phases, with an ubiquitous presence of neoformed fluorite. The occurrence at Fiano quarries (the so-called "Tufare") is the classical locality for these rock xenoliths. Similar rocks were also found in the CI of the Caserta area, and in the Latium region (Colli Albani). This research aims both at a crystal chemical study of fluorophlogopite occurring in the Fiano xenoliths, and at a geochemical and volcanological survey, to constrain the petrogenesis processes related to this rare F-, Mg-rich assemblage and to CI.

The analysed samples belong to two lithotypes: mica-bearing clasts and variably metamorphosed carbonate blocks. The former lithotype is represented by abundant fluorite, followed by fluorophlogopite, F-rich chondrodite, fluoborite, diopside and (Fe,Mg)-oxides. Minor to trace contents of calcite, humite, tremolite, and grossular also occur. Carbonate rocks can show calcite only, or also trace amounts of fluorite. The Fiano micas composition approaches that of the Vesuvius micas from the 1872 eruption (Balassone et al., 2013). The micas belong to the 1M polytype and have crystal chemical features typical of fluorophlogopites i.e., low *c* lattice parameter (~ 10.13 Å), (~ 2.060 Å) and (~ 3.135 Å) distances. New data on minor to ultratrace elements amounts found in the studied clasts, together with Carbon and Oxygen isotope data will be reported and interpreted in a petrogenetic and volcanological frame.

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## A Raman spectroscopic study of Cr-bearing natural spinels with $0.03 < \text{Cr} < 1.68$ apfu

Lenaz D.\*<sup>1</sup> & Lughì V.<sup>2</sup>

1. Dipartimento di Matematica e Geoscienze, Università di Trieste. 2. Dipartimento di Ingegneria e Architettura, Università di Trieste.

Corresponding email: [lenaz@units.it](mailto:lenaz@units.it)

Keywords: Cr-spinels, Raman spectroscopy, structure.

Cr-bearing spinels can be found in different geological environments, usually related to mafic and ultramafic rocks. In nature, several cations can enter into the structure originating a solid solution with a general formula  $(\text{Mg}, \text{Fe}^{2+})(\text{Al}, \text{Cr})_2\text{O}_4$ . Other cations such as  $\text{Fe}^{3+}$  or Ti can be present in low amounts - although in some cases the  $\text{Fe}^{3+}$  content can be very high. They can also be found in metamorphosed rocks, and in sedimentary rocks as a detrital mineral, due to its high resistance to weathering and breakage. In the last decade some Raman spectroscopy studies took into consideration natural Cr-spinels found in meteorites, in mafic rocks and in archaeological stone artifacts. In all natural spinels and almost all of the synthetic ones, even if the vibrational modes are easily assigned, the presence of several cations within the structure has generated difficulties of interpretation of the Raman shifts due to the possibility for several cations to enter the octahedral and tetrahedral sites. Lenaz and Lughì (2013) verified the effects on Raman shifts of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  for two synthetic series. The first one,  $\text{MgCr}_2\text{O}_4 - \text{Fe}^{2+}\text{Cr}_2\text{O}_4$ , is characterized by the sole substitution of Mg by  $\text{Fe}^{2+}$  into the tetrahedral site, while in the second,  $\text{MgCr}_2\text{O}_4 - \text{MgFe}^{3+}_2\text{O}_4$ ,  $\text{Fe}^{3+}$  substitutes for Cr.

For this study we analyzed more than 300 different natural Cr-bearing spinels with  $0.03 < \text{Cr} < 1.68$  atoms per formula unit coming from mantle xenoliths, alpine peridotites, ophiolites, layered complexes and meteorites in order to better define the behavior of the Raman modes according to the chemical composition and structure of these crystals. In many cases, the studied spinels had been previously analyzed by single crystal X-ray diffraction and electron microprobe; in this study, we will attempt to correlate the Raman results to the order-disorder phenomena and the chemistry of spinels.

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## Clinopyroxenes from Pico Volcano (Azores Island, Portugal): crystal chemistry and water content

Nazzareni S.\*<sup>1</sup>, Barbarossa V.<sup>1</sup>, Skogby H.<sup>2</sup> & Zanon V.<sup>3</sup>

1. Department of Physics and Geology University of Perugia. 2. Museum of Natural History, Stockholm, Sweden. 3. CVARG, Ponta Delgada, Portugal.

Corresponding email: [sabrina.nazzareni@unipg.it](mailto:sabrina.nazzareni@unipg.it)

Keywords: clinopyroxenes, volcanic rocks, water content, IR, SC-XRD.

The Pico volcanic island is located in the central Azores archipelago (Portugal). It is formed by a perfect conical stratovolcano and an elongated ridge constituted by cinder cones aligned along NW-SE trending faults, and associated to fissural eruptions.

Clinopyroxenes, as an early forming phase, can incorporate H<sup>+</sup> that may be used to calculate the volatile content and contribute to the knowledge of evolution processes during magma crystallisation and ascent.

We focused on cpxs from this area of the island due to the particularly high content of this phase in erupted material. Samples are millimetric euhedral phenocrysts from a cumulitic lava flows and centimetric euhedral crystals from the Pic16 mugearite lava flow erupted during the 1718 eruption. We performed polarized FTIR, Mössbauer, SC-XRD, EPMA on the same cpx crystal.

Diopside (Wo45-46 En45-48 Fs06-09) in composition, the cpxs showed very weak or absent OH<sup>-</sup> vibrational bands in the IR spectra (except in Pic16) with a H<sub>2</sub>O content ranging from 0 to 91 ppm.

These low contents indicate H<sup>+</sup> loss during ascent to surface or post eruptive re-equilibration, which may occur via the redox reaction  $\text{Fe}^{2+} + \text{OH}^- = \text{Fe}^{3+} + \text{O}^{2-} + \frac{1}{2}\text{H}_2$ . In order to restore H<sup>+</sup> that was possibly lost, we performed thermal annealing experiments under H<sub>2</sub> gas flux at 700°C and 800°C. All the samples increased their hydrogen content and saturated after 65-83 hours, depending on crystal thickness. The new range of water thus obtained is 93-170 ppm for the cumulitic lava and 182 ppm for Pic16.

Mössbauer analysis gave a Fe<sup>3+</sup>/Fe<sub>tot</sub> ratio for untreated cpxs between 18.8-25.8%, after the thermal annealing the ratio remains constant or slightly decrease.

Using the H-saturation values and the partition coefficients of Wade et al. (2008) we calculated 0.75-1.21 H<sub>2</sub>O wt% in melt, which is slightly lower than the range measured in melt inclusions in olivines from the Pico fissural eruptions (Metrich et al. 2014).

The Pico primary magmas were produced at 3GPa and 1352-1362°C, by a very low melting degree of a mantle source with 350 to 630 ppm of H<sub>2</sub>O, then melts ascended up to 18 km, where olivine and clinopyroxene crystallised and accumulated in a storage areas (Zanon & Frezzotti 2013). The crystal chemistry of cpxs suggests that they crystallized at 18 km depth and that the H<sup>+</sup> loss occurred during the ascent or a late stage of eruption.

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## Diamond-olivine host-inclusion system: crystallography and depth of formation

Nestola F.\*<sup>1</sup>, Alvaro M.<sup>1</sup>, Nimis P.<sup>1</sup>, Angel R.J.<sup>1</sup>, Milani S.<sup>1</sup>, Bruno M.<sup>2</sup>, Prencipe M.<sup>2</sup> & Harris J.W.<sup>3</sup>

1. Dipartimento di Geoscienze, Università di Padova. 2. Dipartimento di Scienze della Terra, Università di Torino  
3. School of Geographical and Earth Sciences, University of Glasgow.

Corresponding email: [fabrizio.nestola@unipd.it](mailto:fabrizio.nestola@unipd.it)

Keywords: Diamond, olivine, depth, pressure, diffraction, orientation.

Diamond is probably the most deepest and oldest material able to reach the Earth's surface. Thanks to its ability to include any type of inclusion during its ascent it provides the unique direct sampling of our planet interior. Indeed, much of what is believed about the genesis and distribution of diamond in the Earth's mantle has therefore been deduced indirectly from the characterisation of its mineral inclusions. However, there is still an important debate about the temporal growth relationships between diamond and its inclusions and about the real depth at which diamonds can form. In detail, it is often assumed that the inclusions were formed at the same time as the host diamond (i.e. *syngenetic*), and do not represent pre-existing material that was passively incorporated into the growing diamond (i.e. *protogenetic* inclusions). Two main arguments have been used in favour of syngeneses. (1) It has been claimed that inclusions normally exhibit specific orientations relative to the diamond hosts. (2) Inclusions often display a morphology of the diamond host (i.e. typical "cubo-octahedral" shape).

We have measured the crystallographic orientation of 47 inclusions of olivine in 21 different diamonds by single-crystal X-ray diffraction. We found no recurrent crystallographic orientations between olivine and diamond (as instead reported in some literature data) ruling out any possible epitaxial relationship. However, multiple olivine inclusions in a single diamond often show similar orientation to one another.

Concerning the depth at which the diamonds form it is reported that about 94% of diamonds are subcratonic, with depths of formation ranging between 120 and 250 km, and only 6% of them could be considered "super-deep diamonds" (see recent paper on Nature, Pearson et al., 2014). However, it is very difficult using chemical geothermobarometer approach to provide the real depth of formation of diamonds and recent the method based on inclusion-host elasticity (see Angel et al., 2014) is representing an extremely valid alternative to get the pressure of diamond formation.

We have measured the pressure of formation on four of the above 21 diamonds from Udachnaya applying the method based on inclusion-host elasticity to the diamond-olivine pair and found a pressure of formation very similar for all the diamonds, which could suggest that at Udachnaya diamonds form under the same pressure.

Pearson D.G., Brenker F.E., Nestola F., McNeill J., Nasdala L., Hutchison M.T., Matveev S., Mather K., Silversmit G., Schmitz S., Vekemans B., Vincze L. 2014. Hydrous mantle transition zone indicated by ringwoodite included within diamond. *Nature*, 507, 221-224.

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## How deep (and hot) is a diamond? The current state of diamond thermobarometry

Nimis P.\*

Dipartimento di Geoscienze, Università di Padova.

Corresponding email: [paolo.nimis@unipd.it](mailto:paolo.nimis@unipd.it)

Keywords: diamond, thermobarometry, Earth's mantle.

A good understanding of the distribution of diamond in Earth's mantle provides constraints for the evaluation of diamond potential of economic targets and for the assessment of the deep carbon cycle in ancient Earth. Much of what we know about the depth distribution of diamond is derived from the study of rare mineral inclusions that are amenable to conventional two-phase thermobarometry. However, non-touching inclusions were not necessarily in equilibrium at their encapsulation time, whereas touching inclusions could reequilibrate after entrapment. Moreover, since diamonds can form under a wide range of redox conditions, the unknown  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  ratios in the inclusions may lead to large uncertainties on  $T$  estimates based on Fe–Mg exchange thermometry and, in turn, on  $P$  estimates.

The development of single-mineral thermobarometers applicable to isolated inclusions has in part overcome the equilibrium issue. However, as yet only chromian clinopyroxene allows to estimate both  $P$  and  $T$  with a precision comparable, if appropriate analytical conditions are used, to that of conventional methods. In fact, no effective barometers exist for some of the most abundant inclusion types, such as olivine and the eclogitic minerals.

An additional problem is whether the inclusions are syngenetic with diamond or they represent passively captured pre-existing material. In the latter case, incomplete chemical resetting during rapid diamond growth may prevent determination of the conditions of diamond formation. Recent studies suggest that the imposition of diamond morphology on the inclusion (the most widely used criterion for syngenesi) is not unique to syngenetic inclusions, casting doubts on the real significance of  $P$ - $T$  data extracted from many reported "syngenetic" inclusions in diamonds.

The determination of the remnant  $P$  on the inclusion, e.g., using data from X-ray diffractometry, birefringence analysis or Raman spectroscopy, provides an alternative way to diamond barometry using elasticity theory. Application of this methodology is still at its infancy, because of uncertainties in the thermoelastic behaviour of the minerals, potential non-elastic relaxation and technical limitations. It is a field of on-going development, which may eventually allow evaluation of the depth of provenance of diamonds containing minerals that are chemically insensitive to  $P$ , such as the abundant upper-mantle olivine or the super-deep ferropericlase.

Although available data suggest that lithospheric diamonds may come from any depth below the graphite–diamond transition, owing to the above limitations recognition of subtle inhomogeneity in the vertical distribution of diamond (or of specific diamond populations) remains challenging. Further development of conventional and non-conventional thermobarometric methods may allow us to increase the statistical significance of the diamond  $P$ - $T$  record and may eventually contribute to refine models of diamond formation in the sub-cratonic mantle.

## Zircon beyond geochronology: inherited and antecrystic zircons as igneous petrogenesis tools

Paoli G.\*<sup>1</sup>, Rocchi S.<sup>1</sup>, Jacobs J.<sup>2</sup> & Ksienzyk A.<sup>2</sup>

1. Dipartimento di Scienze della Terra, Università di Pisa. 2. Department of Earth Science, University of Bergen, Norway.

Corresponding email: [gabriele.paoli@unifi.it](mailto:gabriele.paoli@unifi.it)

Keywords: Tuscan Magmatic Province, zircon, U-Pb geochronology.

Advances in U-Pb zircon geochronology led to the awareness that zircon crystals in an igneous rock commonly belong to different populations issuing from complex diverse histories. Thus, dates from autocrysts (that are associated only with the latest pulse of magma) indicate crystallization age, while dates on populations of antecrysts (that crystallized from an earlier pulse of magma and which are incorporated in a later pulse) or of inherited crystals/cores (that survived several processes, from sedimentary to anatectic) can give informations about former processes.

The aim of this study is twofold: (i) using dates obtained for inherited zircon crystals/cores in anatectic rocks to unravel the nature/age of the continental crust involved in anatexis; (ii) using dates obtained for antecrystic zircons to shed light on the temporal evolution of the igneous process.

This study has been carried out on a young igneous system, the Tuscan Magmatic Province, which is mostly composed of anatectic acidic and hybrid rocks. The analysed samples are from intrusive bodies (Monte Capanne and Porto Azzurro monzogranites) and hypabissal rocks (San Martino and Portoferraio porphyries) from Elba Island, as well as from volcanic centres from southern Tuscany (San Vincenzo and Roccastrada rhyolites). Internal morphologies have been investigated by SEM-cathodoluminescence and they have been used as a guide for the selection of potential antecrysts or relict crystal cores where to determine U-Pb ages by means of high-resolution laser-ablation ICP-MS.

After a careful screening of analytical data, the obtained dates have been grouped into two sets: “young” ages, close to the established emplacement age, interpreted to represent antecryst ages, and significantly older ages from inherited zircons.

Inherited zircons and cores have an overall age distribution including components that have all been found in detrital zircons from the Tuscan Metamorphic Basement (studied in a companion work), such as neat Panafrican (late Neoproterozoic-Ordovician) and Variscan signatures. The known Tuscan Basement is thus a plausible candidate as a source rock for anatectic melts.

For “young” antecryst ages, a time gap is observed between zircon ages from the same sample, and between these ages and the final solidification/eruption age as well. Such an age distribution of most of the antecrystic zircon grains has been interpreted in recent works (Fish Canyon Tuff, Colorado) as an evidence for the assembling of magma bodies over a timescale hundreds of ky by the amalgamation of small pulses of magma. Among the Tuscan Magmatic Province, the San Vincenzo rhyolite is the best example of magma that was stored as a crystal mush and repeatedly fed, undergoing local thermal oscillations that enabled zircons to grow intermittently over an extended period of time.

## Compositional variations of sapphirine in metamorphic rocks

Podlesskii K.K.\*

Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry, Russian Academy of Sciences, Moscow, Russia.

Corresponding email: [kkp@igem.ru](mailto:kkp@igem.ru)

Keywords: sapphirine, metamorphism, P-T conditions.

Based on compilation of published microprobe analyses of sapphirine and coexisting phases from metamorphic rocks worldwide (now available as an open Internet database at <http://database.iem.ac.ru/sapphirine>), compositional variations of this mineral have been considered in terms of petrogenetic conditions. Being associated with aluminium- and/or magnesium-rich minerals such as spinel, orthopyroxene, cordierite, garnet, clinopyroxene, olivine, kornerupine, osumilite, plagioclase, K-feldspar, biotite, gedrite, chlorite, talc, clinohumite, sillimanite, kyanite, mullite, and corundum, sapphirine occurs in both silica-saturated and silica-deficient rocks that have undergone different tectono-metamorphic histories. The  $\text{Fe}^{3+}/\text{Fe}$  ratio for sapphirine, as calculated from the total iron content according to stoichiometric criteria (Droop, 1987), is normally higher than that for coexisting Fe-Mg minerals, including spinel. No correlation between  $\text{Fe}^{3+}/\text{Fe}$  and  $\text{Mg}/(\text{Mg}+\text{Fe})$  ratios have been traced for the compiled compositions of sapphirine. The extensive Tschermak substitution characteristic for this mineral is demonstrated by drastic changes from its rather low Si contents in eclogite assemblages to relatively silica-rich compositions in high-temperature granulites. The P-T range of formation of sapphirine-bearing assemblages have been estimated from below 700°C and 5 kbar to above 1000°C and 10 kbar. Controversial thermodynamic models of sapphirine solid solution (Wheller & Powell, 2014; Podlesskii, 2010) arising from insufficient experimental data seem to allow too much freedom for interpreting the P-T-X phase relations.

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Wheller C.J. & Powell R. 2014. A new thermodynamic model for sapphirine: calculated phase equilibria in  $\text{K}_2\text{O-FeO-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O-TiO}_2\text{-Fe}_2\text{O}_3$ . *Journal of Metamorphic Geology*, 32(3), 287-299.

## Phase diagrams for $\text{CaCO}_3$ and $\text{CaCO}_3 + \text{H}_2\text{O}$ and their bearing on the genesis of carbonatitic melts

Poli S.\*

Dipartimento di Scienze della Terra, Università degli Studi di Milano.

Corresponding email: [stefano.poli@unimi.it](mailto:stefano.poli@unimi.it)

Keywords: calcite, aragonite, carbonatite.

Phase transformations in the system  $\text{CaCO}_3$  and  $\text{CaCO}_3 + \text{H}_2\text{O}$  have been of primary concern for Earth scientists since early XIX century. Sir J. Hall performed the first investigations in this system in 1798 and pursued various attempts at defining decarbonation reactions and melting of calcite with water in externally heated gun barrels, successfully performing the first high pressure experiments in geoscience.

Despite two centuries passed, experimental results on phase transformations in  $\text{CaCO}_3$  are still extremely contradictory. Discrepancy between *ex-situ* and *in-situ* determination of the reaction calcite = aragonite is in the order of 3 GPa at 1200 °C. Experimental data on melting of calcite with an aqueous fluid differ by 300 °C and aragonite melting is unknown. Uncertainties on the phase diagram for  $\text{CaCO}_3$  and  $\text{CaCO}_3 + \text{H}_2\text{O}$  have profound consequences in predicting the fate of altered oceanic crust and of metasedimentary materials re-introduced in the mantle at subduction zones.

Multianvil experiments were performed at 4.2 GPa on a model bulk composition in the system  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O-CO}_2$ , obtained from natural calcite,  $\text{Al}(\text{OH})_3$  and silica. Stoichiometric proportions are intended to produce at run conditions kyanite +  $\text{CaCO}_3$  + an aqueous fluid.  $\text{Al}_2\text{SiO}_5$  saturation prevents the formation of portlandite and offers a basis for modelling melting of impure marbles. Furthermore the usage of  $\text{Al}(\text{OH})_3$  in the starting material allows an accurate control of  $\text{H}_2\text{O}$  added, fixed at 10 wt% in the present study. This amount is expected to produce largely  $\text{H}_2\text{O}$ -undersaturated melts, on the basis of solubility data determined at low pressure.

Aragonite + kyanite + fluid, and minor lawsonite and grossular form at 700 °C and 800 °C, respectively. At 900 °C a complex sequence of quenching textural features is observed; “chains” and dendrites of  $\text{CaCO}_3$  grow nucleating from liquid-solid interface; they are followed by growth of Si-Al-bearing fibres; finally spheres of silica precipitate from the residual fluid exsolved from the liquid carbonate phase.

Estimates of liquid – solid proportions, retrieved by image analysis, at known bulk  $\text{H}_2\text{O}$  content, along with the solid – pore volume proportions in the liquid region of the run charge provide constraints for  $\text{H}_2\text{O}$  solubility in  $\text{CaCO}_3$  liquid. Contrarily to early suggestions of supercritical behaviour in the system  $\text{CaCO}_3 - \text{H}_2\text{O}$  above 4 GPa, our data still support the occurrence of a univariant solidus reaction with clear distinction between fluid and liquid phases in the model system investigated.

The model system investigated here and the minimum temperatures of melting found represent the upper bound of the formation of hydrous Ca-carbonate melts able to metasomatise the mantle at subduction zone environments generating carbonate pyroxenites, a fertile  $\text{CO}_2$  source for volatile-rich magmatism.

## Crystal-chemistry of Cr-diopsides included in spinel-peridotite mantle xenoliths from Cameroon, Libya and Morocco (Africa): petrogenetic implications

Princivalle F.\*<sup>1</sup>, De Min A.<sup>1</sup>, Marzoli A.<sup>2</sup>, Youbi N.<sup>3-4</sup> & Lenaz D.<sup>1</sup>

1. Department of Mathematics and Geosciences, Università di Trieste. 2. Department of Geosciences, Università di Padova. 3. Department of Geology, Faculty of Sciences-Semlalia, Cadi Ayyad University, Marrakech, Morocco.  
4. Department of Geology, University of Lisbon, Portugal.

Corresponding email: [princiva@units.it](mailto:princiva@units.it)

Keywords: Cr-diopsides, mantle-xenoliths, Africa.

Three series of C2/c clinopyroxenes (cpx) enclosed in spinel peridotite xenoliths from Lake Nyos (Cameroon; CA), Waw-En-Namus (Libya; LB hereafter) and Tafraoute and Bou-Ibalrhathene (Morocco; MOR) have been investigated by single-crystal X-ray diffraction, and electron microprobe, to provide a new knowledge of the mantle beneath North-Western Africa continent. These cpx were also compared with previously studied cpx from Mt. Nji (Lnji) and other cpx worldwide.

The here studied cpx have been selected considering that the mantle xenoliths sampled by alkaline lavas are coming from different geological occurrences. In fact MOR should reflect cratonic conditions and LB metacratonic while CA are from the Cameroon volcanic line whose products outcrop within a polycyclic mobile belt.

The compositional and structural studies reveal that the three series have: 1) comparable chemistry in terms of major elements (Ca = 0.729-0.835; Mg = 0.795-0.919 a.p.f.u.), 2) are hosted in protogranular textured xenoliths and 3) have pressure equilibration ranging between 10 and 21 kb (Mercier formulation).

T site volume decreases with Al<sup>IV</sup> content and LB cpx show lower volume and Al content with respect to those from MOR and CA. Samples from MOR and CA have Al<sup>IV</sup> content similar to Lnji cpx even if these latter show a slightly higher V(T). Notably, the high V(T) and Al<sup>IV</sup> content of Lnji cpx was interpreted as the effect of a crystallization at high pressure of alkaline magmas, which intruded, as small-volume melts, peridotite mantle.

V(M1) site volume increase is well related to the decrease of R<sup>3+</sup> content. In particular LB and MOR cpx span from 0.157 to 0.251 a.p.f.u., whereas CA and Lnji cpx from 0.221 to 0.257 a.p.f.u.. CA cpx behavior is similar to those of Lnji cpx trending towards cpx crystallized in mantle condition, and not like peridotitic cpx residual after basaltic extraction.

As far as concern the V(M2) site volume for MOR and CA cpx it is positively related to Ca+Na content, whereas for LB and Lnji cpx it increases with virtually constant Ca+Na content (about 0.920 and 0.910 a.p.f.u., respectively).

Inter-crystalline temperature and pressure conditions, calculated through Mercier formulation, are in the range 850-1100 °C and 10-21 Kbar for all investigated cpx. Intra-crystalline temperature, are different for the three cpx suites, (700-1000, 579-700 and 450-780 for LB, MOR and CA cpx, respectively), and this may reflect different cooling history and/or equilibration temperatures into the mantle suffered by the host rocks.

In summary, the three cpx suites show characteristics for some aspects similar each other and also similar to those of Lnji cpx, suggesting they were brought to the surface from a heterogeneous mantle. This heterogeneity may be related to the "small-volume melt metasomatism" which enriched the sub-continental lithosphere during the Pan African event.

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## Structure, composition and origin of yangzhumingite and phlogopite from the Kvaløya lamproite (North Norway)

Schingaro E.\*<sup>1</sup>, Kullerud K.<sup>2-3</sup>, Lacalamita M.<sup>1</sup>, Mesto E.<sup>1</sup>, Scordari F.<sup>1</sup>, Zozulya D.<sup>4</sup>, Erambert M.<sup>5</sup> & Ravna E.J.K.<sup>2</sup>

1. Dipartimento di Scienze della Terra e Geoambientali, Università di Bari. 2. Department of Geology, University of Tromsø, Norway. 3. Norwegian Mining Museum, Norway. 4. Geological Institute, Kola Scientific Centre, Russian Academy of Sciences, Russia. 5. Department of Geosciences, University of Oslo, Norway.

Corresponding email: [emanuela.schingaro@uniba.it](mailto:emanuela.schingaro@uniba.it)

Keywords: Lamproite, Kvaløya Island, Yangzhumingite, Tetraferrifluorophlogopite.

This study reports the first single crystal structure refinement of a natural yangzhumingite found in a lamproitic dyke at the Kvaløya Island (North Norway), as well as a complete structural characterization of the associated phlogopite. Specifically, three types of micas (yangzhumingite, light brown phlogopite and dark brown phlogopite) underwent petrographic and crystal chemical analyses by integrating multiple analytical techniques: electron microprobe, single crystal X-ray diffraction, inductively coupled plasma mass spectrometry, Mössbauer and micro-Fourier Transform infrared spectroscopy.

The micas are separated into three different groups on the basis of the <sup>V</sup>Fe and Mg versus Si content. Yangzhumingite composition is intermediate between those of  $\text{KMg}_{2.75}(\text{Si}_{3.5}\text{Al}_{0.5})\text{O}_{10}\text{F}_2$  and  $\text{KMg}_{2.50}\text{Si}_4\text{O}_{10}\text{F}_2$  synthetic compounds studied by Toraya et al., 1976, 1978, respectively. Light and dark brown phlogopite are both Mg-rich tetraferrifluorophlogopite, the latter having a greater Fe content. The main features of the infrared spectra of yangzhumingite and the light brown phlogopite show the occurrence of OH<sup>-</sup> absorption bands respectively at: ~3586 cm<sup>-1</sup> which correlates well with the measured F content: 3707 cm<sup>-1</sup> and 3686 cm<sup>-1</sup> assigned mainly to  $3\text{Mg}^{2+}\text{-K}^+\text{-OH}^-$  (phlogopitic) environment.

Structural analyses, performed only on yangzhumingite and the light brown phlogopite because dark brown phlogopite is poorly crystallized, show that both samples are 1M polytypes with the expected space group C2/m. Yangzhumingite has cell parameters  $a = 5.2677(3)$ ,  $b = 9.1208(5)$ ,  $c = 10.1652(6)$  Å,  $\beta = 100.010(4)^\circ$  whereas light brown phlogopite has  $a = 5.3202(3)$ ,  $b = 9.2128(4)$ ,  $c = 10.1971(5)$  Å,  $\beta = 100.080(4)^\circ$ . Crystal chemical features are compatible with the following major substitution mechanisms:  $2\text{XIIK}^+ \leftrightarrow \text{VI}^{\text{R}^{2+}} + \text{VI}^{\text{[ ]}}$  (where  $\text{R}^{2+} = \text{Mg, Fe}$ ),  $\text{OH}^- \leftrightarrow \text{F}^-$  for yangzhumingite and  $2\text{VI}^{\text{R}^{2+}} \leftrightarrow \text{VI}^{\text{Ti}^{4+}} + \text{VI}^{\text{[ ]}}$  (Ti-vacancy),  $\text{OH}^- \leftrightarrow \text{F}^-$  for light brown phlogopite.

The three types of mica reported here formed at relatively constant low pressure, but over a large temperature range in equilibrium with a grain boundary fluid that underwent significant changes in composition during reaction progress. Light brown phlogopite cores and dark brown phlogopite rims formed during crystallization from the lamproitic magma, while yangzhumingite formed as a result of reactions between the already formed phlogopites and the highly reactive fluid that was derived from the volatile-rich lamproite magma.

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## **A FESEM-FIB-EDS investigation on fibrous and acicular volcanic orthopyroxenes from Etnean products, Italy**

Stelluti I.\*<sup>1</sup>, Mura F.<sup>2</sup> & Gianfagna A.<sup>1</sup>

1. Dipartimento di Scienze della Terra, "Sapienza" Università di Roma. 2. Laboratorio di Nanotecnologie e Nanoscienze della Sapienza, "Sapienza" Università di Roma.

Corresponding email: [igor.stelluti@uniroma1.it](mailto:igor.stelluti@uniroma1.it)

Keywords: etnean minerals, fibrous pyroxenes.

Present work concerns the continuation of the study of these particular ferroan orthopyroxenes, which have been investigated by Field Emission Scanning Electron Microscopy (FESEM) combined with Focused Ion Beam (FIB) and with Energy Dispersive X-ray Spectroscopy (EDS). These analytical techniques have allowed a detailed study of the external morphology, besides to compositional variations from the surface to the internal parts of the crystals, thanks to the FIB cutting. The study revealed differences in morphology and composition between the fibrous and the acicular orthopyroxenes. The crystals with acicular habit (width  $\approx 2-3 \mu\text{m}$ ), often twinned and sometimes flattened, has a ferroan-enstatite composition with an iron content higher than the fibrous crystals, and are characterized by the presence of parallel lamellae exolutions between them, which extend along the "c" axis of the mineral growth. The exolutions are often visible on the surface of the crystal, making striated morphologies, and their chemical composition, even though with similar spectrum EDS of ferroan-enstatite, presents an iron content higher than the host mineral. In effect, these exolutions could be simple iron oxides in following to element migration. The fibrous orthopyroxene variety (thinner than the prismatic type - width  $\approx 0,5 \mu\text{m}$ ) shows an internal compositional homogeneity with a lower iron content (FeO  $\approx 1 \text{ wt}\%$ ). From these new experimental evidences on morphologies, dimensions, chemical compositions and iron behaviour, we can advance further hypothesis on the crystallization process: 1) a secondary process of alteration interested the prismatic and acicular crystals, which allowed migration of iron and formation of exolutions; 2) consequent formation of oxides with iron 3+ (hematite); 3) high speed of crystallization during the final stage of the magmatic process, with fibrous enstatite formation and low iron content.

A crystal-chemistry study of the acicular and fibrous opx is necessary to confirm or not these hypothesis.

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Stelluti I., Viti C. & Gianfagna A. 2013. Mineralogical characterization and crystallization kinetics of fibrous and acicular volcanic orthopyroxenes from Mt. Etna, Sicily, Italy. Goldschmidt 2013.

## Natural evidence of kimberlite-garnet reactions in the upper mantle

Zibera L.\*<sup>1</sup>, Nimis P.<sup>2</sup>, Zanetti A.<sup>3</sup>, Marzoli A.<sup>2</sup> & Sobolev N.V.<sup>4</sup>

1. School of Earth Sciences, University of Bristol. 2. Dipartimento di Geoscienze, Università di Padova  
3. IGG-CNR Pavia. 4. Sobolev Institute of Geology and Mineralogy, Novosibirsk.

Corresponding email: [luca.zibera@bristol.ac.uk](mailto:luca.zibera@bristol.ac.uk)

Keywords: Garnet, Kimberlite, Trace elements.

Percolation of melts in the Earth's upper mantle leaves geochemical and mineralogical imprints on both the melts and the mantle rocks that need to be interpreted using the available natural samples. Kimberlites, which have the deepest origin of all terrestrial magmas, provide the unique opportunity to study the melt-rock reactions down to the deepest portions of the cratonic lithospheric mantle. The imprints of these reactions are potentially recorded in the kimberlite-hosted mantle xenoliths and in the kimberlitic melts themselves, but they are often obscured by the processes occurring during and after the kimberlite eruption. Garnet and clinopyroxenes, which are two important constituents of the peridotitic mantle, are more resistant to these processes and are in fact commonly found in kimberlites as xenocrysts derived from the disaggregation of the former mantle rocks. Here we focus on the garnet xenocrysts suite of the Zagadochnaya kimberlite (Yakutia, Russia). This is a good case study to investigate the melt percolation processes in the upper mantle, because these samples preserve the clear evidence of garnet-melt reactions occurred at mantle depths shortly before the kimberlite eruption.

All analysed garnet grains are of peridotitic origin and most of them are strongly zoned, showing domains where the original (Ca, Cr)-rich garnet has been replaced by (Ca, Cr)-poor garnet + clinopyroxene + spinel ( $\pm$  phlogopite  $\pm$  amphibole  $\pm$  Ti oxides). These domains are often located at the edges of the grains and in some cases extend pervasively throughout the entire grain. The trace element contents of the secondary garnets, which are systematically higher with respect to the primary hosts, are compatible with equilibrium with the Zagadochnaya kimberlite. This observation, combined with other supporting textural and mineralogical evidence (Nimis et al., 2009; Zibera et al., 2013), indicate that these replacement reactions were driven by melts closely related to the host Zagadochnaya kimberlite and that they occurred at mantle depths shortly before the eruption. The wide spectrum of textural, mineralogical, and major and trace element features of these microxenoliths makes this case study suitable for the application of forward modeling of petrogenetic processes. Therefore numerical simulations of trace element transfer will be tested, which can potentially help to identify the melt-rock reactions that occurred in the mantle shortly before the eruption of the kimberlite.

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Zibera L., Nimis P., Zanetti A., Marzoli A. & Sobolev N.V. 2013. Metasomatic processes in the central Siberian cratonic mantle: evidence from garnet xenocrysts from the Zagadochnaya kimberlite. *J. Pet.*, 54, 2379-2409.

## SESSIONE S17

### **The oceanic lithosphere: formation, evolution and fate**

#### *CONVENORS*

*M. Chiari (CNR-IGG Firenze)*

*M. Marroni (Univ. Pisa)*

*R. Tribuzio (Univ. Pavia)*

## **Modes of ophiolite emplacement in the Tethyan Belt: Implications for palaeogeography and geodynamic reconstructions**

Argnani A.\*

ISMAR, CNR Bologna.

Corresponding email: [andrea.argnani@ismar.cnr.it](mailto:andrea.argnani@ismar.cnr.it)

Keywords: Ophiolite emplacement, Tethyan belt, palaeogeography.

Ophiolite belts cropping out in mountain ranges have classically been considered as evidence of the closure of a former ocean since the early days of Plate Tectonics (e.g., Dewey, 1977). The articulate mountain belt that extends from the Mediterranean region to the Himalayas, and further to the east, has been shaped by the convergence towards Eurasia of a set of southern plates (chiefly Africa, Arabia, and India), ultimately leading to continental collision. The oceanic Tethyan realm, originated during the breakup of Pangea, was consumed during this long-lasting process of plate convergence, leaving sparse vestiges of its original complex palaeogeography (e.g., Sengor, 1985). The Mediterranean Tethyan belt, in particular, offers many examples of ophiolite units dotting the Alpine mountains. Although these ophiolite units originated within the same oceanic realm, they display different ages and geochemical affinity, ranging from MORB to SSZ. But a feature that is perhaps more relevant for palaeogeographic reconstruction is the nature of ophiolite emplacement. Along the Mediterranean Tethyan belt two main types of ophiolite occurrence can be encountered, in spite of some local variety.

In one instance the ophiolites appear as large slivers which have been emplaced onto a passive margin sedimentary succession, and have been capped and sutured by shallow water carbonate sediments. Ophiolites of this type crop out in the Dinarides and Hellenides, with Jurassic age. These ophiolites come from the upper plate and show little or no metamorphism. The age of metamorphic soles indicates that these ophiolites were originated by intra-oceanic subduction, and their emplacement do not mark a collisional suture.

The other major type of emplacement is related to continental collision, when a subductive accretionary wedge is shoved onto a passive continental margin. A subduction initially located at the continental margin is the premise for this type of emplacement. The ophiolite rocks of this type are typically coming from the lower plate, and suffer from variable degree of metamorphism during accretion. Disrupted ophiolites, in blocks of various size often arranged as melange, are accreted in the frontal part of the accretionary wedge. Larger slabs of ophiolite are present in the deeper part of the accretionary wedge; these rocks experienced HP/LT metamorphism in the subduction channel, before being underplated and eventually exhumed. Ophiolites of this type are typically present in the western Mediterranean (Alps, Apennines and Corsica).

The two modes of ophiolite emplacement imply that subduction initiated at different position within the Tethyan ocean, and this issue has major relevance on palaeogeographic reconstructions and geodynamic interpretations.

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## Subsolidus and partial melting experiments on a natural pyroxenite at 1-1.5 GPa

Borghini G.\*<sup>1</sup>, Fumagalli P.<sup>1</sup> & Rampone E.<sup>2</sup>

1. Dipartimento di Scienze Terra, Università di Milano. 2. Dipartimento di Scienze della Terra, dell'Ambiente e della Vita, Università di Genova.

Corresponding email: [giulio.borghini@unimi.it](mailto:giulio.borghini@unimi.it)

Keywords: Experimental Petrology, pyroxenites, mantle partial melting.

Pyroxenite layers embedded in mantle peridotites represent a diffuse lithological heterogeneity in the upper mantle and they are often invoked as a minor but important component in the mantle source of oceanic basalts, as main responsible for their chemical and isotopic variability (e.g. Lambart et al., 2013). Pyroxenite layers in ophiolitic mantle sequences of the Northern Apennines (NA, Italy) have been recently interpreted as the result of deep infiltration of low-MgO melts in the peridotites, thus representing a natural portrait of the so-called “stage 2 pyroxenite”, a potential enriched component in the basalts mantle sources (Mallik & Dasgupta, 2012; Lambart et al., 2012). This study aims to define i) the subsolidus phase assemblage, ii) melt productivity and iii) composition of partial melts of a stage2-type pyroxenite by high pressure and temperature synthesis of a natural NA pyroxenite. Experiments were carried out at P from 1 to 1.5 GPa and T from 1100 to 1330°C, using both single-stage and end-loaded piston cylinders. As starting material we used a glass obtained by complete melting of rock powder sample in a furnace at 1500°C (at FMQ fO<sub>2</sub> conditions) and rapid quench in dry ice. Resulting glass has X<sub>Mg</sub>=0.83, CaO=14.4 wt%, Al<sub>2</sub>O<sub>3</sub>=10.1 wt% and Na<sub>2</sub>O=0.3 wt%, similar to bulk compositions of several worldwide pyroxenites. To promote the nucleation of the minor phases in subsolidus experiments, gel is seeded with 1% of a mixture of synthetic pure spinel (50%) and Dora-Maira pyrope (50%). A layer of carbon vitreous spheres (dMg in olivine and pyroxenes) and first mass balance calculation support approach to equilibrium. At near-solidus T, a spinel-bearing assemblage is stable at 1.0 GPa, whereas garnet+spinel-bearing assemblage is stable at 1.5 GPa. Glass appears in experiments between 1150-1200°C at 1.0 GPa, and 1200-1250°C at 1.5 GPa. At 1 GPa, pyroxenite GV10 produces i) very low melt fraction (F > 5 wt%) at 1200°C, ii) a low-X<sub>Mg</sub> (≅ 0.43), Al-rich melt for low melt fraction (F = 8.9 wt%; T = 1250°C), iii) a high-X<sub>Mg</sub> high-CaO melt for high partial melting degrees (F = 56.7 wt%), iv) melt fraction of about 80 wt% at 1330°C. Preliminary results of this study indicate that high degrees of partial melting of a stage2-type pyroxenite produces melts with composition close to that of near-solidus partial melts from fertile peridotites (Falloon et al., 2008).

Borghini G., Rampone E., Zanetti A., Class C., Cipriani A., Hofmann A.W., Goldstein S.L. & Godard M. Chemical and isotopic heterogeneity in meter-scale pyroxenite-peridotite mantle sequences from Northern Apennine ophiolites (Italy). This conference.

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## Chemical and isotopic heterogeneity in meter-scale pyroxenite-peridotite mantle sequences from Northern Apennine ophiolites (Italy)

Borghini G.<sup>\*1-2-3</sup>, Rampone E.<sup>2</sup>, Zanetti A.<sup>4</sup>, Class C.<sup>3</sup>, Cipriani A.<sup>3-5</sup>, Hofmann A.W.<sup>3-6</sup>, Goldstein S.L.<sup>3</sup> & Godard M.<sup>7</sup>

1. DISTAV- Università di Genova. 2. LDEO- Columbia University, USA. 3. Dipartimento di Scienze Terra, Università di Milano. 4. CNR-IGG Pavia. 5. DSCG, Università di Modena e Reggio Emilia. 6. MPI für Chemie- Mainz, Germany. 7. UMR CNRS- Universite Montpellier, France.

Corresponding email: [giulio.borghini@unimi.it](mailto:giulio.borghini@unimi.it)

Keywords: small-scale mantle heterogeneity, pyroxenite-peridotite sequence, isotope geochemistry.

Deep melt intrusion and melt-peridotite interaction are considered the most efficient processes in creating small-scale heterogeneity in the upper mantle. Pyroxenite-peridotite mantle sequences of External Liguride Units (Northern Apennines, Italy) record the chemical and isotopic variability inherited from their deep lithospheric origin representing an excellent study case to investigate the origin of pyroxenites and how their emplacement modify the chemical and isotopic composition of the upper mantle. Pyroxenites range from spinel-bearing websterite to clinopyroxenite and occur as cm-thick layers (up to 40 cm) parallel to tectonite foliation. In spite of partial subsolidus low-P re-equilibration (spinel- to plagioclase-facies), most of the pyroxenites record chemical features inherited from a precursor garnet-bearing assemblage. Mass balance calculations provide up to about 40% of garnet in the original mineralogy, thus supporting that pyroxenites originated from melt segregation in mantle peridotites at rather high pressures ( $P > 1.6$  GPa). Tholeiitic affinity and rather low  $X_{Mg}$  ( $< 62$ ) of the pyroxenite parental melts suggest that these latter were produced by partial melting of an heterogeneous (SE) pyroxenite-bearing mantle, then reacted in-situ with the host peridotite. Melt-peridotite interaction is indicated by chemical modification of wall-rock peridotites which show i) modal orthopyroxene enrichment at the expense of olivine, ii) higher Al, Ca, Si contents and slightly lower Mg# of bulk rocks, and iii) Al-richer spinel and lower-Mg# pyroxenes, with respect to the pyroxenite-free country peridotites. In the modified peridotites, clinopyroxene porphyroclasts record a trace element gradient resulting from percolative reactive flow of pyroxenite melt up to about 20 cm from the pyroxenite-peridotite boundary. Sr and Nd isotopic compositions fall within the MORB field ( $^{87}Sr/^{86}Sr = 0.7023-0.7029$ ;  $^{143}Nd/^{144}Nd = 0.5134-0.5128$ ).  $^{143}Nd/^{144}Nd$  ratios in peridotites and pyroxenite on few meters scale cover almost the entire Nd isotopic variability documented in abyssal peridotites. Pyroxenite intrusion modified the host peridotites, lowering their  $^{143}Nd/^{144}Nd$  as a combined effect of the systematic LREE enrichment (i.e. Nd/Sm increase) and radioactive decay (Borghini et al., 2013). Sm/Nd errorchrons defined by pyroxenites and modified peridotites yield a small range of ages between 424-452 Ma (errors  $< \pm 50$  Ma). This constrains the timing of pyroxenite emplacement that widely predates the low-P evolution related to rifting and opening of Jurassic Ligurian Tethys, as indicated by plagioclase-clinopyroxene-whole rock Sm-Nd internal isochrones ( $178 \pm 25$  Ma). Hf isotope analysis performed on separated clinopyroxenes from the same set of samples indicate that  $^{176}Hf/^{177}Hf$  ratios of pyroxenites and peridotites well correlate with the  $^{143}Nd/^{144}Nd$  ratios, showing a large variability at the massif scale.

Borghini G., Rampone E., Zanetti A., Class C., Cipriani A., Hofmann A.W. & Goldstein S.L. 2013. Meter-scale Nd isotopic heterogeneity in pyroxenite-bearing Ligurian peridotites encompasses global-scale upper mantle variability. *Geology* 41, 1055-1058.

## Age and geochemistry of chert-basalt associations in the ophiolitic complexes of the Izmir-Ankara Mélange (East of Ankara, Turkey)

Bortolotti V.<sup>1</sup>, Chiari M.\*<sup>2</sup>, Göncüoğlu M.C.<sup>3</sup>, Marcucci M.<sup>1</sup>, Principi G.<sup>1</sup>, Saccani E.<sup>4</sup>,  
Tekin U.K.<sup>5</sup> & Tassinari R.<sup>4</sup>

1. Dipartimento di Scienze della Terra- Università di Firenze. 2. IGG-CNR Firenze. 3. Geological Engineering Department- Middle East Technical University Ankara, Turkey. 4. Dipartimento di Fisica e Scienze della Terra- Università di Ferrara. 5. Geological Engineering Department- Hacettepe University Ankara, Turkey.

Corresponding email: [mchiari@geo.unifi.it](mailto:mchiari@geo.unifi.it)

Keywords: Ophiolites, Izmir-Ankara Mélange, Turkey.

In this work, we present the preliminary age data of the radiolarian cherts deposited on the top of basalts belonging to the Eastern Ankara Mélange (part of the Izmir-Ankara Mélange). Petrological studies on basalts were carried out in order to constrain the tectonic setting of formation of the studied basalt-chert sequences. Nine sections were sampled to the East of Ankara and twenty seven samples were collected for biostratigraphic and geochemical analyses.

The oldest radiolarian cherts dated in the present paper are referable to Late Triassic (Section 6: late Norian) and are associated with basaltic rocks with OIB character. OIB type volcanic rocks are also found in other sections and are associated with cherts of Late Jurassic (Section 3: middle-late Oxfordian to late Kimmeridgian-early Tithonian) and Early Cretaceous (Section 1: late Valanginian to latest Valanginian-earliest Hauterivian) ages.

E-MORB type rocks are associated with radiolarian cherts of Cretaceous age (Section 4: late Barremian and Section 7: Valanginian to middle Aptian-early Albian), whereas the oldest N-MORBs were found in a section of Late Jurassic age (Section 5: early-early late Tithonian). Other N-MORBs are associated with radiolarian cherts of Early Cretaceous age (Section 8: late Valanginian-early Barremian). P-MORBs type rocks were found only in a section of Middle Jurassic age (Section 2: early-middle Bajocian to late Bathonian-early Callovian age).

In this work, we document the occurrence of OIB-type rocks of Late Triassic and of rocks showing different geochemical affinities (N-, E-, P-MORBs and OIB) generated in the same time span (Middle-Late Jurassic - Early Cretaceous). N-MORBs are compatible with composition of melts generated by partial melting of a depleted MORB mantle source. In contrast, OIBs are compatible with partial melting of enriched-type mantle source. E-MORBs may have derived from mantle source slightly enriched with respect to DMM source, whereas P-MORBs are compatible with melts generated from a mantle source significantly enriched, compared to DMM.

The chemical differences shown by the distinct rock-types can be related either to differences in source composition or different tectonic settings of formation, which may have existed during the Late Jurassic - Early Cretaceous time span.

## Multistage asthenospheric melt/rock reaction in the ultraslow eastern SWIR mantle

Brunelli D.\*<sup>1-2</sup>, Verzani A.<sup>1</sup>, Spallanzani R.<sup>1</sup>, Seyler M.<sup>3</sup> & Cannat M.<sup>4</sup>

1. Dipartimento di Scienze Chimiche e Geologiche, Università degli Studi di Modena e Reggio Emilia. 2. Istituto di Scienze Marine, Geologia Marina, CNR, Bologna. 3. UFR Sciences de la Terre, UMR 8217 CNRS-Universite' Lille 1, France. 4. Equipe de Géosciences Marines, Institut de Physique du Globe de Paris, France.

Corresponding email: [daniele.brunelli@unimore.it](mailto:daniele.brunelli@unimore.it)

Keywords: SWIR, mantle partial melting, melting modelling, trace element.

Very small amounts of melt are produced during mantle upwelling beneath the ultraslow spreading South West Indian Ridge. Sectors of this Oceanic Ridge are characterized by nearly amagmatic spreading with rare limited eruptions of basalts spotting a mantle-derived serpentinitic crust. A large peridotite dataset was recovered during the Smoothseafloor French expedition led by D. Sauter and M. Cannat in 2005 (Sauter et al., 2013). Mantle-derived rocks show a significant modal variability from the sample to the dredge scale with frequent occurrences of millimetric to centimetric spinel-bearing pyroxenitic veins. Mantle residua record a multistage reactional history between small amount of transient melts and variably depleted mantle parcels. Incomplete mineral replacements are widespread showing that both pyroxenes are repeatedly dissolved and recrystallized leaving poekilitic pyroxene and spinel textures. Reacting conditions are modelled assuming an incremental open-system melting model under variable critical porosity/F ratios (Seyler et al., 2011; Brunelli et al., 2014). Incoming melts result to be generated by low degrees of melting in the garnet field then reacting with the rock under near-batch conditions, i.e. at low rates of melt extraction with respect to the actual rock porosity. As a consequence Na (and LREE) countertrends with melting indicators as mineral Cr# and concentration of the moderately incompatible elements (HREE, HFSE). This results in rotation of the REE patterns around a pivot element instead of showing progressive depletion as expected after suboceanic mantle decompression.

Brunelli D., Paganelli E. & Seyler, M. 2014. Percolation of enriched melts during incremental open-system melting in the spinel field: A REE approach to abyssal peridotites from the Southwest Indian Ridge. *Geoch. et Cosmoch. Acta*, 127, 190–203. doi:10.1016/j.gca.2013.11.040.

Sauter D., Cannat M., Searle R. 2013. Continuous exhumation of mantle-derived rocks at the Southwest Indian Ridge for 11 million years. *Nature Geosci.*, 6(4), 1–7. doi:10.1038/ngeo1771.

Seyler M., Brunelli D., Toplis M. J. & Mével C. (2011). Multiscale chemical heterogeneities beneath the eastern Southwest Indian Ridge (52°E–68°E): Trace element compositions of along-axis dredged peridotites. *Geochem. Geophys. Geosyst.*, 12, Q0AC15. doi:10.1029/2011gc003585.

## Astenospheric processes beneath the ultraslow Smoothseafloor region in the eastern South West Indian Ridge

Brunelli D.\*<sup>1-2</sup>, Verzani A.<sup>1</sup>, Spallanzani R.<sup>1</sup>, Seyler M.<sup>3</sup> & Cannat M.<sup>4</sup>

1. Dipartimento di Scienze Chimiche e Geologiche, Università degli Studi di Modena e Reggio Emilia. 2. Istituto di Scienze Marine, Geologia Marina, CNR, Bologna. 3. UFR Sciences de la Terre, UMR 8217 CNRS-Université Lille 1, Villeneuve d'Ascq CEDEX, France. 4. Equipe de Géosciences Marines, Institut de Physique du Globe de Paris, Univ Paris Diderot, Paris, France.

Corresponding email: [daniele.brunelli@unimore.it](mailto:daniele.brunelli@unimore.it)

Keywords: mantle partial melting, smoothseafloor, South West Indian Ridge, peridotite, trace element.

Mantle melting at ultraslow spreading ridges is constrained by the low potential temperature and thicker-than-normal LID that limits the extent of the melting column. As a result very small amounts of melts are produced inhibiting the formation of a “normal” oceanic lithosphere and leading to a purely tectonic seafloor extension dominated by serpentinization: the recently investigated Smoothseafloor type spreading (Sauter et al., 2013). At depth the reaction of very small amounts of percolating melts and host asthenospheric mantle leaves traces of the melt/rock reactions as incomplete mineral replacement and strongly variable modal distribution at short scale (dm). Enstatitic, and to a less extent diopsidic, pyroxenes appear to be repeatedly dissolved and recrystallized leaving poekilitic pyroxene and spinel leftovers. Melts enriched in incompatible elements are possibly generated in the garnet field then reacting with the rock under near-batch conditions, i.e. at low rates of melt extraction with respect to the actual rock porosity (Brunelli et al., 2014). Prolonged pyroxenes' dissolution-recrystallization results in enhanced enrichment of the most incompatible elements in the percolating melts that only occasionally are extracted from the system. As a consequence Na (and LREE) countertrends with the melting indicators as mineral Cr# and concentration of the moderately incompatible elements (HREE, HFSE). Accordingly the associated basalts are characterized by a strong Na enrichment and compositional trends separated from those generated in the surrounding regions.

Brunelli D., Paganelli E. & Seyler M. 2014. Percolation of enriched melts during incremental open-system melting in the spinel field: A REE approach to abyssal peridotites from the Southwest Indian Ridge. *Geochimica et Cosmochimica Acta*, 127, 190–203. doi:10.1016/j.gca.2013.11.040

Sauter D., Cannat M., Rouméjon S., Andreani M., Birot D., Bronner A., Searle R. 2013. Continuous exhumation of mantle-derived rocks at the Southwest Indian Ridge for 11 million years. *Nature Geoscience*, 6(4), 1–7. doi:10.1038/ngeo1771.

## Rare occurrences of Early Jurassic radiolarian cherts in the Dinaric-Hellenic Belt, an open problem

Chiari M.\*<sup>1</sup>, Baumgartner P.O.<sup>2</sup>, Bernoulli D.<sup>3</sup>, Bortolotti V.<sup>4</sup>, Muttoni G.<sup>5</sup>, Principi G.<sup>4</sup> & Treves B.<sup>1</sup>

1. IGG-CNR Firenze. 2. UNIL- Université de Lausanne, Switzerland. 3. Geologisches Institut- Universität Basel, Switzerland. 4. Dipartimento di Scienze della Terra- Università di Firenze. 5. Dipartimento di Scienze della Terra "A. Desio"- Università di Milano.

Corresponding email: [mchiari@geo.unifi.it](mailto:mchiari@geo.unifi.it)

Keywords: Maliac-Vardar Ocean, Dinaric-Hellenic belt, Early Jurassic.

The Dinaric-Hellenic mountain belt formed through the closure of the Maliac-Vardar Ocean and the collision of Adria with microplates (Tisia, Dacia) positioned between Eurasia and the main branch of the Neo-Tethys. The ophiolites derived from the Maliac-Vardar Ocean are now scattered over different tectono-stratigraphic units (Bortolotti et al., 2013): i) a *mélange* below the major ophiolite nappe (sub-ophiolitic *mélange*); ii) a unit of Triassic ocean-floor ophiolites; iii) metamorphic soles underlying the major ophiolite nappes; within the major ophiolite assemblage; iv) a Jurassic fore-arc ophiolite unit (with MOR and SSZ magmatic sequences); v) a Jurassic intra-oceanic-arc ophiolite unit (with only SSZ magmatic sequences) and vi) a Jurassic back-arc basin ophiolite unit (with BABB and CAB magmatic sequences).

During the last 30 years, several authors studied the Dinaric-Hellenic ophiolite sequences where radiolarian cherts are overlying or interbedded with basalts in several locations, e.g. Serbia (Zlatibor), Albania (Mirdita), Greece (northern Pindos Mountains, Vourinos, Othrys, Koziakas, Argolis, Evvia, Guevgueli), aiming at reconstructing the geodynamic history of the Dinaric-Hellenic belt. Numerous sections were studied and rich faunas of Triassic and Jurassic age were found in the radiolarian cherts; however, only in two stratigraphic sections, at Angelokastron and Vothiki (Argolis), radiolarites of *Early Jurassic* age were found.

At Angelokastron, the Early Jurassic cherts were found in a small quarry, where, included in a matrix of dark reddish-brown cherty shales, fragments of chert and chert nodules impregnated by ferro-manganese oxides occur (Chiari et al., 2013). The examined samples indicate four age groups for the nodules, and a Middle Jurassic (middle Bathonian) age for the siliceous matrix in which they are embedded. The first age group includes radiolarians of Late Triassic (late Norian–Rhaetian) age; the second group of Early Jurassic (late early to late Pliensbachian and probably middle-late Toarcian) age; the third group comprises species of early Middle Jurassic (Aalenian-Bajocian) age; the fourth group finally consists of late Middle Jurassic (Bajocian-Bathonian) taxa. The Mn-impregnated chert nodules indicate that from Late Triassic to Middle Jurassic a deep oceanic basin existed in the area.

Only another small outcrop in the Argolis Peninsula gave a very poorly preserved radiolarian assemblage of probable Early Jurassic age. The sample comes from a thin, tectonized chert horizon intercalated in a massive basalt in a little quarry near the village of Vothiki, and has been dated as ?Sinemurian.

The scarcity of Early Jurassic cherts in the entire Dinaric-Hellenic belt poses some significant questions: is the extreme scarcity of Early Jurassic radiolarites due to stratigraphic or tectonic causes? More specifically, is this scarcity due to a lack of sedimentation or secondary tectonic elimination? In the first hypothesis, we should look for paleoenvironmental and/or paleoceanographic changes that may have controlled Early Jurassic radiolarian productivity and deposition. In the second case, the tectonic evolution of the basin may have caused subduction of some Early Jurassic parts of the Vardarian oceanic basin, with the possible incorporation of the Early Jurassic portions of the radiolarite sequences into the Middle Jurassic metamorphic soles, where radiolarites could not thus far be dated.

Bortolotti V., Chiari M., Marroni M., Pandolfi L., Principi G. & Saccani E. 2013. Geodynamic evolution of the ophiolites from Albania and Greece, (Dinaric-Hellenic Belt): one, two or more oceanic basins? *International Journal of Earth Sciences* (Geol. Rundsch.), 102, 783-811.

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## Crustal velocity model for the Ionian Sea inferred from new OBS/H data: evidences of Ionian upper mantle serpentinization?

D'Alessandro A.\*, Mangano G. & D'Anna G.

Istituto Nazionale di Geofisica e Vulcanologia, Roma.

Corresponding email: [antonino.dalessandro@ingv.it](mailto:antonino.dalessandro@ingv.it)

Keywords: Ionian Crust, upper mantle serpentinization, P- and S-wave arrival times inversion.

The lack of seafloor stations in the Ionian Sea not allowed to locate moderate magnitude earthquakes and characterize the regional seismogenetic structure in this area (D'Alessandro et al., 2011a, 2011b, 2013a). Within the monitoring activities carried out in cooperation with the Dipartimento di Protezione Civile (Italy) and within the European project NERIES (activity NA6), the Istituto Nazionale di Geofisica e Vulcanologia (Italy) deployed in May 2007 three broadband OBS/H in the Southern Ionian Sea (D'Alessandro et al., 2009, 2012, 2013b). Simultaneous inversion of P- and S-wave arrival times, collected during a long time OBS/H monitoring campaign, yields 1D P- and S-wave velocity models for the Ionian lithosphere. The 1D model highlights the presence of a two layers with high seismic P-wave velocity (S1 and S2, 6.3-6.7 and 7.5 km/s, respectively) in the Ionian lower crust. This two layers, with thickness of about 3.3 km and 5 km, respectively, are characterized by low values of the S-wave velocity (S1=3.05-3.2 km/s, S2=3.85 km/s) and high values of  $V_p/V_s$  (S1=2.06-2.09, S2=1.95). This is characteristic feature often encountered in passive continental margins and are generally interpreted as partly serpentinized peridotite. The  $V_p$ ,  $V_s$  and  $V_p/V_s$  values of S1 are consistent with 55-65% serpentinization while that of S2 are consistent with 15–25% serpentinization of the mantle. Water needed to serpentinize peridotites may be supplied from the continental lower crust, through cracks and faults from above or from the rising plume.

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D'Alessandro A., Papanastassiou D., Baskoutas I. 2011b. Hellenic Unified Seismological Network: an evaluation of its performance through SNES method, *Geophys. J. Int.*, vol. 185, n. 3, pp. 1417-1430.

D'Alessandro A., Mangano G, D'Anna G. 2012. Evidence of persistent seismo-volcanic activity at Marsili seamount, *Ann. of Geophys.*, 55, 2, 213-214.

D'Alessandro A., Gervasi A., Guerra I. 2013. Evolution and strengthening of the Calabrian Regional Seismic Network, *Advances in Geosciences*, 36, 11-16.

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## Experimentally-derived Ca-Na partitioning between plagioclase and clinopyroxene: a new geobarometer for mantle rocks

Fumagalli P.\*<sup>1</sup>, Borghini G.<sup>1</sup>, Rampone E.<sup>2</sup> & Poli S.<sup>1</sup>

1. Dipartimento di Scienze della Terra, Università di Milano. 2. DIPTERIS, Università di Genova.

Corresponding email: [patrizia.fumagalli@unimi.it](mailto:patrizia.fumagalli@unimi.it)

Keywords: Plagioclase-peridotites, mantle exhumation, geobarometer.

The crystallization of plagioclase-bearing equilibrium assemblages in mantle peridotites is commonly considered witness of lithospheric mantle exhumation at shallow depth. Previous experimental works have found systematic compositional variations in coexisting minerals at decreasing pressure within the plagioclase stability field, similar to what observed in equilibrated plagioclase peridotites. In particular Ca-Na partitioning between plagioclase and clinopyroxene is strictly dependent on pressure, with plagioclase composition varying significantly ( $An=59-83$ ) in a narrow pressure range, thus envisaging a potential geobarometer to estimate plagioclase-facies equilibrium pressures. Nevertheless, the composition of plagioclase at variable bulk  $Na_2O/CaO$  ratios has been not fully discerned yet, making this approach directly applicable to a limited bulk composition range. Here, we present the results of new experiments on a Na-enriched lherzolite (bulk  $Na_2O/CaO$  ratio = 0.13), representative of many refertilized lithospheric peridotites at extensional settings, thus enlarging significantly our investigated compositional spectrum ( $Na_2O/CaO = 0.08 - 0.13$ ).

The starting bulk compositions have been selected in order to cover the variability of natural occurrences. A fertile lherzolite, FLZ, and a depleted lherzolite, DLZ (Borghini et al., 2010) correspond to a spinel lherzolite from Suvero (External Liguride ophiolites, Northern Apennine, Italy) and to a Depleted MORB Mantle (Wasilenky et al. 2003) respectively. In order to investigate the effect of the bulk  $Na_2O/CaO$  on the plagioclase to spinel transition, an extra-fertile bulk composition was considered by adding  $Na_2O$  to FLZ (HNa-FLZ).

As expected, the increase of bulk  $Na_2O/CaO$  extends plagioclase stability to higher P as compared with FLZ; in HNa-FLZ the plagioclase-spinel transition occurs between 0.9-1.0 GPa, 1100°C.

$Ca/(Ca+Na)$  decreases with pressure in plagioclase and clinopyroxene in all the investigated bulks, suggesting a sensitive pressure dependent relation. A slight dependence on bulk  $Na_2O/CaO$  might be envisaged. However, the unexpected occurrence of amphibole in HNa-FLZ needs to be taken into account as additional Ca,Na-bearing phase.

Thermodynamic modelling fails in reproducing in details the isopleths of  $XCa_{(plag)}/XCa_{(cpx)}$ . This is likely due to the fact that available solution models for orthopyroxene do not consider CaO, which instead might be present in experimental and natural orthopyroxenes (from about 0.4 to 1.6 wt.%).

Experimental data suggest that Ca-Na partitioning between plagioclase and clinopyroxene is only slightly affected by the bulk  $Na_2O/CaO$ : at 1100°C: the ratio  $XCa_{(plag)}/XCa_{(cpx)}$  of 0.65 translates into an equilibrium pressure of 0.7 GPa for HNa-FLZ and about 0.8 GPa for FLZ, with a difference of less than 0.1 GPa.

Borghini G., Fumagalli P., & Rampone E. 2010. The stability of plagioclase in the upper Mantle: subsolidus experiments on fertile and depleted lherzolite *J. Petrol.*, 51, 229-254.

## **IODP Expedition 345: Primitive Layered Gabbros From Fast-Spreading Lower Oceanic Crust**

Ildefonse B.\*<sup>1</sup>, Gillis K.M.<sup>2</sup>, Snow J.E.<sup>3</sup>, Klaus A.<sup>4</sup> & the IODP Exp 345 Scientific Party

1. Géosciences Montpellier, Université Montpellier 2 & CNRS, Montpellier, France. 2. SEOS, University of Victoria, Victoria, BC, Canada. 3. Earth & Atmospheric Sciences, University of Houston, Houston TX. 4. IODP, Texas A&M University, 1000 Discovery Drive, College Station, TX.

Corresponding email: [ildefonse@um2.fr](mailto:ildefonse@um2.fr)

Keywords: IODP, Integrated Ocean Drilling Program, Ocean Crust, Lower Gabbros, Layered Gabbros.

The lower ocean crust formed at fast-spreading ridges is composed of plutonic rocks whose mineral assemblages, textures and compositions record the history of melt transport and crystallization between the mantle and the seafloor. Owing to the nearly continuous overlying extrusive upper crust, sampling in situ the lower crust is challenging. Integrated Ocean Drilling Program (IODP) Expedition 345 recovered the first significant sections of primitive, modally layered gabbroic rocks from the lowermost plutonic crust formed at a fast-spreading ridge, and exposed at the Hess Deep Rift (Gillis et al., *Nature*, 2014, doi:10.1038/nature12778). The primary science results were obtained from coring of two ~110 m deep reentry holes and one 35-m-deep single-bit hole, all co-located within an ~100-m-wide area on the southern slope of the inarift ridge.

Olivine gabbro and troctolite are the dominant rock types recovered, with minor gabbro, clinopyroxene oikocryst-bearing gabbroic rocks, and gabbronorite. All rock types are primitive to moderately evolved, with Mg# 89-76, and exhibit cumulate textures. Spectacular modal and grain size layering, prevalent in >50% of the recovered core, confirm a long held paradigm that such rocks are a key constituent of the lowermost ocean crust formed at fast-spreading ridges.

Geochemical analysis of these primitive lower plutonics, in combination with previous geochemical data for shallow-level plutonics, sheeted dikes and lavas, provides the best constrained estimate to date of the bulk composition of crust formed at a fast-spreading ridge. Simple crystallization models using this bulk crustal composition as the parental melt accurately predict the composition of both the lavas and plutonics. However, the recovered rocks show unanticipated early crystallization of orthopyroxene, challenging current models of melt extraction from the mantle and mid-ocean ridge basalt differentiation.

The core recovered at Site U1415 originated at a stratigraphic level at least 2 km beneath the sheeted dike-plutonic transition, representing intervals of the lower half to one third of the EPR plutonic crust. A more precise depth cannot be assigned as the results of Expedition 345 (e.g., magnetic inclinations) and site survey indicate that the sampled units are tilted, mass-wasted blocks. However, sampling four large blocks of relatively fresh rocks proved facilitated observations of the wide variety and complexity of rock types and textures present in fast spread primitive lowermost crust.

## **The Tethyan seawater retained in serpentinites of the Hyblean basement (south-eastern Sicily): its role in the igneous activity, tectonic behaviour and oil settings**

Manuella F.C.\*<sup>1</sup>, Scribano V.<sup>2</sup> & Carbone S.<sup>2</sup>

1. Via Dell'Oro, 137 – Catania. 2. Dipartimento di Scienze Biologiche, Geologiche e Ambientali (DBGA) - Università degli Studi di Catania.

Corresponding email: [fmanuella@alice.it](mailto:fmanuella@alice.it)

Keywords: Hyblean Plateau, Serpentinite, Permian Tethys, Hydrocarbons, Igneous activity.

The study of the xenolith suite found in the Hyblean diatremes (SE Sicily), Upper Tortonian in age, revealed that the unexposed Permo-Triassic basement of the region consists of serpentinitized peridotites and minor gabbros, suggesting the development of oceanic core complex structures (Scribano et al., 2006a,b) in the Paleo-Mesozoic, ultra-slow spreading, Ionian-Tethys Ocean. A recent interdisciplinary study pointed out that serpentinites are the dominant rocks forming the Hyblean-Pelagian basement down to a mean depth of 19 km, representing the Moho interpreted as a serpentinitization front (Manuella et al., 2013). The basaltic magma-serpentinite interaction could be responsible of various geochemical and rheological modifications of the former. The serpentinite dehydration originated pressurized vapour whose violent expansion generated the Hyblean diatremes (Scribano et al., 2007). At the regional scale, repeated events of hydration/dehydration generated volume changes of huge masses of serpentinites, which can account the vertical tectonic style of the Hyblean area through geological time. Finally, the finding of hydrocarbons in some Hyblean mafic and ultramafic xenoliths suggests that serpentinitization process promoted the abiogenic production of hydrocarbons via Fischer-Tropsch reaction (Ciliberto et al., 2009; Scirè et al., 2011). Thus, serpentinites may represent both source and reservoir rocks of hydrocarbons in south-eastern Sicily.

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## Tectonic setting and geochemical characteristics of the basic rocks from the Intra-Pontide Suture Zone in Northern Turkey

Marroni M.\*<sup>1</sup>, Sayit K.<sup>2</sup>, Gönçüoğlu M.C.<sup>2</sup>, Pandolfi L.<sup>1</sup>, Ellero A.<sup>3</sup>, Ottria G.<sup>3</sup> & Frassi C.<sup>1</sup>

1. Dipartimento di Scienze della Terra, Università di Pisa. 2. Department of Geological Engineering, Middle East Technical University, Ankara, Turkey. 3. Istituto di Geoscienze e Georisorse, CNR, Pisa.

Corresponding email: [marroni@dst.unipi.it](mailto:marroni@dst.unipi.it)

Keywords: ophiolite, Intra-Pontide suture, Turkey.

The Intra-Pontide Suture Zone (IPSZ) is the less known one among the suture zones present in Turkey. The IPSZ is well exposed along the Daday-Arac-Kursunlu and Tosya – Emirköy geotraverses where several tectonic units can be recognized. Most of these units are characterized by the occurrence of basic rocks reflecting distinct tectonic origins and geochemical signatures. The study of the basic rocks emerges as an important tool for the geodynamic reconstruction as it can reveal the occurrence of different types of oceanic basins, the development of a magmatic arc or the presence of rifting-related magmatism. The study of the geotraverses indicates that the imbricate stack of the IPSZ consists of four distinct tectonic units whose successions bear basic rocks: the Aylı Dağ ophiolite Unit, the Arkot Dağ Mélange and two metamorphic units, referred to as Daday and Devrekani Units. This imbricate stack is probably the result of several episodes of out-of-sequence thrusts that affected the whole IPSZ.

The Aylı Dağ Unit includes an about 5 km-thick ophiolite sequence topped by the middle Bathonian to early Callovian radiolarian cherts. In addition, a metamorphic sole is present at the base of the serpentized peridotites. The geochemical evaluation of pillow-basalts and dykes highlights subduction-related characteristics, similar to IAT- and BABB-type lavas generated above intra-oceanic subduction systems.

The Arkot Dağ Mélange consists of an assemblage of slide-blocks, with different size and lithology, enclosed in a Late Santonian sedimentary matrix. The slide-blocks also include ophiolitic lithologies, mainly represented by basalts, but gabbros and peridotites are also found. The slide-blocks of basalts display affinities to IAT- and BABB-type magmas, signifying the involvement of subduction component, whereas no MORB-like basalt have been found.

The Daday unit is characterized by metasedimentary and metabasic rocks deformed under blueschist to sub-greenschist metamorphic facies conditions. The metasedimentary rocks include mica-bearing schists, fine-grained marbles and black quartzites. The metabasic lithologies, on the other hand, comprise actinolite-bearing schists and Na-amphibole-bearing varieties possibly derived from basaltic and gabbroic protoliths. The metabasic rocks have a wide range of chemical compositions, displaying N-MORB-, E-MORB-, OIB- BABB- and IAT-type signatures.

The Devrekani Unit is represented by an assemblage of amphibolites, marbles and micaschists showing a metamorphic climax developed under upper amphibolite facies in the Late Jurassic time. The amphibolites display E-MORB-, OIB- BABB- and IAT-type signatures.

The geochemical signature of the studied basic rocks provide the evidence that all the basic rocks from the tectonic units of IPSZ are derived by a supra-subduction zone. This finding can provide new insights for the reconstruction of the geodynamic history of the Intra-Pontide domain.

## Petrographic and geochemical characteristics of the Mt. Pollino ophiolitic rocks (Basilicata, Southern Italy)

Mazzeo F.C.\*<sup>1</sup>, D'Antonio M.<sup>1</sup>, Petrosino P.<sup>1</sup> & Zanetti A.<sup>2</sup>

1. Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università degli Studi di Napoli Federico II

2. Institute of Geosciences and Earth Resources, CNR, Pavia.

Corresponding email: [fabiocarminemazzeo@libero.it](mailto:fabiocarminemazzeo@libero.it)

Keywords: Mt. Pollino, Ligurian Tethys, Serpentinized peridotite, Ophiolitic rocks.

In Italy, ophiolites occur in scattered outcrops located mainly in the Western Alps and Northern Apennine. In Southern Apennine, ophiolite outcrops are very rare, occurring only in Southern Campania, Basilicata and Northern Calabria. Southern Apennine ophiolites consist of a serpentinized peridotite basement and a reduced crustal sequence characterized by lack of sheeted-dyke complexes, relatively small volumes of gabbros intruded in the peridotite basement, and a discontinuous basaltic and oceanic sediments cover. They are believed to represent fragments of Tethys oceanic crust that were obducted on continental crust during the closure of the Ligurian branch of Tethys. A thorough petrological investigation has been carried out on ophiolites that crop out widely on Timpa delle Murge Hill, along the boundary between Basilicata and Calabria, close to Mt. Pollino. All peridotite samples contain large amount of serpentine, and are characterized by millimeter-sized porphyroclasts of olivine and orthopyroxene, varying from anhedral to subhedral and showing internal deformation. Clinopyroxene is present as large crystals or as exsolution lamellae in orthopyroxene. Spinel is typically anhedral. Some peridotites show the presence of anhedral crystals of amphibole in accessory amounts. The REE contents of clinopyroxene are about 10 xChondrite I (CI) in the MREE and HREE regions where the patterns are almost flat, while the LREE contents are considerably depleted, with a significant difference between peridotites with amphibole ( $La_N = 1-4$ ) and peridotites without amphibole ( $La_N = 0.05-0.5$ ). Bulk rocks show excellent correlations in major oxides and some trace elements plotted against MgO. Incompatible elements, as well as Al, Ca, Si, Sc, and V show negative covariance with MgO. In contrast, the compatible elements Ni and Co show positive covariance with MgO. The positive relationship occurring between Fo content of olivine and Cr# of spinel confirms that such trends are related to variable degrees of partial melting, i.e. 8% for peridotites with amphiboles and about 20% for peridotites without amphibole. However, the degree of partial melting inferred on the basis of LREE concentrations of clinopyroxenes is much lower than that recorded by spinel-olivine equilibrium (maximum ~4% near-fractional melting of a spinel-facies DM for both amphibole-bearing and amphibole-free peridotites). The observed decoupling between the degrees of partial melting estimated on the basis of bulk rock and clinopyroxene chemistry allow us to interpret the depleted spinel peridotites of Mt. Pollino as the result of a reactive melt/rock interaction with depleted melts of MORB affinity, occurred at spinel-facies conditions after an earlier melt extraction. In places, the already re-fertilised peridotites experienced the percolation of late hydrous melts/fluids that determined the amphibole segregation, in association with further re-enrichment of LILE and LREE in clinopyroxenes.

## Refertilization of subcontinental mantle recorded by the lherzolite-websterite-hornblendite association from St. Lucia (Corsica)

Montanini A.\*<sup>1</sup>, Tribuzio R.<sup>2-3</sup>, Zanetti A.<sup>3</sup> & Zibra I.<sup>4</sup>

1. Dipartimento di Fisica e Scienze della Terra, Università di Parma. 2. Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia. 3. Istituto di Geoscienze e Georisorse - CNR, U.O.S. di Pavia. 4. Geol. Survey of Western Australia, Dept. of Mines and Petroleum, Australia.

Corresponding email: [alessandra.montanini@unipr.it](mailto:alessandra.montanini@unipr.it)

Keywords: mantle, trace element geochemistry, continental margin.

The St. Lucia nappe from Alpine Corsica consists of late-Variscan lower crust exhumed along the European rifted margin of the Ligurian Tethys and Mesozoic sediments (Beltrando et al., 2013). The basement includes a High Grade Mafic Complex and a Granitoid Complex of Early Permian age. The base of the Mafic Complex is associated with mantle slices consisting of mylonitic spinel-bearing lherzolites and mm- to cm-thick websterite and hornblendite layers concordant with the foliation of the host rocks. The mylonite microstructure in the peridotites is characterized by aligned porphyroclasts of pyroxene ( $\pm$  spinel) in a fine-grained polyphase matrix composed of olivine + pyroxenes + spinel. Large exsolved orthopyroxene (Opx) porphyroclasts mantled by neoblastic Cpx + Opx + spinel testify a low-strain spinel tectonite stage predating the mylonite deformation. Major element compositions of olivine, Cpx and spinel porphyroclasts of the lherzolites indicate a fertile geochemical signature. The websterites are Opx-poor rocks containing Al-Ti-rich Cpx porphyroclasts, Cr-poor spinel, disseminated kaersutite and accessory Fe-Ni sulphides. Spinel-facies mylonite recrystallization in both lherzolites and websterites occurred at  $\sim$ 850-900°C. The hornblendites are composed of K<sub>2</sub>O-rich kaersutite + Ti-rich phlogopite + ilmenite. Cpx porphyroclasts from the lherzolites have heterogeneous trace element compositions pointing to four different geochemical signatures. Type 1 Cpx is strongly LREE-depleted (CeN/SmN down to 0.05) with nearly flat MREE-HREE at 8-10 times chondrite. Type 2 Cpx is moderately LREE-depleted (CeN/SmN = 0.31-0.49), whereas Type 3 has nearly flat LREE. Type 4 Cpxs are weakly LREE depleted, peak at MREE and have variable HREE (YbN = 7-12). The websterite Cpxs display convex-upward REE patterns and higher concentrations of incompatible trace element. The kaersutite from the hornblendites are enriched in Rb, Ba, U, Nb, Ta, LREE and depleted in HREE with respect to the websterite ones. The peridotite protholiths are consistent with residual rocks after low degrees of near-fractional melting of spinel facies DM. Type 4 Cpx from the lherzolites likely reflect equilibrium with percolating MORB-type melts. Putative liquids in equilibrium with Cpx and kaersutite from the websterites and the hornblendites have transitional to alkaline affinity. Our study has evidenced that the St. Lucia mantle slices underwent injections of melts with MORB to alkaline affinity forming different kinds of magmatic layers, which were associated with metasomatic haloes in the ambient peridotite.

Beltrando M., Zibra I., Montanini A. & Tribuzio R. 2013. Crustal thinning and exhumation along a fossil magma-poor distal margin preserved in Corsica: a hot rift to drift transition, *Lithos*, 168-169, 99-112.

## Geologic and petrographic study of the Lower Shear Zone in the Monviso Ophiolitic Massif (western Alps): insights into the subduction dynamics

Rapa G.<sup>1</sup>, Groppo C.<sup>1</sup> & Rolfo F.\*<sup>1-2</sup>

1. Dipartimento di Scienze della Terra, Università di Torino. 2. IGG-CNR, Torino.

Corresponding email: [franco.rolfo@unito.it](mailto:franco.rolfo@unito.it)

Keywords: Monviso Ophiolitic Massif, Eclogitic breccia, Subduction processes.

The Monviso Ophiolitic Massif is one of the best preserved relics of the oceanic crust in the Western Alps that formed during opening of the Mesozoic Western Alpine Tethys and underwent eclogite-facies metamorphism during the Eocene Alpine subduction.

We have performed detailed fieldwork and petrographic studies across a major shear zone of the Monviso Ophiolitic Massif, i.e. the Lower Shear Zone (LSZ) as defined by Angiboust et al. (2011), in the upper Bulè Valley. This shear zone mainly consists of strongly foliated serpentinitic schists hosting numerous blocks and lenses of MgAl-metagabbros, FeTi-metagabbros (eclogites), eclogitic breccias and metabasites, and is interposed between the serpentinites of the Basal Serpentinite Unit and the MgAl-metagabbros of the Lago Superiore Unit.

Both the units and the interposed shear zone show exceptionally well preserved mineral assemblages and microstructures formed during subduction under eclogite-facies conditions. In the FeTi-metagabbros the eclogitic assemblage consists of garnet, omphacite, Mg-chlorite, zoisite and rutile, ± blue amphibole, ± phengite, ± lawsonite. In the MgAl-metagabbros, the Fe-poor bulk composition hampered the growth of garnet in equilibrium with omphacite: the eclogitic assemblage thus consists of omphacite, zoisite, Mg-chlorite, talc, blue amphibole and rutile, ± jadeite, ± phengite.

Eclogitic breccias have been recognized both as blocks within the serpentinitic schists of the LSZ, and as boudinated levels within the MgAl-metagabbros of the Lago Superiore Unit. These peculiar rocks suggest that the metamorphic evolution under eclogite facies conditions was particularly complex. Eclogitic breccias consist of centimetric clasts of milonitic eclogites surrounded by an oriented matrix with omphacite, lawsonite, rutile, ± garnet. This is the evidence that a brittle deformation occurred under lawsonite-eclogite facies conditions and was interposed between two ductile deformation events, both occurred under eclogite facies conditions. These observations are in agreement with those of Angiboust et al. (2011), who described similar eclogitic breccias from the same LSZ, north of the Bulè Valley. However, according to our data, the eclogitic breccias are not only limited to the LSZ, but are locally observed also in the structurally upper Lago Superiore Unit.

The presence of eclogitic breccias in the Monviso Ophiolitic Massif is particularly important for the interpretation of the subduction dynamics, and suggests a local brittle behavior of the oceanic crust during subduction, potentially linked to seismic phenomena.

Angiboust S., Agard P., Raimbourg H., Yamato P. & Huet B. 2011. Subduction interface processes recorded by eclogite-facies shear zones. *Lithos*, 127, 222-238.

Rapa G. 2014. Studio geologico-petrografico dell'alto Vallone Bulè, Massiccio Ofiolitico del Monviso (Alpi Occidentali). Tesi di Laurea Magistrale, Scuola di Scienze della Natura, Torino.

## Dating HP metamorphism in Zermatt-Saas ophiolites from Valtournanche

Rebay G.\*<sup>1</sup>, Tiepolo M.<sup>2</sup>, Zanoni D.<sup>3</sup>, Langone A.<sup>2</sup> & Spalla M.I.<sup>3-4</sup>

1. Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia. 2. IGG-CNR, Pavia. 3. Università degli Studi di Milano, Dipartimento di Scienze della Terra "A. Desio". 4. IDPA-CNR, Milano.

Corresponding email: [gisella.rebay@unipv.it](mailto:gisella.rebay@unipv.it)

Keywords: Dating HP metamorphism, Zermatt-Saas, Valtournanche.

The Zermatt-Saas (ZS) Zone is a remnant of the Tethyan oceanic crust that was variously affected by oceanic metamorphism prior to subduction and is now part of the orogenic suture that developed in the Western European Alps during the Alpine subduction and collision (Dal Piaz et al., 2001 and references therein). The Zermatt-Saas rocks preserve a dominant HP to UHP metamorphic imprint overprinted by greenschist facies metamorphism. The age of the oceanic protoliths varies between 164 and 153 Ma (Rubatto et al., 1998) whereas the HP metamorphism is constrained between 44 and 40 Ma (i.e. Rubatto et al., 1998; Dal Piaz et al., 2001).

Ophiolite rocks in upper Valtournanche are dominated by a regional S2 foliation mapped with spatial continuity in serpentinite, metarodingite and eclogite. S2 is defined by HP parageneses in all lithotypes, and developed under  $2.5 \pm 0.3$  GPa and  $600 \pm 20$  °C during Alpine subduction (Rebay et al., 2012). Rarely clinopyroxene and zircon are found in the S2 foliation of serpentinites. Trace element composition of clinopyroxene suggest that they crystallised from a melt in equilibrium with plagioclase; most likely they represent relicts of gabbroic assemblages. The clinopyroxene porphyroclasts show rims indented within S2 with compositions compatible with clinopyroxene grains defining S2, suggesting that they recrystallised during Alpine subduction.

Zircon cores show, under CL, sector zoning typical of magmatic growth. U-Pb dates suggest their crystallisation during Middle Jurassic. Magmatic cores have thin fringe overgrowths parallel to the S2 foliation. U-Pb concordant analyses on these domains reveal an Upper Cretaceous crystallisation. This date likely represents the HP to UHP Alpine re-equilibration.

Therefore, some sections of the ZS have likely experienced HP to UHP metamorphism earlier than previously thought. Remarkably, these new dates are similar to those recorded for the HP re-equilibration in the continental crust of the Sesia-Lanzo Zone (i.e. Rubatto et al., 1999 and refs therein).

Dal Piaz G.V., Cortiana G., Del Moro A., Martin S., Pennacchioni G. & Tartarotti P., 2001. Tertiary age and paleostructural inferences of the eclogitic imprint in the Austroalpine outliers and Zermatt-Saas Zone ophiolite, western Alps. *Int. J. Earth Sci.*, 90, 668-684.

Rebay G., Spalla M.I. & Zanoni D. 2012. Interaction of deformation and metamorphism during subduction and exhumation of hydrated oceanic mantle: Insights from the Western Alps. *J. Metamorphic Geol.*, 30(7), 687-702.

Rubatto D., Gebauer D. & Compagnoni R. 1999. Dating of eclogite facies zircons: the age of Alpine metamorphism in the Sesia-Lanzo Zone (Western Alps). *Earth Planet. Sci. Letters*, 167, 141-158.

Rubatto D., Gebauer D. & Fanning M. 1998. Jurassic formation and Eocene subduction of the Zermatt-Saas-Fee ophiolites: implications for the geodynamic evolution of the Central and Western Alps. *Contrib. Miner. Petrol.*, 132, 269-287.

## The embryonic oceanic crust from the Balagne ophiolite (Corsica)

Renna M.R.\*<sup>1</sup>, Sanfilippo A.<sup>2</sup>, Tiepolo M.<sup>3</sup>, Tribuzio R.<sup>3-4</sup>

1. Dipartimento di Fisica e di Scienze della Terra-Università di Messina. 2. Department of Earth Sciences-Kanazawa University. 3. IGG-CNR Pavia. 4. Dipartimento di Scienze della Terra e dell'Ambiente-Università di Pavia.

Corresponding email: [mrenna@unime.it](mailto:mrenna@unime.it)

Keywords: basalt-sedimentary succession, Jurassic ophiolite, U-Pb zircon dating.

The Balagne ophiolite is considered a marginal paleo-geographic domain of the Jurassic Ligurian Piedmontese basin, proximal to the European continental margin (Durand-Delga et al., 1997; Marroni and Pandolfi 2003). It preserves a basalt-sedimentary succession characterized by the association of pillow and massive basalts with deposits of ophiolitic breccias and continental-derived sediments. At the top of the succession, the pillow basalts are covered by a sedimentary sequence made up of Middle Jurassic to Early Cretaceous pelagic deposits. The ophiolitic breccias occur in the lower portion of the basalt-sedimentary succession and contain clasts of clinopyroxene-rich gabbros, gabbro-norites, oxide-gabbros, albitites and basalts. In the lower portion of the succession, two levels of siliciclastic sediments are also present. Most massive basalts are present in the upper portion of the basalt-sedimentary succession. The latter is associated with a tectonic slice mainly consisting of an intrusive sequence overlain by pillow basalts. The intrusive sequence is made up of gabbro-norites, oxide-gabbros to albitites on top, showing similar structures and compositions to the gabbroic clasts from the ophiolitic breccias. Preliminary *in situ* U-Pb zircon dates from an albitite of the tectonic slice show a Middle-Upper Jurassic crystallization age for the intrusive sequence, which is coeval to the gabbroic sequences from the ophiolites of the Alpine-Appennine belt. U-Pb geochronology of zircons from the siliciclastic sediments mostly reveals Early to Middle Permian age, thereby suggesting the Corsica batholith as the original source material. The whole-rock compositions of the massive basalts display slight LREE, Nb and Zr enrichment relative to N-MORB and homogeneous initial Nd isotope ratios consistent with an origin from an asthenospheric MORB-type mantle source. Clinopyroxenes from the basalts and the gabbros have nearly parallel incompatible trace element patterns showing slight LREE enrichment relative to clinopyroxene at equilibrium with typical N-MORB. The parental melts of the basalts and the gabbros from the Balagne ophiolites may have formed by low degrees of asthenosphere partial melting, in conjunction with thick lithosphere and low asthenosphere ascent. The early stages of the basalt-sedimentary succession development were most likely characterized by intense tectonic activity with supplies from different topographic highs consisting of lower oceanic crust and of continental-derived material.

Durand-Delga M., Pybernès B. & Rossi P. 1997. Arguments en faveur de la position, au Jurassique, des ophiolites de Balagne (Haute-Corse, France) au voisinage de la marge continentale européenne. C.R. Sci. Paris, Ser. IIa, 325, 973-981.

Marroni M. & Pandolfi L. 2003. Deformation history of the ophiolite sequence from the Balagne Nappe, northern Corsica: insights in the tectonic evolution of Alpine Corsica. Geol. J., 38, 67-83.

## **Ghostlike boninitic magmatism in the Cretaceous southern Neo-Tethys. New evidence from the Zagros ophiolites (Iran)**

Saccani E.\*<sup>1</sup> & Allahyari K.<sup>2</sup>

1. Dipartimento di Fisica e Scienze della Terra, Università di Ferrara. 2. Faculty of Earth Science, Shahid Beheshti University, Tehran, Iran.

Corresponding email: [sac@unife.it](mailto:sac@unife.it)

Keywords: Ophiolite, Zagros belt, Iran.

Ophiolites cropping out along the Main Zagros Thrust Zone (MZTZ) represent portions of the southern Neo-Tethys Ocean, which existed between the Arabian and Eurasian continental margins. Several authors suggested that an intra-oceanic supra-subduction zone setting (SSZ) developed in this ocean during the Late Cretaceous. However, in contrast to many other ophiolites (e.g., Albanide-Hellenide), volcanic rocks, which typically characterize SSZ settings (i.e., island arc tholeiites and boninites) are lacking. Nonetheless, the volumetrically most abundant rock-type in the MZTZ ophiolites consists of very depleted mantle harzburgites, which have chemical features that are typical for residual mantle after boninitic-type melts extraction. Therefore, though boninitic lava flows are lacking in the MZTZ ophiolites, the occurrence of boninitic magmatism at a regional scale can be envisaged. In this contribution, we review the available data on the Kermanshah and Sarve-Abad ophiolites (SW Iran) in search for evidence for the existence of boninitic magmatism in the southern Neo-Tethys.

The Kermanshah ophiolites include SSZ sequences largely consisting of depleted mantle harzburgites, which display a significant depletion in incompatible elements and rare earth element (REE), coupled with a marked LREE enrichment with respect to MREE. REE modeling shows that they may represent a residual mantle after 25 – 30% removal of boninitic-type melts. The mineral chemistry of Cr-spinels also supports this conclusion.

The Sarve-Abad ophiolites include cumulitic lherzolites bearing minor dunite and chromitite lenses in places. The crystallization order in ultramafic cumulates is: olivine ± Cr spinel + clinopyroxene ± orthopyroxene, which is typical for boninitic melts. The mineral chemistry of Cr-spinel, pyroxenes, and olivine is compatible with a genesis from a boninitic-type melt. Indeed, the calculated TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> compositions and Mg# in the parental melt that was in equilibrium with these minerals are consistent with boninitic-type compositions. Whole-rock geochemistry show low incompatible element content and a general enrichment in Th with respect to Ta and Nb. Chondrite-normalized REE patterns are consistent with boninitic-type parental melts. REE petrogenetic modeling indicates that the Sarve-Abad ultramafic cumulates may have formed by small degrees (5-15%) of fractional crystallization from typical boninitic melts.

In conclusion, several lines of evidence indicate that episodes of boninitic magmatism occurred within the southern Neo-Tethys Ocean during the Late Cretaceous. Some hypotheses explaining the lacking of boninitic lavas or dykes in the MZTZ ophiolites can be postulated (e.g., short lived intra-oceanic subduction, transition from intra-oceanic to continental subduction). However, further investigations should be made for testing their tectono-magmatic and geodynamic consistence.

## **Discriminating between different types of ophiolitic basalts and their tectonic significance using a new method based on Th-Nb and Ce-Dy-Yb**

Saccani E.\*

Dipartimento di Fisica e Scienze della Terra, Università di Ferrara

Corresponding email: [sac@unife.it](mailto:sac@unife.it)

Keywords: Basalt, Ophiolite, Discrimination diagram, Trace elements, Plate tectonics.

Ophiolites are interpreted to form in a wide variety of plate tectonic settings including oceanic spreading ridges, hot spots, and supra-subduction zone (SSZ) environments, such as intra-oceanic arcs, continental arcs, forearcs, and back-arcs. Hence, different rocks or rock associations found in ophiolitic complexes preserve records of tectono-magmatic events that occurred during distinct phases of oceanic development, from continental rifting to oceanic spreading, subduction, accretion and continental collision. Recognition of the tectonic affinity of ancient ophiolites is therefore a fundamental problem for all scientists working on this topic. To this purpose, tectonic discrimination diagrams based on major and/or trace elements have been a common technique for addressing this problem since the early 70s. In this work, a new discrimination diagram using absolute measures of Th and Nb is proposed and is applied to ancient ophiolites to best discriminate a large number of different ophiolitic basalts. This diagram was obtained using >2000 ophiolitic basalts (spanning in age from Proterozoic to Cenozoic) and was tested using ~560 modern rocks from known tectonic settings. Data consist of ten different basaltic varieties, including two types that have never been considered before, which are: a) medium-Ti basalts (MTB) generated at nascent forearc settings; b) a type of mid-ocean ridge basalts showing garnet signature (G-MORB) that characterizes Alpine-type (i.e., non volcanic) rifted margins and ocean-continent transition zones (OCTZ). In this diagram, basalts generated in subduction-unrelated settings can be distinguished from subduction-related basalts with a misclassification rate <1%. This diagram highlights the chemical variation of oceanic and OCTZ basalts from depleted compositions to progressively more enriched compositions reflecting, in turn, the variance of source composition. Chemical contributions of enriched components (plume-type components) to mantle sources can therefore be identified. Enrichment of Th relative to Nb is effective for highlighting crustal input via subduction or crustal contamination. Basalts formed at continental margin volcanic arcs can be distinguished from those generated in intra-oceanic arcs in supra-subduction zones (SSZ) with a misclassification rate <1%. Within the SSZ group, two sub-settings can be recognized. They are: a) SSZ characterized by chemical contribution from subduction-derived components (forearc and intra-arc) characterized by island arc tholeiitic (IAT) and boninitic basalts; b) SSZ with no contribution from subduction-derived components (nascent forearc) characterized by MTBs and depleted-MORBs. Two additional discrimination diagrams are proposed: a) boninite and IAT basalts can be discriminated with a confidence level >99.5% using a Dy-Yb diagram; b) G-MORBs and N-MORBs can be discriminated using a Ce/Yb-Dy/Yb diagram.

## **Mantle-crust interactions in the oceanic lithosphere: constraints from minor and trace elements in olivine**

Sanfilippo A.<sup>1</sup>, Tribuzio R.\*<sup>2</sup> & Tiepolo M.<sup>3</sup>

1. School of Natural System, Kanazawa University, Japan. 2. Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia. 3. C.N.R. - Istituto di Geoscienze e Georisorse, Pavia.

Corresponding email: [tribuzio@crystal.unipv.it](mailto:tribuzio@crystal.unipv.it)

Keywords: olivine, dunite, troctolite.

Minor and trace element compositions of olivines were used as probes into the melt-rock reaction processes occurring at the mantle-crust transition in the oceanic lithosphere. We studied mantle and lower crustal sections from the Jurassic ophiolites of Alpine-Apennine belt, which are considered to be lithospheric remnants of a slow-spreading basin. Olivines from depleted mantle plagioclase-harzburgites and associated replacive dunitic conduits (Fo = 91-89 mol%) and olivines from olivine-rich troctolites and troctolites (Fo = 88-84 mol%) within km-scale gabbroic bodies were analyzed.

Positive correlations among the concentrations of Mn, Ni, Co, Sc and V characterize the olivines from the dunites. These chemical variations are reconciled with formation by melts produced by a mixed source melted under different pressure conditions and made up of a depleted peridotite and a pyroxene-rich, garnet-bearing component. We propose that partial melts extracted from the asthenosphere did not fully aggregate within the mantle before they form the oceanic crust.

The olivines from the olivine-rich troctolites and the troctolites have lower Ni contents and higher concentrations of Mn and incompatible trace elements (Ti, Zr, Y and HREE) than the olivines from the dunites. In addition, the olivines from the olivine-rich troctolites and the troctolites commonly show heterogeneous Ti, Zr, Y and HREE compositions, which produce variable Ti/Y and Zr/Y values. The chemical variations observed for these olivines cannot be only related to fractional crystallization. We correlate these olivine compositional characteristics with events of reactive melt migration occurred during the formation of the primitive lower oceanic crust. The migrating melts may have formed at the mantle-crust transition via interaction with mantle peridotites during periods of low melt supply.

## Ultra-depleted peridotites of New Caledonia: a reappraisal

Secchiari A.<sup>\*1-2</sup>, Bosch D.<sup>2</sup>, Cluzel D.<sup>3</sup>, Macera P.<sup>4</sup> & Montanini A.<sup>1</sup>

1. Dipartimento di Fisica e Scienze della Terra, Università di Parma. 2. Géosciences Montpellier, Université Montpellier 2, France. 3. Université de la Nouvelle-Calédonie. 4. Dipartimento di Scienze della Terra, Università di Pisa.

Corresponding email: [arianna.secchiari@nemo.unipr.it](mailto:arianna.secchiari@nemo.unipr.it)

Keywords: New Caledonia, Peridotites, Ophiolites.

In spite of pervasive serpentinisation and prominent weathering, the New Caledonia Peridotitic Nappe is one of the largest and best exposed supra-subduction mantle section in the world and hence provides a unique insight on upper mantle processes. The sequence is dominated by harzburgite-dunite association and minor lherzolites, but it also includes mafic/ultramafic cumulates.

Recent geochemical studies revealed that harzburgites experienced several phases of melting, melt-rock interaction and re-melting, that led to overall ultra-depletion, making their geochemical characterization an analytical challenge.

This presentation deals with the preliminary results of a reappraisal based upon a new set of un-serpentinised, or only slightly serpentinised, peridotite samples collected on the whole island.

Harzburgites are highly refractory rocks, as attested by the absence of primary clinopyroxene, very high Fo content in olivine (90.7-92.9 mol%), high Mg# in orthopyroxene ( $[Mg/(Mg+Fe)] = 91.0-92.7$ ) and Cr# in spinel ( $[100 \cdot Cr/(Cr+Al)] = 40-71$ ).

Secondary, interstitial and undeformed clino- and orthopyroxenes have also been observed in harzburgites. These phases indicate percolation after partial melting and re-equilibration at lithospheric conditions. Their chemical compositions, i.e. low Al<sub>2</sub>O<sub>3</sub> and CaO contents in orthopyroxene and very low Na<sub>2</sub>O and TiO<sub>2</sub> in clinopyroxene, suggest a metasomatic origin by SiO<sub>2</sub>-rich fluids and/or depleted melts in a subduction-related setting.

In contrast, lherzolites exhibit a fairly fertile nature, indicated by lower Fo in olivine (88.5-90.0), low Cr# in spinel ( $[100 \cdot Cr/(Cr+Al)] = 13-17$ ) and relatively high Na<sub>2</sub>O (up to 0.80 wt%) and Al<sub>2</sub>O<sub>3</sub> (3.1-6.7 wt%) in clinopyroxene.

The peridotites are low strain tectonites with porphyroclastic textures partially overprinted by mosaic equigranular textures. They record an asthenospheric HT origin followed by sub-solidus re-equilibration, as also testified by geothermometric estimates (930–1145°C and 870-1080°C on porphyroclastic assemblages for harzburgites and lherzolites respectively; 830°C-980°C for spinel facies recrystallization in both lithotypes).

Mineral compositional variations (e.g. Mg# (Ol) vs Cr# (Spl), Cr# (Spl) vs Mg# (Spl)), show that most investigated harzburgites plot in the field of fore-arc peridotites, while lherzolites are more akin to (variably refertilized) abyssal peridotites. These features have also been confirmed by whole-rock REE contents, that display U-shaped pattern for harzburgites, commonly attributed to a fore-arc setting and abyssal-type patterns for lherzolites.

These results are consistent with multi-stage history of melting, deformation, recrystallization and melt-rock interaction. Major and trace elements combined with radiogenic isotope analyses (in progress) will provide a clue for deciphering the depletion vs. refertilization evolution of the different peridotite types and will add new constraints on their geodynamical significance.

## The magmatic-hydrothermal transition in the lower oceanic crust: clues from the Ligurian ophiolites, Italy

Tribuzio R.<sup>1,2</sup>, Renna M.R.\*<sup>3</sup>, Dallai L.<sup>4</sup> & Zanetti A.<sup>2</sup>

1. Dipartimento di Scienze della Terra e dell'Ambiente-Università di Pavia. 2. IGG-CNR Pavia. 3. Dipartimento di Fisica e di Scienze della Terra-Università di Messina. 4. IGG-CNR Pisa.

Corresponding email: [mrenna@unime.it](mailto:mrenna@unime.it)

Keywords: Alpine Jurassic ophiolites, hornblende chemistry, O and Sm-Nd isotopes.

The gabbroic bodies from the Jurassic Ligurian ophiolites are structurally and compositionally similar to the gabbroic sequences from the oceanic core complexes of the Mid Atlantic Ridge. The high temperature cooling evolution of the Ligurian gabbros is locally associated with formation of hornblende-bearing felsic dykes and hornblende vein networks. The hornblende veining is correlated with widespread development of hornblende as coronas/pseudomorphs after the igneous clinopyroxene in the host gabbros. We also found hornblende-rich gabbros as dykes/sills within mantle peridotites.

The hornblendes from the felsic dykes and the hornblende gabbros are characterized by low Mg#, CaO and Al<sub>2</sub>O<sub>3</sub>, negligible Cl, and high TiO<sub>2</sub>, K<sub>2</sub>O, REE, Y, Zr and Nb. The whole-rock Sm-Nd isotopic compositions of the felsic dykes and the hornblende gabbros define a Jurassic isochron with a MORB-type initial <sup>143</sup>Nd/<sup>144</sup>Nd ratio. The δ<sup>18</sup>O of the hornblendes and coexisting zircons from these rocks do not decipher the presence of a seawater component in these melts. We propose that the felsic dykes and the hornblende gabbros formed by SiO<sub>2</sub>-rich silicate melts derived from high degree fractional crystallization of MOR-type basalts.

The vein and the coronitic/pseudomorphous hornblendes show high Mg# and CaO, significant Cl and low TiO<sub>2</sub> and K<sub>2</sub>O. The coronitic/pseudomorphous hornblendes have trace element compositions similar to those of the clinopyroxenes from the gabbros and δ<sup>18</sup>O close to that of seawater, thereby documenting an origin by reaction between migrating seawater-derived fluids and the host gabbros. The vein hornblendes commonly show slight LREE enrichment and relatively high values of Nb and δ<sup>18</sup>O. The crystallization of these hornblendes most likely required the involvement of both seawater and magmatic components.

## **Relationships between embryonic and slow spreading oceanic crust in the Jurassic Ligurian-Piedmontese basin: constraints from U-Pb zircon geochronology**

Tribuzio R.\*<sup>1</sup>, Garzetti F.<sup>1</sup>, Corfu F.<sup>2</sup> & Tiepolo M.<sup>3</sup>

1. Dipartimento di Scienze della Terra e dell'Ambiente - Università di Pavia. 2. Department of Geosciences - University of Oslo, Norway. 3. C.N.R. - Istituto di Geoscienze e Georisorse Pavia.

Corresponding email: [tribuzio@crystal.unipv.it](mailto:tribuzio@crystal.unipv.it)

Keywords: Ophiolite, rift, seafloor spreading.

The fragments of Jurassic oceanic crust exposed in eastern Liguria (Northern Apennine, Italy) are either associated with continental lithosphere material, or bear structural and compositional resemblances to slow spreading oceanic crust. To constrain time and spatial relationships between these embryonic and slow spreading type domains in the Jurassic basin, we carried out a U-Pb geochronological study of zircons. Zircons were separated from eight intrusive rocks and analyzed for U-Pb isotopes by laser ablation ICPMS and isotope dilution TIMS. Zircons were also investigated for morphology, internal structures, inclusions and chemistry, thereby revealing remarkable similarities to zircons collected from modern oceanic crust. The U-Pb zircon dates indicate a short time span for the formation of the oceanic crust in the eastern Liguria ophiolites, thereby arguing against a ca. 30 Ma time span as previously thought. Implications for the geological evolution of the Jurassic basin are discussed.

## **SESSIONE S18**

### **The geological cycle of C and Earth degassing: what do we (really) know?**

*CONVENORS*

*L. Dallai (CNR-IGG, Pisa)*

*F. Frondini (Univ. Perugia)*

*S. Tumiati (Univ. Milano)*

## New geological, geophysical and biological insights on the hydrothermal system of the Panarea – Basiluzzo Volcanic complex (Aeolian Islands, Tyrrhenian Sea)

Bortoluzzi G.\*<sup>1</sup>, Spagnoli F.<sup>1</sup>, Aliani S.<sup>1</sup>, Romeo T.<sup>2</sup>, Canese S.<sup>2</sup>, Esposito V.<sup>2</sup>, Grassi M.<sup>3</sup>, Masetti G.<sup>3</sup>, Dialti L.<sup>4</sup>, Cocchi L.<sup>5</sup>, Muccini F.<sup>5</sup>, Lacono V.<sup>6</sup>, Yakimov M.<sup>6</sup>, La Spada G.<sup>6</sup>, Ligi M.<sup>1</sup>, Giordano P.<sup>1</sup>, Franchi F.<sup>1</sup>, Ferrante V.<sup>1</sup>, Borgognoni L.<sup>1</sup>, Tudino T.<sup>1</sup>, Guideri M.<sup>4</sup>, Ivaldi R.<sup>4</sup>, Filippone M.<sup>3</sup>, Pratellesi M.<sup>3</sup>, Marziani F.<sup>7</sup>, Niccolini A.<sup>7</sup>, Barbieri E.<sup>8</sup>, Capaccioni B.<sup>9</sup> & Andaloro F.<sup>2</sup>

1. Istituto di Scienze Marine - CNR Arsenale, Venezia. 2. Istituto Superiore per la Protezione e la Ricerca Ambientale, STS Palermo, Milazzo. 3. Marina Militare Italiana, Nave Ammiraglio Magnaghi. 4. Istituto Idrografico della Marina, Passo Osservatorio, Genova. 5. Istituto Nazionale di Geofisica e Vulcanologia, Roma. 6. Istituto per lo studio dell'Ambiente Marino Costiero - CNR, Messina. 7. Marina Militare Italiana, Nave Aretusa. 8. Dipartimento Scienze Chimiche e Geologiche, Università di Modena. 9. Dipartimento Scienze Biologiche, Geologiche e Ambientali, Università di Bologna.

Corresponding email: [giovanni.bortoluzzi@bo.ismar.cnr.it](mailto:giovanni.bortoluzzi@bo.ismar.cnr.it)

Keywords: Volcanic arc, hydrothermal systems, CO<sub>2</sub> degassing.

Since the exhalative crisis of 2002 cruises were carried out to investigate morphology, magnetic and gravity fields, fluid escape, plume anomalies, biological and microbiological activity, benthic fluxes, early diagenesis, mineralogy and geochemistry of water and sediments of the hydrothermal system of Panarea. The volcanic complex was mapped by multibeam, including backscatter analysis, and magnetometric surveys were done to detect low magnetization in areas with hydrothermal activity, i.e., vents, sulphide deposits, chimney fields. CTD by ship and on ROV detected acidic plumes at bottom (minimum pH value 6.5) and mid depths.

An Automatic Benthic Chamber was deployed on a terrace (40m) and in depressions with gas-charged and hydrothermally altered sediments (80m). At the 40m site, strong releases of Dissolved Inorganic Carbon (DIC) and Fe, Mn, Zn (75.7, 2.0, 2.9, 3.4  $\mu\text{mol m}^{-2} \text{day}^{-1}$ ) were found. Average decrease of pH in the chamber was  $\sim 4$  units  $\text{day}^{-1}$  with a  $\text{H}^+$  benthic flux of 0.32  $\mu\text{mol m}^{-2} \text{day}^{-1}$ . DIC values of seawater had average 2.3, increasing to 3.1 on degassing vents, while 7.5  $\mu\text{mol}$  was measured on top of a bubbling core.

ROV dives explored and sampled several sites; active chimneys (black, red crusts and yellowish-orange precipitates at top) were recovered on the SE flanks of Basiluzzo; pH value of 5 was measured aboard on sediments. XRD and XRF data on the external crust showed Fe-Mn oxyhydroxides, including goethite and opal, with Co, Ce, Sr, Zn and Cu enrichments, whereas the inner part are depleted of Fe, Mn and other metals, mostly under detection limits. SEM imagery shows porous filamentous minerals, probably bacterial in origin. Dives to SW discovered fields of partially or totally relict chimneys at the same depth ( $\sim 200\text{m}$ ). Chimneys are present on the edges of slope failures and settled on areas of relative lower positive magnetic anomaly, indicating possible shallow depth level of hydrothermal alteration. Reddish crusts and sediments, and acid, gas boiling water (pH 5.5) were cored at 90 m depth upslope of the 'active' chimneys; upslope from the 'relict' chimney's fields, oxidized-normal sediments were found.

Biological investigations on the sediments revealed a community strongly dominated by the amphipod *Ampelisca ledoyeri* (43.8 % of the total abundance), probably dwelling in the tube-patches. Rare species were detected on the chimney's samples.

The phylogenetic diversity of microbial communities in the precipitates collected on chimneys and on Bottaro vent was analyzed by bacterial and archaeal 16S rDNA clone libraries, showing a dominance of sulfur-oxidizing epsilon and gamma proteobacteria. Very interesting groups of archaea were revealed including methanotrophic Thermoplasmatales and members of SM1 candidate division. Overall prokaryotic diversity was found similar to that of deep sea hydrothermal vents and other sulfidic habitats. White microbial mats were found in an area S of Panarea, on a N-S oriented fracture.

## CO<sub>2</sub> release and carbonation of Tuscan serpentinites

Boschi C.\*<sup>1</sup>, Dallai L.<sup>1</sup>, Dini A.<sup>1</sup>, Rielli A.<sup>2</sup> & Ruggieri G.<sup>2</sup>

1. Istituto di Geoscienze e Georisorse – CNR, Pisa . 2. School of Geosciences - Monash University, Melbourne, Australia. 3. Istituto di Geoscienze e Georisorse – CNR, Firenze.

Corresponding email: [c.boschi@igg.cnr.it](mailto:c.boschi@igg.cnr.it)

Keywords: magnesite deposits, serpentinites, CO<sub>2</sub> release.

Serpentinite-hosted magnesite deposits are known from almost all the serpentinite outcrops in Tuscany (Monti Livornesi, Colline Metallifere, Elba Island). The inland Tuscan magnesite deposits are considerably large, being represented by tens of veins up to 15 m thick and 800 m on strike that were exploited over a vertical extent of at least 100 m. All the ore bodies show similar mineralogy and have a general sub-vertical attitude trending NNW–SSE, coherent with the main extensional, high-angle faults in the region. The deposits are not directly in contact with Neogene–Quaternary magmatic rocks, but they are placed at the northern periphery of the active Larderello–Travale geothermal field where granite intrusions were cored at depth of about 3300–4800 m. These deposits were derived from serpentinite silicification–carbonation of the Ligurian ophiolites, and represent a natural analogue of *in situ* CO<sub>2</sub> mineral sequestration. Serpentinite host rocks were transformed to a brownish friable mineral assemblage of opal, chromian montmorillonite, Fe-rich magnesite and minor iron sulfides and oxides. The pervasive alteration of serpentinite was accompanied by the formation of a network of magnesite and dolomite veinlets, and large magnesite–dolomite veins along major structures. The mineral assemblage observed both in veins and in host rock is indicative of low-temperature hydrothermal alteration driven by Si- and CO<sub>2</sub>-rich fluids under relatively low pH conditions.

The origin of the hydrothermal fluid is most probably related to the Tertiary to present Tuscan magmatic activity. In particular, the presence of low temperature fluids could be connected to the peripheral hydrothermal circulation (lateral flow) of high-temperature magmatic-hydrothermal field, as Larderello-Travale geothermal field. Here, we present the geological, petrological and geochemical characteristic of the Tuscan serpentinite-hosted magnesite deposits and we discuss their strict relationship with a peripheral hydrothermal circulation and with a regional release of CO<sub>2</sub>.

## CO<sub>2</sub> fluxes from Earth degassing in Italy

Cardellini C.\*<sup>1</sup>, Chiodini G.<sup>2</sup>, Frondini F.<sup>1</sup> & Caliro S.<sup>2</sup>

1. Dipartimento di Fisica e Geologia, Università di Perugia. 2. INGV Napoli, Osservatorio Vesuviano.

Corresponding email: [carlo.cardellini@unipg.it](mailto:carlo.cardellini@unipg.it)

Keywords: CO<sub>2</sub> fluxes, Earth degassing, non volcanic emissions, volcanic emissions, gas flux.

CO<sub>2</sub> Earth degassing is contributed by the combined action of two distinct source processes: active volcanoes (volcanic CO<sub>2</sub>), and tectonically active areas of the world (non-volcanic CO<sub>2</sub>). Even if it has long been recognized that Earth degassing may represent a not-trivial contribution to the global CO<sub>2</sub> budget, also nowadays, the magnitude of both contributions is however poorly constrained.

Central and southern Italy are affected by an active and intense process of CO<sub>2</sub> Earth degassing from both volcanic and non volcanic sources as revealed by recent studies focussed on the quantification of both CO<sub>2</sub> fluxes by point emission and soil diffuse degassing, and on the quantification of deeply derived CO<sub>2</sub> dissolved by the groundwater.

Regional scale studies in non volcanic areas of central and southern Italy, based on mass balance of carbon dissolved by groundwater, highlights the presence of two large CO<sub>2</sub> degassing structures (Tuscan Roman degassing structure, TRDS, and Campania degassing structure, CDS) that, for the magnitude and for the geochemical-isotopic features, were related to a regional process of mantle degassing. Quantitative estimates provided a regional CO<sub>2</sub> flux of about 9 Gt/y affecting the region (62000 km<sup>2</sup>), an amount globally relevant, being ~ 10% of the present-day global CO<sub>2</sub> discharge from subaerial volcanoes.

In addition to the large amounts of carbon dissolved by regional aquifers, the TRDS and CDS are also characterised by the presence of many cold gas emissions where the CO<sub>2</sub> is released by both vents and soil diffuse degassing. Both anomalous soil CO<sub>2</sub> degassing and CO<sub>2</sub> rich groundwater are different manifestations of the same process. In fact when the deeply produced gas is able to rise toward the surface, it can be dissolved by groundwaters or emitted directly to the atmosphere from gas emissions, depending on the magnitude of the gas flux rate and on the geological, structural and hydrogeological settings.

Measurement performed by the accumulation chamber shows soil CO<sub>2</sub> fluxes of order of magnitude higher than the typical biogenic CO<sub>2</sub> fluxes, characterise different sized areas which extension and shape are mainly related to tectonic structures. The first on-line catalogue of Italian gas emissions recently realised, reports on the existence of about 270 gas manifestations. Even if for only a limited number (~50) of such manifestations quantitative estimations of CO<sub>2</sub> fluxes are available considering that these contribute for fluxes in the range of some tenths of a some hundreds tons per day, it is likely that the cumulative contribution of the 270 manifestation would be large, and highly significant to the total CO<sub>2</sub> budget.

Large amounts of CO<sub>2</sub> is also discharged by soil diffuse degassing at the quiescent volcanoes. Specific surveys on the Campanian volcanoes pointed out the relevance of this process that in the case of Solfatara of Pozzuoli volcano, provide a CO<sub>2</sub> flux comparable to an erupting volcano.

The estimations of the fluxes of deep CO<sub>2</sub> in Italy points out the relevance of non-volcanic CO<sub>2</sub> degassing and of soil diffuse degassing from volcanoes, suggesting the actual underestimation of the Earth degassing process at global scale, arising from the lack of specific and systematic studies in the numerous "degassing areas" of the world.

## **MAGA, a new database of gas emissions from natural systems: a collaborative web environment for collecting data**

Cardellini C.\*<sup>1</sup>, Chiodini G.<sup>2</sup>, Frigeri A.<sup>2</sup>, Frondini F.<sup>1</sup>, Bagnato E.<sup>4</sup> & Aiuppa A.<sup>4</sup>

1. Dipartimento di Scienze della Terra, Università di Perugia. 2. INGV Napoli, Osservatorio Vesuviano  
3. Istituto di Astrofisica e Planetologia Spaziali, INAF, Roma. 4. DiStEM, Università di Palermo.

Corresponding email: [carlo.cardellini@unipg.it](mailto:carlo.cardellini@unipg.it)

Keywords: CO<sub>2</sub> emissions, gas emissions, CO<sub>2</sub> global budget, data science, data base.

The data on volcanic and non-volcanic gas emissions available online are, as today, are incomplete and most importantly, fragmentary. Hence, there is need for common frameworks to aggregate available data, in order to characterize and quantify the phenomena at various scales. A new and detailed web database (MAGA: MAPPING GAS emissions) has been developed, and recently improved, to collect data on carbon degassing from volcanic and non-volcanic environments. MAGA database allows researchers to insert data interactively and dynamically into a spatially referred relational database management system, as well as to extract data. MAGA kicked-off with the database set up and with the ingestion in to the database of the data from: i) a literature survey on publications on volcanic gas fluxes including data on active craters degassing, diffuse soil degassing and fumaroles both from dormant closed-conduit volcanoes (e.g., Vulcano, Phlegrean Fields, Santorini, Nisyros, Teide, etc.) and open-vent volcanoes (e.g., Etna, Stromboli, etc.) in the Mediterranean area and Azores, and ii) the revision and update of Googas database on non-volcanic emission of the Italian territory (Chiodini et al., 2008), in the framework of the Deep Earth Carbon Degassing (DECADE) research initiative of the Deep Carbon Observatory (DCO).

For each geo-located gas emission site, the database holds images and description of the site and of the emission type (e.g., diffuse emission, plume, fumarole, etc.), gas chemical-isotopic composition (when available), gas temperature and gases fluxes magnitude. Gas sampling, analysis and flux measurement methods are also reported together with references and contacts to researchers expert of each site. In this phase data can be accessed on the network from a web interface, and data-driven web service, where software clients can request data directly from the database, are planned to be implemented shortly. This way Geographical Information Systems (GIS) and Virtual Globes (e.g., Google Earth) could easily access the database, and data could be exchanged with other database. At the moment the database includes: i) more than 1000 flux data about volcanic plume degassing from Etna and Stromboli volcanoes, ii) data from ~ 30 sites of diffuse soil degassing from Neapolitan volcanoes, Azores, Canary, Etna, Stromboli, and Vulcano Island, several data on fumarolic emissions (~ 7 sites) with CO<sub>2</sub> fluxes; iii) data from ~ 270 non volcanic gas emission site in Italy.

We believe MAGA data-base is an important starting point to develop a large scale, expandable data-base aimed to excite, inspire, and encourage participation among researchers. In addition, the possibility to archive location and qualitative information for gas emission/sites not yet investigated, could stimulate the scientific community for future researches and will provide an indication on the current uncertainty on deep carbon fluxes global estimates.

## Measuring carbon dioxide and heat fluxes at orogene scale: the case of central Apennines

Chiodini G.\*<sup>1</sup>, Caliro S.<sup>1</sup>, Cardellini C.<sup>2</sup>. & Frondini F.<sup>2</sup>

1. INGV, Osservatorio Vesuviano. 2. Università di Perugia.

Corresponding email: [giovanni.chiodini@ov.ingv.it](mailto:giovanni.chiodini@ov.ingv.it)

Keywords: CO<sub>2</sub>, heat flux, Apennines.

Geological and geophysical studies hypothesized that the intrusion of Tyrrhenian asthenosphere is one of the factor controlling the Apennine orogenesis. This hypothesis are supported by the researches that we devoted in the last decade to quantify the rate of CO<sub>2</sub> and heat released in the Apennine belt. Carbon dioxide Earth degassing process was quantified on the base of the carbon mass balance of regional aquifers. The deeply derived CO<sub>2</sub> resulted in  $\sim 2\text{-}2.5 \times 10^{11}$  mol/a that represents a significant proportion (2% to 15%) of the estimated present-day total CO<sub>2</sub> discharge from the sub aerial volcanoes of the Earth. The groundwaters enriched in CO<sub>2</sub> systematically display a slight temperature anomaly, which becomes significant when the differences between the water temperatures at the springs and the temperature of corresponding recharging meteoric waters are compared. These temperature differences, together with the hydrogeologic parameters of the different aquifers, have been used to compute the total amount of heat by geothermal warming which results of  $\sim 2.1 \times 10^9$  Js<sup>-1</sup>, implying that a large sector of the Apennines is affected by heat fluxes higher than 300 mWm<sup>-2</sup>. These are in absolute very high values, for instance they are higher than the average heat fluxes of the famous geothermal provinces of Tuscany and Latium.

This finding is in some way surprising because so far the central Apennines was though to be a cold area. This high heat and CO<sub>2</sub> flux opens a new vision of the Apennines belt and requires the existence, at depth, of a thermal and fluid source such as a large magmatic intrusion. Recent tomographic images of the area confirm the presence of such intrusion visible as a broad negative velocity of seismic waves. This study reveals how the investigations based on groundwater systems are important for a more reliable estimation of both deep CO<sub>2</sub> and heat fluxes in orogenes.

## From mantle to magma: a comparison between volatile content in mantle xenoliths, basic lavas and melt inclusions from Northern Victoria Land, Antarctica

Giacomoni P.P.\*<sup>1</sup>, Coltorti M.<sup>1</sup>, Bonadiman C.<sup>1</sup>, Ferlito C.<sup>2</sup> & Pelorosso B.<sup>1</sup>

1. Dep. of Physics and Earth Sci., Univ. of Ferrara. 2. Dep. of Biol. and Earth Sci., Univ. of Catania.

Corresponding email: [pierpaolo.giacomoni@unife.it](mailto:pierpaolo.giacomoni@unife.it)

Keywords: Lithospheric mantle, melt inclusions, volatile content, basic magmatism.

The Trans-Antarctic Rift is the most extended continental break up on Earth. However, the origin of the magmatism and the nature of the mantle sources are still poor understood. This study offers an innovative view on the petrologic features of mantle xenoliths, basic lavas and olivine-hosted melt inclusions (MI) in the same lavas from Northern Victoria Land (NVL). Samples were collected from various localities, such as Baker Rocks, Harrow Peaks, Greene Point, Shield Nunatak, Eldridge Bluff and Handler Ridge during two expeditions funded by the Italian Antarctic Program (PNRA).

Mantle xenoliths are anhydrous and hydrous spinel-bearing lherzolites and harzburgites. Few samples are Fe-rich peridotites. Amphibole is the main volatile-bearing mineral, although few crystals of phlogopite were also found. Volatile content in amphibole were determined by SIMS at IGG-CNR laboratory in Pavia, while water contents in NAMs were determined at the Department of Earth and Space Science, University of Hefei (China).

Lavas are olivine-phyric (up to 15 %vol) with minor clinopyroxene and plagioclase in a glassy to microcrystalline plagioclase-dominated groundmass; opaque minerals are mostly magnetites and subordinately ilmenites. Samples are nepheline-normative basanites (42.4-44.8 SiO<sub>2</sub> wt%; 3.11-6.19 Na<sub>2</sub>O+K<sub>2</sub>O wt%) and alkaline basalts (44.9-48.7 SiO<sub>2</sub> wt%; 2.81-4.55 Na<sub>2</sub>O+K<sub>2</sub>O wt%). Samples from Handler Ridge are more primitive and richer in alkaline, with the highest TiO<sub>2</sub> content (3,55-3,65 wt%). They are also enriched in Rb, Ba, Nb, La, Zr despite their primitive features.

Olivine-hosted melt inclusions (MI) were analyzed for major element and volatiles (H<sub>2</sub>O, CO<sub>2</sub>, S, F, and Cl) after HT (1300°C) and HP (6 Kbar) homogenization at Rensselaer Polytechnic Institute (New York, USA). They are compositionally comparable to host lavas but show a wider range of variability. At least two populations have been identified, sometimes coexisting in the same sample, following two distinct compositional trends: a high- and a low-Fe-Ti-K trend. Volatile content in MI has been determined by SIMS at Woods Hole Oceanographic Institute (Massachusetts, USA). The H<sub>2</sub>O content ranges from 0.70 wt% to 1.19 wt% and CO<sub>2</sub> from 25 ppm to 341 ppm (H<sub>2</sub>O/CO<sub>2</sub>~1). At comparable H<sub>2</sub>O contents few samples show a remarkable higher CO<sub>2</sub> values (1322 ppm to 3905 ppm) with a H<sub>2</sub>O/CO<sub>2</sub> molar ratio down to 0.8. F and Cl content varies from 990 ppm to 10 ppm and from 570 ppm to 38 ppm respectively.

A comparison between volatile budget in the mantle sources and that analyzed in MI were developed, after modelling the metasomatic and melting processes which affected this portion of the lithospheric mantle. The Fe-Ti-K-rich melt observed in MI was also tentatively proposed as the metasomatic agent responsible for the genesis of the Fe-rich xenoliths.

## Metamorphic CO<sub>2</sub> production in scapolite-bearing calc-silicate rocks from the central-eastern Himalaya

Groppo C.\*<sup>1</sup>, Rolfo F.<sup>1-2</sup>, Mosca P.<sup>2</sup> & Castelli D.<sup>1-2</sup>

1 Department of Earth Sciences, Università di Torino. 2 IGG – CNR, Torino.

Corresponding email: [chiara.groppo@unito.it](mailto:chiara.groppo@unito.it)

Keywords: orogenic CO<sub>2</sub> cycle, metamorphic CO<sub>2</sub> degassing, scapolite-bearing calc-silic.

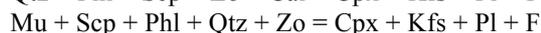
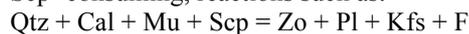
The “long-term carbon cycle” operates over millions of years and involves the slow exchange of carbon between rocks and the surficial system; the volume of CO<sub>2</sub> involved in these processes is still far from being constrained. So far, the degassing flux was mainly estimated based on the flux emitted by volcanoes in different geodynamic contexts, and additionally include carbon from the mantle and carbon degassed from subduction zones. This estimated flux does not take into account CO<sub>2</sub> derived from orogenic zones, where organic-rich sediments and limestone may be buried at depths at which CO<sub>2</sub> is formed by metamorphic reactions. However, recent studies suggest that metamorphic degassing from active collisional orogens supplies a significant fraction of the global solid-Earth derived CO<sub>2</sub> to the atmosphere, thus playing a fundamental role, even in today’s Earth’s carbon cycle (Gaillardet & Galy, 2008).

In order to test if calc-silicate rocks may act as metamorphic CO<sub>2</sub>-source rocks, a petrologic study of K-feldspar+scapolite-bearing calc-silicate rocks from eastern Nepal Himalaya has been performed. These rocks occur as tens to hundreds of meter thick levels hosted in anatectic Ky-Sil- bearing gneisses.

Mineral assemblage consists of Kfs + Cpx + Scp + Cal + Pl + Qtz ± Zo, and later Ep and green Amp. Clinopyroxene often shows oriented inclusions of Phl + Scp + Cal ± Mu ± Qtz, whereas zoisite includes Scp + Qtz + Ca + Na-rich Pl and is intergrown with Kfs and Ca-rich Pl. Clinopyroxene is often partially replaced by later green Ca-Amp ± Ep, whereas scapolite is locally partially replaced by symplectitic aggregates of Pl + Cal. In addition to ubiquitous titanite, strongly pleochroic allanite and bluish to colorless tourmaline locally occur, whereas graphite is always absent.

The Kfs+Scp-bearing calc-silicate rocks can be modeled in the NCKMAS-CO<sub>2</sub>-H<sub>2</sub>O system, including Pl and Scp solid solutions, in addition to a fluid of variable composition. In such complex system, the use of mixed-volatile phase diagram projections (in which the volatile composition of the system is projected onto the P–T coordinate frame: Connolly & Trommsdorff, 1991), is the best approach for simultaneously considering the effects of the three variables P, T and X<sub>fluid</sub> on phase relations.

Preliminary petrologic data demonstrates that Kfs+Scp- bearing calc-silicate rocks may act as CO<sub>2</sub>-source during prograde heating, releasing internal-derived CO<sub>2</sub>-rich fluids (XCO<sub>2</sub>=0.5-0.6) through Cpx, Kfs and Zo -forming, and Scp -consuming, reactions such as:



Gaillardet J. & Galy A. 2008. Himalaya-carbon sink or source? *Science*, 320, 1727-1728.

Connolly J.A.D. & Trommsdorff V. 1991. Petrogenetic grids for metacarbonate rocks: pressure–temperature phase-diagrams for mixed-volatile systems. *Contrib. Mineral. Petrol.*, 108, 93-105.

## Carbonate, not carbonatite, at Villamayor volcano (Calatrava Volcanic District, Central Spain)

Lustrino M.\*<sup>1</sup>, Prelevic D.<sup>2</sup>, Agostini M.<sup>3</sup> & Gaeta M.<sup>1</sup>

1. Dipartimento di Scienze della Terra, Università di Roma La Sapienza. 2. Geocycles Research Centre and Institute of Geosciences, University of Mainz, Germany. 3. IGG-CNR, Pisa.

Corresponding email: [michele.lustrino@uniroma1.it](mailto:michele.lustrino@uniroma1.it)

Keywords: Carbonatite, Petrology, Leucitite.

The Moron de Villamayor Volcano (~9 Ma) represents the oldest volcanic activity in the Calatrava Volcanic field, Central Spain. The products of this activity have been classified in literature as leucitites despite a minor presence of modal groundmass leucite (<5 vol. %), the low K<sub>2</sub>O content (average 3.3 wt%) and the low K<sub>2</sub>O/Na<sub>2</sub>O ratio (<1.8). The lava flows of this small volcano are strongly porphyritic with the presence of subhedral to euhedral olivine phenocrysts and cumulate crystals. A recent paper (Humphreys et al., 2010) classifies these rocks as leucitites and considers the olivine phenocrysts as mantle debris. The carbonate inclusions are considered to represent the relict of Ca-carbonatitic magma crystallizing calcite and, in one single case, aragonite. We challenge the Humphreys et al (2010) hypothesis for several reasons:

1) The olivine crystals cannot be considered mantle xenocrysts because of their low forsterite content (72-89 mol% Fo) and relatively high CaO (>0.2 wt%).

2) Olivine crystals are considered liquidus phases (euhedral crystals with plateau Mg/Fe ratios to normal zoning) or cumulitic phases remobilized after arrival of new magma batches (subhedral to euhedral shape with plateau Mg/Fe to inverse zoning in the outermost rim).

3) The rare mica occasionally associated with carbonate within olivine has much lower Mg# (73-84) compared to mantle phlogopite (Mg# = 89-95) and is indistinguishable from groundmass biotite.

4) Also the other mineral phases associated with carbonates as inclusions in olivine are chemically indistinguishable from groundmass phases.

5) The calculated leucitite composition (obtained subtracting 30% olivine, considered xenocrysts by Humphreys et al., 2010) is too much MgO-poor (0.52 wt%) for the calculated SiO<sub>2</sub> (46.65 wt%). This is not compatible with a mantle melt.

6) The carbonate present in the Moron de Villamayor mantle sources, in equilibrium with the leucititic magma cannot be Mg-free as the Ca-carbonate (calcite and aragonite) found as inclusions in olivine crystals.

7) The SrO content of the carbonate inclusions is generally low (generally <0.2 wt%) and never exceeding 0.54 wt%, values, compatible with sedimentary carbonates.

8) The LAM-ICPMS incompatible trace element contents of calcite indicate nearly sterile compositions, with very low REE contents (La down to 0.01 ppm).

We propose a sedimentary origin for the carbonate mineral inclusions in olivine. In our model sedimentary carbonate is scraped off the country rocks and partially digested by the ultrabasic melt. When in contact with the carbonate xenocrysts the olivine growth is stopped, producing the typical hollow body euhedral shape of the Moron de Villamayor olivine.

Humphreys E.R., Bailey K., Hawkesworth C.J., Wall F., Najorka J. & Rankin A.H.. 2010. Aragonite in olivine from Calatrava, Spain—Evidence for mantle carbonatite melts from >100 km depth. *Geology*, 38, 911-914.

## C-O-H fluids and redox processes at subduction zones

Malaspina N.\*<sup>1</sup>, Tumiati S.<sup>2</sup>, Fumagalli P.<sup>2</sup> & Poli S.<sup>2</sup>

1. Dipartimento di Scienze dell'Ambiente e del Territorio e di Scienze della Terra, Università degli Studi di Milano Bicocca. 2. Dipartimento di Scienze della Terra, Università degli Studi di Milano.

Corresponding email: [nadia.malaspina@unimib.it](mailto:nadia.malaspina@unimib.it)

Keywords: C-O-H fluids, carbonate, diamond, redox state, oxygen fugacity.

C-O-H fluids are released by dehydration, partial melting and/or decarbonation of the slab and transferred to the mantle, where they interact with the surrounding rocks, prompting the growth of carbonates, hydrous minerals and C polymorphs. In the pure C-O-H system, C-saturated fluid speciation is a function of the oxygen chemical potential. Therefore, in natural systems, the fluid speciation can be imposed by the redox state of the rock-forming phases. Alternatively, C-O-H fluids may control the bulk oxidation state of the rock system by redox reactions with the mineral phases. Complexities in the speciation of such fluids are demonstrated by discoveries of hydrates, carbonates and carbon polymorphs in polyphase inclusions, and also by high-pressure H<sub>2</sub>- or CH<sub>4</sub>-bearing fluid inclusions in mantle harzburgites, suggesting that the composition of C-bearing hydrous fluids closely relates to the oxidation state of the system. We selected three case studies of garnet-bearing ultramafic rocks (Ulten zone, Italy; Sulu, China; Bardane, Norway), which record metasomatic processes driven by C-O-H fluids at the interface between a subducting slab and the overlying mantle wedge. All these rocks contain carbonates (dolomite-only at P < 1.9 GPa at 900 °C, magnesite-only at P > 2.4 GPa at 900 °C, dolomite + magnesite in between) and hydrous phases (amphibole, phlogopite) equilibrated at some stages in the garnet stability field. The fO<sub>2</sub> values, estimated by analysing the Fe<sup>3+</sup> content (skiagite mole fraction) in garnet, indicate that the Ulten and Sulu peridotites record high oxygen fugacities (FMQ to FMQ+2) and a retrograde path with decreasing P and T. The fO<sub>2</sub> values obtained for the Bardane garnet websterites, which record a prograde path with increasing T and P, are up to -2 log units lower than the FMQ. When combined with data for subduction-zone systems (arc lavas and their mantle sources), the studied ultramafic rocks define a trend of decreasing fO<sub>2</sub> with increasing pressure.

The Bardane websterites contain C-polymorphs in polyphase inclusions, which precipitated from entrapped metasomatic fluids at ultrahigh pressures. The calculated C-O-H fluid phase in equilibrium with the solid phases consists of mixtures of H<sub>2</sub>O and CO<sub>2</sub>. Semi-quantitative estimates for the Ulten and Sulu peridotites, in which C-polymorphs have not been found, and petrographic constraints for the Ulten peridotites indicate that the C-O-H component of the fluid could consist of H<sub>2</sub>O+CO<sub>2</sub>.

## Subduction zones and the deep carbon cycle

Manning C.E.\*

Department of Earth, Planetary, and Space Sciences-University of California, Los Angeles.

Corresponding email: [manning@epss.ucla.edu](mailto:manning@epss.ucla.edu)

Keywords: subduction, carbon cycle, dissolution.

Most studies conclude that the mantle is gaining carbon because more carbon is subducted than is degassed by volcanism. A key component of these budgetary analyses is the estimation of the carbon lost from slabs and degassed at arc volcanoes. But this hinges on the assumption that there is a 1:1 correspondence between carbon derived from subducting lithosphere and carbon degassed at arc volcanoes, and that the carbon transfer mechanism involves only molecular CO<sub>2</sub>. Neither of these assumptions is valid. The first is problematic because arc magmas may attain deep fluid saturation, a significant fraction of arc magma does not erupt, and arc crust is permeable to fluids. These considerations point to diffuse loss and deep storage of potentially significant carbon that does not contribute to degassing at volcanic centers. The second problem arises because assessment of the supply of carbon from subducting slabs arbitrarily limits consideration to CO<sub>2</sub> in molecular fluids, which underestimates the mass of carbon that can be mobilized. Theoretical and experimental results show that carbon solubilities are likely higher than these models predict. Total dissolved carbon depends on the solubilities of all carbon species (e.g., CO<sub>2</sub>aq, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, etc), which are controlled by pH, fO<sub>2</sub>, halogens, and dissolved cations. Controls on these variables in subduction zones can combine to elevate carbonate mineral solubility. For example, the calculated pH of model slab mineral assemblages of jadeite, white mica and quartz along slab-top geotherms show that the CaCO<sub>3</sub> solubility is higher at silicate-buffered pH than at the more alkaline pH of otherwise pure H<sub>2</sub>O saturated only in CaCO<sub>3</sub>, or than in molecular mixing models. Carbonate solubility is also enhanced by alkali halide salts. At a given pressure and temperature, calcite solubility increases in proportion to the square of salt mole fraction for NaCl, KCl, LiCl, and their mixtures. At fixed P, T, and X<sub>salt</sub>, solubility decreases as LiCl > NaCl > KCl, consistent with Pearson Hard-Soft Acid-Base rules. Ion pairing and reduction of carbonate or CO<sub>2</sub> to CH<sub>4</sub> will further increase solubility. Models including the above effects yield carbon solubility approaching 1 wt% in some slab fluids. Carbon carried by subduction-zone fluids and deep degassed magmatic volatiles likely play important roles in the deep carbon cycle, and must be taken into account in assessing the gain or loss of carbon by the mantle.

## Hydrous carbonatitic liquids from epidote-dolomite eclogites: new perspectives on carbon transfer at subduction zones

Poli S.\*

Dipartimento di Scienze della Terra, Università degli Studi di Milano.

Corresponding email: [stefano.poli@unimi.it](mailto:stefano.poli@unimi.it)

Keywords: subduction, carbon, carbonatite.

Current knowledge on the solidus temperature for carbonate-bearing rocks suggests that carbonatitic liquids should not form in a subducted oceanic lithosphere, unless anomalous thermal relaxation occurs. For a mildly warm subduction path, COH-bearing basaltic eclogites are expected to lose all H<sub>2</sub>O component at epidote breakdown, located at approx. 2.8-3.0 GPa. Above this pressure limit, the solidus is that of a carbonated basaltic eclogite which shows a minimum temperature of 1020 °C at 4.0-4.5 GPa. However, the oceanic crust includes a range of gabbroic rocks, altered on rifts and transforms, with large amounts of An-rich plagioclase. It has been shown that epidote disappearance with pressure depends on the normative anorthite content of the bulk composition considered; we therefore expect that altered gabbros might display a much wider pressure range where epidote persists, potentially affecting the solidus relationships. Notably, this applies to epidote rocks formed in hydrothermal environments at oceanic settings, then recovered in high-pressure and ultra-high pressure terrains.

New experimental data from 3.7 to 4.6 GPa, 750°C to 1000 °C are intended to unravel the effect of variable bulk and volatile compositions in model eclogites, enriched in the normative anorthite component (An<sub>37</sub> and An<sub>45</sub>). Experiments are performed in piston cylinder and multianvil machines apparatus, using both single and, buffered, double capsule techniques.

Garnet, clinopyroxene and coesite form in all syntheses. Lawsonite was found to persist at 3.7 GPa, 750 °C, with both dolomite and magnesite; at 3.8 GPa, 775-800 °C, fluid saturated conditions, epidote coexists with kyanite, dolomite and magnesite. The anhydrous assemblage garnet, omphacite, aragonite, kyanite is found at 4.2 GPa, 850 °C. At 900 °C, fluid-rich conditions, a silicate fluid/melt of granitoid composition, a carbonatitic melt and Na-carbonate are observed. Close to fluid-saturation, 3.8-4.2 GPa, 900 °C, garnet and Na-rich clinopyroxene coexist with a carbonatitic melt, dolomite and aragonite. The carbonatitic melt is enriched in Ca compared to melts previously obtained in dry carbonated experiments. Sandwich experiments, producing large quantities of liquid, demonstrate attainment of equilibrium and the supercritical nature of the carbonate liquid produced.

The subsolidus breakdown of epidote in the presence of carbonates at depths exceeding 120 km provides a major source of COH fluids at subarc depth. In warm subduction zones, the possibility of extracting hydrous carbonatitic liquids from a variety of gabbroic rocks offers new scenarios on the metasomatic processes in the lithospheric wedge of subduction zones and a new mechanism for recycling carbon. Such liquids are expected to be extremely reactive in a percolated mantle wedge, where they generate carbonate pyroxenites, a fertile CO<sub>2</sub> source for magmatism at subduction zones.

## Soil gas geochemistry and C isotopic signature in Medolla (Modena) area

Sciarra A. \*, Cantucci B., Galli G., Cinti D., Pizzino L. & Quattrocchi F.

Istituto Nazionale di Geofisica e Vulcanologia – Roma.

Corresponding email: [alessandra.sciarra@ingv.it](mailto:alessandra.sciarra@ingv.it)

Keywords: soil gas, C isotope.

Several soil surveys were performed in Medolla (Modena), a peculiar area characterized by spotty high soil temperature, coupled to gas emission and lack of vegetation, to determine the origin of these phenomena.

In this area gas fluxes (CO<sub>2</sub> and CH<sub>4</sub>) measurements, soil gas concentrations (He, H<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>) and their isotopic analyses ( $\delta^{13}\text{C}-\text{CH}_4$ ,  $\delta\text{D}-\text{CH}_4$  and  $\delta^{13}\text{C}-\text{CO}_2$ ) were performed in October and December 2008, and repeated in May 2012, September 2012, June 2013 afterwards the 2012 Emilia seismic sequences.

Chemical composition of soil gas are dominated by CH<sub>4</sub> that ranges from 0.34 to 764,269 ppmv/v, with CO<sub>2</sub> concentration ranging from 0.024 to 3 %v/v. Very anomalous fluxes (138 g/m<sup>2</sup>day of CO<sub>2</sub>, 51.77 g/m<sup>2</sup>day of CH<sub>4</sub>) and concentrations are recorded in the spot area.

In the surrounding area CO<sub>2</sub> and CH<sub>4</sub> values are very low, within the typical range of vegetative and of organic exhalation of the cultivated soil.

After the seismic sequence the CH<sub>4</sub> and CO<sub>2</sub> fluxes are increased of one order of magnitude in the spotty areas, whereas in the surrounding area the values are within the background. On the contrary, CH<sub>4</sub> concentration decrease (40%v/v in the 2012 surveys) and CO<sub>2</sub> concentration increase until to 12.7%v/v (2013 survey).

Isotopic analysis were carried out only on samples with anomalous values. October/December 2008 data hint a thermogenic origin of CH<sub>4</sub> probably linked to leakage from a deep source. Conversely, 2012/2013 isotopic data indicate a typical biogenic origin (i.e. microbial hydrocarbon production) of the CH<sub>4</sub>, as recognized elsewhere in the Po Plain and surroundings.

The  $\delta^{13}\text{C}-\text{CO}_2$  value suggests a prevalent shallow origin of CO<sub>2</sub> (i.e. organic and/or soil-derived) probably related to anaerobic oxidation of heavy hydrocarbons.

Obtained results highlight a different behavior before and after the seismic events, proved also by the different carbon isotopic signature of CH<sub>4</sub>. These variations could be produced by increasing of bacterial (e.g. peat strata) and methanogenic fermentation processes in the first meters of the soil.

## Experimental determination of carbon-saturated COH fluids speciation at 1 GPa

Tiraboschi C.\*<sup>1</sup>, Tumiati S.<sup>1</sup>, Recchia S.<sup>2</sup>, Fumagalli P.<sup>1</sup> & Poli S.<sup>1</sup>

1. Dipartimento di Scienze della Terra, Università di Milano. 2. Dipartimento di Scienza e Alta Tecnologia, Università dell'Insubria.

Corresponding email: [carla.tiraboschi@unimi.it](mailto:carla.tiraboschi@unimi.it)

Keywords: COH fluids, speciation, experiments.

The quantitative assessment of species in COH fluids is crucial in modelling mantle processes. For instance, H<sub>2</sub>O/CO<sub>2</sub> ratio in the fluid phase influences the location of the solidus and of carbonation/decarbonation reactions in peridotitic systems (Wyllie, 1978). In the scientific literature, the speciation of COH fluids has been generally assumed on the basis of thermodynamic calculations using equations of state of simple H<sub>2</sub>O-non-polar gas systems (e.g., H<sub>2</sub>O-CO<sub>2</sub>-CH<sub>4</sub>). Only few authors dealt with the experimental determination of high-pressure COH fluid species at different conditions, using diverse experimental and analytical approaches (e.g., piston cylinder+capsule-piercing+gas-chromatography/mass-spectrometry; cold-seal+silica glass capsules+Raman). We performed experiments on COH fluids using a capsule-piercing device inspired by Taylor & Foley (1994) coupled with quadrupole mass spectrometry. This type of analyzer ensures superior performances in terms of selectivity of molecules to be detected, high acquisition rates and extended linear response range. Experiments were carried out in a rocking piston cylinder apparatus at pressure of 1 GPa and temperatures from 800 to 900°C. Carbon-saturated fluids were generated through the addition of oxalic acid dihydrate (C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O) and graphite. Single/double capsules and different packing materials (BN and MgO) were used to evaluate the divergence from the thermodynamic speciation model. Moreover, to assess the effect of solutes on COH fluid speciation we also performed a set of experiments adding synthetic forsterite to the charge. To determine the speciation we assembled a capsule-piercing device that allows to puncture the capsule in a gas-tight vessel at 80°C. The extraction Teflon vessel, similar to that described by Manning & Boettcher (1994) for dissolution experiments, is composed of a base part, where the capsule is allocated on a steel support, and a top part where a steel drill is mounted. To release the quenched fluids from the capsule, the base part of vessel is hand-tighten to the top part, allowing the steel pointer to pierce the capsule. The evolved gases are then conveyed to a quadrupole mass spectrometer through a heated line to avoid the condensation of water. Our results suggest that fluid speciation can diverge considerably compared to the thermodynamic model depending on the experimental strategies adopted and on the presence of solutes in complex COH systems.

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Wyllie P.J. 1978. The effect of H<sub>2</sub>O and CO<sub>2</sub> on planetary mantles. *Geophys. Res. Lett.*, 5, 440-442.

## COH serpentinites and metasomatic rocks from Cogne (Aosta Valley, Western Italian Alps): Insights into seafloor fluid-rock interactions

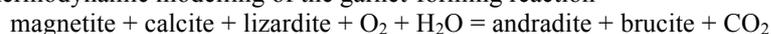
Tumiati S.<sup>1</sup>, Martin S.\*<sup>2</sup>, Rossetti P.<sup>3</sup> & Carbonin S.<sup>2</sup>

1. Dipartimento di Scienze della Terra, Università di Milano. 2. Dipartimento di Geoscienze, Università di Padova. 3. Dipartimento di Scienze della Terra, Università di Torino.

Corresponding email: [silvana.martin@unipd.it](mailto:silvana.martin@unipd.it)

Keywords: COH fluids, magnetite, serpentinite

The serpentinites of Cogne contain magnetite, serpentine, calcite, graphite, brucite, chlorite, diopside, and andradite/hydroandradite garnet. These mineralogical assemblages result from oceanic serpentinization and metasomatic processes, mediated by hydrothermal-vent fluids on the Tethyan seafloor. Fluid speciation and redox potential are strictly linked to each other in carbon-saturated COH (GCOH) fluids. If the redox buffer capacity of rocks can be overwhelmed, as in the case of high fluid/rock ratios, COH fluids can control externally the redox potential of rocks. The speciation of the COH fluid and therefore the redox conditions in force during the oceanic serpentinization and metasomatism recorded by the Cogne rocks can be unravelled by the mineral assemblages observed. Thermodynamic modelling of the garnet-forming reaction



suggests that the formation of andradite at T ranging from 250 to 400 °C is possible only for very low  $X_{\text{CO}_2}$  [ $=\text{CO}_2/(\text{H}_2\text{O}+\text{CO}_2)$ ] in the fluid ( $\log X_{\text{CO}_2} = -5$  to  $-4$ ), which is comparable to the present-day seawater. Thermodynamic modelling of GCOH fluids at 500 bar and 350 °C shows that this  $\text{CO}_2$  content is consistent with  $f_{\text{O}_2}$  conditions broadly approaching the FMQ buffer, which well agrees with estimates concerning oceanic hydrothermal vents and with the sulphide parageneses found at Cogne. The constraints to the fluid speciation allowed the construction of a fluid-saturated, isobaric (500 bar) T-X diagram, ranging from two representative bulk-rock compositions: (1) a typical magnetite- and sulphide-bearing serpentinite and (2) an andradite-, diopside- and calcite-bearing metasomatic rock. At composition (1), T-X diagram represents a model for the serpentinization of a peridotite in a pure FMS+COH system. When oceanic peridotite undergoes hydration, it becomes a magnetite±brucite-bearing serpentinite. Prograde forsterite is expected to grow at the expenses of brucite and lizardite above ~ 400 °C. In fact, we observed olivine (Fo98) neoblasts developing after brucite. Towards composition (2), at T below 400 °C and for low degrees of metasomatism, the expected association should contain clinocllore and calcite in addition to lizardite, magnetite and brucite. Higher degrees of metasomatism will stabilize andradite at T < 360 °C and diopside at T > 360 °C in brucite-free rocks. Eventually, for (2) andradite and diopside coexist even at T < 360 °C, and calcite disappears. At T < 300 °C, diopside should be replaced by amphibole, never observed in the investigated samples of Cogne.

In conclusion, thermodynamic modelling suggests that mineral assemblages observed at Cogne match a process of seafloor serpentinization and Ca (±Al) metasomatism at 300–360 °C conveyed by carbon-saturated COH hydrothermal vent fluids characterized by  $\text{CO}_2$  contents comparable to present-day seawater, capable to fix the redox potential of rocks close to the FMQ buffer.

## Co-seismic carbonate melting along natural faults

Viganò A.\*<sup>1</sup>, Tumiati S.<sup>2</sup>, Martin S.<sup>3</sup>, Rigo M.<sup>3</sup>, Prosser G.<sup>4</sup> & Zanchetta S.<sup>5</sup>

1. Sezione Centro di Ricerche Sismologiche, Istituto Nazionale di Oceanografia e di Geofisica Sperimentale. 2. Dipartimento di Scienze della Terra, Università degli Studi di Milano. 3. Dipartimento di Geoscienze, Università degli Studi di Padova. 4. Dipartimento di Scienze, Università degli Studi della Basilicata. 5. Dipartimento di Scienze dell'Ambiente e del Territorio e di Scienze della Terra, Università degli Studi di Milano-Bicocca.

Corresponding email: [alfio.vigano@retesismicatrento.org](mailto:alfio.vigano@retesismicatrento.org)

Keywords: Carbonate rock, Pseudotachylytes, Faults.

Seismic faulting in carbonates produces different fault rocks due to competing chemico-physical processes (e.g., mechanical comminution, thermal decomposition and melting), which tend to prevail mainly as a function of ambient temperature and pressure, presence and composition of fluids, and rock material properties. Viganò et al. (2011) recently reported the occurrence of carbonate pseudotachylytes, i.e. products of friction-induced melting of carbonate rocks.

Here we present two examples of natural faults where co-seismic carbonate melting occurred: (i) the Canalone Porta fault (CPF, Grigna Massif, Italy; Viganò et al., 2011) and (ii) the Pietra Grande thrust (PGT, Brenta Dolomites, Italy; Castellarin et al., 1993).

The studied faults developed within dolomitic and marly limestones (CPF) and limestones and dolomitic limestones (PGT) of middle Triassic and Triassic–Early Jurassic age, respectively. At the outcrop scale, faults show reddish infillings forming fault- and injection-veins. At the micro-scale, veins consist of a fine-grained reddish matrix containing carbonate clasts of different size. Veins usually show chilled margins and typical wall rocks vary from fractured carbonate of the damage zone to protocataclasite, cataclasite and fault breccia.

Even if bulk chemical and mineralogical compositions of host rocks and carbonate pseudotachylytes are mostly the same, the fine-grained matrix is characterized by a second-generation nanometer-sized Ca-carbonate aggregates with different compositions compared to clasts. A K-bearing aluminosilicate amorphous phase bounds aggregates and clasts in the fine-grained matrix. We suggest that this glass was obtained by disequilibrium melting of mainly muscovite and quartz of the host rock.

The temperature attained by the Canalone Porta fault by calcite–dolomite solvus geothermometry on nanometer-sized Ca-carbonates is up to 720 °C, above the eutectic melting temperature of dolomite with water at pressure of 0.2 GPa (cf. Lee et al., 2000). Regarding the almost pure calcite composition of the Pietra Grande fault rocks, petrological models similarly suggest a melting temperature of about 740 °C for the join calcite–water system at 1 kbar (Wyllie and Tuttle, 1960).

Castellarin A., Piccioni S., Prosser G., Sanguinetti E., Sartori R. & Selli L. 1993. Mesozoic continental rifting and Neogene inversion along the South Giudicarie Line. *Mem. Soc. Geol. It.*, 49, 125-144.

Lee W.-J., Fanelli M.F., Cava N. & Wyllie P.J. 2000. Calciocarbonatite and magnesiocarbonatite rocks and magmas represented in the system CaO-MgO-CO<sub>2</sub>-H<sub>2</sub>O at 0.2 GPa. *Miner. Petrol.*, 68, 225-256.

Viganò A., Tumiati S., Recchia S., Martin S., Marelli M. & Rigon R. 2011. Carbonate pseudotachylytes: evidence for seismic faulting along carbonate faults. *Terra Nova*, 23, 187-194.

Wyllie P.J. & Tuttle O.F. 1960. The system CaO–CO<sub>2</sub>–H<sub>2</sub>O and the origin of carbonatites. *J. Petrol.*, 1, 1-46.

## **SESSIONE S19**

### **Fluids in the Earth's crust and Mantle**

*CONVENORS*

*O. Bartoli (Univ. Padova)*

*N. Malaspina (Univ. Milano Bicocca)*

## The H<sub>2</sub>O content of granite embryos

Bartoli O.\*<sup>1</sup>, Cesare B.<sup>1</sup>, Remusat L.<sup>2</sup>, Acosta-Vigil A.<sup>3</sup> & Poli S.<sup>4</sup>

1. Dipartimento di Geoscienze, Università di Padova. 2. Muséum National d'Histoire Naturelle, Laboratoire de Minéralogie et Cosmochimie du Muséum. 3. Instituto Andaluz de Ciencias de la Tierra, Consejo Superior de Investigaciones Científicas-Universidad de Granada. 4. Dipartimento di Scienze della Terra, Università di Milano.

Corresponding email: [omar.bartoli@unipd.it](mailto:omar.bartoli@unipd.it)

Keywords: melt inclusions, granite H<sub>2</sub>O content, crustal melting.

Quantification of H<sub>2</sub>O contents of natural granites has been an on-going challenge owing to the extremely fugitive character of H<sub>2</sub>O during cooling and ascent of melts and magmas. Here we approach this problem by studying granites in their source region (i.e. the partially melted continental crust) and we present the first NanoSIMS analyses of anatectic melt inclusions (MI) hosted in peritectic phases of migmatites and granulites. These MI which totally crystallized upon slow cooling represent the embryos of the upper-crustal granites (Cesare et al., 2009; Bartoli et al., 2013). The approach based on the combination of MI and NanoSIMS has been here tested on amphibolite-facies migmatites at Ronda (S Spain) that underwent fluid-present to fluid-absent melting at ~700 °C and ~5 kbar. Small (≤ 5 μm) crystallized MI trapped in garnet have been remelted using a piston-cylinder apparatus and they show leucogranitic compositions. We measure high and variable H<sub>2</sub>O contents (mean of 6.5±1.4 wt%) in these low-temperature, low-pressure granitic melts. We demonstrate that, when the entire population from the same host is considered, MI reveal the H<sub>2</sub>O content of melt in the specific volume of rock where the host garnet grew. Mean H<sub>2</sub>O values for the MI in different host crystals range from 5.4 to 9.1 wt%. This range is in rather good agreement with experimental models for granitic melts at the inferred P-T conditions. Our study documents for the first time the occurrence of H<sub>2</sub>O heterogeneities in natural granitic melts at the source region (Bartoli et al., 2014). These heterogeneities are interpreted to reflect the birth of granitic melts under conditions of “mosaic” equilibrium, where the distinct fractions of melt experience different buffering assemblages at the micro-scale, with concomitant differences in melt H<sub>2</sub>O content. These results confirm the need for small-scale geochemical studies on natural samples to improve our quantitative understanding of crustal melting and granite formation. The same approach adopted here can be applied to MI hosted in higher-temperature, granulite-facies rocks that represent the parents of many upper-crustal granites. This will result in a better understanding of formation and evolution of granitic magmas.

Bartoli O., Cesare B., Poli S., Bodnar R.J., Acosta-Vigil A., Frezzotti M.L. & Meli S. 2013. Recovering the composition of melt and the fluid regime at the onset of crustal anatexis and S-type granite formation. *Geology*, 41, 115-118.

Bartoli O., Cesare B., Remusat L., Acosta-Vigil A. & Poli S. 2014. The H<sub>2</sub>O content of granite embryos. *Earth Planet. Sci. Lett.*, 395, 281-290.

Cesare B., Ferrero S., Salvioli-Mariani E., Pedron D. & Cavallo A. 2009. Nanogranite and glassy inclusions: the anatectic melt in migmatites and granulites. *Geology*, 37, 627-630.

## The “spongy” behaviour of serpentinized mantle rocks at the plate interface setting: geochemical and tectonic implications

Cannaò E.\*<sup>1</sup>, Agostini S.<sup>2</sup>, Scambelluri M.<sup>1</sup> & Tonarini S.<sup>2</sup>

1. Dipartimento di Scienze della Terra, dell'Ambiente e della Vita, Università di Genova.  
2. IGG-CNR Pisa.

Corresponding email: [enrico.cannaò@unige.it](mailto:enrico.cannaò@unige.it)

Keywords: High pressure ultramafic rocks, plate interface, fluid-mediated mass transfer.

A “spongy” behaviour of serpentinized mantle rocks has been recently advocated to explain fluid and element (e.g. B, Sr, Pb) transfer from slab to mantle in subduction zones (Deschamps et al., 2011). In this scenario, km-thick hydrated layers in the supra-subduction mantle wedge, as well as melanges hosting serpentinized mantle rocks can play a key role. In such environments, mixing of slab derived fluids with mantle and/or geochemical mixing of different element reservoirs in subduction channel melanges significantly affect subduction recycling.

Here we present the study of two plate interface environments: (I) serpentinite-rich, represented by the high-pressure Ligurian serpentinites (Erro-Tobbio, ET, and Voltri Units, VU); (II) metasediment-dominated top slab mélange, represented by the de-serpentinized garnet peridotite and chlorite harzburgite bodies (with eclogite and metaroddingite layers) embedded in metasediments from Cima di Gagnone (CdG, Adula Unit).

The Ligurian serpentinites derive from oceanic slab and mantle wedge tectonically coupled and dragged to depth during Alpine subduction: they may represent the hydrated precursors of the CdG peridotites. The ET serpentinites show high [B], positive  $d^{11}\text{B}$  and limited enrichment in Pb and Sr isotopic ratio: they are interpreted as supra-subduction mantle flushed by slab fluids. The VU serpentinites show comparable values of [B],  $d^{11}\text{B}$  and Pb and slightly higher Sr isotopic ratio. This geochemical signature may reflect interaction with slab fluids enriched in heavy B-rich and in crustal radiogenic Sr, suggestive of mantle evolving atop the slab.

High-pressure metaperidotite and mafic rocks from CdG show low [B], negative  $d^{11}\text{B}$  and high Sr and Pb isotopic ratios. The host metasediments have higher [B], negative  $d^{11}\text{B}$  and distinctly higher Sr and Pb isotopic ratios. The geochemical signature of the CdG rocks, points to exchange between mantle and sedimentary/crustal reservoirs during prograde subduction burial.

The evidence presented here for a number of Alpine ultramafic rocks suggests that slices of serpentinized mantle of different size and provenance (slab and wedge) were accreted to plate interface domains since the early stages of subduction. These serpentinized rocks took up slab fluids and elements during burial (spongy rocks) thus becoming key fluid-mobile element reservoirs for arc magmatism.

Deschamps F., Guillot S., Godard M., Andreani M. & Hattori K. 2011. Serpentinites act as sponges for fluid-mobile elements in abyssal and subduction zone environments. *Terranova*, 23, 171-178.

## Volatile concentrations of silicate melt inclusions: Deep insights into processes in active volcanic systems

Esposito R.\*<sup>1</sup>, Moore L.<sup>2</sup>, Steel-MacInnis M.<sup>3</sup>, Cannatelli C.<sup>1</sup>, Bodnar R. J.<sup>2</sup>, Lima A.<sup>1</sup> & De Vivo B.<sup>1</sup>

1. DISTAR, Università degli Studi di Napoli Federico II. 2. Department of Geosciences, Virginia Tech, USA. 3. Institute for Geochemistry and Petrology, ETH Zürich, Switzerland.

Corresponding email: [rosario.esposito3@unina.it](mailto:rosario.esposito3@unina.it)

Keywords: Melt inclusions, melt inclusion assemblage (MIA), pre-eruptive volatile contents, magma degassing pattern.

In the last few decades, many volcanologists, petrologists and geochemists have focused on understanding the volatile (H<sub>2</sub>O-CO<sub>2</sub>-S-Cl-F) evolution of active volcanic systems using silicate melt inclusions (MI). The prominence of MI studies is not surprising because MI often provide the only means to measure directly the volatile contents dissolved in deep, undegassed melts. MI represent aliquots of melt trapped during crystal growth (and, more rarely, during crystal dissolution). Ideally, this aliquot of melt would be considered representative of the melt in equilibrium with the growing crystal at the time of trapping. Thus, the volatile concentrations of MI are commonly coupled with the silicate melt composition to estimate depths of crystal formation based on experimentally derived volatile solubility models. The volatile contents of MI can also be used to infer the magma dynamics of past eruptions, in an effort to better predict the characteristics of future eruptions. Furthermore, volatile concentrations of MI can be used to decipher physical and chemical processes in deep volcanic plumbing systems, such as volatile fluxing from deep source regions to shallow magma reservoirs and to reveal the oxidation state of deep magmas.

One common feature of MI volatile data presented in the literature is the high variability of concentrations observed in a typical dataset. On one hand, such variability can reflect varying pressure, temperature, oxidation state, and/or silicate melt composition during the evolution of the magmatic system, recorded by MI trapped in phenocrysts grown at different stages in the magma reservoir. Such variability itself may thus allow researchers to investigate different magmatic processes using MI. On the other hand, a growing body of evidence suggests that similar variability in volatile concentrations of MI can result from modifications of MI after trapping (e.g., post entrapment crystallization, diffusive loss, etc.). Therefore, in order to draw robust inferences concerning magmatic evolution based on volatile concentrations of MI, methods are needed to distinguish the "primary" signal (representing deep magmatic processes) from potential post-entrapment modification effects.

In this study, we review methods that can be used to assess the reliability and optimize the interpretation of volatile contents of MI. Firstly, we highlight the importance of petrographic examination of MI to collect robust data. We review the concept of melt inclusion assemblages (MIA), representing groups of MI that were trapped all at the same time during the magmatic evolution, and thus, at the same physical and chemical conditions (e.g., MI trapped along a growth zone of a phenocryst). If MI in a single MIA record the same volatile contents, an inclusionist can be confident that those MI faithfully record representative concentrations of the melt in equilibrium with the growing phenocryst. Conversely, if MI in a single MIA show variable volatile concentrations, an inclusionist should be cautious of whether these MI record a representative composition. Commonly, identifying melt inclusion assemblages (especially in juvenile phenocrysts) can be challenging; therefore, we review alternative means to establish time correlations among studied MI (e.g., cathodoluminescence imaging). Next, we highlight the importance of bubbles in bubble-bearing MI, and discuss how we can estimate the original CO<sub>2</sub> concentration of bubble-bearing MI. Finally, we review the importance of major/trace element compositions of MI and mineral hosts for interpreting the volatile concentrations of MI. To demonstrate how data from MI can be effectively interpreted, we include MI data from the Phlegrean Volcanic District in Italy as a case study.

## Water in the oceanic lithosphere: a trilogy

Faccenda M.\*

Dipartimento di Geoscienze, Università di Padova.

Corresponding email: [manuele.faccenda@gmail.com](mailto:manuele.faccenda@gmail.com)

Keywords: water, fluid flow, slab hydration/dehydration, seismological observations, deep earthquakes, mantle.

I will review the geological and geophysical phenomena associated with water in the oceanic lithosphere that can be grouped into three different categories: those related to 1) the storage of water in the oceanic lithosphere at the surface, 2) the subduction of a hydrated slab and 3) its dehydration that ultimately leads to mantle regassing (Faccenda, 2014). Widespread hydration of the uppermost oceanic lithosphere occurs at mid-ocean ridges and more pervasively at the trench-rise system in response to bending-related fracturing and faulting. The amount of water stored in the upper lithosphere appears to be proportional to the spreading slowness and amount of bending. Hydrothermal alteration of the oceanic plate may also occur more locally along transform margins, fracture zones and volcanic ridges. Subduction of a hydrated slab should be observed from a reduction of seismic velocities, anomalous  $V_p/V_s$  ratios and seismic anisotropy in its uppermost portions, and shift of the main phase transformation boundaries characteristic of the mantle. Because of the increased buoyancy and weakness, hydrated or wet slabs should tend to stagnate over the 660 km discontinuity, favouring layered mantle convection patterns. Slab dehydration takes place according to the plate thermal regime function of the slab age and sinking velocity. Hydrous minerals in the oceanic crust and mantle are stable down to maximum 300 km and 1200 km depth, respectively, after which minor amounts of water can be retained in nominally anhydrous minerals. There is abundant geophysical evidence for dehydration of the slab crust and sub-Moho mantle, while fragmentary and often indirect evidence supports the presence of water in the lower plane of the Double Seismic Zone and at depths > 300 km.

Faccenda M. 2014. Water in the slab: a trilogy. *Tectonophys.*, 614, 1-30.

## Fluid inclusions as tracers for the chemical-physical behaviour of deep-subduction fluids

Ferrando S.\*<sup>1</sup> & Frezzotti M.L.<sup>2</sup>

1. Dipartimento di Scienze della Terra, Università di Torino. 2. Dipartimento di Scienze dell'Ambiente e del Territorio e di Scienze della Terra, Università di Milano Bicocca.

Corresponding email: [simona.ferrando@unito.it](mailto:simona.ferrando@unito.it)

Keywords: ultra-high-pressure metamorphism, mantle metasomatism, element recycling.

Fluids released from the slab by progressive dehydration reactions during deep subduction can have strong petrological and geochemical effects, inducing metasomatism into the mantle wedge. Deep-subduction fluids must be considered an integral part of the HP-UHP phase assemblages and, in the last twenty years, their chemical-physical properties have been subject of experiments, thermodynamic models, and field studies.

Deep-subduction fluids are almost ubiquitously trapped in eclogite-facies crustal suites as inclusions that still preserve firsthand information on their chemical composition and origin. Thus, data from natural fluid inclusions can be combined with those from experiments and thermodynamics to investigate the chemical-physical properties of fluids released during subduction, their solvent and transport capacity, and the subsequent implications for the element recycling.

Three distinct populations of fluid inclusions have been observed in HP and UHP metamorphic rocks: i) chloride-bearing aqueous fluid inclusions and/or gaseous fluid inclusions, ii) multiphase-solid inclusions, and iii) melt inclusions. Their study reveals that the chemical composition of natural deep-subduction fluids is more complex than that considered by experiments. At forearc depths, moderate concentrations of chlorides, Si, Al, and alkalis,  $\pm$  non-polar gases are present in water-dominated solutions; at subarc depths, mobile water-rich phases gradually increases the amounts of aluminosilicate components (e.g., Si, Al, Ca, Fe, alkalis, Ti, Zr,  $(\text{SO}_4)^{2-}$ ,  $(\text{CO}_3)^{2-}$ ) and trace elements at rising temperature. Trace element patterns show enrichments in LILE, U, Pb, LREE, and depletion in HFSE, and result chemically controlled by stabilization/destabilization of some hydrous and accessory minerals. These data are in agreement with experiments of mineral dissolution and element fractionation at deep subduction and also support experiments and thermodynamics on physical properties of deep-subduction fluids. At forearc depths, fluids are supposed to have properties similar to crustal fluids, i.e. dominated by halide ligands. In contrast, element solubility and transport of aqueous fluids released at subarc depths are supposed to be governed by polymerization, which is directly proportional to pressure and temperature. On the contrary, the finding of substantial amounts of dissolved oxidized carbon in natural fluid inclusions from deep-subducted rocks reveals that the deep transport of carbonates by aqueous fluids is a relevant process, and implies a reconsideration of the petrological models supporting liberation of C into the mantle wedge as  $\text{CO}_2$ .

Although hampered by some analytical difficulties, in the coming years the research on fluid inclusions in HP-UHP metamorphic rocks will provide exciting new results, supplying the added value to experimental and thermodynamic data.

## Melting of continental crust at mantle depth: nanogranites from leucogranulites of the Orlica–Śnieżnik Dome (Bohemian Massif)

Ferrero S.\*<sup>1</sup>, O'Brien P.<sup>1</sup>, Walczak K.<sup>2</sup>, Wunder B.<sup>3</sup>, Ziemann M.<sup>1</sup> & Hecht L.<sup>4</sup>

1. Universität Potsdam, Institut für Erd- und Umweltwissenschaften, Potsdam, Deutschland. 2. Institute of Geological Sciences, Polish Academy of Sciences, Krakow, Poland. 3. Helmholtz-Zentrum Potsdam, Deutschland. 4. Museum für Naturkunde, Leibniz-Institut für Evolutions- und Biodiversitätsforschung, Berlin, Deutschland.

Corresponding email: [sferrero@geo.uni-potsdam.de](mailto:sferrero@geo.uni-potsdam.de)

Keywords: Nanogranites, partial melting, granitoids.

Crystallized MI, or “nanogranites” (Cesare et al., 2009; Ferrero et al., 2012), were identified within HP felsic granulites from Orlica–Śnieżnik Dome, NE Bohemian Massif (Walczak, 2011). The investigated samples are Grt+Ky leucogranulites originated from a granitic protolith, with assemblage Qtz+Pl+Kfs+Grt+Ky+Ttn+Rt+Ilm. Nanogranites occur in garnet as primary inclusions, and consist of Qtz+Ab+Bt+Kfs±Ep±Ap. Such assemblage results from the crystallization of a melt generated during a partial melting reaction; the same reaction is also responsible for the production of the host garnet, interpreted therefore as a peritectic phase. Besides nanogranites, former presence of melt is supported by the occurrence of tiny pseudomorphs of melt-filled pores (Holness & Sawyer, 2008) and euhedral faces in garnet. Garnet composition, with Grs =0.28–0.31, phase assemblage (kyanite, ternary feldspar) and classic thermobarometry suggest that partial melting took place at  $T \geq 875^\circ\text{C}$  and  $P \sim 2.4\text{--}2.8$  GPa, under eclogite-facies conditions. Although other authors reported palisade quartz after coesite in this area (see e.g. Bakun-Czubarow, 1992), no clear evidence of UHP conditions have been identified during this study. Piston cylinder re-homogenization experiments were performed on MI-bearing garnet chips to obtain the composition of the pristine anatectic melt. Data from experiments show that nanogranites can be re-melted through piston cylinder experiments at  $T \geq 875^\circ$  and confining pressure of 2.7 GPa under dry conditions. The homogenized nanogranites can be analyzed by EMP means and they show a syenitic/granitic composition with water  $\leq 8$  wt%. Water presence in the glass has been also confirmed by Raman investigation.

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## Volatile content in mantle amphiboles from Harrow Peaks, Northern Victoria Land (Antarctica)

Gentili S.\*<sup>1</sup>, Comodi P.<sup>1</sup>, Bonadiman C.<sup>2</sup>, Biagioni C.<sup>3</sup>, Zucchini A.<sup>1</sup> & Coltorti M.<sup>2</sup>

1. Dipartimento di Fisica e Geologia, Università di Perugia. 2. Dipartimento di Fisica e Scienze della Terra, Università di Ferrara. 3. Dipartimento di Scienze della Terra, Università di Pisa.

Corresponding email: [silvia.gentili@studenti.unipg.it](mailto:silvia.gentili@studenti.unipg.it)

Keywords: amphibole, crystal chemistry, oxygen fugacity, lithospheric mantle water activity.

This contribution reports a crystal-chemical study of four mantle amphiboles from three spinel-bearing lherzolites and one harzburgite from Harrow Peaks, Antarctica (HP, 74 02.785S 164 47.466E, q. 335m). The experiments were carried out by means of single crystal X-ray diffraction, electron microprobe analyses, secondary ion mass spectrometry (SIMS) and <sup>57</sup>Fe Mössbauer spectroscopy.

Amphiboles represent the main hydrous metasomatic minerals and texturally occur both disseminated in the peridotite matrix and/or in fair veinlets.

Their accurate crystal-chemical characterization is crucial to better understand the mechanism of amphiboles formation in relation to water activity (and partitioning) in peridotite ambient and their ultimately effects in controlling the mantle redox conditions.

HP amphiboles are compositionally referred to pargasite ( $Mg\# [MgO/(MgO+FeO) \text{ mol}\%] = 87.5-90.2$  and  $TiO_2 = 2.74-4.20 \text{ wt}\%$ ) and kaersutite (HP164:  $Mg\# 80.1$  and  $TiO_2 = 5.30 \text{ wt}\%$ ). The outcome crystal chemistry was carried out by minimizing the differences between theoretical and experimental site scatterings and it shows high concentrations in  $Fe^{3+}$  preferred ordered in C site, a partial vacancy in A site and M4 site disordered with the presence of Ca, Na and  $Fe^{2+}$ .

The degree of dehydrogenation determined by SIMS ranges from 0.820 to 0.989 and 0.682  $O_3(O^{2-})$  a.p.f.u. in pargasites and kaersutite. F ranges from 0.020 to 0.042 a.p.f.u and 0.111 a.p.f.u.; whereas Cl ranges from 0.007 to 0.017 and 0.020 a.p.f.u., in pargasites and kaersutite respectively.

The  $a_{H_2O}$  was determined from dehydration equilibrium among end-member components assuming that pargasites are in equilibrium with the anhydrous peridotitic phases (at least for Fe/Mg and Ti). This assumption is not applicable to the lherzolite HP164: kaersutite contains too much Ti and  $Fe^{3+}$  to be in equilibrium with the metasomatic parageneses (mainly clinopyroxene). The equilibrium temperatures, calculated by ol-sp Fe-Mg distribution ( $P=15 \text{ Kbar}$ ) are in the range of 916-966 °C. The  $a_{H_2O}$  calculated for HP pargasite-bearing peridotites is in the range of 0.091-0.105. The oxygen fugacity of HP xenoliths is also calculated upon the dissociation constant of water (by oxy-amphibole equilibrium). The HP pargasite-bearing peridotites record  $f_{O_2}$  well below the fayalite-magnetite-quartz (FMQ) buffer ( $f_{O_2} = -1.61 - -1.75$ ) and show higher water reactivity at comparable (or slightly more reduced)  $f_{O_2}$  with respect to other mantle fragments from the same region.

Notwithstanding this high water activity, the pyroxene water contents, determined by Fourier transform infrared spectroscopy, appear very low, close to the lower limit of the pyroxene water contents of the intraplate mantle pyroxenes. In fact, Their  $H_2O$  (ppm) content ranges from 172 to 122 for cpx and from 20 to 63 for opx. These values are comparable with those of the nearby locality of Baker Rocks, where  $f_{O_2}$  is comparable but water activity is much lower.

## Slab-derived fluid phase precipitation at high pressures

Malaspina N.<sup>\*1</sup>, Alvaro M.<sup>2</sup> & Nestola F.<sup>2</sup>

1. Dipartimento di Scienze dell'Ambiente e del Territorio e di Scienze della Terra, Università degli Studi di Milano Bicocca. 2. Dipartimento di Geoscienze, Università degli Studi di Padova.

Corresponding email: [nadia.malaspina@unimib.it](mailto:nadia.malaspina@unimib.it)

Keywords: Polyphase inclusion, epitaxial growth, X-ray diffraction, subduction fluid.

Remnants of the fluid phase at ultrahigh pressure (UHP) in subduction environments may be preserved as primary polyphase inclusions in UHP minerals. These inclusions show the same textural features as fluid inclusions and locally may enclose UHP daughter minerals. Detailed textural studies, as well as experimental attempts to homogenise such inclusions, demonstrate that polyphase inclusions derive from solute-rich aqueous fluids or hydrous melts. However, the mode of precipitation of daughter minerals from these solute-rich hydrous fluids has never been investigated yet.

A case study is represented by garnet orthopyroxenites from the Maowu Ultramafic Complex (China). They derive from harzburgite precursors metasomatised at ~ 4 GPa, 750 °C by a silica- and incompatible trace element-rich fluid phase, sourced from the associated crustal rocks (Malaspina et al., 2006). This metasomatism produced poikilitic orthopyroxene and inclusion-rich garnet porphyroblasts. Solid polyphase primary inclusions in garnet display negative crystal shapes and constant volume ratios of infilling minerals (spinel: 10–20 vol.%; amphibole, chlorite, talc, mica: 80–90 vol.%). Experimental homogenisation of polyphase inclusions demonstrated that derive from trapped solute-rich aqueous fluids (Malaspina et al., 2006).

To constrain the possible mode of precipitation of daughter minerals, significant contribution could be given by the analysis of the growth relationships between host and inclusions. As demonstrated by Nestola et al. (2013) for the case of diamond and their olivine inclusions, the use of 'state of the art' single-crystal X-ray diffraction to collect data simultaneously on both host and inclusion phases, allows to obtain "orientation matrixes" of both phases thus retrieving their reciprocal crystallographic orientation. We performed a single-crystal X-ray diffraction experiment by Synchrotron Radiation at DLS-Diamond Light Source. Combination of the EMPA analyses, Raman Spectroscopy and X-ray diffraction allowed unique identification of each mineral phase and its orientation with respect to the host. Applying this methodology we have been able to infer the possible epitaxial growth of spinel-garnet; gedrite-pargasite and spinel-gedrite pairs which share preferred crystallographic orientation. Such information is crucial to evaluate any recurrent orientation, ruling out epitaxial growth relationships, shedding light on the temporal growth relations between host and inclusion that could not be otherwise evaluated.

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## Evidence for strong depletion, followed by multiple refertilisation, in the mantle column of the extra-Andean backarc (Paso de Indios, Argentina)

Mazzucchelli M.<sup>\*1-3</sup>, Ponce A.D.<sup>2</sup>, Bertotto G.W.<sup>2</sup>, Zanetti A.<sup>3</sup>, Brunelli D.<sup>1-4</sup>, Giovanardi T.<sup>5</sup>, Aragón E.<sup>6</sup> & Bernardi M.I.<sup>2</sup>

1. Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia. 2. Instituto de Ciencias de la Tierra y Ambientales de La Pampa (CONICET-UNLPam), Argentina. 3. Istituto di Geoscienze e Georisorse - CNR, U.O.S. di Pavia. 4. CNR Istituto di Scienze Marine, Bologna. 5. Instituto de Geociências, Universidade de São Paulo, Brazil. 6. Centro de Investigaciones Geológicas (CONICET-UNLP), Buenos Aires, Argentina.

Corresponding email: [maurizio.mazzucchelli@unimore.it](mailto:maurizio.mazzucchelli@unimore.it)

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In the central part of the Chubut province, close to the town of Paso de Indios, there are several outcrops of Cenozoic basalts carrying spinel-facies ultramafic xenoliths. In this area, located in the extra-Andean back-arc region, basaltic necks and dikes outcrop between 43° 36' – 43° 50' S and 68° 53' – 69° 02' W, along with remnants of lava flows divided in two groups of Paleocene and Eocene age. This volcanism was generated by extensional tectonic related to a transform plate margin episode that affected the southern South America active margin from the Paleocene to the Oligocene, as the Aluk plate detached and a slab window opened beneath the study area.

Here, the petrochemical processes experienced by spinel-facies mantle xenoliths, hosted in Eocene basalts of the Matilde lava flow remnants, the León volcano and the Chenque dike, are presented.

The studied samples are mainly spinel-facies harzburgites and clinopyroxene(Cpx)-poor lherzolites, with some dunites. The Chenque xenoliths mainly present porphyroclastic to equigranular texture, whereas those from Matilde and León volcanoes have coarse-grained to porphyroclastic textures. Estimated equilibrium temperatures based on pyroxenes solvus range from 800 to 940°C.

The refractory character of the mineral assemblages is matched by the major element mineral compositions, which are mostly Al poor and Mg and Cr rich. Spinel composition is consistent with melt extraction from 8 to 14% (Chenque and León) and 14 to 18% (Matilde). The estimated degree of melting rises up to 24% considering the literature spinel data. However, the occurrence of melt-related open-system processes is suggested by local trends of positive correlation between Na and Cr# in Cpx, being fully confirmed by the trace element compositions. Cpxs from a harzburgitic sample from León volcano show composition rich in U, Th, Sr and LREE. The Matilde harzburgites ubiquitously show Cpx with transient U-shaped REE patterns. The LREE fractionation is very strong, with La<sub>N</sub> up to 100 and minimum at the M-HREE region between 0.1-1xCI. The HREE level content (Lu<sub>N</sub> down to 1) is consistent with 20-23% fractional melting of spinel DM. V-to-U-shaped REE patterns are also shown by Chenque lherzolites and harzburgites. Their M-HREE are more fractionated than that expected in residue after spinel facies basal removal, thus suggesting an onset of the partial melting at garnet facies conditions. Other Chenque lherzolites seem to result from a more extensive refertilisation processes led by LREE-enriched to LREE-depleted melts. The latter gave rise to transient LREE-depleted sinusoidal patterns through reaction with the depleted ambient peridotite. It is, thus, concluded that the shallow mantle column beneath Paso de Indios records an incomplete refertilisation of strongly depleted protoliths. This represents a unique example for the Patagonian region, where the mantle is usually completely overprinted by multiple stages of melt/fluid migration.

## The interaction between silicate minerals and C-O-H bearing melts in the Earth's mantle

Novella D.\*<sup>1-2</sup> & Frost D.J.<sup>2</sup>

1. Laboratoire Magmas et Volcans, Université Blaise-Pascal Clermont Ferrand, France. 2. Bayerisches Geoinstitut, Universitaet Bayreuth, Germany.

Corresponding email: [D.Novella@opgc.univ-bpclermont.fr](mailto:D.Novella@opgc.univ-bpclermont.fr)

Keywords: volatiles, kimberlites, incipient melting, H<sub>2</sub>O partitioning.

Melting processes in the mantle are strongly affected by the presence of volatile species such as H<sub>2</sub>O and CO<sub>2</sub>. In this study we conducted experiments to investigate the effect of these volatiles on the melting of mantle rocks at conditions corresponding to the deep upper mantle (~180-400 km). Chemical compositions of small degree hydrous melts that would form at 180 km depth and near adiabatic temperatures were determined in a natural mantle peridotite system. The hydrous melt compositions, on a volatile free basis, are found to be similar to group II kimberlites. The H<sub>2</sub>O concentrations of peridotite mineral phases were measured and the partitioning of H<sub>2</sub>O between peridotite and melts determined. The results indicate that current estimates for the H<sub>2</sub>O content of the depleted mantle (50-200 ppm H<sub>2</sub>O) are insufficient to induce mantle melting at these conditions. Based on inter-mineral H<sub>2</sub>O partitioning a model is constructed that calculate the distribution of H<sub>2</sub>O between peridotite phases as a function of depth at H<sub>2</sub>O-undersaturated conditions. The model indicates that for a fixed mantle H<sub>2</sub>O content the olivine H<sub>2</sub>O content will increase with depth solely due to changes in inter-phase partitioning and mineral modes, providing an explanation for the reduction in seismic anisotropy observed at depths >200 km. Experiments were also conducted at 6 and 13 GPa in the simplified systems MgO-SiO<sub>2</sub>-H<sub>2</sub>O±CO<sub>2</sub>. In the H<sub>2</sub>O-bearing experiments melting phase relations were examined using a thermodynamic model that supports the almost complete dissociation of H<sub>2</sub>O to OH- bonded to melt silicate components at these conditions, although results for forsterite at 13 GPa are inconclusive. H<sub>2</sub>O partition coefficients were determined as a function of temperature for forsterite and enstatite at 6 and 13 GPa and very little temperature dependence was observed except for forsterite at 13 GPa. Experiments in the H<sub>2</sub>O- and CO<sub>2</sub>-bearing system at 13 GPa were performed to investigate the effect of CO<sub>2</sub> on the mineral-melt H<sub>2</sub>O partition coefficient. These results have implications on the formation of volatile bearing melts atop the transition zone.

## The Valdieri marbles: the result of a localised recrystallization and metasomatism related to a focused flow of REE-rich fluids

Rossetti P.\*<sup>1</sup>, Barale L.<sup>1</sup>, Bertok C.<sup>1</sup>, d'Atri A.<sup>1</sup>, Martire L.<sup>1</sup> & Piana F.<sup>2</sup>

1. Dipartimento di Scienze della Terra - Università di Torino. 2. IGG-CNR Pisa.

Corresponding email: [piergiorgio.rossetti@unito.it](mailto:piergiorgio.rossetti@unito.it)

Keywords: Dauphinois domain, Hydrothermal circulation, REE enrichments.

In the Maritime Alps, at the northeastern border of the Argentera crystalline massif, close to Valdieri, two kilometre-scale rock bodies of marbles occur within a carbonate succession referable to the Dauphinois domain. These marbles have been quarried in the past as ornamental stones ("Marmi di Valdieri").

The stratigraphic succession in which the Valdieri marbles occur consists of Middle Jurassic-Upper Cretaceous deep water sediments: dark marls (Entracque Marl, Middle Jurassic-Berriasian) followed by micritic limestones with breccia beds (Lausa Limestone, Valanginian-early Aptian) in turn overlain by dark shales and marls (Marne Nere, Aptian-Cenomanian) and by marly limestones (Puriac Limestone, Turonian-Campanian). The Puriac Limestone is bounded at the top by a regional unconformity, overlain by middle Eocene-Lower Oligocene sediments of the Alpine foreland basin.

Recrystallization affects the Lausa Limestone, the Marne Nere, and the lower and middle portions of the Puriac Limestone, whereas the upper portion of the Puriac Limestone, as well as the overlying Alpine foreland basin succession, seems to be unaffected. Laterally, the marbles rapidly pass to poorly recrystallized limestones and marls of the corresponding stratigraphic intervals.

The lower part of the Valdieri marbles, corresponding to the Lausa Limestone, consists of pure white and grey marbles with rare mm-thick elongated and folded domains strongly enriched in muscovite, K-feldspar, albite and quartz. The upper part, corresponding to the Puriac Limestone, is mostly composed of lens-shaped, cm- to dm-thick granoblastic marble portions, interlayered with mm-thick anastomosed greenish to purple levels. The latter are composed of white mica (muscovite-paragonite s.s.), chlorite and epidote with accessory titanite, tourmaline, apatite and zircon. The epidote, locally abundant, occurs as subhedral crystals up to few millimeters across, undeformed to strongly fractured; it often shows a dark (metamictic?) core surrounded by a clear rim and at least locally overgrows the folded  $S_0$  planes. Preliminary SEM-EDS analyses show that the Fe-rich epidote (very close to the epidote end member) is characterized by an irregular zoning, with abundant small patches (few microns across) strongly enriched in HREE ( $\text{La}_2\text{O}_3 + \text{Ce}_2\text{O}_3 + \text{Nd}_2\text{O}_3$  up to ~13 wt%) and Th ( $\text{ThO}_2$  up to ~2.8 wt%). The marbles are crossed by mm- to dm-thick veins commonly filled with calcite, quartz and locally also Fe-rich carbonate. Veins strongly enriched in epidote (+ calcite + quartz) are found in the upper part. All the veins show equilibrium relationships within the host marble.

The stratigraphic setting and the petrographic features of the Valdieri marbles suggest that their formation probably took place in the Late Cretaceous-Eocene time interval and that it was due to a polyphase metasomatic process related to the localized upflow of REE-rich hydrothermal fluids.

## Solubility of mantle minerals in high-pressure COH fluids

Tiraboschi C.\*<sup>1</sup>, Tumiati S.<sup>1</sup>, Ulmer P.<sup>2</sup>, Pettke T.<sup>3</sup> & Poli S.<sup>1</sup>

1. Dipartimento di Scienze della Terra - Università di Milano. 2. Department of Earth Sciences - ETH Zurich, Switzerland. 3. Institute of Geological Sciences - University of Bern, Switzerland.

Corresponding email: [carla.tiraboschi@unimi.it](mailto:carla.tiraboschi@unimi.it)

Keywords: COH fluids, solubility, subduction.

Fluids play a crucial role in many processes in subduction zones, influencing the melting temperatures and promoting mass transfer from the subducting lithosphere to the overlying mantle wedge. Carbon is a relevant component in deep fluids, as suggested by its occurrence in arc magmas and subduction-related rocks. Compared to H<sub>2</sub>O-only fluids, high-pressure COH fluids are substantially unexplored. For this reason we choose to experimentally investigate the dissolution of mantle minerals, represented by forsterite, enstatite and magnesite in graphite-saturated COH fluids at controlled redox conditions. We conducted experiments at pressures from 1 to 1.5 GPa and temperatures from 700 to 1100°C using a rocking piston cylinder apparatus. Synthetic forsterite, enstatite and natural magnesite were used as starting material. A diamond trap was placed between two layers of mantle minerals to collect fluid and solutes. Carbon-saturated COH fluids were generated starting from oxalic acid anhydrous (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>), water (doped with 580 ppm of Cs) and graphite. Redox conditions were controlled employing the double capsule technique and nickel-nickel oxide buffer ( $\Delta\text{FMQ}=-0.61$  at 800°C;  $\Delta\text{FMQ}=-0.98$  at 900°C). Thermodynamic calculations predict fluids mainly composed of H<sub>2</sub>O and CO<sub>2</sub>, characterized by different XH<sub>2</sub>O contents as a function of *P* and *T*. We analyzed the fluid and solutes using the cryogenic laser ablation ICP-MS technique. With this method the capsule is frozen (*T*=-35°C) prior the opening to allow laser ablation analyses of the frozen fluid. As the temperature reached by the freezing stage is not sufficient to freeze CO<sub>2</sub>, the analyzed solute content refers to the aqueous part of the COH fluid. The concentration of an internal standard (Cs), corrected with a dilution model, was used to retrieve the amount of solutes in the fluid, as Cs fractionates completely into water. The use of a dilution model is necessary because the XH<sub>2</sub>O is not constant and is controlled by the nickel-nickel oxide buffer. The results will highlight the importance of fluids for the mass transport of C, Si and Mg in subduction zones. Comparison with other experimental system (Newton & Manning, 2002) will also be shown.

Newton R.C. & Manning C.E. 2002. Solubility of enstatite + forsterite in H<sub>2</sub>O at deep crust/upper mantle conditions: 4 to 15 kbar and 700 to 900°C. *Geochim. Cosmochim. Ac.*, 66, 4165-4176.

## Ultra-oxidized redox conditions in subduction mélanges? Decoupling between oxygen fugacity and oxygen availability in a metasomatic environment

Tumiati S.\*<sup>1</sup>, Poli S.<sup>1</sup>, Godard G.<sup>2</sup>, Martin S.<sup>3</sup> & Malaspina N.<sup>4</sup>

1. Dipartimento di Scienze della Terra - Università degli Studi di Milano. 2. IGP Paris-Université Paris Diderot. 3. Dipartimento di Geoscienze-Università di Padova. 4. Dipartimento di Scienze dell'Ambiente e del Territorio e di Scienze della Terra-Università di Milano Bicocca.

Corresponding email: [simone.tumiati@unimi.it](mailto:simone.tumiati@unimi.it)

Keywords: manganese, oxygen fugacity, redox.

The manganese ore of Praborna (Italian Western Alps) is embedded within a metasedimentary sequence belonging to a subduction mélange equilibrated at high-pressure conditions (~2 GPa) during the Alpine orogenesis and record environmental conditions typical for a subducting slab setting. The pervasive veining of the ore and the growth of "pegmatoid" HP minerals suggest an open system with large fluid/rock ratio and a strong interaction with slab-derived fluids. This natural case provides an excellent natural laboratory for the study of the oxygen mobility in subducting oceanic slab mélanges at high-*P*, fluid-present conditions. The Mn-rich rocks in contact with the underlying sulphide- and magnetite-bearing metabasites, in textural and chemical equilibrium with the veins, contain braunite ( $\text{Mn}^{2+}\text{Mn}^{3+}_6\text{SiO}_{12}$ ) + quartz + pyroxmangite ( $\text{Mn}^{2+}\text{SiO}_3$ ), and minor hematite, omphacite, the epidote piemontite and spessartine-rich garnet. Similarly to Fe-bearing systems, Mn oxides and silicates can be regarded as natural redox-sensors, capable to monitor a process of fluid infiltration that could fix externally the intensive variable  $f\text{O}_2$  (or  $\mu\text{O}_2$ ). Sulphides are absent in these Mn-rich rocks, sulphates (barite, celestine) occurring instead together with As- and Sb oxides and silicates. On the basis of the observed assemblages, new thermodynamic calculations show that these mélange rocks are characterized by unrealistic ultra-oxidized states (dFMQ up to +12) if the chemical potential of oxygen (or the oxygen fugacity) is accounted for. However, if the molar quantity of oxygen in excess with reference to with reference to a system where all iron and manganese are considered to be ferrous, the ore appears only moderately oxidized, and comparable to typical subduction-slab mafic eclogites. Therefore, oxygen can be hardly considered a perfectly mobile component, even in the most favourable conditions. In the Earth's interior redox reactions take place mainly among solid oxides and silicates, as oxygen is a negligible species in the fluid phase, if any. Therefore, the description of the redox state of petrological systems requires the introduction of the conjugate oxygen molar quantity, becoming the oxygen chemical potential a dependent variable. As a consequence,  $\mu\text{O}_2$ , and therefore  $f\text{O}_2$ , should not be regarded as long-range properties, indicative of the redox state of the entire rock column of a subduction zone, from the dehydrating oceanic crust to the overlying mantle wedge. On a more general basis, the comparison of  $f\text{O}_2$ s retrieved from different bulk compositions and different phase assemblages may lead to apparent redox heterogeneities. On the contrary, the distribution of oxygen is expected to be much more continuous moving from a maximum in the subducted mafic eclogites, formed from the altered oceanic basalts and gabbros, down (upward) to a minimum in the peridotites of the mantle hanging-wall.

## **Fluid-induced leaching of organic matter at HP-LT conditions: a new tile in the deep C cycle**

Vitale Brovarone A.\* & Beyssac O.

IMPMC, UPMC, Paris, France.

Corresponding email: [alberto.vitale-brovarone@impmc.upmc.fr](mailto:alberto.vitale-brovarone@impmc.upmc.fr)

Keywords: Subduction, HP-LT metasomatism, C devolatilization.

At subduction zones, crustal rocks are recycled into the Earth's interior with profound implications for global elemental cycling. This process includes redistribution of carbon from the solid state (e.g. carbonates, graphite, diamond) to the fluid phase (e.g. CO<sub>2</sub>, CH<sub>4</sub>), which deeply participates in the global carbon cycle. In subducting oceanic slabs, C in the solid state mainly occurs as carbonates and organic matter (OM). The participation of carbonates in decarbonation reactions at HP-LT conditions has been recently matter of field-based studies, which in part question more conservative thermodynamic and experimental results. On the contrary, much less is known about the evolution and role of OM in the processes of C recycling at HP-LT conditions. The thermodynamic approach has provided important insights on the evolution of graphite-saturated COH (GCOH) fluids. However, natural example of OM recycling at HP-LT conditions in subduction zones is poor.

The progressive transformation of organic matter from a disordered structure to almost pure, ordered graphite is well established. This process occurs in a wide range of T ranging from diagenesis to T exceeding the peak estimates of most oceanic rocks that are back from HP-UHP conditions (ca. 650 °C). This indicates that, in absence of perturbations induced by changing boundary conditions such as changing redox state or interaction with external fluids, subducted OM is expected to persist in the solid state during HP regional metamorphism.

In this contribution we show that impressive fluid-induced leaching of OM may occur at HP conditions. We present natural evidence for C devolatilization during HP metasomatism of ocean-derived blackschists from Alpine Corsica. This process is accompanied by profound chemical and mineralogical variations in the rock, including hydrous phases such as lawsonite, and affects a significant amount of the HP-LT terranes of Corsica from a minimum P-T condition of ca. 360 °C and 1.6 GPa. Mass balance calculations point to significant CO<sub>2</sub> fluxes produced by this metasomatic process and released toward the forearc or subarc wedge.

**SESSIONE S20**

**Magmatism and Geodynamics of the Mediterranean area**

*CONVENORS*

*M. Lustrino (Univ. Roma La Sapienza)*

*F. Rossetti (Univ. Roma Tre)*

## Subduction-modified and intraplate Neogene magmatism in SE Anatolia

Agostini S.<sup>1</sup>, Di Giuseppe P.\*<sup>2</sup>, Lustrino M.<sup>2</sup>, Savaşçın M.Y.<sup>3</sup>, Önal A.Ö.<sup>4</sup>, Kürüm S.<sup>5</sup>, Karaoğlu Ö.<sup>6</sup> & Manetti P.<sup>7</sup>

1. Istituto di Geoscienze e Georisorse, Consiglio Nazionale delle Ricerche, Pisa. 2. Dipartimento di Scienze della Terra, Università "La Sapienza", Roma. 3. Mahmutiye-Sapanca, Turkey. 4. Tunceli University, Turkey. 5. Fırat University, Turkey. 6. Van University, Turkey. 7. Dipartimento di Scienze della Terra, Università di Firenze.

Corresponding email: [s.agostini@igg.cnr.it](mailto:s.agostini@igg.cnr.it)

Keywords: Eastern Anatolia, Neogene Volcanism, Petrology, Isotope Geochemistry.

Widespread igneous activity occurs from Middle Miocene to Quaternary in Eastern Anatolia. Around Elazığ, Pertek, Tunceli, Mazgirt and Karakoçan areas calc-alkaline and alkali-basaltic rocks with whole-rock chemical compositions ranging from basalts and trachybasalts to andesite and dacite crop out.

On the basis of geochemical and isotopic data, three main groups of rocks have been distinguished. Rocks of the first group occur in Elazığ and Karakoçan areas show high TiO<sub>2</sub> (3.10-1.71), low La/Nb ratios (1.9-0.7), low Sr (<sup>87</sup>Sr/<sup>86</sup>Sr = 0.70331-0.70376), high Nd (<sup>143</sup>Nd/<sup>144</sup>Nd 0.51290-0.51283) and low <sup>207</sup>Pb/<sup>204</sup>Pb isotopic ratios (15.64-15.67), coupled with roughly HIMU-OIB-like pattern in primitive mantle-normalized diagrams, peaking at Nb-Ta. The second group of rocks is found in Tunceli and Bulğurçuk area and marks the transition between intraplate-like and more typical subduction-related magmatic compositions. The TiO<sub>2</sub> content is lower (1.75-1.42), while the La/Nb ratios (2.3-1.3) and <sup>87</sup>Sr/<sup>86</sup>Sr (0.70395-0.70491) as well as <sup>207</sup>Pb/<sup>204</sup>Pb (15.64-15.67) are higher than the first rock group, coupled with lower <sup>143</sup>Nd/<sup>144</sup>Nd (0.51280-0.51268). The third group includes samples from Pertek and Mazgirt area, characterized by low TiO<sub>2</sub> (1.67-0.41), high La/Nb (3.5-2.3), strongly radiogenic <sup>87</sup>Sr/<sup>86</sup>Sr (0.70554-0.70682), lower <sup>143</sup>Nd/<sup>144</sup>Nd (0.51263 to 0.51257) and higher <sup>207</sup>Pb/<sup>204</sup>Pb (15.70-15.72). These features, including positive Pb and K anomalies as well as LILE and Sr enrichment in primitive mantle-normalized diagrams, are compatible with derivation from a subduction-related mantle source.

Despite the supra-subduction tectonic setting of all of the studied samples, rocks of the first group exhibit geochemical and isotope characters typical of mantle source with any or limited modification by subduction-derived fluids. This fact, along with the presence of spatially and temporally overlapping volcanic rocks with very different mineralogical and chemical compositions is a further evidence of the perils in inferring paleotectonic environments on the basis of geochemical constraints only.

The negative correlation of TiO<sub>2</sub> with <sup>87</sup>Sr/<sup>86</sup>Sr and <sup>207</sup>Pb/<sup>204</sup>Pb ratios, as well as the positive correlation of <sup>87</sup>Sr/<sup>86</sup>Sr with Th/Ta and La/Nb speak for the existence of two mantle source end-members, one producing HFSE-rich, LILE-poor, low <sup>87</sup>Sr/<sup>86</sup>Sr, low <sup>207</sup>Pb/<sup>204</sup>Pb intraplate-like magma and the other responsible for the production of HFSE-poor, LILE-rich and radiogenic <sup>87</sup>Sr/<sup>86</sup>Sr and <sup>207</sup>Pb/<sup>204</sup>Pb melts, generated by subduction processes.

## The within-plate Na-alkaline magmatism of the Pelagian Block (Southern Italy): Sr-Nd-Pb and U-series isotope constraints from Pantelleria, Linosa and Pachino-Capo Passero basalts

Avanzinelli R.\*<sup>1</sup>, Braschi E.<sup>2</sup>, Marchionni S.<sup>1</sup>, Bindi L.<sup>1</sup> & Conticelli S.<sup>1</sup>

1. Dipartimento di Scienze della Terra - Università degli Studi di Firenze. 2. IGG-CNR Firenze.

Corresponding email: [riccardo.avanzinelli@unifi.it](mailto:riccardo.avanzinelli@unifi.it)

Keywords: within-plate continental magmatism, Sr-Nd-Pb isotope, HIMU-FOZO, Common Mantle Reservoir, U-series.

The origin of the mantle sources of the Na-alkaline magmas erupted within the Pelagian Block (southern Italy) are here investigated through the determination of Sr, Nd and Pb isotope ratios on basaltic volcanic from Linosa, Pantelleria and Pachino-Capo Passero. Despite their geographical proximity these rocks were erupted over a large time span (Upper Cretaceous to Quaternary). U-series disequilibria have been measured on the recent products of Pantelleria (120-9 ka) volcano in order to constrain the mechanism of mantle melting in relationship to the geodynamic setting of the studied area.

The isotope data, along with trace element ratios are used to assess the possible role of the interaction with the continental crust and/or the Sub-Continental Lithospheric Mantle (SCLM). The data show little variation in Sr and Nd isotopes and a continuous trend towards more radiogenic Pb isotope composition from Linosa to the oldest mafic activity of Pantelleria (i.e. Paleo-Pantelleria) and Pachino-Capo Passero, with intermediate values measured in the youngest Pantelleria lavas (Neo-Pantelleria). The Sr-Nd-Pb isotope compositions of the studied rocks are also compared with literature data from the Canary Islands, as representative of a putative plume component contaminating the mantle region, but some clear distinction, especially in terms of Pb isotopes are observed.

The increasing FOZO-like character of the studied magmas and the variation of some key trace element ratios is interpreted as a feature of the ambient asthenospheric mantle, due to the extremely widespread process of prolonged subduction and recycling of mafic oceanic crust of variable age and composition.

Pantelleria basalts have ubiquitous <sup>230</sup>Th-excess ranging from 7% to 20%. These data suggest the magmas are originated within the asthenospheric mantle, with little or no interaction with either the continental crust or the SCLM.

The Coupled <sup>230</sup>Th-<sup>238</sup>U and <sup>231</sup>Pa-<sup>235</sup>U data in a Pantelleria sample were used to perform quantitative dynamic melting models in order to constrain physical parameters of mantle melting in the Sicily Channel. The combined modelling yielded positive solutions only for high  $D_U/D_{Th}$  ( $\geq 2.5$ ) and low melting rates ( $-4 \text{ kg/m}^3/\text{a}$ ). These data argue against any important role for amphibole in the genesis of these magmas and are consistent with a peridotite source possibly well mixed with recycled components. The modelled values of melting rate can also be converted into estimates of the upwelling rate of the mantle that are compatible with slow passive upwelling along the Sicily Channel rift.

## **Metasedimentary and igneous xenoliths from the volcano of Tallante (Betic Cordillera, Spain): a reappraisal based on isotopic analyses**

Bianchini G.\*<sup>1</sup>, Braga R.<sup>2</sup>, Langone A.<sup>3</sup> & Natali C.<sup>1</sup>

1. Dipartimento di Fisica e Scienze della Terra, Università di Ferrara. 2. Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Bologna. 3. CNR-IGG, Pavia.

Corresponding email: [bncglc@unife.it](mailto:bncglc@unife.it)

Keywords: Magmatism and geodynamics, Betic Cordillera, xenoliths.

Deep seated xenoliths entrained by volcanics provide information on the composition, thermal regime and physical properties of deep inaccessible lithologies. Unfortunately, the approach of study is somewhat limited because: i) xenoliths are rare and not ubiquitous in all volcanic centers; ii) in each volcanic center the xenolith population is often monotonous, i.e. mainly represented by a prevalent lithology. The homogeneity of xenolith suites from distinct volcanic sites is ascribed to the uptake mechanism, mainly related to fluid release and bubble nucleation, which trigger discrete event of crack formation and breaking of the surrounding deep rocks. The specific depth of xenolith formation is distinctive of each magma type, and usually Cenozoic alkaline basalts of the Mediterranean region entrain xenoliths from either the uppermost lithospheric mantle (30-50 Km depth) or the lower crust, and sampling from different depths is rare. In this view, the volcano of Tallante (Pliocene) in the Betic Cordillera (Spain) represents a peculiar occurrence, where alkaline basalts uprising from mantle sources exhumed an extremely heterogeneous xenolith association, including protogranular peridotites, felsic metasedimentary rocks, as well as diverse cumulitic igneous rocks such as amphibole-clinopyroxenites and norite-gabbros. Noteworthy, the numerous studies available in the literature mainly focused on the peridotite xenoliths and failed to consider in a coherent framework the total xenolith suite of Tallante and to explain its extreme variability. Only recently, Bianchini et al. (2013) proposed that the extreme xenoliths heterogeneity recorded at Tallante could be related to the specific geodynamic setting, located along a collisioned belt, where the crust-mantle boundary is possibly characterized by an intimate association of crustal and subcrustal lithologies, interlayered as result of orogenic processes. This contribution presents new Sr-Nd isotopic analyses carried out on metasedimentary and igneous xenoliths, as well as in-situ U-Pb dating of a zircon grain from a gabbroic xenolith. The new data, discussed taking into account the most recent geophysical evidence (Thurner et al., 2014) give insights to refine the pre-existing petrological hypotheses, in the general geological framework of the Betic orogenic belt.

Bianchini G., Braga R. & Langone A. 2013. Crustal xenoliths from Tallante (Betic Cordillera, Spain): insights into the crust-mantle boundary. *Geol. Magaz.*, 150, 952-958.

Thurner S., Palomeras I., Levander A., Carbonell R., & Lee C.-T. Ongoing lithospheric removal in the western Mediterranean: Evidence from Ps receiver functions and thermobarometry of Neogene basalts (PICASSO project).

## Geochemistry of submarine mafic lavas from Pantelleria Island, Sicily Channel

Calarco M.<sup>1</sup>, Chiocci F. L.<sup>2</sup>, Conte A.M.\*<sup>3</sup>, Fonseca F.<sup>2</sup>, Martorelli E.<sup>4</sup>, Perinelli C.<sup>2</sup> & Sposato A.<sup>4</sup>

1. D'Appolonia S.p.A. Genova. 2. Dipartimento di Scienze della Terra, Sapienza Università di Roma.  
3. IGG, CNR Roma. 4. IGAG, CNR Roma.

Corresponding email: [aidamaria.conte@uniroma1.it](mailto:aidamaria.conte@uniroma1.it)

Keywords: Pantelleria Island, submarine volcanism, mafic magmas.

Detailed investigations of the submarine portions of Pantelleria were carried out in 2006 and 2008 (aboard R/V Urania) using a 50 kHz multibeam bathymetric system and collecting seafloor samples by dredging, grabbing and coring. In particular, more than 50 dredge samples including scoriaceous and massive lavas were recovered on the NW portion of the volcano. Here, numerous volcanic centers were identified, including the vent of the last known eruption (1891). The NW monogenetic volcanic field likely formed during a discontinuous activity punctuated by several eruptions close in space and, probably, in time.

In order to reconstruct the submarine volcanic activity of Pantelleria, several mafic lava collected from these volcanic cones and along the NW slope have been analyzed in their petrography and geochemistry and compared with the literature data of analogous subaerial products from the NW of the island. Samples from the cones are scoriaceous basalts and basanites with sub-aphyric to porphyric texture (P.I.~5-15vol%) in which plagioclase, clinopyroxene±olivine±oxides occur as phenocrysts, microphenocrysts and microlites. Vesicles of most of these samples are totally or partially filled with secondary minerals (i.e., carbonate and/or motukoreaite). In addition, the composition of scoriaceous lavas is similar to those of 1891 products (Conte et al., 2014).

The massive lavas from the slope are weakly porphyritic basalts (P.I.≤10vol%) with phenocrysts of plagioclase>olivine> clinopyroxene and ± oxides, set in a microcrystalline groundmass made up of the same minerals. Their higher olivine amount respect to the scoriaceous products, along with the higher Mg# and Cr and Ni contents, testify a more primitive character. Noteworthy, the massive basalts are characterized by a lower TiO<sub>2</sub> and P<sub>2</sub>O<sub>5</sub> contents than those of the scoriaceous lavas (TiO<sub>2</sub>~2.55wt%-P<sub>2</sub>O<sub>5</sub>~0.55wt% and TiO<sub>2</sub>~4.3wt%-P<sub>2</sub>O<sub>5</sub>~1.80wt%, respectively).

The chemical differences observed between submarine massive and scoriaceous lavas were found respectively in the older (~120 to 50 ka) and younger (~30 to 10 ka) mafic sub-aerial products outcropping in the NW part of Pantelleria, which are characterized by higher TiO<sub>2</sub> (>3wt%) and P<sub>2</sub>O<sub>5</sub> (>1wt%) contents, and lower TiO<sub>2</sub> (<3wt%) and P<sub>2</sub>O<sub>5</sub> (<0.7wt%) contents, respectively. Therefore, we infer that the massive basalts from the NW submarine slope were fed by magmas similar to the younger sub-aerial products and the scoriaceous lavas of the NW volcanic field, including the historical 1891 eruption products, were fed by a reservoir filled by a magma geochemically very similar to that which had fed the older sub-aerial mafic units.

Conte A.M., Martorelli E., Calarco M., Sposato A., Perinelli C., Coltelli M., Chiocci F.L. 2014. The 1891 submarine eruption offshore Pantelleria Island (Sicily Channel, Italy): Identification of the vent and characterization of products and eruptive style. *Geochemistry, Geophysics, Geosystems*, accepted May 29, 2014.

## Newly discovered submarine volcanoes north of Ventotene extend the Pontine volcanism offshore Gaeta (Tyrrhenian Sea, Italy)

Conti A.\*<sup>1</sup>, Bigi S.<sup>1</sup>, Cocchi L.<sup>2</sup>, Ligi M.<sup>3</sup>, Muccini F.<sup>2</sup>, Bortoluzzi G.<sup>3</sup>, Cuffaro M.<sup>4</sup>, Doglioni C.<sup>1</sup>, Scrocca D.<sup>4</sup>, Loreto M. F.<sup>3</sup>, Giordano P.<sup>3</sup>, Ferrante V.<sup>3</sup>, Conte A.M.<sup>5</sup> & Perinelli C.<sup>1</sup>

1. Dipartimento di Scienze della Terra, Università La Sapienza, Roma. 2. Istituto Nazionale di Geofisica e Vulcanologia, Roma2, Fezzano (La Spezia). 3. Istituto di Scienze Marine, CNR, Bologna. 4. Istituto di Geologia Ambientale e Geoingegneria, CNR, Sez. Sapienza, c/o Dipartimento di Scienze della Terra, Università La Sapienza. 5. Istituto di Geoscienze e Georisorse, CNR, UOS Sapienza, c/o Dipartimento di Scienze della Terra, Università La Sapienza.

Corresponding email: [alessia.conti@uniroma1.it](mailto:alessia.conti@uniroma1.it)

Keywords: New submarine volcanoes, Pontine islands, arc-related volcanism.

Newly acquired high-resolution bathymetric data covering the upper part of the continental shelf off Gaeta, combined with magnetic data and multichannel seismic reflection profiles, have revealed an elongated partially-buried structural high oriented NW-SE. A 200 m-high cone and an elliptical feature mark the summit of this structure. Morphology and positive magnetic anomalies (> 150 nT) suggest that they are two volcanic edifices. Both volcanoes have flat summits lying at a depth of ~170 m, with a diameter of 1.5 km and with major and minor axis of 5 and 2 km, respectively. A multichannel seismic line runs SE-NW along the axis of the 20 km-long structural high. The seismic line crosses the lower northern flank of the elliptical edifice bounded to the south-east by a major normal fault trending SW-NE that offsets the Ventotene Basin basement by over 1 km. Further to the north the seismic line intersects another normal fault with similar orientation. This fault separates the aforementioned volcanic edifice from the sub-circular volcanic apparatus shaping its southeastern flank. Well stratified contourites cover the flanks of the sub-circular volcanic cone, whereas a ring-like depression due to erosion surrounds the cone.

The newly discovered submarine volcanoes are located 25 km north of Ventotene Island extending Pontine volcanism landward. The Pontine Archipelago forms a 50-km-long chain running parallel to the Tyrrhenian coast and connecting the Vavilov abyssal plain with the continental platform. The western Pontine islands (Ponza, Palmarola and Zannone) are dominated by silica-rich submarine volcanic units. The magmatic activity of Ponza began 4.2 Ma with emplacement of rhyolitic hyaloclastites and ended 1 Ma with a trachytic event. Palmarola island consist of rhyolitic hyaloclastites and domes dated between 1.6 and 1.5 Ma. The eastern Pontine (Ventotene and Santo Stefano) are dominated by alkali-potassic subaerial deposits dated between 0.9 to 0.3 Ma.

The flat, shallow tops of the newly discovered volcanoes are interpreted as wave-cut marine terraces due to lower sea level in the past. Marine terraces with similar depths have been already noted on the flanks of Ventotene. This, together with the normal polarity of the magnetic anomalies, suggests that volcanic activity in this sector of the Gaeta bay was contemporaneous with that of Ventotene (Middle Pleistocene). Further studies in this new volcanic area, in particular geochemical work, may have important implications on the evolution of the east-directed back-arc-related opening of the Tyrrhenian Sea. In fact, changes in space and time of the Pontine magmatism has been related to the tectonic evolution of the area, with emplacement of volcanic units that range from syn-collisional to post-collisional setting.

## The evolution of the magmatic feeding system of the Ustica Island (Southern Tyrrhenian Sea, Italy)

de Vita S.\*<sup>1</sup>, D'Antonio M.<sup>2</sup>, Civetta L.<sup>2</sup> & Orsi G.<sup>2</sup>

1. Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Napoli Osservatorio Vesuviano. 2. Dipartimento di Scienze della Terra dell'Ambiente e delle Risorse, Università degli Studi "Federico II" di Napoli.

Corresponding email: [sandro.devita@ingv.it](mailto:sandro.devita@ingv.it)

Keywords: Tyrrhenian Sea, Ustica, Transtensional tectonics.

Volcanism at Ustica has been related to the activation of left-transtensional faults, linked to the anticlockwise rotation of the Italian peninsula and opening of the Tyrrhenian basin. It started more than 1 Ma ago and extinguished at 130 ka. Volcanism on the island can be subdivided in three periods, based on major and trace elements and total alkali variations vs. stratigraphic height.

During the first period (750-475 ky) there was the emplacement of units characterized by poor compositional variations, although showing appreciable intra-formational variability. The second period (around 425 ka) is marked by the only eruption of trachytic magma occurred on the island, whose deposits show a decreasing differentiation degree from base upward, suggesting the existence of a compositionally zoned magma chamber. The volcanic units emplaced during the third period (420 – 130 ky) are the product of less differentiated magmas, although they show a greater compositional variability, mainly in the differentiation degree, between one unit, and the previous and following ones.

Sr isotopic ratios individuate well defined fields for rocks belonging to different periods in the plots vs. SiO<sub>2</sub> and P<sub>2</sub>O<sub>5</sub>. The rocks of the first period have this ratio on average higher than the rocks belonging to the third period. The most differentiated product of the Ustica volcanic sequence, represented by the trachytic Grotte del Lapillo pyroclastic unit, is characterized by Sr isotopic ratios that vary significantly with the stratigraphic height, suggesting open-system evolution processes. Based on chemical composition of the erupted products, their stratigraphic height, and vent position, each period can be subdivided in cycles in which the first erupted magmas are systematically less differentiated than the final ones.

Taking also into account the absolute ages of the erupted products, it is possible to formulate the following hypothesis on the evolution of the Ustica magmatic feeding system. During the first period, due to the intense tectonic activity related to the opening of the Tyrrhenian sea, almost continuous eruptions were fed by poorly evolved magmas, which had no time to differentiate in shallow- level reservoirs. Only short episodes of stagnation at variable depth could have occurred during this period, accompanied by moderate crystal fractionation and assimilation processes. After a period of quiescence that lasted about 50 ka, the eruption of trachytic magma could be related to a stasis in the regional tectonic activity, which allowed the stagnation of magma and the formation of a compositionally zoned magma chamber.

After this eruption, volcanism renewed with close eruptions fed by poorly evolved magmas, which were however characterized by more efficient differentiation processes, likely related to the formation of small-scale magma chambers.

## Subduction-related enrichment of the Neapolitan volcanoes (Southern Italy) mantle source: new constraints on the characteristics of the slab-derived components

D'Antonio M.\*<sup>1</sup>, Mazzeo F.C.<sup>1</sup>, Arienzo I.<sup>2</sup>, Aulinas M.<sup>3</sup>, Di Renzo V.<sup>4,5</sup> & Gimeno D.<sup>3</sup>

1. Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università degli Studi di Napoli Federico II. 2. Istituto Nazionale di Geofisica e Vulcanologia, sezione di Napoli Osservatorio Vesuviano. 3. Departamento de Geoquímica, Petrología i Prospecció Geològica, Facultat de Geologia, Universitat de Barcelona, Spain. 4. Analisi e Monitoraggio Del Rischio Ambientale (AMRA) center, Napoli. 5. Dipartimento di Ingegneria Civile, Design, Edilizia e Ambiente, Seconda Università degli Studi di Napoli, Aversa (CE).

Corresponding email: [masdanto@unina.it](mailto:masdanto@unina.it)

Keywords: Neapolitan volcanic area, Basilicata ophiolites, subduction slab derived melts and fluids.

The Neapolitan volcanic area (Southern Italy) has been the site of an intense Plio-Quaternary magmatic activity with a subduction-related signature. The high-Mg, K-basaltic lithic lava fragments dispersed in hydromagmatic tuff of the Solchiaro eruption (22 ka, Procida Island) are the least evolved volcanic rocks of the Neapolitan volcanic area and provide constraints on the nature and role of both pre-enrichment mantle and subduction-related components. Their average values of HFSE ratios such as Nb/Yb, Nb/Y, and Zr/Hf, relative to typical EMM and Canary Islands OIB, would seem to indicate an EMM-like, spinel peridotite pre-enrichment source for the Procida and, by inference Somma-Vesuvius, mafic magmas. In order to constrain the characteristics of subduction-slab derived components added to this mantle sector, new geochemical and Sr-Nd-isotopic data have been acquired on meta-sediments and pillow lavas from Timpa delle Murge ophiolites, representing fragments of Tethyan oceanic crust obducted during the Apennine orogenesis, and that may be similar to sediments subducted during the closure of Tethys ocean. Based on trace elements compositions (Th/Nd, Yb/Th, Ba/Th) the addition of three distinct subduction components to the mantle wedge underlying the Neapolitan volcanic area can be hypothesized: partial melts from shales, aqueous fluids from shales, and partial melts from limestone. Trace elements and Sr-Nd-isotopic ratios suggest a greater role for melts from pelitic sediments, relative to melts from limestones, and aqueous fluids, whereas seem to rule out a significant role for altered oceanic crust. Modeling based on variations of trace elements and isotopic ratios indicates that the pre-subduction mantle source of the Phlegrean Volcanic District and Somma-Vesuvius was enriched by 2-3% of subducted slab-derived components that might have stabilized amphibole and/or phlogopite in the mantle. The partial melting degree of this enriched source (amphibole-bearing spinel peridotite) should have been 2.5% to generate the Procida primary magmas. Modeling based on trace element contents and  $^{87}\text{Sr}/^{86}\text{Sr}$ - $^{143}\text{Nd}/^{144}\text{Nd}$  values constrains the age of the enrichment event to about 45 Ma ago, confirming that the Plio-Quaternary magmatism of the Neapolitan area is post-collisional, and suggesting that the origin of the subduction-derived enriching agents can be related to the closure of Tethys. A model of 1% partial melting of a source with the same chemical composition as that inferred for the PVD, but with different mineralogy (phlogopite-bearing spinel peridotite) reproduces the same trace elements distribution pattern of the olivine-hosted shoshonitic melt inclusions from the 1906 AD lava flow of Somma-Vesuvius. EC-AFC modeling suggests that these primitive melts were subsequently modified at mid-lower crust depth, with assimilation of 1.4% of continental crust.

## **Mantle dynamic in the Mediterranean**

Faccenna C.\*<sup>1</sup>, Becker T.W.<sup>2</sup>, Billi A.<sup>3</sup>, Boschi L.<sup>4</sup>, Capitanio F.A.<sup>5</sup>, Funicello F.<sup>1</sup>, Jolivet L.<sup>6</sup>, Piromallo C.<sup>7</sup>,  
Rossetti F.<sup>1</sup> & Serpelloni E.<sup>7</sup>

1. Dipartimento di Scienze, Università Roma TRE, Rome. 2. Department of Earth Sciences, University Southern California, CA, USA. 3. Consiglio delle Nazionali Ricerche, IGAG, Rome. 4. ISTEP, UPMC-CNRS, UMR 7193, Paris, France. 5. School of Geosciences, Monash University, Clayton, Australia. 6. Univ d'Orléans, ISTO, UMR 7327, 45071, Orléans, France. 7. Istituto Nazionale di Geofisica e Vulcanologia.

Corresponding email: [faccenna@uniroma3.it](mailto:faccenna@uniroma3.it)

Keywords: Mediterranean, mantle, tectonics.

The Mediterranean offers a unique opportunity to study the driving forces of tectonic deformation within a complex mobile belt. Lithospheric dynamics are affected by slab rollback and collision of two large, slowly moving plates, forcing fragments of continental and oceanic lithosphere to interact. This paper reviews the rich and growing set of constraints from geological reconstructions, geodetic data, and crustal and upper mantle heterogeneity imaged by structural seismology. We proceed to discuss a conceptual and quantitative framework for the causes of surface deformation. Exploring existing and newly developed tectonic and numerical geodynamic models, we illustrate the role of mantle convection on surface geology.

## Petrological characterization of the upper Miocene Rodna-Bârgău sub-volcanic district (Eastern Carpathians, Romania)

Laiena F.\*<sup>1</sup>, Fedele L.<sup>1</sup>, Seghedi I.<sup>2</sup> & Morra V.<sup>1</sup>

1. Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università degli Studi di Napoli Federico II.

2. Institute of Geodynamics, Bucharest, Romania.

Corresponding email: [fabio.laiena@unina.it](mailto:fabio.laiena@unina.it)

Keywords: petrology, Eastern Carpathians, Rodna-Bârgău, amphibole.

During Neogene, the Eastern Carpathians were the locus of abundant igneous activity with subduction-related geochemical characteristics. Among the various districts, the Rodna-Bârgău sub-volcanic complex represents a potentially key-area due to its peculiar position at the junction point between ALCAPA, Tisza-Dacia and East European plates, the exclusively sub-volcanic nature of its products, compared with the mainly effusive nature of the products from the other districts and the occurrence of a wide range of chemical compositions coupled with xenoliths of various nature, testifying complex low-pressure evolution. Despite this, little attention has been so far devoted to the study of the products of the area, which still remain poorly characterized. The present work is thus aimed to a full petrological investigation of the products of the Rodna-Bârgău district, which will possibly shed some new light on the magmatic and geodynamic evolution of the entire Carpathian arc.

The preliminary analyses on representative samples allowed the recognition of numerous petrographic types, ranging from basalt/microgabbro to mainly andesite/microdiorite up to dacite/granodiorite and rhyolite/microgranite. Rock compositions show a well defined calcalkaline serial affinity in which, however, a clear distinction between a low-K and a high-K magmatic suites can be observed. Rocks of the first series are amphibole-bearing andesites/microdiorites, dacites and rhyolites/microdiorites with  $\text{SiO}_2 = 58.0-74.6$ ,  $\text{MgO} = 3.36-0.09$  and  $\text{K}_2\text{O} = 1.49-2.93$  wt.%, whereas rocks of the high-K suite are microgabbros, amphibole-bearing basaltic andesites/andesites and dacites with  $\text{SiO}_2 = 53.4-64.1$ ,  $\text{MgO} = 10.2-2.18$  and  $\text{K}_2\text{O} = 1.29-3.23$  wt.%. Intermediate-evolved terms of the two series are remarkably different also on petrographic grounds, given that 1) low-K rocks ( $\text{K}_2\text{O} = 1.71-3.23$  wt.%) display a yellow-pale green tschermakite to Mg-hornblende amphibole ( $\text{Si} = 6.01-6.94$ ,  $\text{K} = 0.03-0.09$  a.p.f.u.), whereas high-K ones ( $\text{K}_2\text{O} = 1.16-1.46$  wt.%) feature a green hastingsite-pargasite ( $\text{Si} = 5.82-6.36$ ,  $\text{K} = 0.16-0.34$  a.p.f.u.); 2) low-K andesites display rare Na-rich alkali feldspar ( $\text{Or} \sim 49$ ) in the groundmass, whereas high-K equivalents have higher abundances of a K-richer variety ( $\text{Or} \sim 70$ ); 3) accessory biotite ( $\text{Mg}\# = 0.57-0.61$ ) is present only in high-K andesites and dacites. Incompatible element abundances suggest subduction-modified magma sources and again indicate a clear distinction between the two rock series, with rocks of the high-K suite displaying a stronger enrichment in LILE (e.g.,  $\text{Rb} = 34-57$  and  $56-118$  ppm,  $\text{Ba} = 359-631$  and  $578-819$  ppm, in least evolved and intermediate-evolved terms, respectively) and LREE (e.g.,  $\text{La}_N = 22.7-31.6$  and  $30.6-44.4$ ,  $\text{Nd}_N = 12.1-14.9$  and  $13.0-20.0$ ) with respect to those of the low-K one ( $\text{Rb} = 27-46$  and  $38-107$  ppm,  $\text{Ba} = 158-288$  and  $253-619$  ppm,  $\text{La}_N = 15.3-22.4$  and  $17.0-42.6$ ,  $\text{Nd}_N = 8.1-11.2$  and  $9.7-13.4$ , respectively for intermediate and evolved rocks).

## $^{40}\text{Ar}$ - $^{39}\text{Ar}$ dating of Marsili seamount (Tyrrhenian Sea)

Laurenzi M.A.<sup>1</sup>, Marani M.\*<sup>2</sup> & Trua T.<sup>1-3</sup>

1. Istituto di Geoscienze e Georisorse, CNR, Pisa. 2. Istituto di Geologia Marina, CNR, Bologna  
3. Dipartimento di Fisica e Scienze della Terra, Università di Parma.

Corresponding email: [michael.marani@ismar.cnr.it](mailto:michael.marani@ismar.cnr.it)

Keywords:  $^{40}\text{Ar}$ - $^{39}\text{Ar}$  dating, Marsili seamount, Tyrrhenian Sea.

Marsili seamount, a huge volcanic edifice about 60 km long and 20 km wide, rises from the 3500 m deep seafloor of the homonymous basin to about 500 m below sea level. Its products range from medium- to low K basalts to high-K andesites, the latter sampled only in the summit area of the volcano (Marani & Trua, 2002).

Very few chronological constraints on its development are available in the literature. Poorly defined K/Ar ages, younger than 0.1-0.2 Ma, are reported for shallow lava scoriae by Selli et al. (1977). Cocchi et al. (2009) place the start of the vertical growth of the seamount at the beginning of the Jaramillo subchron and the maximum accretion within the Brunhes chron. Furthermore, the magnetic chronology of the Marsili basin is presently debated (Nicolosi et al., 2006; Cocchi et al., 2009; Florio et al., 2011).

Some fresh samples, dredged in past cruises (Marani et al., 1999), have been selected for  $^{40}\text{Ar}$ - $^{39}\text{Ar}$  dating, with the aim to attempt to clarify seamount growth. The often altered state of the samples and the inability to place them exactly on the volcanic edifice are limiting factors, constraining the choice of samples and the volcanological interpretation of their results. The only reliable datum obtained up to now is from a calc-alkaline basalt dredged in the NE steep flank, at 3050-2725 m depth. Pooled data from two step-heating experiments identifies an isochron of  $213 \pm 22$  ka ( $1\sigma$ ), which represents the first direct dating of Marsili basalts.

This research is part of the the Flagship Project "RITMARE", coordinated by CNR (Italy).

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## **$^{40}\text{Ar}$ - $^{39}\text{Ar}$ geochronology and evolution of the Cimini volcanic district (Central Italy)**

Laurenzi M.A.<sup>1</sup>, Mattioli M.\*<sup>2</sup>, Bonomo R.<sup>3</sup>, Ricci V.<sup>3</sup> & Vita L.<sup>3</sup>

1. Istituto di Geoscienze e Georisorse, CNR, Pisa. 2. Dipartimento di Scienze della Terra, della Vita e dell'Ambiente, Università di Urbino, PU. 3. Servizio Geologico d'Italia, ISPRA (Istituto Superiore per la Protezione e la Ricerca Ambientale), Roma.

Corresponding email: [michele.mattioli@uniurb.it](mailto:michele.mattioli@uniurb.it)

Keywords: Cimini volcanic district,  $^{40}\text{Ar}$ - $^{39}\text{Ar}$  geochronology, stratigraphy.

The Cimini volcanic district (CVD) is located in Central Italy and belongs to the Tuscan Magmatic Province (Miocene-Middle Pleistocene). It is characterized by several phases of activity during which lava domes, lava flows and ignimbrites have been erupted (Lardini & Nappi, 1987). Conticelli et al. (2013) indicate that the Cimini volcanic rocks range from ultrapotassic to potassic, where shoshonitic lavas represent the most primitive products and trachytic lava domes are the rocks richest in silica. Although some age determinations were made in the past for the CVD, evidencing a quite long eruptive history (see Fornaseri, 1985, for a review), a great uncertainty persisted on the age, as well as on the stratigraphy of the Cimini volcanic activity. To solve such doubts, a  $^{40}\text{Ar}$ - $^{39}\text{Ar}$  geochronological study has been performed in the framework of the new sheet No. 345 "Viterbo" of the Geological Map of Italy at 1:50,000 scale. The accurate geological survey at 1:10,000 scale allowed an improvement of the stratigraphy and a detailed and representative sampling of the whole volcanic sequence.

Fourteen  $^{40}\text{Ar}$ - $^{39}\text{Ar}$  datings evidence an interval of activity of about 0.07 Ma, from 1.36 to 1.29 Ma, a period by far shorter than previously thought. Lava domes, which constitute a well preserved dome field, display the widest age dispersion (1.36÷1.29 Ma), while the ignimbritic and lava flows are all in the age interval 1.31÷1.29 Ma. The integration of geochronological and field data opens up to different interpretations about the eruptive history of the CVD than previously thought. The activity started with the growth of trachytic lava domes, followed by explosive eruptions that gave rise to pyroclastic flows which deposited a thick and widespread ignimbritic cover of latitic to trachytic composition. The building of further trachytic lava domes continued after this explosive stage. Latitic, olivine-latitic and shoshonitic lavas, coming from Mt. Cimino dome, are subsequent to the ignimbritic eruption, but both age data and field evidences are unable to fully elucidate their mutual relations and those with some of the last lava domes. However, some evidences question the allocation of olivine-latites and shoshonites as final products. The new datings enlarge the age gap between the end of the CVD and the beginning of the nearby Vico volcanic activity (0.42 Ma, Laurenzi & Villa, 1987).

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## Magmatism in central Mediterranean: can we change the subduction paradigm?

Lustrino M.<sup>1</sup> & Chiarabba C.\*<sup>2</sup>

1. Dipartimento di Scienze della Terra, Università di Roma La Sapienza. 2. INGV, Roma.

Corresponding email: [claudio.chiarabba@ingv.it](mailto:claudio.chiarabba@ingv.it)

Keywords: magmatism, subduction, lithosphere delamination, central Mediterranean.

We review geophysical and petrological data that can support an evolutionary model for the Apennine system based on delamination of continental lithosphere. What is classically interpreted as subduction-related magmatism, i.e., partial melting of a mantle wedge metasomatized by coeval subduction, could be instead be considered as partial melting of mantle sources modified by no longer active (Alpine or Hercynian) subduction systems.

This may force a change in the current paradigm that explains the calcalkaline, high-K calcalkaline, potassic and ultrapotassic Cenozoic igneous activity of western Mediterranean in terms of subduction-related processes.

While coeval subduction can explain the early-middle Miocene igneous activity in Sardinia and the late Pleistocene volcanism in the Aeolian Islands, the distribution of many subduction-related igneous districts of western Mediterranean is not consistent with paleogeographic reconstructions. Excluding the naïve geochemical models invoking the presence of alleged mantle plumes, geochemical and petrological arguments simply indicate tapping of mantle sources modified by interaction with crustal lithologies, not a direct connection with active or recent subduction processes.

Magmas generated by subduction-modified mantle sources, not genetically related with coeval subduction systems, are present in the early Oligocene northern Apennines and the late Eocene Provençal-Sardinian margins. The subduction-related igneous activities along the Alpine Chain and in the Algerian Kabylies are tectonically unrelated with subduction (being post-collisional or emplaced too much closer to the trench or even in foreland position). Also the calcalkaline, potassic to ultrapotassic volcanic activity of the Betic Chain cannot directly be explained by subduction processes because these terminated more than 30 Myr before.

So far, high velocity mantle anomalies in tomographic models have been interpreted as remnants of subducted lithosphere, sustaining an East-directed and West-directed subduction-retreat model in the Apennine-Maghrebide and Betic-Rif systems. Consistent traces for prolonged Ionian subduction are outlined by high velocity anomalies in the mantle in the southern Tyrrhenian Sea region only, without continuity with the rest of the Apennines. Geophysical data likely indicate that the Apennines belt is delaminating and continental lithosphere plunges down to 100 km depth in front of a fossil Alpine belt, dismembered during the Tyrrhenian Sea opening. The Pleistocene volcanism is sourced in the hydrated and chemically heterogeneous patches of the uppermost mantle, outlined by high-resolution Vp/Vs models.

## Leucitites and leucitites within and around the Mediterranean

Lustrino M.<sup>1</sup>, Agostini S.\*<sup>2</sup> & Prelevic D.<sup>3</sup>

1. Dipartimento di Scienze della Terra - Università degli Studi di Roma La Sapienza. 2. Istituto di Geoscienze e Georisorse - CNR – Pisa. 3. Geocycles Research Centre and Institute of Geosciences - University of Mainz - Mainz Germany.

Corresponding email: [s.agostini@igg.cnr.it](mailto:s.agostini@igg.cnr.it)

Keywords: Alkaline magmatism, Mediterranean, petrology.

Leucitites crop out in few localities within and around the circum-Mediterranean area: Central Spain (Calatrava), Central Germany (West and East Eifel), Eastern Germany (Saxony; Hammerunterwiesenthal), Czech Republic (Doupovské hory Mts.), Southern Hungary (Bár), Central Italy (Ernici Mts. and Alban Hills volcanoes), Southern Kosovo (Devaje-Visočica), Western Turkey (Kirka-Afyon-Isparta) and NW Iran (Eslamieh Peninsula). We tentatively differentiate them in "anorogenic" and "orogenic" leucitites, depending on the proximity from active or recent subduction zones. Anorogenic leucitites are characterized by higher TiO<sub>2</sub> (1.9-3.6 wt%), Fe<sub>2</sub>O<sub>3</sub>tot (9.7-13.6 wt%), MgO (8.5-19.3 wt%), but lower Al<sub>2</sub>O<sub>3</sub> (8.5-14.3 wt%), K<sub>2</sub>O (0.5-4.3 wt%) and K<sub>2</sub>O/Na<sub>2</sub>O ratios (0.1-1.9) compared with orogenic leucitites. Compared with orogenic leucitites, the anorogenic leucitites have also lower Rb (13-303 vs. 96-670 ppm), Th (all but two samples 6-41 vs. 14-106 ppm), Pb (all but three samples 6-34 vs. 28-211 ppm), Ba/Nb (6-19 vs. 42-193), La/Nb (0.7-1.2 vs. 1.1-9.5), Zr/Nb (1.5-6.5 vs. 4.9-29.8), Th/Ta (1-12 vs. 8-108) higher Nb (54-172 vs. 4-60 ppm), Ta (3.4-9.9 vs. 0.6-3.4 ppm), Nb/U (all but two samples 19-51 vs. 1-17), Ta/Yb (2.2-4.5 vs. 0.2-1.7) and Nb/Nb\* (0.7-3.0 vs. 0.04-0.6).

This survey evidences the following important features: 1) Not all the leucitites are ultrapotassic rocks; 2) Some rocks classified in literature as leucitites are instead leucite-bearing basanites, tephrites, tephriphonolites and K-trachybasalts, given the abundant presence of feldspatic minerals; 3) Some rocks classified as basanites-tephrites should rather be defined leucitites because of the absence or paucity of feldspars; 4) leucitites are not confined in the foidite field of TAS diagram only, but spread towards silica-richer compositions; 5) rocks classified as leucitites emplaced in the foreland of subduction zones or in intraplate settings are not true leucitites. These can be easily distinguished from true leucitites, emplaced above active or recent subduction zones or along ancient sutures on the basis of several major and trace element constraints; 6) Rocks classified in different terms (e.g., leucite-basanite, tephrite, leucitite, leucite-nephelinite, phonotephrite, leucite-lamproite) generally have roughly the same incompatible element content, therefore can be related to similar petrogenetic processes, independently from the given rock name.

## The siderite mineralizations in the Southern Alps: a signal of the Permo-Triassic rifting?

Montorfano C.<sup>1</sup>, Toffolo L.\*<sup>2</sup>, Martin S.<sup>2</sup>, Secco L.<sup>2</sup>, Carugati G.<sup>1</sup>, Vezzoli L.<sup>1</sup> & Frizzo P.<sup>2</sup>

1. Dipartimento di Scienze della Terra, Università dell'Insubria, Como. 2. Dipartimento di Geoscienze, Università di Padova.

Corresponding email: [luca.toffolo@studenti.unipd.it](mailto:luca.toffolo@studenti.unipd.it)

Keywords: Southern Alps, siderite, ICP-Mass microchemistry.

Siderite mineralizations are distributed along the Southern Alps between Lake Como and Eastern Dolomites, mostly along major faults as Orobic, Val Trompia and Valsugana lineaments. They are dominantly unconformable veins in the Southalpine basement of Lake Como (Dongo, Val Cavargna) and Val Trompia (Torgola and Pineto) and in Late Permian rocks of the Orobic Alps (Lorio and Torsolazzo), or as stratiform conformable ore bodies within Lower Triassic Servino Formation carbonatic rocks (Manina, Fusio, Fura, San Vittore) (Cassinis et al., 1997; Brigo & Venerandi, 2005). Similar setting is described for siderite veins and strata-bound mineralizations in the Eastern Dolomites (Santa Lucia, Transacqua and Valle del Mis). Several publications describe the setting and the characteristics of the siderite, because the mining activity for iron extraction has been active since XV century. This work is aimed to define structural, stratigraphical and geochemical correlations among the siderite mineralizations of the Southern Alps that support a common time and process of genesis.

The composition of the siderite is rather homogeneous but it is enriched in Mn when it forms strata-bound ores in carbonatic rocks, whereas it is enriched in Mg when it forms veins cross-cutting the basement.

The Mn increasing trend in the siderites associated to carbonatic rocks of Early Trias age (Servino) is confirmed by a  $\delta^{13}\text{C}$  concordant trend. According to Frizzo & Scudeler Bacelle (1983), siderite appears to have invaded the carbonatic rocks and impregnate them more or less extensively.

The origin of Fe and Mg of the siderite remains unclear. Hydrothermal solutions charged of Fe and Mg, at presumed low temperature, traveled across the upper crust in a large portion of the Southern Alps, mostly where extension faults were active since Late Permian and some basin (e.g. Collio) were locally opening. In some places veins cut basement and Permian granodiorite as at Introbio.

A specific time range, spanning from Late Permian to Early Triassic in Lombardy, and to Middle Triassic in the Eastern Dolomites is recorded. The time of siderite impregnation ended with the beginning of the Triassic magmatism in Lombardy and Veneto regions. The siderite mineralizations are a geodynamic indicator in the Southern Alps, possibly related to the Permo-Triassic rifting process.

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## Deciphering the tectonometamorphic evolution of the Alboran Domain (Betic-Rif orogen, western Mediterranean): a clue from granite magmatism

Rossetti F.\*<sup>1</sup>, Dini A.<sup>2</sup>, Lucci F.<sup>1</sup>, Bouybaouene M.<sup>3</sup>, Gerdes A.<sup>4</sup>, Phillips D.<sup>5</sup> & Theye T.<sup>6</sup>

1. Dipartimento di Scienze Geologiche-Università Roma Tre. 2. IGG-CNR Pisa

3. Département de Géologie-Université de Rabat Morocco. 4. Institute für Geowissenschaften-Goethe Universität Frankfurt. 5. School of Earth Sciences-The University of Melbourne Australia. 6. Institut für Mineralogie und Kristallchemie-Universität Stuttgart Germany.

Corresponding email: [federico.rossetti@uniroma3.it](mailto:federico.rossetti@uniroma3.it)

Keywords: Granite magmatism, Structures, U-Pb geochronology, Ar-Ar geochronology, Alpine orogeny, Mediterranean.

The Betic-Rif orogen forms the western termination of the Alpine orogenic system in the Mediterranean region. Still under debate are timing and structures of the high-grade metamorphism (Alpine vs. pre-Alpine) in the metamorphic core of the orogen (Alboran Domain). A major source of ambiguity results from interpretation of the metamorphic history of the granulite-facies envelopes surrounding the peridotite bodies exposed within the two arms of the Alboran Domain (Ronda and Beni Bousera). We report occurrence of two distinct generations (hereafter referred as Type-1 and Type-2, respectively) of peraluminous granitic bodies intruded within the Beni Bousera peridotites and their amphibolite-to-granulite facies envelope (northern Morocco). These granitic bodies are central to reconstruction of the high-grade evolution of the Alboran Domain, because they provide first-order structural markers to assess the *P-T-t* history of the high-grade terranes. We document their structural relationships with the host rocks, petrography, geochemistry and timing of granite emplacement is constrained by integrated U-Pb-Th zircon/monazite and <sup>40</sup>Ar/<sup>39</sup>Ar dating. Type-1 consists of small (m to dm in size), variably-deformed leucocratic sheets and stocks, which occur exclusively within the granulite envelope, where they locally preserve intrusive relationships with the migmatitic country rocks. Their modal mineralogy consists of Qz (30-50%), K-Fsp (30-35%), Pl (10-25%), and Ky, Grt, Tor, Zrn and Fe-Ti oxides as minor phases (<10%). On the Q'-ANOR classification diagram, they range in composition from granodiorites to syenogranites. Type-2 consists of steeply-dipping dyke arrays discordantly intruded in the Beni Bousera units (including the peridotites) under the control operated by regional strike-slip tectonics. They consist of modally abundant K-Fsp (25-50%), Qz (20-30%), Pl (5-35%) ± Bt ± Mu ± Crd ± And ± Fe-Ti oxides, Zrc and Mnz (<15%). On the Q'-ANOR diagram, they range from alkali-feldspar granites to granodiorites. The Sr and Nd isotope systematics points to melting of fertile metasedimentary sources excluding derivation from the refractory host rocks. The geochronological results indicate granite emplacement occurred during two distinct episodes of crustal melting, in Hercynian (*c.* 290 Ma) and Alpine (*c.* 22 Ma) times for the Type-1 and Type-2, respectively. These data (i) provide conclusive evidence for preservation of a Hercynian high-grade signature in the Alboran Domain of the Betic-Rif chain, (ii) impose to revise significance of the regional, Early Miocene high-grade and partial melting events in terms of a late-stage thermal pulse that affected a polymetamorphic (Hercynian and Alpine) nappe pile, and (iii) emphasise role of strike-slip tectonics during the Neogene syn-to-post-orogenic Alpine evolution of the western Mediterranean. This study also provides first-order constraints to arrive to a feasible tectono-metamorphic model for the Alpine orogeny in the western Mediterranean.

## Occurrence of several explosive eruptions from Marsili seamount: new geochemical data of the Marsili volcanic activity during the last 6.7 ka B.P.

Tamburrino S.\*<sup>1</sup>, Insinga D.D.<sup>1</sup>, Vallefucio M.<sup>1</sup>, Ventura G.<sup>2</sup>, Sprovieri M.<sup>3</sup>, Tiepolo M.<sup>4</sup> & Passaro S.<sup>1</sup>

1. IAMC-CNR, Calata Porta di Massa, Napoli. 2. INGV, Roma. 3. IAMC-CNR, U.O.S. di Capo Granitola, Campobello di Mazara (TP).  
4. IGG-CNR, U.O.S. di Pavia.

Corresponding email: [stella.tamburrino@iamc.cnr.it](mailto:stella.tamburrino@iamc.cnr.it)

Keywords: Marsili explosive events, major and trace elements, Y-1.

The Marsili oceanic-like basin (Southern Tyrrhenian Sea, Italy) is an about 2 Ma old back-arc related to the north-westward subduction of the Ionian lithosphere below the Calabrian Arc (Ventura et al., 2013 and reference therein). Several studies focused on the geodynamic interpretation of that area, which is characterized by coexisting active volcanism, compressive and extensional deformations and slab rollback processes. The evolution of the Marsili Seamount (MS), which is located in the central sector the back-arc basin, is still debated. MS is one of the largest volcano of Mediterranean Area and Europe, measuring about 70 km in length and 30 km in width with the top at ~500 m b.s.l.. The about 1 to 0.03 Ma fissural and central MS activity form a complex segmented volcanic structure (Ventura et al., 2013). Effusions of lava flow represent the main eruptive style along with minor explosive eruptions that produced fall and flow deposits in historical time (Iezzi et al., 2014). The composition of the products ranges from medium-K calcalkaline basalts to high-K calcalkaline andesites related to both IAB and OIB-like mantle sources (Trua et al., 2011).

In this contribution, we present new stratigraphic and geochemical data, as well as AMS <sup>14</sup>C dating from a 2.35 cm deep-sea gravity core "Marsili1" recovered at 940 m b.s.l. in the MS central area. In particular, major and trace element glass composition (EMPA and LA-ICP-MS) of five tephra layers recovered along the core are reported. The geochemical features of the tephra layers allow in identifying MS and Mt. Etna as source areas. On the base of AMS <sup>14</sup>C dating, the MS tephra layers emplaced between 2 and 7 ka B.P., whereas the Etna distal layer can be correlated with the Y-1 marker layer (ca. 17 ka B.P.). Our results testify, within the recent MS activity, recurrent explosive eruptions in historical time. The occurrence of submarine explosive eruptions in the last 7 ka implies an evaluation of the potential hazards.

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## **Alpine Tethys closure as revealed by amphibole-rich mafic and ultramafic rocks from the Adamello and the Bergell intrusions (central Alps)**

Tiepolo M.\*<sup>1</sup>, Tribuzio R.<sup>2-1</sup>, Ji W.-Q.<sup>3</sup>, Wu F.-Y.<sup>3</sup> & Lustrino M.<sup>4-5</sup>

1. C.N.R. – Istituto di Geoscienze e Georisorse – U.O.S. Pavia. 2. Dipartimento di Scienze della Terra e dell’Ambiente, Università di Pavia. 3. Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing, China. 4. Dipartimento di Scienze della Terra, Università degli Studi di Roma La Sapienza. 5. C.N.R. - Istituto di Geologia Ambientale e Geoingegneria, Roma.

Corresponding email: [tiepolo@crystal.unipv.it](mailto:tiepolo@crystal.unipv.it)

Keywords: Adamello, Bergell, Zircon, U-Pb, Hf isotopes.

U-Pb ages and Hf isotope data were carried out on zircon from amphibole-rich mafic to ultramafic rocks from the Adamello batholith and the Bergell pluton, the largest Paleogene intrusions of the Alpine orogen. The <sup>206</sup>Pb/<sup>238</sup>U age pattern of U-Pb concordant dates from the Adamello mafic rock shows a major crystallization event at ~41 Ma and older age peaks at ~50 and ~45 Ma. Hornblende and amphibole gabbro samples of the Adamello batholith have zircon with initial ε<sub>Hf</sub> of ~+9.0 and ~+7.0, respectively. Amphibole gabbro and diorite samples of the Bergell pluton yield a younger age of ~31 Ma and have zircon with lower initial ε<sub>Hf</sub> (~+4.0).

We propose that the amphibole-rich rocks from the Adamello batholith originated from a depleted mantle source activated by the subduction of the Ligurian-Piedmontese basin. The amphibole-rich rocks from the Bergell pluton formed 10-15 Ma later than the Adamello counterparts by melts derived from a mantle sector metasomatized by the subduction of the Valais Basin. The enriched Hf isotopic signature of the amphibole rich rocks from the Bergell pluton is therefore interpreted to reflect the peculiar lithostratigraphy of the Valais Basin or a primary feature of the newly activated mantle source.

The Periadriatic magmatic province of the Alpine Orogen cannot be considered the magmatic response to a single tectonic event. This study is further evidence that amphibole-rich mafic and ultramafic rocks associated with orogenic granitoid plutons worldwide are a fundamental geochronological and petrological tool to interpret large scale tectonic processes during continental assembly.

## **The Tertiary dike magmatism in the central Southern Alps: Geochronological data and Geodynamic significance**

Zanchetta S.\*, Bergomi M.A. & Tunesi A.

Dipartimento di Scienze dell'Ambiente e del Territorio e di Scienze della Terra - Università degli Studi di Milano-Bicocca.

Corresponding email: [stefano.zanchetta@unimib.it](mailto:stefano.zanchetta@unimib.it)

Keywords: Southern Alps, dike magmatism, U-Pb ages.

The relationships between tectonics and magmatic activity in the Alps are still debated. Despite an active subduction since the Late Cretaceous, no arc-related magmatism is recorded prior of the Middle Eocene. The emplacement of plutons along the Insubric Fault in a short time span (~ 34-28 Ma) has been generally interpreted in terms of the slab break-off model. The Tertiary magmatism, however, is also characterized by occurrence of widespread calcalkaline dikes not necessarily intruded along the Insubric Fault. The geochemical features of dikes vary from the different areas and are interpreted in terms of mantle source heterogeneity and degree of crustal contamination. U-Pb zircon dating of studied dikes indicates intrusion ages in the 42-34 Ma time interval. These data provide evidence for a pre-Oligocene magmatic activity that was not solely limited to the Adamello batholith. Moreover, dikes roughly rejuvenate from S to N, in an opposite direction with respect to the Alpine subduction polarity. Thus, a more complex geodynamic scenario than the slab break-off model must be envisaged. The absence of arc-magmatism prior to the Middle Eocene can be explained by the low-angle subduction of the Tethyan slab that confined the mantle partial melting zone away from the orogenic wedge. The onset of the Apennines subduction at 55-50 Ma caused the Alpine slab to retreat. The partial melting zone progressively migrated beneath the orogenic wedge and finally reached the axial belt in the Late Eocene, when the Alpine collision was completed. Only at this stage slab break-off occurred and promoted the intrusion of the Periadriatic plutons.

## Sources, migration mechanisms and geodynamic environment of K-LILE-Mg-rich melts: Evidence from the Finero Complex (Southern Alps)

Zanetti A.\*<sup>1</sup>, Giovanardi T.<sup>2</sup>, Mazzucchelli M.<sup>1-3</sup>, Tiepolo M.<sup>1</sup>, Dallai L.<sup>4</sup>, Wu F.Y.<sup>5</sup>, Morishita T.<sup>6</sup>,  
Langone A.<sup>1</sup> & Vannucci R.<sup>7</sup>

1. IGG, CNR Pavia. 2. Instituto de Geociências, Universidade de São Paulo, Brazil. 3. Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia. 4. IGG-CNR Pisa. 5. Chinese Academy of Sciences, Beijing (China). 6. University of Kanazawa (Japan). 7. Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia.

Corresponding email: [zanetti@crystal.unipv.it](mailto:zanetti@crystal.unipv.it)

Keywords: Mantle Metasomatism, Southern Alps, Lamproitic Magmatism.

The Finero Complex is located in the northern sector of the Ivrea-Verbanò Zone (IVZ, Southern Alps). It outcrops with an antiformal structure showing a mantle unit at the core and a layered mafic-ultramafic intrusion on the flanks, i.e. the Finero Mafic Complex. The youngest unit of the latter (i.e. the External Gabbro) emplaced at the bottom of the continental basement at 232±3 Ma (Zanetti et al., 2013).

The Finero Complex records the unique worldwide example of subcontinental lithospheric mantle column in off-craton setting extensively metasomatised with segregation of phlogopite-bearing mineral assemblages.

Presently, there is a large consensus in considering that the mantle unit experienced a multi-stage melt migration in a supra-subduction environment (Zanetti et al., 1999).

However, the sequence of metasomatic stages and the mechanisms of melt migration are poorly constrained. Besides, the nature of the crustal component(s) (oceanic vs. continental crust) occurring in the ascending melts is still controversial, rendering doubtful the geodynamic reconstruction.

This contribution is aimed at providing new data about field relationships, petrographic features, major and trace elements mineral chemistry of the main lithologies of the mantle unit (e.g. phlogopite-amphibole-bearing harzburgites, dunites with chromitite and pyroxenite bands, phlogopite-bearing websterite, orthopyroxenites), as well as about the O isotope mineral composition and in-situ U-Pb and Lu-Hf isotope data for zircons from chromitite layers.

Our investigation points out that the mantle unit experienced a virtually complete metasomatic recrystallization as a result of a discrete number of episodes of pervasive-to-channelled porous flow migration of hydrous melts, alternated with stages of melt migration in open fractures. The latter mechanism formed pyroxenites usually containing Opx, Cpx, Amph and Phl. Both peridotites and pyroxenites display a similar geochemical signature, characterized by low contents in Al, Ti, Nb, Ta, HREE and Y, associated to large content in Mg, K, Th, U, Sr, Pb, Ba and LREE. The finding of  $\delta^{18}\text{O}_{\text{Opx}}$  vs. SMOW‰ up to +8 and of negative  $\epsilon_{\text{Hf}}$  in chromitite zircons suggest that large volumes of crustal component were present in the migrating melts. New U-Pb zircon data for the chromitite layers provide Lower Jurassic ages.

The sources of the migrating liquids, the age and the geodynamic environment of the mantle metasomatism, as well as the age of the crustal accretion of the mantle unit will be addressed. In particular, it will be stressed out the possibility that the K-LILE-Mg-enriched melt migration took place in a late-orogenic environment, similarly to the high-MgO ultrapotassic, lamproitic magmatism widespread in different Mediterranean areas from Oligocene to Pleistocene in association with shoshonitic and calc-alkaline rocks.

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## Structural level of Tertiary magma emplacement as a tool to unravel the late orogenic tectonics of the Western Alps

Zanoni D.\*<sup>1</sup>, Roda M.<sup>2</sup> & Spalla M.I.<sup>1-3</sup>

1. Università degli Studi di Milano - Dipartimento di Scienze della Terra, "A. Desio". 2. Universiteit Utrecht - Fac. of Geosciences, Utrecht, The Netherlands. 3. CNR-IDPA, Milano.

Corresponding email: [davide.zanoni@unimi.it](mailto:davide.zanoni@unimi.it)

Keywords: Biella and Traversella plutons, Alpine geodynamics, late orogenic magmatism.

The Biella and Traversella plutons (Zanoni et al., 2008; Zanoni, 2010 and refs. therein) are Periadriatic intrusives of the Alps, emplaced in the internal part of the HP continental Sesia Lanzo Zone. During the Alpine subduction and exhumation the Sesia Lanzo Zone records a polyphasic tectonometamorphic evolution. Pluton cooling involved contact metamorphism overprinting eclogitic to greenschist facies assemblages in country rocks. On the basis of the amount and type of contact metamorphic assemblages the aureole extent was mapped and the variation of thermal peak validated by numerical modeling. Relationships of structural record in country and plutonic rocks suggest that generally the intrusion of both plutons postdates the ductile deformations of the country rocks and that the brittle deformation mainly postdates magma emplacement. These structural and metamorphic relationships between plutonic and country rocks are consistent with magma intrusion taking place at shallow crustal levels, as corroborated by thermobarometrical estimates (Zanoni et al., 2010). This emplacement history indicates that the intrusion of Biella and Traversella bodies occurred when the Sesia Lanzo Zone had almost completed its exhumation within the subduction channel under a low thermal state (e.g. Roda et al., 2012 and refs therein). Numerical modeling suggests that Biella and Traversella stocks intruded a crust characterized by a thermal gradient consistent with that induced by a slab breakoff, as already proposed for the Periadriatic magmatism (Von Blanckenburg & Davies, 1995). Tertiary plutons of Western Alps emplaced at shallower crustal levels than in Central Alps (Rosenberg, 2004 and refs. therein) suggesting a slower exhumation of the western portion of Alpine axial zone over the last 30 Ma.

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## SESSIONE S21

**The role of metamorphic petrology in understanding Earth evolution,  
mass transfer and orogenic processes. A tribute to Bruno Lombardo**

### *CONVENORS*

*M. Scambelluri (Univ. Genova)*

*C. Groppo (Univ. Torino)*

*G. Ortolano (Univ. Catania)*

## Isomekes: A chemically-independent method for geobarometry of UHPM rocks

Alvaro M.\*<sup>1</sup>, Angel R.J.<sup>1</sup>, Mazzucchelli M.L.<sup>2</sup>, Nestola F.<sup>1</sup> & Nimis P.<sup>1</sup>

1. Dipartimento di Geoscienze, Università di Padova. 2. Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia.

Corresponding email: [matteo.alvaro@unipd.it](mailto:matteo.alvaro@unipd.it)

Keywords: Inclusion, inclusion-host system, isomeke, elasticity, ultra high-pressure metamorphic rocks, quartz.

Conventional thermo-barometric methods are challenged in ultra high-pressure metamorphic (UHPM) terranes as the temperatures of deep subduction often exceed the closure temperature of geothermobarometers and minerals may undergo discontinuous reactions or re-equilibration during both prograde and retrograde paths. Furthermore, some minerals are not suitable for conventional thermobarometry. We therefore need an independent method to determine P and T that does not rely on chemical equilibrium. The elastic behavior of mineral inclusions trapped in host minerals contained in UHPM rocks provides such an alternative.

Minerals trapped as inclusions within other host minerals develop residual stresses on exhumation as a result of the differences between the thermo-elastic properties of the host and inclusion phases. For example, a quartz trapped in a garnet at 1.7 GPa and 600 °C will exhibit a residual pressure of 1.06 GPa at room conditions. The key to interpreting this residual pressure is that when the inclusion was trapped, the host and inclusion had the same P and T, and the inclusion fitted perfectly within the cavity in the host. Measurement of the residual stress in the inclusions can therefore, in combination with the equations of state (EoS) of the two phases, be used to infer the P and T of entrapment. First we calculate the pressure  $P_{\text{foot}}$  at room-T at which they would have the same pressure, temperature, and volume. Possible entrapment conditions lie on a line in P-T space passing through  $P_{\text{foot}}$ , along which the fractional volume changes of the host and inclusion are the same. Such a path is known as an 'isomeke' (Adams et al., 1975), a curved line in P-T space that can be calculated directly from the EoS of the host and the inclusion. The intersection of isomekes for two host-inclusion pairs trapped at the same time, or with an independent P or T estimate is sufficient to uniquely define a point in the P-T history of the assemblage.

This approach can also be used to calculate the stress on mineral inclusions during the prograde history of the rock. For the Kulet whiteschist (Parkinson, 2000), calculations performed with EoSFit7c (Angel et al., 2014) show that at peak metamorphic conditions (about 780 °C and 35 kbar) an isolated quartz inclusion deep in the garnet cores would experience a pressure of about 1.7 GPa and would thus remain well within the stability field of quartz.

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## **Tectonostratigraphy and metamorphic evolution of the northern Monviso Meta-ophiolite Complex (inner Western Alps)**

Balestro G.\*<sup>1</sup>, Borghi A.<sup>1</sup>, Festa A.<sup>1</sup>, Gattiglio M.<sup>1</sup> & Vaggelli G.<sup>2</sup>

1. Dipartimento di Scienze della Terra - Università di Torino. 2. CNR - Istituto di Geoscienze e Georisorse.

Corresponding email: [gianni.balestro@unito.it](mailto:gianni.balestro@unito.it)

Keywords: HP meta-ophiolite, Western Alps, Monviso.

The Monviso Meta-Ophiolite Complex is a remnant of the Piedmont-Ligurian oceanic lithosphere that was subducted below the Adria plate and, during continental collision, tectonically juxtaposed on the paleo-European continental margin units. The northern sector of the Monviso Meta-Ophiolite corresponds to a stack of six tectonic units consisting of serpentinite, metagabbros, metabasalt and metasediments, that were affected by three main tectonometamorphic stages. The first subduction-related stage (D1) was characterized by the development of an early syn-eclogitic foliation (S1), overprinting primary surfaces (i.e. S0 sedimentary bedding and magmatic foliation). The occurrence of garnet-, omphacite-, talc- and lawsonite-assemblage in a Fe-Ti metagabbro particularly indicates P-T peak conditions of 2.5-2.7 GPa for 550-570 °C. The subsequent exhumation-related stage (D2), occurred under epidote-blueschist to greenschist-facies transition, extensively overprinted the D1 structures and mineral assemblages. The D2 was characterized by the development of a regional foliation (S2) that is parallel both to the contacts between the different tectonic units and to the axial plane of map-scale West-verging folds. The D1 and D2 were followed by a late-metamorphic stage (D3) which occurred at shallower crustal levels, developing westward extensional shear zones. Restoring deformation, the northern sector of the Monviso Meta-Ophiolite can be referred to an original ocean seafloor where an exhumed mantle was connected to a basalt-rich ridge segment through an articulated transition zone, formed during intra-oceanic faulting and characterized by different sedimentation processes. This portion of oceanic lithosphere was likely subducted as an almost coherent slice and dismembered into different tectonic units during collision- and exhumation-related deformation.

## Petrological constraints on the geological history of the Gran Paradiso Massif

Ballèvre M. \*, Manzotti P., Le Bayon B., Pitra P. & Poujol M.

Géosciences Rennes, Université de Rennes 1, France.

Corresponding email: [michel.ballevre@univ-rennes1.fr](mailto:michel.ballevre@univ-rennes1.fr)

Keywords: petrology, Gran Paradiso, Western Alps.

The Gran Paradiso Massif consists of two main superimposed units, namely the Gran Paradiso Unit and the Money Unit (Compagnoni, Elter and Lombardo, 1974).

Pre-Alpine history - In the Gran Paradiso Unit, a regional metamorphism of amphibolite-facies grade (~650°C – 6 kbar) is recognized in low-strain volumes. Its age is still unknown, possibly associated with the Variscan orogeny. Porphyritic granitoids intruded during the Middle Permian age producing contact metamorphism at ~700°C – 2.5 kbar (Gabudianu Radulescu et al., 2011) implying that the regional metamorphic rocks were already partly exhumed during the Middle Permian.

In the Money Unit, the sequence consists of (i) graphite-bearing, polygenic conglomerates, (ii) alkaline metarhyolites, (iii) paragneisses associated to amphibolites, and (iv) graphite-poor, monogenic, metaconglomerates (Manzotti et al., 2014a). In the meta-conglomerates, detrital garnet grains (with Alpine garnet overgrowths) are found (Manzotti and Ballèvre, 2013). A LaICP-MS study of the detrital zircons has allowed to assess the Late Carboniferous to Early Permian palaeo-topography in the (future) Alpine region. The volcano-sedimentary sequence is lately intruded by the Erfault metagranite.

Alpine history - In the Gran Paradiso Unit, an early eclogite-facies event is recognized (Compagnoni and Lombardo, 1974; Dal Piaz and Lombardo, 1986) in the polycyclic rocks, and the Permian metagranites. Estimated P-T conditions for the eclogite-facies event vary substantially from one author to the other. In the Money Unit, peak P conditions of the early stage (garnet-chloritoid assemblages in the pelitic matrix of the meta-conglomerates) are lower than those recorded in the Gran Paradiso Unit. These data allow to refine a geometrical and kinematical model for the Western Alps.

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## The role of melt inclusions in understanding crustal melting

Bartoli O.\*<sup>1</sup>, Cesare B.<sup>1</sup>, Acosta-Vigil A.<sup>2</sup>, Ferrero S.<sup>3</sup> & Poli S.<sup>4</sup>

1. Dipartimento di Geoscienze, Università di Padova. 2. Instituto Andaluz de Ciencias de la Tierra, Consejo Superior de Investigaciones Científicas-Universidad de Granada. 3. Institut für Geowissenschaften, Universität Potsdam. 4. Dipartimento di Scienze della Terra, Università di Milano.

Corresponding email: [omar.bartoli@unipd.it](mailto:omar.bartoli@unipd.it)

Keywords: crustal melting, nanogranite, peritectic minerals.

The recent recognition of melt inclusions (MI) in peritectic minerals of high-grade, partially melted metasedimentary rocks has opened up new possibilities to constrain petrological and tectonic processes during crustal melting. In slowly-cooled regional rocks MI are crystallized to a cryptocrystalline assemblage of quartz, feldspars and one or two micas named “nanogranite”. More rarely, in some exceptional geological contexts such as anatectic enclaves hosted in lavas, melt can be quenched to glass during eruption of the host volcanic rocks. Unlike inclusions in igneous rocks, formed by magma cooling and crystallization, MI in migmatites and granulites are trapped during incongruent melting, along the up-temperature path of anatexis. Because of such peculiar origin, they can provide key microstructural and chemical information.

Microstructurally, when they appear trapped within potential peritectic minerals (garnet, cordierite, spinel, ilmenite) and display textural features pointing to a primary origin, MI demonstrate the growth of their host in the presence of melt. Therefore MI represent one of the most reliable microstructural criteria for the former presence of melt in a rock, particularly in cases where deformation and/or recrystallisation have erased previously present igneous microstructures. Not only MI indicate that a rock was partially melted, but also they add constraints to the mineral(s) which coexisted with the melt. An unexpected outcome is that garnet can trap the earliest formed, low-T melts, with muscovite still stable or soon after its disappearance.

Chemically, as the composition of anatectic MI is representative of that of the bulk melt in the system during anatexis, these tiny objects (rarely exceeding 15 mm) represent embryos of anatectic granites. With an appropriate characterization and analytical strategy they can provide the missing information on the primary composition of natural crustal melts before they undergo modification processes such as cumulus, fractional crystallization, mixing or entrainment of exotic material. Information on primary compositions includes the concentrations of volatile components, and hence the nature of the fluid regime during anatexis. While glassy inclusions can be analyzed directly, nanogranites need to be rehomogenized and then quenched. Remelting is done in a piston cylinder, to prevent the decrepitation of inclusions and loss of volatiles. Inclusions can then be analyzed for major and trace elements, and also for H<sub>2</sub>O: most melts are leucogranitic and peraluminous, but show important variations in normative Qtz-Ab-Or proportions (with some tonalitic compositions), as well as in H<sub>2</sub>O contents.

This presentation will summarize some key results from MI occurrences at El Hoyazo and Ronda (Spain), the KKB of India, the Ivrea Zone (Italy) and Kali Gandaki (Nepal).

## **Petrographic study of xenoliths from deep crustal levels of northern Karakorum (Shaksgam Valley, Xinjiang, China)**

Botta S.<sup>1</sup>, Groppo C.<sup>1</sup>, Ferrando S.\*<sup>1</sup>, Frezzotti M.L.<sup>2</sup> & Rolfo F.<sup>1-3</sup>

1. Dipartimento di Scienze della Terra, Università di Torino. 2. Dipartimento di Scienze dell'Ambiente e del Territorio e di Scienze della Terra, Università di Milano Bicocca. 3. IGG, CNR Torino.

Corresponding email: [simona.ferrando@unito.it](mailto:simona.ferrando@unito.it)

Keywords: Tibetan Plateau, minette, HP dehydration melting.

Xenoliths hosted in post-collisional volcanic and subvolcanic rocks, that sample the lower crust and the upper mantle on their way up to the surface, give direct information on the structure and on the mineral and fluid composition of the deep core of the orogens.

The Tibetan Plateau, the highest and largest topographic feature on Earth, represents the archetypal product of continent-continent collision. It consists of several terranes progressively accreted onto the stable North Asian Siberian–Mongolian craton since the Early Mesozoic. The limited occurrence of exhumed deep crustal rocks hampers the direct characterisation of the deeper crust and upper mantle beneath the orogen. However, post-collisional volcanic rocks are widespread in the whole Tibetan Plateau, and ultrapotassic dykes hosting lower crustal xenoliths have been reported from many terranes (e.g. Hacker et al., 2000). Post-collisional potassic and ultrapotassic dykes have been also found in the Karakoram terrane (Pognante, 1990) but so far, no crustal xenoliths have been reported.

We present preliminary petrographic data on crustal xenoliths hosted by lamprophyric dykes from the Shaksgam valley, northern Karakorum (Xinjiang, China), in order to provide a first characterisation on the deep crust beneath the western segment of the Himalayan-Tibetan collisional belt.

The lamprophyric dykes are mostly porphyritic minettes, consisting of abundant phlogopite fenocrysts set in a fine-grained groundmass consisting of Kfs + Phl ± augitic or aegirinic Cpx ± Amp ± Pl. The lamprophyric dykes host various types of xenoliths sourced at different depths, from deep to intermediate to lower crustal levels, and variably affected by contact metamorphism induced by the dyke intrusion.

In this study, only xenoliths from the deep crustal level are considered. Apatite-bearing clinopyroxenite is mostly composed of clinopyroxene (> 90 vol%), apatite and minor phlogopite. Basic granulite consists of clinopyroxene, garnet, plagioclase and magnetite. Acid granulite contains Qtz and Pl, and is characterised by abundant Kfs (up to 40 vol%) and zoned garnet (up to 30 vol%), by the almost complete lack of hydrous minerals (biotite < 2 vol%), and by the local occurrence of relict kyanite. Rutile and graphite included in Grt are common accessory minerals. Microstructures and mineral-fluid assemblages suggest that these acid granulites may represent the restitic product of a former pelitic protolith that experienced HP dehydration melting. Remnants of the fluid phases present in the system at deep crustal levels are represented by primary inclusions in Grt.

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## Tectonic and metamorphic evolution of the Greater Himalayan Sequence in Central Himalaya: the role of the High Himalayan Discontinuity

Carosi R.\*<sup>1</sup>, Montomoli C.<sup>2</sup>, Iaccarino S.<sup>2</sup> & Visonà D.<sup>3</sup>

1. Dipartimento di Scienze della Terra, Università di Torino. 2. Dipartimento di Scienze della Terra, Università di Pisa  
3. Dipartimento di Geoscienze, Università di Padova.

Corresponding email: [rodolfo.carosi@unito.it](mailto:rodolfo.carosi@unito.it)

Keywords: Himalayas, metamorphism, tectonics, exhumation, collision tectonics, P-T-t paths.

The Greater Himalayan Sequence (GHS) is the main metamorphic unit of the Himalayas, running for over 2400 km, bounded to the South by the Main Central Thrust (MCT) and to the North by the South Tibetan Detachment (STD) whose contemporaneous activity controlled its exhumation between 23 and 17 Ma (Godin et al., 2006). Several shear zones and/or faults have been recognized within the GHS, usually regarded as out of sequence thrusts. Recent investigations in the GHS in Central Himalaya allowed the Authors to identify a tectonic and metamorphic discontinuity, above the MCT, with a top-to-the SW sense of shear (Higher Himalayan Discontinuity: HHD) (Carosi et al., 2010; Montomoli et al., 2013;). U-(Th)-Pb *in situ* monazite ages provide temporal constraint of initiation of the HHD at 27-25 Ma, older than the Main Central Thrust, and continuing up to 17 Ma. Data on the P and T evolution testify that this shear zones affected the tectono-metamorphic evolution of the belt and different P and T conditions have been recorded in the hanging-wall and footwall of the HHD. The correlation of the HHD with several other discontinuities recognized in the GHS led to propose that it is a tectonic feature running for several hundreds kilometers, documented at the regional scale and dividing the GHS in two different portions. In Western and Central Nepal the occurrence of even more structurally higher contractional shear zone in the GHS (above the HHD): the Tyar shear zone in the Mugu –Karnali valley and the Kalopani shear zone in the Kali Gandaki valley, points out to an even more complex deformation pattern within the metamorphic core. The actual proposed models of exhumation of the GHS, based exclusively on the MCT and STD activities, are not able to explain the occurrence of the HHD and other in-sequence shear zones. Any model of the tectonic and metamorphic evolution of the GHS should account for the occurrence of the tectonic and metamorphic discontinuities within the GHS and its consequences on the metamorphic paths and on the assembly of Himalayan belt.

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## High-resolution structurally-controlled ELA-ICP-MS zircon and monazite dating

Casini L.\*<sup>1</sup>, Maino M.<sup>2</sup>, Oggiano G.<sup>1</sup>, Cannas Aghedu L.<sup>1</sup> & Langone A.<sup>3</sup>

1. DipNeT - Università di Sassari. 2. Dipartimento di Scienze della Terra, Università di Pavia. 3. IGG, CNR Pavia.

Corresponding email: [casini@uniss.it](mailto:casini@uniss.it)

Keywords: zircon dating, Variscan, Sardinia.

Zircon dating by ICP-MS methods is a robust approach to constrain the age of magmatic or high-grade ( $T > 0.5 T_m$ ) metamorphic events. Actually, this requires averaging the concordant Th-U-Pb and Pb-Pb ages of a representative population of zircon grains extracted from a 2 – 5 kg sample. Zircon separation involves crushing, grinding and heavy-liquids/magnetic separation processes. Although suitable crystals – i.e. zircons with a clear magmatic habitus – may be selected during hand-picking, there is no way to control the structural site where a given crystal came from. This limitation generally has no consequence for poorly evolved magmatic mafic to intermediate rocks. The liquidus-solidus temperatures of mafic melts are in fact above the temperature for U and Pb diffusion in zircon and monazite. Therefore, most crystals formed or were likely re-equilibrated during the crystallization of melt, yielding to simple Gaussian or log-normal age distributions. Felsic rocks such as S- and I-type granites, granulites and migmatites, instead, often record complex P-T-t paths involving multiple partial melting or HT events. This results in a large age distribution characterized by several clusters that may be difficult to link to specific tectonic events. A way around this analytical limit would be dating zircon grains in thin section; however, most rocks contain less than 2 – 5 suitable zircon grains per thin section, making this method incredibly time-consuming and unworkable.

In this report, it is presented an optimization scheme that allow for efficient structurally-controlled zircon and monazite dating of rocks using conventional ELA-ICP-MS apparatus. The procedure is based on micro-drilling of crystals from polished 120 mm-thick thin sections. For the purposes of demonstration, several zircon and monazite grains were selected by SEM-EDX and C-L analysis from three different microstructural sites of a Variscan migmatitic orthogneiss (northern Sardinia). The first population of zircons drilled from the unmelted domain of the orthogneiss retain only lower Ordovician ages ( $480.7 \pm 2.9$  Ma) that can be readily interpreted as the protholith age (Oggiano et al., 2010). The second population drilled from thin (0.1 – 1.5 cm) pseudotachylites that cut across the Late Devonian– Early Carboniferous orthogneiss fabric (Ferrara et al., 1978; Giacomini et al., 2005) gave an upper Mississippian age ( $324.5 \pm 7.6$  Ma). Monazite grains sampled from the younger leucosomes show slightly younger ages ( $313.3 \pm 3.3$  Ma), in perfect agreement with the field relationships.

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## **Bruno Lombardo (1944 – 2014)**

Castelli D.\*

Dipartimento di Scienze della Terra, Università di Torino.

Corresponding email: [daniele.castelli@unito.it](mailto:daniele.castelli@unito.it)

Bruno Lombardo, for 35 years Research Fellow at C.N.R., the Italian Research Council, has been an outstanding representative of a generation of earth scientists to whom we are indebted for a consistent synthesis of field observations coupled with a deep petrologic knowledge. Born in Cuneo, in the very core of his beloved Alps, he graduated at the University of Torino in 1970 with a thesis on the Gran Paradiso Massif under Ezio Callegari and Roberto Compagnoni. After a two-year fellowships at the Institute of Petrography of Torino, in 1972 he moved to the C.N.R. “Centro di Studio sui Problemi dell'Orogeno delle Alpi Occidentali” (later part of the C.N.R. “Istituto di Geoscienze e Georisorse”), a position which he held until he retired in 2007. As petrologist and Alpine field geologist who devoted his research to orogenic belts, Bruno Lombardo leaves a significant body of work on the Alps, the Himalaya and Antarctica. Pursuing his first studies on the Gran Paradiso, the crystalline rocks of Western Alps have been an ever-present subject within his whole scientific career, with fundamental studies on the origin and metamorphic evolution of Gran Paradiso – Monte Rosa – Dora-Maira Massifs, the Argentera Massif, the Sesia Zone, and the Piedmont ophiolite basin. A major turning point of his research interests can be traced back to 1975 when Bruno joined the Italian C.A.I.-C.N.R. Lhotse Expedition to study the Higher Himalaya and the Tibetan Series of Eastern Nepal. The outstanding mountain scenery and the geology of the Everest-Makalu region lured him to come back to Himalaya some sixteen times between 1975 and 2006, to investigate the geology and metamorphic evolution of High Himalayan Crystallines in the same Everest-Makalu region and Southern Tibet (Everest region and Kharta Valley) and, to the East, in Sikkim and Bhutan Himalaya. During his expeditions, he also studied the basement nappes of NW Himalaya (Zaskar and Nanga Parbat-Haramosh Massif) and Karakorum (Chogo Lungma Glacier, Deosai Plateau and Hunza Valley). In 1985, the invitation to join the first Italian Antarctic Expedition to Northern Victoria Land was another capstone of his scientific activity. He also participated to the 2nd and 4th expeditions and, thanks to his great skills and experience, gave significant contributions in modelling the metamorphic evolution of Wilson Terrane and its relationships with the East Antarctic craton. During this pioneering time of the Italian research activity in Antarctica, he was also appointed project leader of the basement rocks Petrology, Geochemistry and Geochronology division, the P.N.R.A. - National Antarctic Research Program, and member of the C.N.R. Polar Board. Through all his research work, Bruno Lombardo has been able to develop a vast network of scientific collaborations and relationships. All colleagues and friends will miss such a good, intelligent, tenacious, learned, calm and curious research companion.

## Partial to complete deprotonation of staurolite during crustal anatexis: nanoSIMS analysis and experimental constraints

Cesare B.\*<sup>1</sup>, Schmidt M.W.<sup>2</sup>, Remusat L.<sup>3</sup>, Barich A.<sup>4</sup>, Bartoli O.<sup>1</sup>, Acosta-Vigil A.<sup>4</sup>, Poli S.<sup>5</sup> & Garrido C.J.<sup>4</sup>

1. Dipartimento di Geoscienze, Università di Padova. 2. Geowissenschaften ETH, Zurich. 3. CNRS and MNHN, Paris, France. 4. IACT-CSIC, Granada, Spain. 5. Dipartimento di Scienze della Terra, Università di Milano.

Corresponding email: [bernardo.cesare@unipd.it](mailto:bernardo.cesare@unipd.it)

Keywords: Anatexis, Hydrogen, Staurolite.

Staurolite is a common mineral in amphibolite-facies metapelites, but owing to the multiple substitutions allowed by its complex crystal chemistry, it may be stable also in mafic systems at high pressure, or in partially melted Al-rich compositions. In the latter, experiments have so far demonstrated the supersolidus stability of staurolite in the range 700-825°C and 6-12 kbar. Throughout its wide P-T stability field, staurolite also displays huge variations of the H content (from 2.7 to 6.0 atoms per 48 oxygens) that appear to be positively correlated with P and negatively with T. However, direct analysis of H has been performed only in a limited number of studies, and never in staurolite stable at supersolidus conditions.

We report the preliminary results of NanoSIMS analysis of H in staurolite coexisting with melt from two experimental run series. The first sample results from the melting of fine-grained powder of a graphitic metapelite at 893°C and 8 kbar. The staurolite from the starting material has an  $X_{\text{Fe}}$  of 0.83, and an average H<sub>2</sub>O content of 2.2 wt.% (inferred from EMP total closure), that would correspond to 4 atoms H per 48 oxygens. During the experiment the assemblage melt-Qtz-Grt-Sil-Ilm-Crn-Her-St is produced, and St is partially to completely rimmed by hercynitic spinel. The staurolite is much more magnesian ( $X_{\text{Fe}}$  0.67-0.72) and contains only 1300 ppm (0.13 wt.%) H<sub>2</sub>O, with a 1s error of 0.06 wt.%. These values correspond to 0.24 atoms H per 48 oxygens. Along with the dramatic deprotonation demonstrated by NanoSIMS, the experimental staurolite shows higher total contents of Al and (Fe+Mg), in agreement with previously proposed exchange vectors for deprotonation.

The second sample consists of fragments of garnet with *nanogranite* inclusions from the migmatites around the Ronda Peridotite (Spain), which were brought to 850°C and 15 kbar in order to remelt the polycrystalline inclusions in garnet. In the remelted inclusions, the formation of thin (Fe of 0.57, and H<sub>2</sub>O contents of 1.3 wt.%, that correspond to 2.35 atoms H per 48 oxygens. Also this staurolite is richer in Al (>18.5 atoms) with respect to common compositions.

These results suggest that, similarly to other hydroxylated minerals like biotite, also staurolite undergoes a progressive T-dependent deprotonation, and that this process may reach completion with the occurrence of H-free terms at (U)HT supersolidus conditions.

## Microstructures in granulitized kyanite-eclogite from NE sardinia, Italy: insights into the reconstruction of metamorphic evolution

Cruciani G.\*<sup>1</sup>, Franceschelli M.<sup>1</sup>, Groppo C.<sup>2</sup>, Scodina M.<sup>1</sup> & Spano M.E.<sup>1</sup>

1. Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari. 2. Dipartimento di Scienze della Terra, Università di Torino.

Corresponding email: [gcrucian@unica.it](mailto:gcrucian@unica.it)

Keywords: kyanite-eclogite, P-T path, Variscan orogeny.

The studied kyanite-eclogites are massive to poorly foliated rocks cropping out a few kilometers north of Olbia, NE Sardinia. They consist of garnet, kyanite, clino/orthopyroxene + plagioclase symplectites and amphibole. Other minerals identified are sapphirine, spinel, corundum, epidote, biotite, ilmenite, titanite and chlorite. Garnet occurs as millimeter-sized zoned porphyroblasts (core: Grs<sub>27-26</sub>, Pyr<sub>23</sub>; rim: Grs<sub>18</sub>, Pyr<sub>37</sub>). The garnet crystals preserve armoured relics of kyanite and omphacite as well as several inclusions of quartz, epidote, amphibole, apatite, and rutile. Kyanite is also found in rounded to elongated crystals in the matrix. The kyanite-eclogites are characterized by the occurrence of amazing microstructures rarely observed in other eclogitic samples from Variscan Sardinia (Cruciani et al., 2012). These striking microstructures include: (i) spinel, sapphirine and corundum coronitic assemblages around kyanite, and (ii) double layered-coronas of amphibole and plagioclase around garnet. In the first ones a variable degree of kyanite replacement can be observed in different microdomains. When kyanite is still preserved, the corona around kyanite consists of a thin layer of spinel+plagioclase (Ab<sub>5-10</sub>) symplectite, in turn surrounded by sapphirine + plagioclase (Ab<sub>20</sub>) symplectite. When kyanite is no more present, in the nucleus of the corona an intergrowth of acicular corundum crystals and Ca-rich plagioclase (Ab<sub>13</sub>) is observed. All these microstructures are surrounded by a continuous thin layer of Na-rich plagioclase (Ab<sub>60</sub>). The double layer-coronitic microstructures around garnet consist of an inner corona of Ca-rich plagioclase (bytownite) and Al-rich amphibole (Al-pargasite, tschermakite or Mg-hornblende, X<sub>Mg</sub>: 0.7-0.8) adjacent to the garnet, in turn surrounded by an outer corona made up of Ca-Na plagioclase (andesine) and amphibole of the same composition. Preliminary P-T conditions estimated by thermodynamic modelling (method of Cruciani et al., 2008) indicate that garnet core and omphacite formed at P-T conditions of 1.8-2.0 GPa and ~ 650°C. The occurrence of orthopyroxene and sapphirine indicates a temperature of 700-800°C and P < 1.5 GPa for the symplectitic assemblages. The composition of coronitic amphibole and plagioclase points to P-T conditions of 0.9-1.1 GPa and 630-730°C for the development of coronas in contact with garnet.

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Cruciani G., Franceschelli M., Groppo C., Spano M.E. 2012. Metamorphic evolution of non-equilibrated granulitized eclogite from Punta de li Tulchi (Variscan Sardinia) determined through texturally controlled thermodynamic modelling. *J. Metam. Geol.*, 30, 667-685.

## Carbonatites, silicate melt and fluid produced during anatexis in the middle crust: a case study from Oberpfalz (Bohemian Massif)

Ferrero S.\*<sup>1</sup>, O'Brien P.<sup>1</sup>, Hecht L.<sup>2</sup>, Ziemann M.<sup>1</sup> & Wunder B.<sup>3</sup>

1. Universität Potsdam, Institut für Erd- und Umweltwissenschaften, Potsdam, Deutschland. 2. Museum für Naturkunde, Leibniz-Institut für Evolutions- und Biodiversitätsforschung, Berlin, Deutschland. 3. Helmholtz-Zentrum Potsdam, GFZ, Potsdam, Deutschland.

Corresponding email: [sferrero@geo.uni-potsdam.de](mailto:sferrero@geo.uni-potsdam.de)

Keywords: Nanogranites, Carbonatite, Anatexis.

In the last decades our understanding of partial melting processes in the lower crust profited from the investigation of fluid inclusions (Touret et al., 2009) and more recently of anatectic melt inclusions (Cesare et al., 2011) within enclaves and high-grade terranes. The latter finding allowed us to directly analyse the original anatectic melt (Ferrero et al., 2012; Bartoli et al., 2013) preserved within peritectic phases, before fractionation, mixing and contamination processes took place. Furthermore, the occurrence of primary fluid inclusions (FI) and anatectic melt inclusions (MI) within enclaves allowed the characterization of the COH fluid present during anatexis under fluid+melt immiscibility conditions (Ferrero et al., 2014).

Primary crystallized MI, or “nanogranites”, and FI have been identified to occur as clusters in garnet from stromatic migmatites (Zeilengneise) from Oberpfalz, Eastern Bavaria (Moldanubian Zone). During the late Carboniferous, these Grt+Bt+Sill+Crd+Spl metapelitic gneisses underwent HT/MP metamorphism, followed by a HT/LP event (Tanner & Behrmann, 1995). Nanogranites,  $\leq 20 \mu\text{m}$  in size, consist of Qtz+Bt+Wm+Ab $\pm$ Ap, and show abundant nanoporosity, localized in the quartz. Fluid inclusions are smaller, generally  $\leq 10 \mu\text{m}$ , and contain CO<sub>2</sub>+N<sub>2</sub>+CH<sub>4</sub> plus siderite, pyrophyllite and cristobalite, mineral phases not observed in the surrounding rock or as mineral inclusion in garnet. Polycrystalline inclusions containing Cc+Wm+Chl $\pm$ Qz, commonly  $\leq 10 \mu\text{m}$  in diameter, occur in the same cluster with MI and FI. Microstructural features, negative-crystal shape and the well-developed crystalline faces of calcite within inclusions suggest that they may result from the crystallization of a carbonate-rich melt. The lack of arrays of carbonate-bearing MI, verified by cathodoluminescence investigation, supports their primary nature, i.e. they formed during garnet growth. This would suggest the occurrence of a silicate melt and a carbonate-rich melt during anatexis at relatively shallow crustal levels, but this hypothesis needs to be further tested through re-homogenization experiments by piston cylinder means.

Bartoli O., Cesare B., Poli S., Bodnar R.J., Acosta-Vigil A., Frezzotti M.L. & Meli S. 2013. Recovering the composition of melt and the fluid regime at the onset of crustal anatexis and S-type granite formation. *Geology*, 41, 115–118.

Cesare B., Ferrero S., Salvioli-Mariani E., Pedron D. & Cavallo A., 2009. Nanogranite and glassy inclusions: the anatectic melt in migmatites and granulites. *Geology*, 37, 627–630.

Ferrero S., Bartoli O., Cesare B., Salvioli Mariani E., Acosta-Vigil A., Cavallo A., Groppo C. & Battiston S. 2012. Microstructures of melt inclusions in anatectic metasedimentary rocks. *Journal of Metamorphic Geology*, 30, 303–322.

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Tanner D.C. & Behrmann J.H. 1995. The Variscan tectonics of the Moldanubian gneisses, Oberpfalzer Wald: a compressional history. *Neues Jahrbuch für Geologie und Paläontologie. Abhandlungen*, 197, 331–355

Touret J.L.R. 2009. Mantle to lower-crust fluid/melt transfer through granulite metamorphism. *Russian Geology and Geophysics*, 50, 1052–1062.

## REE distribution among zircon, amphibole and garnet in Variscan granulites from southern Calabria (Italy)

Fornelli A.\*<sup>1</sup>, Langone A.<sup>2</sup>, Micheletti F.<sup>1</sup> & Piccarreta G.<sup>1</sup>

1. Dipartimento di Scienze della Terra e Geoambientali. 2. IGG-CNR, Pisa-Pavia.

Corresponding email: [annamaria.fornelli@uniba.it](mailto:annamaria.fornelli@uniba.it)

Keywords: REE, amphibole, garnet, zircon.

Two samples of mafic and intermediate granulites with porphyroblastic garnet were investigated for REE distribution among the mineral phases. The granulites underwent Variscan metamorphism experiencing compressive events ~350 Ma ago and decompressional stages up to 280 Ma (Fornelli et al. 2012). The studied samples having comparable REE contents, differ for the presence (sample Tur76A) or absence (sample GRT3) of amphibole. In the amphibole-bearing sample garnet is REE-rich ( $\Sigma\text{REE}=206$  ppm at core and 756 ppm at rim) but distinctly poorer than in the amphibole-free sample ( $\Sigma\text{HREE}=2463$  ppm at core and 14784 ppm at rim). Both garnets show a continuous symplectitic corona formed by plagioclase and biotite with or without amphibole. They have a rim rich in REE with engulfments characterized by REE distribution comparable with that of core. The abundance and distribution of REE in the coeval zircons dated around 300 Ma from the two samples, are different: (1) in the amphibole-free sample,  $\Sigma\text{REE}$ 's range from 1180 to 439 ppm and define steep patterns with low LREE and high HREE contents; (2) in the amphibole-bearing sample, REE contents are lower ranging from 207 ppm to 361 ppm. Amphibole, present only in the sample Tur76A, shows different composition in the diverse sites: 1) in garnet, amphibole displays on average  $\text{REE}=464$  ppm,  $\text{Yb}_N/\text{Gd}_N=0.26$  and  $\text{Eu}/\text{Eu}^*=0.56$ ; 2) in matrix it contains slightly lower REE (420 ppm) but higher values of  $\text{Yb}_N/\text{Gd}_N$  (1.17) and lower  $\text{Eu}/\text{Eu}^*$  (0.43); 3) two types are present in symplectite around garnet showing similar patterns at different level of abundance of MREE-HREE ( $\text{REE}=493$  ppm,  $\text{Eu}/\text{Eu}^*=0.43$ ,  $\text{Yb}_N/\text{Gd}_N=0.49$  and  $\text{REE}=680$  ppm,  $\text{Eu}/\text{Eu}^*=0.38$ ,  $\text{Yb}_N/\text{Gd}_N=0.7$ ).

Summing up it appears that: 1) amphibole under granulite facies conditions is rich in REE and, when present, it causes a decrease of REE in garnet and zircon; 2) the outer rim of garnet is affected, due to dissolution, by intracrystalline REE diffusion with increase of REE during the first stage of decompression (~300 Ma); 3) subsequently towards the end of decompression (280 Ma), dissolution was more effective and more rapid than diffusion and produced engulfments depleted in REE; 4) in the corona firstly formed amphibole poorer in REE and, finally, when dissolution of garnet was more rapid than REE diffusion, amphibole taken more REE; 5) amphibole tends to be richer than garnet for MREE's; 6) the elemental ratios between zircon dated 305-303 Ma in the inner rim of garnet and in corona probably indicate the initial stage of decompression; 7) the two kinds of amphiboles from corona having different distribution coefficient with garnet, seem to indicate that especially MREE's tend to increase with increasing geothermal gradient during post-peak decompression.

Fornelli A., Pascazio A., Piccarreta G. 2012. Diachronic and different metamorphic evolution in the fossil Variscan lower crust of Calabria. *Int. J. Earth Sci.*, Vol. 101, pp 1191-1207.

## The stability of Cr-chlorite and other hydrates in subduction mélanges: and experimental study in the system $\text{Cr}_2\text{O}_3\text{-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$

Fumagalli P.\*<sup>1</sup>, Poli S.<sup>1</sup>, Fischer J.<sup>1</sup>, Merlini M.<sup>1</sup> & Gemmi M.<sup>2</sup>

1. Dipartimento di Scienze della Terra, Università di Milano. 2. Center for Nanotechnology Innovation@NEST, Istituto Italiano di Tecnologia, Pisa.

Corresponding email: [patrizia.fumagalli@unimi.it](mailto:patrizia.fumagalli@unimi.it)

Keywords: Subduction mélanges, Earth Mantle, Cr-Chlorite.

The stability of chlorite in the model system MASH is critical in the modelling of the hydration/dehydration sequence in a variable range of lithologies at the slab–mantle interface, where mass transfer in mélange zones generates hybrid rocks. In hydrated ultramafic systems, chlorite (containing 13 wt% of  $\text{H}_2\text{O}$ ) is a good candidate for transferring water beyond the stability field of antigorite, being stable up to 4–6 GPa, 700–800 °C. Although chromium is a minor constituent of the Earth mantle, it is incorporated in almost all major mantle phases, i.e., spinels, garnets, and pyroxenes, and it is expected to substantially modify phase equilibria in both mafic and ultramafic rocks. Chromium solubility in chlorite may further extend its stability and likely influence phase relations.

The solubility of chromium in chlorite as a function of pressure, temperature, and bulk composition was investigated in the system  $\text{Cr}_2\text{O}_3\text{-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ , and its effect on phase relations evaluated. Three different compositions with  $X_{\text{Cr}} = \text{Cr}/(\text{Cr} + \text{Al}) = 0.075, 0.25, \text{ and } 0.5$  respectively, were investigated at 1.5–6.5 GPa, 650–900 °C. Cr-chlorite only occurs in the bulk composition with  $X_{\text{Cr}} = 0.075$ ; otherwise, spinel and garnet are the major aluminous phases. In the experiments, Cr-chlorite coexists with enstatite up to 3.5 GPa, 800–850 °C, and with forsterite, pyrope, and spinel at higher pressure. At  $P=5$  GPa other hydrates occur: a Cr-bearing phase-HAPY ( $\text{Mg}_{2.2}\text{Al}_{1.5}\text{Cr}_{0.1}\text{Si}_{1.1}\text{O}_6(\text{OH})_2$ ) is stable in assemblage with pyrope, forsterite, and spinel; Mg-sursassite coexists at 6.0 GPa, 650 °C with forsterite and spinel and a new Cr-bearing phase, named 11.5 Å phase ( $\text{Mg}:\text{Al}:\text{Si} = 6.3:1.2:2.4$ ) after the first diffraction peak observed in high resolution X-ray diffraction pattern.

Cr affects the stability of chlorite by shifting its breakdown reactions toward higher temperature, but Cr solubility at high pressure is reduced compared with the solubility observed in low pressure occurrences in hydrothermal environments. Chromium partitions generally according to  $X_{\text{Cr}}^{\text{spinel}} \gg X_{\text{Cr}}^{\text{opx}} > X_{\text{Cr}}^{\text{chlorite}} \geq X_{\text{Cr}}^{\text{HAPY}} > X_{\text{Cr}}^{\text{garnet}}$ . At 5 GPa, 750 °C (bulk with  $X_{\text{Cr}} = 0.075$ ) equilibrium values are  $X_{\text{Cr}}^{\text{spinel}} = 0.27$ ,  $X_{\text{Cr}}^{\text{chlorite}} = 0.08$ ,  $X_{\text{Cr}}^{\text{garnet}} = 0.05$ ; at 5.4 GPa, 720 °C  $X_{\text{Cr}}^{\text{spinel}} = 0.33$ ,  $X_{\text{Cr}}^{\text{HAPY}} = 0.06$ , and  $X_{\text{Cr}}^{\text{garnet}} = 0.04$ ; and at 3.5 GPa, 850 °C  $X_{\text{Cr}}^{\text{opx}} = 0.12$  and  $X_{\text{Cr}}^{\text{chlorite}} = 0.07$ . Results on Cr–Al partitioning between spinel and garnet suggest that at low temperature the spinel- to garnet-peridotite transition has a negative slope of 0.5 GPa/100 °C. The formation of phase-HAPY, in assemblage with garnet and spinel, at pressures above chlorite breakdown, provides a viable mechanism to promote  $\text{H}_2\text{O}$  transport in metasomatized ultramafic mélanges of subduction channels.

## The Carboniferous - Permian evolution of the Sardinia Variscan branch: tracing the geodynamic change through U-Pb geochronology and geochemistry

Gaggero L.<sup>1</sup>, Gretter N.\*<sup>2</sup>, Lago M.<sup>3</sup>, Langone A.<sup>4</sup> & Ronchi A.<sup>2</sup>

1. Dipartimento di Scienze della Terra dell'Ambiente e della Vita, Università di Genova. 2. Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia. 3. Department of Earth Sciences, University of Zaragoza, Spain. 4. IGG – CNR, Pavia.

Corresponding email: [nicola.gretter@gmail.com](mailto:nicola.gretter@gmail.com)

Keywords: Permian volcanism, Sardinia, U-Pb geochronology, calc-alkaline series.

A distinctive feature of the Late Variscan geodynamic reorganization in Southern Europe can be found in the progressive collapse of the southern Variscides and the occurrence of a widespread related magmatism (Cortesogno et al., 1998; Buzzi et al., 2008). Prevalent transpressive/transensional tectonic movements drove the build up of continental deposits, infilling a great number of intramontane subsiding basins. In this scenario, the volcanism interbedded within the Late Carboniferous-Early Permian succession of Sardinia basins, is represented by K-normal and high-K calc-alkaline andesites and rhyolites followed by large volumes of rhyolites, and dacites.

Whole rock geochemistry and U-Pb geochronological analysis have been performed from samples collected in the NW Nurra basin and central - SE Perdasdefogu, Escalaplano, Seui-Seulo basins. Thus, trace elements and REE together with major elements have been analysed for 17 selected samples. Consequently, LA-ICP-MS U-Pb zircon dating was carried out. The most likely ages of crystallization have been obtained focusing measurements in outer zircon domains showing well preserved igneous textures. As a preliminary result, the calc-alkaline volcanism occurred at  $299\pm 1$  Ma lasting up to  $297\pm 1$  Ma in the Nurra basin.

Accordingly, the timing of the post Variscan volcanism, records the active tectonics between latest Carboniferous and Permian, constraining the collapse of the Southern Variscides and post-dating the unroofing and erosion of nappes in the External Zone of the belt. Thus, the lower crust results exposed at  $297\pm 1$  Ma in Nurra. In the external zone, the intermediate andesite volcanic rocks emplaced at  $294\pm 2$ , in good agreement with the latest felsic volcanism, as old as  $292\pm 2$  Ma. In this regards, the overlap between the calc-alkaline events and the volcanic/sub-volcanic alkalic one, is not exclusive to Sardinia and Corsica but to Pyrenees. The integration of detailed geochemical analyses (from recent literature) with new radiometric dating, constitutes a consistent dataset for different, though subsequent, volcanic events and provides a robust nail to unravel the plate reorganization between Laurussia and Gondwana during the late Palaeozoic evolution of the Variscan chain.

Buzzi L., Gaggero L. & Oggiano G. 2008. The Santa Giusta ignimbrite (NW Sardinia): a clue for the magmatic, structural and sedimentary evolution of a Variscan segment between Early Permian and Triassic. *Ital. J. Geosci.*, 127(3), 683–695.

Cortesogno L., Cassinis G., Dallagiovanna G., Gaggero L., Oggiano G., Ronchi A., Seno S. & Vanossi M. 1998. The Variscan post-collisional volcanism in Late Carboniferous-Permian sequences of Ligurian Alps, Southern Alps and Sardinia (Italy): a synthesis. *Lithos*, 45, 305–328.

## Olivine fabric as tool to constrain paleopiezometry and crystallization temperature in orogenic peridotites: an example from the Friningen Garnet Peridotite (Central Scandinavian Caledonides)

Gilio M.<sup>\*1-2</sup>, Clos F.<sup>1-3</sup> & Van Roermund H.L.M.<sup>1</sup>

1. Structural Geology and Tectonics, Department of Earth Sciences, Utrecht University, The Netherlands. 2. Dipartimento di Scienze della Terra, Ambiente e Vita, Università di Genova. 3. School of Geosciences, Monash University, Clayton, Australia.

Corresponding email: [mattia.gilio@edu.unige.it](mailto:mattia.gilio@edu.unige.it)

Keywords: Mantle wedge garnet peridotite, Olivine microstructures and fabrics, Scandinavian Caledonides.

The Friningen garnet peridotite (FGP; Seve Nappe Complex, Central Scandinavian Caledonides) is a mantle-wedge garnet peridotite (Van Roermund, 2009) incorporated into the continental crust in a plate interface environment during deep Scandian subduction (Van Roermund, 1989; Gilio and Van Roermund, 2013).

Here we combine 'classic' geothermobarometry and thermodynamic modelling to olivine fabric analysis in order to investigate paleopiezometry and crystallization temperature. These independent methods provide us with new tools to determine P-T histories of much more complex rocks and gain information on tectonic processes and provenance of peridotitic bodies from HP environments.

The FGP shows a complex history of multi-stage crystallization of ol+grt parageneses (Gilio and Van Roermund, 2013). Pre-Caledonian HP-HT metamorphic conditions of  $1150\pm 50^\circ\text{C}$  and  $2.6\pm 1.0$  GPa are determined for the early M1a assemblage (ol+opx+cpx+grt). These physical conditions are followed by an inferred early-Caledonian exhumation event down to  $850\text{-}950^\circ\text{C}$  and 1.5 GPa (M1b). During Scandian times, the FGP was incorporated into the down-going continental crust and dragged down to UHPM condition (M2;  $T=800^\circ\text{C}$  and  $P=3.0$  GPa; Janák et al., 2014). Afterwards, it followed the continental crust into exhumation (M3;  $T=800^\circ\text{C}$  and  $P=1.0$  GPa; Janák et al., 2014) and subsequent nappe stacking.

Three olivine microstructures are developed in the FGP in response to three deformation events under different PT and stress conditions.

1) Coarse grained (10-15 mm) olivine M1 porphyroclasts formed around  $1000\text{-}1100^\circ\text{C}$  under a very low differential stress (1-2 MPa).

2) Medium size (200-1000  $\mu\text{m}$ ) M2 olivine 'foam' microstructure, pervasive throughout the entire body formed around  $780\text{-}880^\circ\text{C}$  under a differential stress of about 10-40 MPa.

3) A fine grained (20-100  $\mu\text{m}$ ) M3 olivine 'foam' microstructure, localised along metric-sized, localized shear zones within sub-crustal levels  $650\text{-}700^\circ\text{C}$  and under a high differential stress (70-100 MPa).

These olivine microstructures are a common feature of several dunitic/harzburgitic bodies in the Scandinavian Caledonides (Clos et al., 2014). Olivine fabric analysis is therefore a very powerful tool to gain insight on crystallization conditions and provenance of ultra-depleted orogenic peridotites, where 'classic' geothermobarometry is useless.

Clos F., Gilio M., Van Roermund H.L.M. 2014. Fragments of deeper parts of the hanging wall mantle preserved as orogenic peridotites in the central belt of the Seve Nappe Complex, Sweden. *Lithos* 192-195, 8-20.

Gilio M. & van Roermund H.L. 2013. The Friningen Garnet Peridotite (central Sweden): a good example of the characteristic PTt path of a cold mantle wedge garnet peridotite. In 10th International Eclogite Conference, 41.

Janák M., Van Roermund H.L.M., Majka J.C., Gee D.G. 2013. UHP metamorphism recorded by kyanite-bearing eclogite in the Seve Nappe Complex of northern Jämtland, Swedish Caledonides. *Gondwana Research* 23(3), 865-879.

Van Roermund H.L.M. 1989. High-pressure ultramafic rocks from the allochthonous nappes of the Swedish Caledonides, in: Grayer R. A. (Eds.), *The Caledonide Geology of Scandinavia*, Graham and Trotman, London, 205-219.

Van Roermund H.L.M. 2009. Mantle-wedge garnet peridotites from the northernmost ultra-high pressure domain of the Western Gneiss Region, SW Norway. *European Journal of Mineralogy* 21, 1085-1096.

## From mega- to microscopic and back: The P-T-t-D history of HP rocks from the Sesia Zone

Giuntoli F.\*, Lanari P., Burn M. & Engi M.

Institut für Geologie, University of Bern, Switzerland.

Corresponding email: [francesco.giuntoli@geo.unibe.ch](mailto:francesco.giuntoli@geo.unibe.ch)

Keywords: Microstructural, geochronology, Sesia Zone.

Dating individual stages of the metamorphic evolution has become a key point to understand metamorphic terranes. The critical aspect remains how to link age data derived from in situ geochronology of accessory minerals (here allanite) with the mineral assemblages and the P-T conditions derived from these.

This field-based study investigates the Sesia Zone, a continental terrane derived from the NW-Adriatic margin and polydeformed at eclogite-facies conditions during Alpine convergence. The samples studied in detail belong to the central part of the Eclogitic Micaschist Complex. Assemblages comprise multiple generations of phengite, garnet, quartz, epidote, chlorite, allanite and rutile, locally with glaucophane and/or jadeite, or chloritoid.

X-ray maps of garnet show complex zoning, with a late Paleozoic porphyroclastic core surrounded by three Alpine overgrowth zones. Inclusions are abundant: Between the core and the first Alpine rim they are quartz only, but rutile crystals are frequent within the second Alpine rim, and glaucophane + phengite locally occur within rim2 or between rim2 and rim3.

These overgrowth zones can be linked to individual HP stages, if the bulk rock composition (based on XRF analyses) is corrected for the effects of the pre-Alpine cores. Rim1 and rim3 are found to have formed during very similar conditions (~600°C and 1.6-1.8 GPa), but rim1 is prograde and rim3 is retrograde. Rim2 may reflect the pressure peak (~600°C and 1.8-2.0 GPa). The Si isopleths of phengites and the glaucophane composition are in line with these HP stages.

The allanite crystals show a core rich in LREE, up to three rim generations with lower LREE contents, and a final rim of clinozoisite. The allanite core includes rutile and HP phengite (Si~3.3 a.p.f.u.). This inclusion suggests a correlation between the 2 alpine rims of the garnet; however work is in progress (e.g. REE pattern in garnet and phengite).

Preliminary Th-Pb ages of allanite cores (in situ LA-ICP-MS analysis) span between 75-60 Ma. These ages compare well with the two HP stages (HP1: ~75 Ma; HP2: ~65 Ma) found in several samples of the Fondo slice of the Sesia Zone (Regis et al., 2014).

Ongoing work aims to integrate these data for individual samples at the regional scale, using the spatial and structural relations mapped in this project. The diversity of the results obtained clearly shows that the Sesia terrain comprises several slices and is not as uniform as previously thought.

Regis D., Rubatto D., Darling J., Cenko-Tok B., Zucali M. & Engi M. 2014. U-Th/Pb petrochronology: Deciphering the metamorphic dynamics in an eclogite facies terrane (Sesia Zone, Western Alps). *Journal of Petrology* (in press).

## Structural, metamorphic and geochronological constraints of the Himalayan metamorphic core (HMC) in Western Nepal (Central Himalaya)

Iaccarino S.\*<sup>1</sup>, Montomoli C.<sup>1</sup>, Carosi R.<sup>2</sup>, Massonne H.J.<sup>3</sup>, Langone A.<sup>4</sup> & Visonà D.<sup>5</sup>

1. Dipartimento di Scienze della Terra, Univ. of Pisa. 2. Dipartimento di Scienze della Terra, Univ. of Torino. 3. Institut für Mineralogie und Kristallchemie, Univ. of Stuttgart, Germany. 4. C.N.R. Istituto di Geoscienze e Georisorse, U.O.S. Pavia. 5. Dipartimento di Geoscienze, Univ. of Padova.

Corresponding email: [iaccarino@dst.unipi.it](mailto:iaccarino@dst.unipi.it)

Keywords: Himalaya, monazite textural geochronology, metamorphism.

The Himalayan belt is often regarded as the premier example of continent-continent collisional tectonics and is seen as a proxy for understanding the evolution of ancient orogenic belts (e.g. Jamieson & Beaumont 2013). Several important geodynamic processes, currently among the major topics of geosciences, like syn-compressional extension, feedback relations between climate and tectonics, rheological implications and exhumation consequences in response to crustal melting, have been developed starting from studies of the Himalayas (e.g. Jamieson & Beaumont 2013). In this contribution we describe the tectono-metamorphic evolution of the Himalayan metamorphic core (HMC) in the Mugu Karnali area in Western Nepal (Montomoli et al., 2013), where a complete and well-exposed cross section of the belt, starting from the Lesser Himalaya up to the Tethyan Sedimentary Sequence (TSS), has been studied. Moreover, in this area, a huge leucogranitic body, the Mugu granite, intrudes the migmatitic portion (in the core of HMC) and probably the base of the TSS.

Combining meso-microstructural observations, pseudosection modeling (as well as MET approach), trace element thermometry (e.g. Zr-in-rutile thermometry, Tomkins et al., 2007) and textural geochronology, we present pressure-temperature-deformation-time (P-T-D-t) paths for representative samples along the whole section, ranging from structurally lower chlorite-garnet-bearing rocks (>500°C, 0.8 GPa) up to kyanite-sillimanite-bearing migmatites (>720°C, 1.1-0.7 GPa) and cordierite-bearing gneiss (c. 650-700°C, 0.6 GPa).

Pseudosection modeling coupled with textural and chemical characterization of monazite grains provides a framework for the rigorous interpretation of the timing of monazite growth along the P-T-D path (e.g. Foster & Parrish, 2003, Spear & Pyle 2010). In this way, time constrained P-T-D paths from different structural positions within the HMC could be compared with particle paths obtained from numerical modeling in order to quantify geodynamic processes at the collisional front of large-hot orogenic belts.

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## Metamorphic evolution of the Cerro del Almirez ultramafic rocks (Betic Cordillera, South Spain) as a proxy to dehydration processes taking place during subduction

López Sánchez-Vizcaíno, V.\*<sup>1</sup>, Gómez-Pugnaire M.T.<sup>2-4</sup>, Padrón-Navarta J.A.<sup>3</sup>, Garrido-Marín C.J.<sup>4</sup>, Marchesi C.<sup>2-4</sup> & Jabaloy A.<sup>5</sup>

1. Departamento de Geología, Universidad de Jaén, Linares (Jaén), Spain. 2. Departamento de Mineralogía y Petrología, Universidad de Granada, Granada, Spain. 3. Géosciences Montpellier, UMR 5243, CNRS-Université Montpellier II, Montpellier, France. 4. Instituto Andaluz de Ciencias de la Tierra, CSIC-Universidad de Granada, Armilla (Granada), Spain. 5. Departamento de Geodinámica, Universidad de Granada, Granada, Spain.

Corresponding email: [vlopez@ujaen.es](mailto:vlopez@ujaen.es)

Keywords: Serpentinites, subduction, metamorphism, dehydration, fluids release.

Serpentinites are the main carriers of water in subduction zones. The dehydration reaction of antigorite (releasing up to ~ 9 wt % H<sub>2</sub>O) affects the composition and rheology of the plates, induces intermediate-depth earthquakes in the slab and plays a fundamental role in the production of arc lavas and in the transference of elements between different domains. The Cerro del Almirez ultramafic massif is the only known locality where the arrested dehydration front due to antigorite breakdown at high pressure conditions has been preserved (Padrón-Navarta et al., 2010). Since the work by Trommsdorff et al. (1998) these outcrops have revealed as a unique setting to investigate the prograde metamorphic evolution from antigorite serpentinite to chlorite harzburgite and its various implications. Atg-serpentinite preserves both prograde mineral assemblages and subduction-related structures. Prior to breakdown, antigorite is Al-rich and exceptionally ordered from a microstructural point of view. Transitional lithologies occur as well preserved layers in between Atg-serpentinite and Chl-harzburgite all along the devolatilization front. The gradual disappearance of antigorite leads to the final prograde assemblage in Chl-harzburgite with two contrasting textures: granofelsic (with coarse, round olivine) and spinifex-like (dendritic-like, cm-sized olivine and orthopyroxene) that occur as interspersed, m-sized boudins. We ascribe these textures to shifts of the growth rate ultimately controlled by variations of the excess fluid pressure and the hydrodynamics of fluid expulsion. Fluids channelling is evidenced by the occurrence of grain-size reduction zones, a few mm to meters wide, with roughly planar conjugate structures. We interpret them as brittle structures generated by hydrofracturing by overpressure fluids in a compressional setting in an otherwise almost impermeable peridotite. This might be an essential mechanism in the first stages of fluid flow through the coldest parts of top-slab mantle in subduction zones. The main geochemical effects of dehydration are, on the one hand, the loss of LREE–MREE, water, and sulfur, which can contribute to <sup>18</sup>O, D, and <sup>34</sup>S enrichments and oxidation of the sub-arc mantle wedge. On the other hand, Chl-harzburgite is enriched in Ti and the most compatible HREEs (Tm, Yb and Lu) as well as in Th, U, Nb, Ta, Pb, Sr due to fluid circulation in an open system, and thus contributing to their recycling in deep regions of the mantle.

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Padrón-Navarta J.A., Tommasi A., Garrido C.J., López Sánchez-Vizcaíno V., Gómez-Pugnaire M.T., Jabaloy A., Vauchez A. 2010. Fluid transfer into the wedge controlled by high-pressure hydrofracturing in the cold top-slab mantle. *Earth Planet. Sci. Lett.*, 297, 271-286.

## Is the Ivrea-Verbanò Zone subdivided in two sectors? New insights from the Kinzigite Formation exposed in the Val Cannobina (northern Italy)

Langone A.\*<sup>1</sup>, Tiepolo M.<sup>1</sup>, Zanetti A.<sup>1</sup>, Mazzucchelli M.<sup>1-2</sup>, Bergamaschi C.<sup>3</sup>

1. IGG-CNR U.O.S. of Pavia, 27100 Pavia - Italy 2. Dipartimento di Scienze Chimiche e Geologiche – Università di Modena e Reggio Emilia 3. Dipartimento di Scienze della Terra e dell'Ambiente - Università di Pavia

Corresponding email: [langone@crystal.unipv.it](mailto:langone@crystal.unipv.it)

Keywords: Ivrea-Verbanò Zone, Val Cannobina, P-T-t reconstructions.

The Ivrea-Verbanò Zone (IVZ, Southern Alps), in northern Italy, is part of the pre-Alpine basement characterized by the exposure of a well-preserved lower crustal section. The middle-lower crustal rocks of the IVZ have commonly been subdivided in three major units, from bottom to top: i) different ultramafic mantle bodies; ii) the Mafic Complex (MC), which represents an intrusive complex (gabbros, norites and diorites); iii) the Kinzigite Formation (KF), consisting of amphibolite- to granulite-facies metapelites with subordinate metabasites, marbles and calc-silicate gneisses.

U-Pb zircon data on the MC indicate an emplacement at 295-280 Ma in the central sector of the IVZ (Peressini et al., 2007, and references therein) and at about 232 Ma in the north-eastern sector (External Gabbro, Finero Complex; Zanetti et al., 2013). The Permian intrusion was coeval with granite intrusions in the middle-upper crust and rhyolitic volcanism, while the Triassic intrusion was concurrent with the activity of (low-/high-temperature) shear zones.

In order to shed light on the observed diachronism of the MC and to provide useful insights on the tectonic evolution, new P-T-t data from the KF exposed in the Val Cannobina (Cursolo-Orasso area) were carried out. Here, the KF shows the narrowest thickness and is partially affected by mylonitic deformation. It mainly consists of micaschists and migmatitic paragneisses, dominant at the higher structural levels (SE), and amphibolites, prevailing at the contact with the MC (lower structural levels; NW; Boriani & Burlini, 1995). Septa, both mafic and metapelitic in composition, occur within the MC and show granulite-facies metamorphism. Metapelites are mainly composed of Pl, Qtz, Bt, Grt and Sil. With increasing the metamorphic grade (towards NW), the abundance of Bt decreases, that of Grt increases and fibrolitic Sil is progressively replaced by prismatic Sil. Preliminary P-T estimates on metapelites indicate P of about 0.4 GPa and T ranging from 620 to 700°C. The septa show T higher than 800°C. Preliminary U-Pb dates on monazite from the migmatitic paragneisses zone indicate that an HT metamorphic event occurred at about 277 Ma, coherently with other areas of the IVZ. A single age at 225±7 Ma obtained from a narrow rim suggests a later perturbation of the U-Pb system.

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Zanetti A., Mazzucchelli M., Sinigoi S., Giovanardi T., Peressini G. & Fanning M. 2013. SHRIMP U-Pb zircon Triassic intrusion age of the Finero Mafic Complex (Ivrea-Verbanò Zone, Western Alps) and its geodynamic implications. *J. Petrol.*, 54, 2235-2265.

## Linking the formation of coronitic microstructures around monazite to the growth of garnet in the Pontremoli well metapelites (Northern Apennines, Italy)

Lo Pò D.\*<sup>1</sup>, Braga R.<sup>1</sup>, Theye T.<sup>2</sup>, Massonne H.-J.<sup>2</sup>, Montanini A.<sup>3</sup> & Molli G.<sup>4</sup>

1. Dipartimento di Scienze Biologiche, Geologiche ed Ambientali, Università di Bologna. 2. Institut für Mineralogie und Kristallchemie, Universität Stuttgart. 3. Dipartimento di Fisica e Scienze della Terra, Università di Parma. 4. Dipartimento di Scienze della Terra, Università di Pisa.

Corresponding email: [deborah.lopo@unibo.it](mailto:deborah.lopo@unibo.it)

Keywords: REE-minerals, garnet zoning, thermodynamic modelling.

The linkage of textural and petrological information, and mineral dating is central to understand the evolution of orogenic belts. In this regard, the relation between zoned metamorphic minerals, that define *P-T* paths, and accessory minerals, that provide geochronological information, is a source of uncertainties, which in turn will affect the quality of the reconstruction of lithospheric processes. In this contribution, a complex polymetamorphic history of a rock is deciphered on the basis of replacement microstructures of monazite, chemical variations in garnet porphyroblasts, and a detailed study of the garnet inclusion mineralogy combined with investigations of element partitioning between garnet and accessory minerals such as REE-rich minerals.

Garnet-bearing metapelites of the Micaschist Complex drilled in the Pontremoli 1 well belong to the Variscan basement of the Northern Apennines (Italy). Samples of these rocks contain coronitic microstructures around monazite grains, consisting of an apatite ring, allanite shell and epidote rim. Garnet porphyroblasts, which show a typical prograde growth zoning, enclose xenotime, allanite and epidote in their inner core, outer core and rim, respectively. Discontinuous variation of Y may be attributed to garnet growth during xenotime breakdown. Moreover, the Ca and P chemical profiles in garnet indicate a simultaneous crystallization of the inner core of garnet and apatite. The garnet composition can thus record modifications in the accessory mineral assemblage. The microstructure and chemistry of the monazite grains suggest that the monazite was an early mineral and underwent partial to total decomposition at peak metamorphic conditions. The chemical age of  $296 \pm 6$  Ma should be older than the garnet-forming metamorphic stage.

Thermodynamic modelling permitted also to obtain a counterclockwise *P-T* path for the studied sample: the prograde evolution developed to a metamorphic peak close to 600°C and 7 kbar, and was followed by the peak pressure stage at 520°C and 8 kbar during which Mg-rich muscovite and chlorite with decussate structure crystallize. The replacement of early monazite by apatite, allanite and epidote, inferred through a correlation with the garnet isopleth *P-T* constraints, occurred during the prograde evolution at 500-600°C and 5-7 kbar. A nearly isobaric cooling is responsible for the late observed stage at 500°C and 2 kbar.

The obtained *P-T* path is different from the previously proposed trajectories for the Variscan basement of the Northern Apennines. The tectonic implications of this polymetamorphic evolution will be discussed.

## Geobarometry for host-inclusion systems: the role of elastic relaxation

Mazzucchelli M.L.\*<sup>1</sup>, Angel R.J.<sup>2</sup>, Alvaro M.<sup>2</sup>, Nestola F.<sup>2</sup> & Nimis P.<sup>2</sup>

1. Dipartimento di Scienze della Terra e dell'Ambiente - Università degli Studi di Pavia. 2. Dipartimento di Geoscienze – Università degli Studi di Padova.

Corresponding email: [mattialuca.mazzucchelli01@universitadipavia.it](mailto:mattialuca.mazzucchelli01@universitadipavia.it)

Keywords: Inclusion, Relaxation, Equations of State.

Conventional thermo-barometric methods can be challenged in UHPM terranes as the temperatures of deep subduction often exceed the closure temperature of geothermobarometers, and they are also afflicted by the effects of further reactions and re-equilibration on exhumation. The elastic behavior of mineral inclusions trapped in host mineral phases contained in UHPM rocks provides an alternative method that is independent of chemistry and chemical equilibria. Minerals trapped as inclusions within other host minerals will develop residual stresses on exhumation as a result of the differences between the thermo-elastic properties of the host and inclusion phases. Measurement of the residual stress in the inclusions in combination with the equations of state (EoS) of the two phases, can be used to infer the pressures of entrapment. However, until now, even the simplest elastic system of a single inclusion embedded in an isotropic host has not been properly addressed for geological systems. Previous analyses (i.e. Zhang, 1998) have relied on the assumption of linear elasticity and invariant elastic properties of the minerals with  $P$  and  $T$ , or assume that the host material is completely rigid. These assumptions are not physically correct.

We will present a solution to the single-inclusion problem that incorporates non-linear elasticity and can be applied to determine the stress distribution in the host and inclusion that arises from any change in  $P$  and  $T$ . Our solution shows that the previous calculations of residual inclusion pressures are incorrect in the relaxation term. The relaxation arises from the difference in stress at the host/inclusion interface that will force the interface outwards thus increasing the radial stress in the host adjacent to the inclusion, and decreasing the  $P$  inside the inclusion. The errors from linear elasticity theory are greater with softer hosts, and when the final conditions are not at ambient  $P$  and  $T$ .

The general form of our solution relies on the concept of the isomeke, a line in  $P$ - $T$  space along which the fractional volume changes of the host and inclusion are the same. This allows our solution to be used in combination with any form of equation of state and/or thermal expansion, and is not restricted to linear elasticity or just invertible EoS. Calculations can be performed with Eosfit7c (Angel et al. 2014).

*This work was supported by ERC starting grant 307322 to Fabrizio Nestola.*

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Zhang Y. 1998. Mechanical and phase equilibria in inclusion–host systems. *Earth and Planetary Science Letters*, 157, 209-222.

## Exhumation of the crystalline core of the Himalaya: relations between the South Tibetan Detachment and leucogranite emplacement in Western Nepal

Montomoli C.\*<sup>1</sup>, Carosi R.<sup>2</sup>, Visonà D.<sup>3</sup>, Iaccarino S.<sup>1</sup> & Langone A.<sup>4</sup>

1. Dipartimento di Scienze della Terra - Università di Pisa. 2. Dipartimento di Scienze della Terra - Università di Torino  
3. Dipartimento di Geoscienze - Università di Padova. 4. IGG-CNR Pavia.

Corresponding email: [chiara.montomoli@unipi.it](mailto:chiara.montomoli@unipi.it)

Keywords: Himalaya, STDS, exhumation.

The architecture of the South Tibetan Detachment System, separating the lower medium to high-grade metamorphic rocks of the Greater Himalayan Sequence (GHS) from the overlying Tethyan Himalayan Sequence (THS) is complex. It is characterized by a lower ductile shear zone, affecting the upper part of the GHS (Carosi et al., 1998) and the amphibolites facies rocks at the bottom of the THS (lower THS) and by an upper brittle fault, above which the very-low-grade to non metamorphic rocks of the THS (upper THS) crop out. According to most workers the High Himalayan granites (HHG), located in the upper part of the GHS, intrude and are deformed by the lower ductile shear zone of the STDS.

We report new data from a geological transect located in Western Nepal where the STDS shows a peculiar structural setting.

In the study area the upper portion of the Greater Himalayan Sequence is made by gneiss, migmatites and calcilicates.

The THS is characterized by a lower portion made by garnet and cordierite bearing gneisses. P-T pseudosection modelling, reveal as the observed assemblage is stable in the range of 0.53-0.65 GPa and 610-720°C.

The upper portion the THS is made by biotite-bearing quartzites, impure limestone, metarenites and subordinate metapelites with a metamorphic assemblage of calcite, quartz, muscovite, biotite ± chlorite and scapolite, indicating greenschist facies conditions. Detrital zircon ages indicate a depositional age from upper Jurassic to lower Cretaceous.

The boundary between the GHS and the THS is intruded by a large leucogranitic body showing a crystallization age at 23-24 Ma (Carosi et al. 2013), constraining the time of youngest shearing event between the two tectonic units.

Dykes from the upper portion of the granite intrude the low-grade metamorphic rocks of the THS causing contact metamorphism within few meters from the granite contact. The low grade foliation is overgrown by biotite and muscovite. The intrusion closest samples show static crystallization of amphibole, clinopyroxene and annealing of calcite-plagioclase-quartz (± kfeldspar) matrix. On the previous samples, in order to quantify the depth of pluton emplacement, a set of geothermobarometric methods have been applied. A broad consistency of all the methods points out a T of equilibration around 600-640°C and a P of nearly 0.5 GPa.

Structural relations and time of emplacement of the leucogranite cast doubts on the exhumation models widely adopted till now for the Himalayan belt.

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## **Petrological and structural studies in the eastern Nepal Himalaya: data for a geological map and constraints for tectonic models**

Mosca P.\*<sup>1</sup>, Groppo C.<sup>2</sup> & Rolfo F.<sup>1-2</sup>

1. Istituto di Geoscienze e Georisorse, UO Torino, CNR. 2. Dipartimento di Scienze della Terra, Università di Torino.

Corresponding email: [p.mosca@csg.to.cnr.it](mailto:p.mosca@csg.to.cnr.it)

Keywords: Himalaya, metamorphism, geological map, tectonic models.

The Himalayan orogen comprises few lithotectonic units extending throughout the length of the chain and separated by major north-dipping tectonic contacts. From lower to upper structural levels (and from south to north) these are the sub-Himalaya, the metamorphic Lesser Himalayan Sequence (LHS) and Greater Himalaya sequence (GHS, subdivided into a lower GHS and upper GHS or Higher Himalayan Crystallines-HHC), and the Tibetan Sedimentary Series.

This contribution discusses petrological and structural data collected from metamorphic units outcropping along several geotraverses in the eastern Nepal Himalaya (e.g. Khimti Khola, Likhu Khola, Dudh Khosi, Arun and Tamur tectonic windows), with the aim of: i) interpreting the geological setting and presenting an original geological map of the eastern Nepal, ii) discussing the P-T metamorphic evolution of the different exposed units, and iii) compare their P-T evolutions with tectonic models proposed for the development of the Himalaya.

At a regional-scale, the investigated area shows a structural setting dominated by a dip to the north of major faults and composite foliations, and the units recorded polyphase ductile to brittle-ductile deformations. The metamorphic grade increases toward higher structural levels, passing from the low- to medium-grade LHS to the high-grade HHC across the lower GHS. The lower GHS is roughly coincident with the Main Central Thrust Zone (MCTZ), a several km-thick shear zone extending along strike all along the Himalayas and driving the southwards extrusion of the high grade rocks over the low grade rocks.

More in detail, along the investigated geotraverses, the metamorphic assemblages range from the low-grade chlorite and garnet zones (LHS), to the medium-grade garnet-biotite, staurolite and kyanite zones (lower part of the MCTZ), up to the sillimanite zone and a further zone of incipient partial melting with breakdown of muscovite and formation of K-feldspar (upper part of the MCTZ). Structurally above the MCTZ, anatexis is widespread in the HHC and is recorded by granulite-facies kyanite-bearing metapelite, in turn followed up section by cordierite-bearing, kyanite-free gneiss.

Structural observations integrated with petrography, mineral chemistry, and petrologic modeling revealed the juxtaposition of rock packages characterized by different P-T evolution and T/depth gradients across the MCTZ and its adjacent domains. A similar setting reveals an imbricate nature of the MCTZ itself, thus emphasizing the complexity of tectonic processes operating during the exhumation of the metamorphic units in the Himalaya.

## Evidence of rodingitization process within Ophiolite Units (Liguride Units, Southern Apennines - Italy)

Ortolano G.<sup>1</sup>, Rizzo G.\*<sup>2</sup>, Sansone M.T.C.<sup>2</sup> & Cirrincione R.<sup>1</sup>

1. Dipartimento di Scienze Biologiche, Geologiche ed Ambientali, Università degli Studi di Catania

2. Dipartimento di Scienze, Università degli Studi della Basilicata, Potenza.

Corresponding email: [giovanna.rizzo@unibas.it](mailto:giovanna.rizzo@unibas.it)

Keywords: Rodingites, ophiolites, southern Apennines.

New petrological data of the ophiolitic sequences from the Liguride Units (Southern Apennine Chain) are here presented in order to investigate some rodingite dykes preserved within un-sheared low strain domains. Liguride Units shows indeed pervasive shear deformations, developed during subduction process reaching HP/LT conditions typical of blueschist facies (Cirrincione & Monaco, 1996). Nevertheless, local low strain domains are preserved and within these, rodingite dikes occur. The rodingite dikes is composed of garnet, prehnite, chlorite, pumpellyite, and quartz. Hydrogrossularite, prehnite, epidote, calcite, and titanite replace plagioclase and produce Ca-rich basic rocks during hydrothermal alteration of sub-greenschist to greenschist facies metabasalts (Sansone et al., 2011).

The process usually is initialized during the early stage of ocean crust evolution and can continue at later stages of the oceanic crust history (Charlou et al., 1998). It is catalyzed by metasomatism, triggered by injection of Ca<sup>2+</sup> ions from high alkaline content fluids, probably released during the ocean-floor metamorphism.

In order to extrapolate new quantitative petrological data from this process, after propaedeutic optical and electron-microprobe analytical sessions, a multivariate statistical data handling of X-ray maps, representative for some garnet-replacing plagioclase microdomains have been carried out by means of X-Ray Micro Analyzer software (Ortolano et al., in press). Obtained results were then used for the computation of useful phase diagrams, able to reconstruct the sequence of the metamorphic reactions evolved during the rodingitization process as a tracer of the original ocean floor metamorphic conditions of the Liguride ocean, today merged into the southern sector of the Apennine chain, evaluating at the same time the potential metamorphic effects operating during the following tectonic staking activity of the Frido Unit (Sansone et al., 2011).

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Sansone M.T.C., Rizzo G., Mongelli G. 2011. Petrochemical characterization of mafic rocks from Ligurian ophiolites, southern Apennines. *Int. Geol. Rev.*, 53, 130-156.

## Sequential atoll-shaped garnets formation from the Aspromonte Peloritani unit (northeastern Sicily-Italy): Petrogenetic and Geothermobarometric implications

Ortolano G.<sup>1</sup>, Visalli R.\*<sup>1</sup>, Cirrincione R.<sup>1</sup> & Rebay G.<sup>2</sup>

1. Università degli Studi di Catania, Dipartimento di Scienze Biologiche, Geologiche e Ambientali. 2. Università degli Studi di Pavia, Dipartimento di Scienze della Terra e dell'Ambiente.

Corresponding email: [v\\_roberto@hotmail.it](mailto:v_roberto@hotmail.it)

Keywords: atoll garnets, image analysis, pseudosections.

Micaschist from Santa Lucia del Mela zone, (Peloritani Mountains), were studied by integrating information obtained from petrographic analysis, image assisted analysis on mineral phases compositions using X-Ray maps and thermodynamic modeling. These rocks are characterized by the presence of atoll garnets, and preserve a continuous array of textures from pristine garnets, to atoll textures, to completely substituted garnets. These textures are linked to the metamorphic evolution of the rocks, consisting of three main stages of metamorphic recrystallization and related deformation are recognized.

The sequence of mineral parageneses recognised to successive deformation events is as follow: D1 is characterised by the assemblage  $wm1 + chl1 + bt1 + pl1 + grt1$  (Inner Core) +  $qtz + ilm + ap$ ; D2 by  $grt2$  (a and b Relic Outer Core and Relic Rim) +  $wm2 + chl2 + bt2 + pl2 + qtz + ilm + ap + hem$ ; D3 (associated to garnet core transformation) by  $grt3$  (New Rim) +  $bt3 + pl3 + wm3 + qtz + chl3 + ilm$ .

On the basis of textural observations and mineral parageneses, the atoll formation is related to the substitution of garnet cores during the D3 stage, with the consumption of garnet cores ( $grt1$ ) and production of new garnet rim  $grt3$  with  $wm$ ,  $bi$ ,  $qtz$  and  $pl$ . The recognition of the different stages of garnet growth and associated parageneses has been obtained using image analysis coupled with compositional maps, performed with a dedicated software (Ortolano et al., in press).

Following the textural and minerochemical analyses, PT conditions associated to the three recrystallization phases have been determined from pseudosections. In order to determine the equilibrium volumes during the different stages of the metamorphic evolution, bulk compositions were determined by XRF and by modal determinations assisted by image analysis. Results indicate that in the Mela rocks is recorded a prograde evolution to amphibolite facies conditions in garnet cores, followed by decompression associated to the heating to lower amphibolite facies, and finally by a temperature increase, probably associated to the intrusion of late Variscan granitoids that are widespread in this unit.

Ortolano G., Zappalà L., Mazzoleni P. (in press). X-Ray Map Analyzer: a new ArcGIS® based tool for the quantitative statistical data handling of X-ray maps (Geo- and Material-science applications).

## Preliminary study on polymorphs of serpentine of the Koniambo Massif (New Caledonia)

Petriglieri J.R.\*<sup>1</sup>, Salvioli-Mariani E.<sup>1</sup>, Mantovani L.<sup>1</sup>, Tribaudino M.<sup>1</sup>, Bersani D.<sup>1</sup>, Lottici P.P.<sup>1</sup> & Laporte-Magoni C.<sup>2</sup>

1. Department of Physics and Earth Sciences- University of Parma. 2. Laboratoire PPME- Université de la Nouvelle Calédonie.

Corresponding email: [jasmine.petriglieri@gmail.com](mailto:jasmine.petriglieri@gmail.com)

Keywords: New Caledonia, harzburgite, dunite, serpentine, Raman spectroscopy.

The Koniambo Massif is part of a mountain chain located along the west coast of Grande Terre island, the main island of New Caledonia archipelago. It is composed of three major lithological assemblages of mantle and crustal origin: a strongly serpentized harzburgite-dunite sequence at the base, followed by a spinel dunite sequence and at the top a succession of layers of harzburgite and minor dunite, which changes to harzburgite on the summit. These associations overlap the Poya Unit, a portion of the upper part of the oceanic crust containing basalts, gabbros and dolerites. The basal unit harzburgite-dunite is totally serpentized and strongly silicified. The overlying dunitites show an homogeneous fine texture: olivine grains altered into serpentine (about 30%) are associated to smaller quantities (less than 1%) of orthopyroxene and spinel. The proportion of orthopyroxene increases from the bottom to the top of the sequence. The upper sequence is mainly composed by harzburgite with alternating layers of dunite, where clinopyroxene is an accessory phase. Rare layers of dunite form thin (< 1 m) and discontinuous horizons. All these sequences represent portions of obducted oceanic plate as a result of compressive tectonics (Ulrich *et al.*, 2010). There are many studies in the literature about the characterization of the minerals of the serpentine family, but a complete methodology, able to distinguish the different polymorphs of the group, is still lacking. This work introduces an innovative analytical strategy that allows to recognize these polymorphs, involving Raman spectroscopy. Samples, coming from the basal and middle sequences of the massif, were studied by means of optical microscopy, SEM-EDS and micro-Raman spectroscopy. Optical microscopy and SEM allow the observation of textural relationships and morphological features of the phases, Raman spectroscopy is essential in the identification of the polymorphs of serpentine group. Raman peaks observed in the high-wavenumber spectral range 3550-3850 cm<sup>-1</sup> associated with OH stretching vibrations, allow the identification of chrysotile, lizardite, antigorite and polygonal serpentine varieties (Auzende *at al.*, 2004). However, whereas spot analyses alone are not fully adequate to investigate the relationship between the different varieties of serpentine in complex samples, two-dimensional Raman maps are very useful. The main advantage is to recognize the serpentine polymorphs directly on the sample, within their textural environment at the micrometer scale.

Auzende A-L., Daniel I., Reynard B., Lemaire C. & Guyot F. 2004. High-pressure behavior of serpentine minerals: a Raman spectroscopic study. *Phys Chem Minerals*, 31, 269-277.

Ulrich M., Picard C., Guillot S., Chauvel C., Cluzel D. & Meffre S. 2010. Multiple melting stages and refertilization as indicators for ridge to subduction formation: The New Caledonia ophiolite. *Lithos*, 115, 223-236.

## Fluid rock interactions as recorded by Cl-rich amphiboles from continental and oceanic crust of Italian orogenic belts

Rebay G.\*<sup>1</sup>, Riccardi M.P.<sup>1</sup> & Spalla M.I.<sup>2-3</sup>

1. Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia. 2. Dipartimento di Scienze della Terra, Università di Milano.  
3. IDPA-CNR, Milano.

Corresponding email: [gisella.rebay@unipv.it](mailto:gisella.rebay@unipv.it)

Keywords: Cl-Amphibole, fluids, metamorphism.

A series of Cl-rich amphiboles coming from oceanic and sub-continental gabbro bodies has been studied in order to compare their microstructural and compositional peculiarities and investigate the fluid-rock interactions in different geodynamic contexts. The first group of amphiboles is within gabbros from the Northern Apennines, and developed subsequently to an hydration event ascribed to oceanic metamorphism (Riccardi, 1994). The second group is found in a slice of continental crust subducted during Alpine collision, within a subcontinental metagabbro from the Sesia-Lanzo Zone of Western Italian Alps. The development of these amphiboles has been ascribed to a hydrothermal event that took place after the exhumation of the metagabbro during pre-Alpine lithospheric extension (Rebay & Spalla, 2001).

The Cl-amphiboles are either found in veins or as rims of zoned amphiboles, where brown-amphibole cores (sometimes Ti-rich), and green amphibole rims, are rimmed by the Cl-rich amphibole. All amphiboles show edenbergite to pargasite compositions, with a direct correlation between Fe and  $Na_A$  vs. Cl content, and inverse correlation of Mg and  $Na_{M4}$  vs. Cl.

A comparison with other Cl-amphiboles that have been observed both in oceanic and continental settings, allow to determine the role played by Cl-rich fluids infiltration in oceanic and continental crust, during lithospheric extension.

The large variations in Si,  $Al^{IV}$ ,  $Al^{VI}$ , Fe, Mg, K and Cl may be related to the  $a_{HCl/fluid}/a_{H_2O/fluid}$  ratio of the fluid in equilibrium with the amphiboles at various stages of the metamorphic evolution. Amphiboles that locally contain extremely high Cl contents (up to 4% wt) could have been in equilibrium with a locally enriched Cl-fluid. As suggested by the fact that the Cl content of amphibole into the veins is generally lower than in amphibole rims, far from the veins, these equilibrium conditions probably were reached at places where the system resulted locally closed. In addition hydration reaction consumed the  $H_2O$  component of the fluid, leaving a Cl-enriched fluid, that then re-equilibrated with the crystallising amphibole. Equilibration temperatures are up to 350°C for the amphiboles from the Apennines, and up to 550°C for those from the Sesia-Lanzo Zone.

Rebay G. and Spalla M.I., 2001. Emplacement at granulite facies conditions of the Sesia-Lanzo metagabbros: early record of Permian rifting? *Lithos* 58, 85-104.

Riccardi M.P. 1994. Gli anfiboli legati al metamorfismo oceanico dei metagabbri ofiolitici dell'Appennino settentrionale: aspetti composizionali e cristallografici. PhD thesis, Pavia.

## Probing deep CO<sub>2</sub> production in a collisional orogen with petrology

Rolfo F.<sup>\*1-2</sup>, Groppo C.<sup>1</sup>, Mosca P.<sup>2</sup> & Castelli D.<sup>1-2</sup>

1. Dipartimento di Scienze della Terra - Università di Torino. 2. IGG-CNR Torino.

Corresponding email: [franco.rolfo@unito.it](mailto:franco.rolfo@unito.it)

Keywords: Metamorphic CO<sub>2</sub>, Calc-silicate rocks, Himalaya.

Active collisional orogens may have strong impact on the global carbon cycle through metamorphic degassing, which would supply a significant fraction of the global solid-Earth derived CO<sub>2</sub> to the atmosphere. The Himalayan belt, a major active “hot” collisional orogen, is a likely candidate for the production of significant amounts of metamorphic CO<sub>2</sub>. Large metamorphic CO<sub>2</sub> fluxes may be triggered by prograde metamorphism of big volumes of impure carbonate rocks. So far, the incomplete knowledge of the nature, magnitude and distribution of the CO<sub>2</sub>-producing processes hampered a reliable quantitative modeling of metamorphic CO<sub>2</sub> fluxes from any collisional orogen.

We focus on the metamorphic decarbonation processes occurring during the Himalayan orogeny and discuss the distribution of metacarbonate rocks, their petrography and petrological data about the nature of the CO<sub>2</sub>-producing reactions.

In the eastern Himalaya, calc-silicate rocks are widespread at different structural levels of the Greater Himalayan Sequence and are intercalated within strongly deformed anatectic metapelites. The studied lithologies are medium- to fine-grained calc-silicate granofels consisting of cm-thick alternated layers differing in mineral modes and compositions; the common equilibrium assemblage consists of Pl + Cpx + Qtz + Grt.

Phase equilibria involving Grt (Grs-Alm s.s.), Zo, Cpx, An, Qtz and Cc in the CFAS–CO<sub>2</sub>–H<sub>2</sub>O system have been investigated using activity-corrected P–T phase diagrams at fixed fluid composition, isobaric T–X(CO<sub>2</sub>) phase diagram sections and phase diagram projections in which fluid composition is not explicitly constrained. The relevance of the Grt-bearing equilibria during metamorphic evolution of calc-silicate rocks is discussed in the light of the observed microstructures and measured mineral compositions.

Petrologic data show that these Grt-bearing calc-silicate rocks may act as CO<sub>2</sub>-source during prograde heating and/or early decompression, releasing internally-derived CO<sub>2</sub>-rich fluids through Grt forming reactions. For suitable bulk rock compositions, the amount of CO<sub>2</sub> released during Grt growth increases with the increase in Grs component. However, in the studied lithologies, coarse-grained graphite is abundant and it has been interpreted as precipitated from the H<sub>2</sub>O–CO<sub>2</sub> fluid released through prograde decarbonation reactions.

The complex interplay between two contrasting processes - i.e. the production of CO<sub>2</sub>-rich fluids versus carbon sequestration through graphite precipitation - must thus be considered when dealing with a global estimate of the role exerted by decarbonation processes on the orogenic CO<sub>2</sub> cycle. Even if calc-silicate rocks may act as a significant CO<sub>2</sub> source during prograde heating, if the system remains closed, fluid–rock interactions may induce hydration of the calc-silicate assemblages and the “in situ” precipitation of graphite, thereby removing carbon from the fluids.

## **Petrology and geochemistry of Alpine peridotites indicate mass transfer during subduction of serpentinized mantle (Cima di Gagnone, Switzerland)**

Scambelluri M.\*<sup>1</sup>, Pettke T.<sup>2</sup>, Cannaò E.<sup>1</sup>, Agostini S.<sup>3</sup>, Tonarini S.<sup>3</sup> & Godard M.<sup>4</sup>

1. University of Genova, Dipartimento di Scienze delle Terra, Ambiente e Vita, Genova, Italy. 2. Institute of Geological Sciences, University of Bern, Bern, Switzerland. 3. IGG CNR Pisa, Italy. 4. Geosciences Montpellier, Université Montpellier 2, Montpellier, France

Corresponding email: [marco.scambelluri@dipteris.unige.it](mailto:marco.scambelluri@dipteris.unige.it)

Keywords: Subduction Mass Transfer Fluids High-pressure Peridotite Serpentinite Trace element.

At Cima di Gagnone, garnet peridotite and chlorite harzburgite lenses within pelitic schists correspond to eclogite-facies breakdown products of hydrated peridotites and are suitable for studying dehydration of serpentinized mantle. Thermobarometry and pseudosection modelling yield peak temperatures of 750-850 C and pressures below 10 GPa. The minimum temperature recorded by the garnet peridotite corresponds to the maximum conditions experienced by the chlorite harzburgite, suggesting that these rocks recrystallized cofacially at 800 C. Alternatively, they might have decoupled during subduction, as achieved in tectonically active plate interface boundaries. The major and rare earth element (REE) variability of the peridotites was mostly acquired during pre-subduction mantle evolution as a result of partial melting and reactive melt flow. The ultramafic suite is also characterized by fluid-mobile element enrichments (B, Pb, As, Sb, Cs, Li, U, Be). Similarity in the U, Pb, B, Li and Sr contents of the Gagnone peridotites to present-day oceanic serpentinites suggests that these elements were partly taken up during initial serpentinization by seawater-derived fluids. Positive Be, As and Sb anomalies and enrichment in radiogenic Sr and Pb of peridotites suggest involvement of fluids equilibrated with crustal (metasedimentary) host rocks during subsequent subduction metamorphism and peridotite entrainment in (meta)sediments. Fluid-mobile element enrichment characterizes all peak eclogitic minerals, implying that multiple hydration events and element influx pre-dated the eclogite-facies dehydration. Peak anhydrous minerals retain B, Li, As and Sb concentrations exceeding primitive mantle values and may introduce geochemical anomalies into the Earth's mantle. The relatively low contents of large ion lithophile elements and light REE in the Gagnone peridotites with respect to much higher enrichments shown by metasomatized garnet peridotite pods hosted in migmatites (Ulen Zone, Eastern Alps) suggest that the crustal rocks at Gagnone did not experience partial melting. The Gagnone garnet peridotite, despite showing evidence for chlorite dehydration, retains significant amounts of fluid-mobile elements documenting that no partial melting occurred upon chlorite breakdown. We propose that the Gagnone ultramafic rocks represent a prime example of multi-stage peridotite hydration and subsequent dehydration in a plate interface setting.

## Mantle wedge and COH fluids: thermodynamic modelling, experiments and natural cases

Tumiati S.\*

Dipartimento di Scienze della Terra, Università di Milano.

Corresponding email: [simone.tumiati@unimi.it](mailto:simone.tumiati@unimi.it)

Keywords: experimental petrology, subduction, COH fluids.

Thermodynamic calculations and experiments predict that high-pressure fluids are dominated by water. Nevertheless, the importance of carbon species has been highlighted in the last years because of the relevant CO<sub>2</sub> content of arc magmas and the observation of carbon-bearing phases in mantle-wedge peridotites (e.g., Ulten zone). In C-free, H<sub>2</sub>O-bearing systems, experiments have shown that the release of volatiles extends over several tens of km depths and result from a succession of continuous and discontinuous reactions involving hydrous phases in the subducted lithosphere, such as antigorite and chlorite in ultramafics; amphibole, lawsonite, zoisite, and chloritoid in mafic rocks. Phengite and biotite are involved in melting reactions of a variety of bulk compositions whenever K is available. In COH-bearing systems, the framework of phase relationships is more complex. COH fluids interact with the mantle-wedge rocks, prompting the growth of carbonates, hydrous minerals and C polymorphs. However, carbonates once formed are refractory and stable at very high pressures. Therefore, it has been proposed that the transport of carbon in the mantle wedge occurs via solute species in aqueous fluids or via advecting rock masses in buoyant “cold plumes” (e.g., Tumiati et al., 2013), but the problem remains still largely unresolved.

Phase relationships in systems bearing COH fluids are strictly dependent on the composition of the fluid itself, i.e., on the speciation of the volatile components of the fluid (H<sub>2</sub>O, CO<sub>2</sub>, CH<sub>4</sub>...) and the presence of solutes deriving from the dissolution of rock-forming minerals. In the scientific literature, the speciation of COH fluids has been generally assessed through thermodynamic calculations using equations of state of simple H<sub>2</sub>O+non-polar gas systems (es. H<sub>2</sub>O-CO<sub>2</sub>-CH<sub>4</sub>), equations that do not consider the complexity related to dissolution processes, which are substantially unexplored in COH fluids. In the pure C-O-H system, C-saturated fluid speciation is a function of the oxygen chemical potential (and therefore oxygen fugacity). Therefore, in natural systems, the fluid speciation can be imposed by the redox state of the rock-forming phases. Alternatively, COH fluids may control the bulk oxidation state of the rock system by redox reactions with the mineral phases. We investigate experimentally the speciation and the dissolution of mantle minerals in COH fluids at buffered *f*O<sub>2</sub> conditions in equilibrium with graphite. Results highlight the importance of fluids for the transport of carbon and other elements in subduction zones. Experimental data, thermodynamic calculations and natural cases will be shown and compared.

Tumiati S., Fumagalli P., Tiraboschi C. & Poli, S. 2013. An experimental study on COH-bearing peridotite up to 3.2 GPa and implications for crust-mantle recycling. *J. Petrol.*, 54, 453-479.

## Lawsonite metasomatism: a new route for volatiles and trace elements in subduction zones

Vitale Brovarone A.\*<sup>1</sup>, Beyssac O.<sup>1</sup> & Alard O.<sup>2</sup>

1. IMPMC, UPMC, Paris, France. 2. Géosciences Montpellier, Université Montpellier II, France.

Corresponding email: [alberto.vitale-brovarone@impmc.upmc.fr](mailto:alberto.vitale-brovarone@impmc.upmc.fr)

Keywords: HP metasomatism, Lawsonite, Volatile recycling

Hybrid rocks formed by fluid-rock interactions at high-pressure (HP) metamorphic conditions are active players in the recycling of volatiles and trace elements in subduction zones. Such rocks include chlorite-talc-amphibole-rich ( $\pm$  carbonate) rocks formed by chemical and mechanical mixing of mafic, ultramafic and sedimentary protoliths. The recent discovery of widespread formation of lawsonite-rich hybrid rocks (Corsica, Guatemala, Urals, Turkey) extends the geological and compositional range of these rocks and their significance for volatile transfer to the deep Earth. We present the geological occurrence of these rocks in the HP units of Alpine Corsica, and their main geochemical features for whole rock and in-situ analyses of zoned lawsonite crystals. Field observations at the belt scale permit to define a metamorphic isograd for lawsonite metasomatism, which was found from a minimum of ca. 360 °C and 1.6 GPa to the maximum P-T conditions of Alpine Corsica, i.e. ca. 530 °C and 2.3 GPa, within a continuous metamorphic gradient. From a geochemical point of view, the whole rock experienced a dramatic chemical modification dominated by Ca gain. Significant mass gain also occurred for a large variety of trace elements, including REE, HFSE and some LILE. Lawsonite may have notable major element zoning, including Fe (up to ca 1.5 wt.%) and Ti (ca. 1 wt.%); some lawsonite crystals in vein also display a marked Cr oscillatory zoning (up to ca. 8 wt.%). In some cases, this variation may be correlated with increasing metamorphic conditions. Moreover, lawsonite compositional zoning permitted to define successive stages of mass transfer during metasomatism. As an example, the trace element composition of different lawsonite zones has remarkable variations, comprising LILE and HFSE. Altogether, these data point to mixed fluid sources including serpentinite-, mafic- and sediment-derived fluids, along channelized fluid pathways. The chemical compositions of the final metasomatic product, which in many cases approach the CASH system, favor (i) the precipitation of lawsonite and the unexpected reincorporation of free water at HP conditions, and (ii) the stability of lawsonite at higher temperature and at greater depth compared to the MORB+H<sub>2</sub>O system. By means of a thermodynamic approach, we quantified the drastic water enrichment across a metasomatic aureole characterized by intense chemical resetting and massive lawsonite precipitation, and its implication for water transfer at depth. We conclude that these hybrid rocks testify for intense geochemical recycling and water transfer to great depth in subduction, with implications for water cycling to the mantle. Moreover, the dramatic water expulsion and fluid overpressure caused by these lawsonite-rich rocks at lawsonite breakdown may cause localized deformation and seismicity at the subduction interface.

## UHT metamorphism of HP rocks? A case study from the Adula nappe complex (Central Alps, N Italy)

Zanchetta S.<sup>1</sup>, Tumiati S.\*<sup>2</sup>, Malaspina N.<sup>1</sup> & Poli S.<sup>2</sup>

1. Dipartimento di Scienze dell'Ambiente e del Territorio e di Scienze della Terra, Università degli Studi di Milano-Bicocca. 2. Dipartimento di Scienze della Terra, Università degli Studi di Milano.

Corresponding email: [simone.tumiati@unimi.it](mailto:simone.tumiati@unimi.it)

Keywords: Garnet peridotite, UHT metamorphism, Adula nappe.

The Adula-Cima Lunga nappe complex represents the highest of the Lower Penninic units of the Central Alps. Garnet lherzolite bodies crop out at three localities, from west to east: Cima di Gagnone, Alpe Arami and Mt. Duria. This study concerns an outcrop close to Monte Duria, where retrogressed garnet lherzolites occur as m-to hm-sized boudins hosted within amphibole-bearing gneisses that contain also some dm-to-m-sized boudins of more or less preserved eclogites. This rock association is in turn embedded within the migmatitic gneisses that form most of the southern sector of the Adula nappe. Petrographic and chemical analyses indicate that garnet peridotite is composed of olivine (XMg=0.88), orthopyroxene, clinopyroxene and garnet (Py 68; Cr<sub>2</sub>O<sub>3</sub> up to 1.45 wt%) with inclusions of Cr-rich spinel (up to Cr/(Al+Cr)=0.55) surrounded by kelyphitic symplectites of opx + cpx/amph + spl. These reaction produced double coronas, one composed of opx (former ol) and one composed of cpx + opx + spl. In one kelyphite, we observed the uncommon occurrence of ZrO<sub>2</sub> (baddeleyite) and ZrTi<sub>2</sub>O<sub>6</sub> (srilankite). Tiny crystals of these two Zr-bearing phases (~1 µm) are invariably located in the opx corona after ol. The cpx + opx + spl corona (after grt) contains, instead, zircon. Baddeleyite should have formed through a reaction of the type Mg<sub>2</sub>SiO<sub>4</sub> + ZrSiO<sub>4</sub> = MgSiO<sub>3</sub> + ZrO<sub>2</sub>. ZrO<sub>2</sub> and ZrTi<sub>2</sub>O<sub>6</sub> display a low amount of solid solution. These compositions are consistent with T below 1200°C, but an improvement of the thermodynamic model is needed in order to better constrain the T of the granulitic overprint on the basis of these Zr-bearing phases.

In eclogites, the HP association consists of garnet (Py<sub>40</sub>Alm<sub>37</sub>Sp<sub>20</sub>), omphacite (preserved as inclusion, containing Jd<sub>30</sub> and XMg 0.87), kyanite, K-feldspar, zoisite and minor quartz. Omphacite is almost always replaced by cpx (Jd<sub>5</sub>) + plag (An<sub>55</sub>) symplectites. Garnet is surrounded by plag (An<sub>33</sub>) + opx (En<sub>70</sub>) symplectites, more often by amphibole+plagioclase. Kyanite is replaced by plag (An<sub>84</sub>) + spinel ± sapphirine ± corundum. The spinel-sapphirine Fe-Mg thermometer suggests T of about 850°C for this granulite-facies overprint. Corundum-bearing symplectites after kyanite are common at the contact between eclogites and the host amphibole-bearing gneiss. In this contact, cm-sized emerald green zoisite has been found, replaced by anorthitic plagioclase ± clinopyroxene ± spinel ± calcite.

The observed assemblages point to a diffuse static granulitization of both peridotites and eclogite of Mt. Duria, suggesting a nearly isothermal decompression from peak-pressure conditions. The surrounding migmatitic gneiss do not display evidence of such granulitic event, recording T < 700°C.

The mechanism and timing of emplacement of the garnet peridotite and associated HP-HT rocks in the country migmatites, and whether or not the subduction event is related to the Alpine or to an older orogenic cycle are still a matter of debate.

**SESSIONE S22**

**Volcano laboratories: where geology, geophysics and  
geochemistry gather together**

*CONVENORS*

*G. De Natale (INGV-Osservatorio Vesuviano, Napoli)*

*M. Viccaro (Univ. Catania)*

## **Magma system conditions and ascent time during the Monte Nuovo eruption (Campi Flegrei, Southern Italy): an experimental and CSD study**

Arzilli F.<sup>1-3</sup>, Piochi M.\*<sup>2</sup>, Mormone A.<sup>2</sup>, Agostini C.<sup>3</sup> & Carroll M.R.<sup>3</sup>

1. Elettra-Sincrotrone Trieste S.C.p.A., Basovizza (Trieste). 2. Istituto Nazionale di Geofisica e Vulcanologia, sezione Osservatorio Vesuviano, Napoli. 3. School of Sciences and Technology - Geology Division, Università di Camerino.

Corresponding email: [monica.piochi@ov.ingv.it](mailto:monica.piochi@ov.ingv.it)

Keywords: Campi Flegrei, experiments, phono-trachyte, alkali-feldspars, CSD.

Processes of unrest, ascent dynamics and eruption of magmas govern the transition from quiescent to active volcanic systems. The knowledge of these processes is fundamental for understanding geochemical and geophysical signals that are observed at high risk volcanoes.

Here we present results from petrological and experimental studies on the phono-trachytic products, representative of those commonly erupted at the Campi Flegrei. In particular, we focus on the Monte Nuovo eruption for which robust background information exists in the literature, including historical chronicles, stratigraphical, textural and petrological studies. This low intensity and magnitude eruption is particularly interesting because it occurred after 3000 years of volcanic quiescence and the reported ground level movements and seismicity have characteristics comparable to the present bradyseisms.

Cooling and decompression experiments on a phono-trachytic composition reproduce the melt evolution in response to an instantaneously applied thermodynamic driving force (undercooling –  $\Delta T$ ). Natural and synthetic products have been characterized by B-SEM investigations, image analysis, Crystal Size Distribution study, X-ray diffractometry, and mineral and glass geochemistry.

Experimental and natural samples are texturally and chemically comparable allowing us to estimate the pre-eruptive conditions of the magma and the timescales of the eruptive process during the Monte Nuovo event in agreement with historical chronicles. Magma crystallization time was estimated from size distribution of feldspar microlites quenched in the matrix of juvenile fragments, by experimentally knowing the relation between population density, sizes and growth rates of alkali feldspar. As a whole, the experimental conditions reproduce the later evolution state of the phono-trachytic magmas, particularly, shortly before and during eruptions. Thus, this study offers a set of pressure (water saturated), temperature and undercooling ( $\Delta T$ ) conditions, useful to constrain the timescale and to better understand the behaviour of Phlegraean magma, starting from the texture of their eruptive products.

## Melting of Plume Residue beneath the Afar: Implications for Axial Basalts Geochemistry

Barbieri E.\*<sup>1</sup>, Brunelli D.<sup>1-2</sup>, Cipriani A.<sup>1-3</sup> & Mazzucchelli M.<sup>1</sup>

1. Dipartimento di Scienze Chimiche e Geologiche, Università degli Studi di Modena e Reggio Emilia. 2. Istituto di Scienze Marine, Geologia Marina, CNR. 3. Lamont-Doherty Earth Observatory of Columbia University, USA.

Corresponding email: [emiliano.barbieri@unimore.it](mailto:emiliano.barbieri@unimore.it)

Keywords: Afar, Ethiopia, Erta Ale.

The Afar is the place to investigate both the evolution of the lithosphere from continental break up to incipient seafloor spreading and the interaction between rifting processes and a mantle plume.

The plume has been evoked as one of the main factors involved in the development of the Afar, but its persistence beneath the depression is still a matter of debate. Recent studies have shown the lack of a well developed plume structure beneath the Afar (Hammond et al., 2013), thus suggesting its partial exhaustion. Geophysical investigations hint at an uppermost mantle dominated by broad asthenospheric upwelling (Rychert et al., 2012; Hammond et al., 2013) affected by decompression melting, feeding the magma chambers stored within both the crust and mantle, and the Afar plume magmatism. However, modern basalts erupted along the northern Afar show a strong enrichment in incompatible and trace elements that partially disagree with a shallow depleted mantle reservoir.

Recent geochemical analyses indicate that part of the mantle melting process, still occurs at greater depths (> 80 km) (Ferguson et al., 2013) and several authors suggest the presence of focused diapiric upwelling (Hammond et al., 2013), which probably enhances the melting at greater depths.

EMPA and LA-ICP-MS were used to investigate the composition of modern lavas sampled from the Erta Ale Chain and the Asal region in 2011 and 2013. The plume markers are recognizable but with less intensity compared to the Oligocene High Ti lavas, according to the lower activity of the Afar hot spot. Our results suggest a hybrid source characterized by two main reservoirs: an enriched mantle melting in the grt field and a shallow depleted mantle. We elaborated a numerical model that predicts the composition of the axial basalts through the mixing of melts obtained by melting of these theoretical reservoirs.

We propose for the Afar region the presence of isolated volumes of enriched material genetically related to the remains of the plume. These bodies generate enriched melts that pollute the liquids obtained by the surrounding asthenosphere before they reach the surface. Isotopic investigations are in progress and will help to better define the involvement of each reservoir.

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## Unravelling the hidden origin and migration of plagioclase phenocrysts by in-situ Sr isotopes: the case of final dome activity at Nisyros volcano, Greece

Braschi E.\*<sup>1</sup>, Francalanci L.<sup>1-2</sup>, Tommasini S.<sup>2</sup> & Vougioukalakis G.E.<sup>3</sup>

1. C.N.R., Istituto di Geoscienze e Georisorse, sezione di Firenze. 2. Dipartimento di Scienze della Terra, Università degli Studi di Firenze.  
3. IGME, Athens, Greece.

Corresponding email: [eleonora.braschi@igg.cnr.it](mailto:eleonora.braschi@igg.cnr.it)

Keywords: In situ Sr isotopes, crystal migration, dusty sieved plagioclase.

*In-situ* Sr isotope analyses, along with textural and compositional characteristics, of plagioclase phenocrysts occurring in the rhyodacite dome-lavas and associated mafic enclaves, erupted during the last magmatic activity at Nisyros volcano (Greece) have been studied in detail.

Dome-lavas and enclaves have a paragenesis dominated by plagioclase. We recognize five different types of plagioclase based on their specific textures and composition. Dome-lava plagioclases (Type-1) are mainly large (1-5mm), subhedral, clear and poorly zoned crystals with low-An content (An<sub>25-35</sub>), whereas the plagioclase phenocrysts (Type-4 and Type-5) and groundmass plagioclase microlites occurring in the enclaves have high-An content (An<sub>75-95</sub>). In both dome-lavas and enclaves two other types of plagioclase do also occur: (i) plagioclase phenocrysts with size and core composition similar to those of Type-1 having a dusty sieve zone (DSZ) at the rims (Type-2); (ii) plagioclases with a DSZ affecting the entire crystal but a thin rim (Type-3). The drilled plagioclases have <sup>87</sup>Sr/<sup>86</sup>Sr negatively correlated with their An content. Low-An cores of Type-1 and Type-2 have quite homogeneous <sup>87</sup>Sr/<sup>86</sup>Sr (0.7044-0.7046), whose values are more radiogenic than their host magmas (0.70403-0.70408) and similar to those of the previous Upper Pumice (UP) rhyolite magma (0.70438-0.70456). The DSZs of Type-2 and Type-3 show lower and scattered <sup>87</sup>Sr/<sup>86</sup>Sr (0.70397-0.70426) with intermediate and variable An content. High-An cores of Type-4 and Type-5 have the least radiogenic Sr isotope composition (0.70379) in equilibrium with that measured in the enclaves (0.70384-0.70389). We demonstrate that Type-1 plagioclase crystallizes in the previous Upper Pumice (UP) rhyolitic magmas, and Type-2 plagioclase derives from entrainment of Type-1 into the still molten enclave magma. The DSZs originated in response to the interaction between the low-An plagioclase and the enclave mafic melt in which dissolution, and re-crystallization acted together as function of the interaction time.

Type-1 and Type-2 plagioclases record, therefore, a long-lived timescale of events starting from their crystallization in the UP rhyolite, representing the original silica-rich magma from which the dome-lava melts derived by open system evolutionary processes (e.g. mixing, mingling and crystal migration), caused by successive refilling of mafic enclave-forming magma. It is noteworthy that the occurrence of DSZs with different width (Type-2 and Type-3) could indicate different interaction timescales between the single crystals and the enclave melt (from few hours to some 40 days).

These micro-analytical data contribute to the understanding of the origin of the rhyodacitic dome-lavas at Nisyros volcano and to set robust constraints on the dynamics of mingling/mixing processes in terms of crystal exchange pathways and enclave disaggregation.

## The CFDDP 506 m drilling mud and cores at Campi Flegrei (Italy): volcanological and environmental clues on the eastern sector of the caldera

De Natale G.<sup>1</sup>, Troise C.<sup>1</sup>, Piochi M.\*<sup>1</sup>, Mormone A.<sup>1</sup>, Aiello G.<sup>2</sup>, Barra D.<sup>1,2</sup>, de Vita S.<sup>1</sup>, Di Vito M.A.<sup>1</sup>, Isaia R.<sup>1</sup>, Mark D.F.<sup>3</sup>, Smith C.V.<sup>4</sup>, Wiersberg T.<sup>5</sup>, Somma R.<sup>1</sup>, Tramelli A.<sup>1</sup>, Carlino S.<sup>1</sup>, Caputo T.<sup>1</sup>, Erzinger J.<sup>4</sup>, Jurado Rodriguez M.J.<sup>6</sup> & Marturano A.<sup>1</sup>

1. Istituto Nazionale di Geofisica e Vulcanologia, Osservatorio Vesuviano, Napoli. 2. Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università Federico II, Napoli. 3. NERC Argon Isotope Facility, SUERC, University of Glasgow, UK. 4. Research Laboratory for Archaeology and the History of Art, University of Oxford, UK. 5. Deutsches GeoForschungsZentrum GFZ Telegrafenberg, Germany. 6. Institut de Ciències de la Terra Jaume Almera, Institut de Ciències de la Terra Jaume Almera, CSIC, Spain.

Corresponding email: [monica.piochi@ov.ingv.it](mailto:monica.piochi@ov.ingv.it)

Keywords: Campi Flegrei, CFDDP, mud drilling, cores, volcanism, paleoenvironments.

The Campi Flegrei caldera, inhabited by more than 350.000 people, is one of the most studied volcanic areas in the world. Nonetheless, several aspects about the tectonics, the nature of the deformation (net uplift of c.a 4 m between 1950 and 2013) and the volcanic system are still matter of debate.

This contribution presents the results of a 506m deep pilot well drilled in the Bagnoli Plain, in the Campi Flegrei caldera, c.a 1.6 km away from its eastern border. The drilling was conducted in the frame of the Campi Flegrei Deep Drilling Project (CFDDP), which is funded and supported by the INGV and the ICDP.

The obtained results are derived from analysis of cuttings, cores and geophysical logs. Stratigraphic, volcanological and geo-environmental information have been constrained from mineralogy, paleontology, Sr-isotope geochemistry and <sup>40</sup>Ar/<sup>39</sup>Ar geochronology. Measurements of gasses within the drilling mud and geophysical data collected with the down hole logging also provide information on the geothermal system. Furthermore, 4 seismic stations were installed around the drilling site, in addition to the monitoring permanent network. No induced seismicity occurred during the drilling activity. Power Spectral Density of the recorded signal evidences sea waves (below 1 Hz) and anthropic (around 8 Hz) seismic noise. The network detection threshold, as a function of the earthquake magnitude and hypocentral distance, was computed to understand the limits of the instrumentation used.

The CFDDP drilling penetrated essentially pyroclastic rocks younger than 47.8 ka. The clast type, characteristics, texture, mineralogy, and log-derived compositional contents are similar to those documented in the literature for the Phlegraean area. Based on lithological and log data, the general sequence is as follows: i) a basal gray pumice-bearing tuff at the base; ii) a greenish tuff between 470 and 270 m, progressively less altered; iii) a ~60 m-thick monotonous level of brown dense to vesicular glass fragments; iv) unit with an abundance of microfossils in association with dominantly sub-rounded or rounded vesicular to dense heterogeneous grains in the 255-36 m depth range, and carbon, wood fragments and peat in the shallowest portion; and v) superficial products that differ for the relative abundance of variably angular vesicular to dense and porphyritic fragments.

Characterization of sediments indicates sub-aerial conditions or aggressive environments between 245 and 506 m of depth, while the shallowest 245-36 m bgl interval shows a succession of subaerial and subaqueous paleoenvironments. The reconstructed stratigraphic sequence allows us to highlight some important features about the evolution of the eastern sector of the caldera. The results have implications on the origin and structure of the caldera, on the pre-caldera volcanic history, on the recent caldera dynamics and on the hazard assessment.

## **The Punta Chiarito Tephra (Ischia, Italy): eruption dynamics and emplacement mechanism inferred from stratigraphic, sedimentologic and petrological data**

de Vita S.\*<sup>1</sup>, Sansivero F.<sup>1</sup>, Piochi M.<sup>1</sup> & Minin G.<sup>2</sup>

<sup>1</sup> Istituto Nazionale di Geofisica e Vulcanologia - Sezione di Napoli Osservatorio Vesuviano. <sup>2</sup> Associazione Culturale Borbonica Sotterranea.

Corresponding email: [sandro.devita@ingv.it](mailto:sandro.devita@ingv.it)

Keywords: Ischia, eruption dynamics, resurgent calderas.

Volcanism in resurgent calderas is a common feature, in which areal distribution of vents, style of volcanism and chemical composition of the erupted magmas, can be strongly influenced by the local stress field induced by resurgence mechanism and dynamics. In the Ischia resurgent caldera almost all the volcanic vents of the past 5 ky are located in the lowland bordering eastward the resurgent block. The Punta Chiarito Tephra (ChT) is the sole pyroclastic deposit of this period exposed in the western sector of the island, over an area of at least 5 km<sup>2</sup>. The ChT has been archeologically dated at the end of the 8<sup>th</sup> century b.C. as it buried a human settlement of this age.

Here we present the results of an integrated stratigraphical, sedimentological, petrological and volcanological study, carried out on this tephra.

The ChT has been subdivided in Eruption units and sub-units according to the observed sedimentological features. Clasts morphology, degree of vesiculation and sedimentary structures, analyzed both in the field and laboratory through grainsize and SEM analyses, allowed the reconstruction of the eruption dynamics, type of fragmentation, transport mechanisms and depositional processes. The variations of geometrical and sedimentological characteristics (shape, thickness, grainsize, sedimentary structures) of each unit, together with direction of provenance of ballistic clasts, were used to constrain the position of the eruption vent, presently buried under landslides.

Mineralogical, geochemical and isotopic determinations allowed the characterization of both the juvenile products and the composition of the erupted magma in the frame of the evolution of the magmatic system of Ischia in the past 5 ky.

The ChT sequence was generated by a sequence of magmatic and phreatomagmatic explosions that extruded a homogeneous alkali-trachytic, well-vesicular and porphyritic magma. The eruption began with a phreatomagmatic phase, which generated the basal surge of Member A. A violent strombolian-to-subplinian eruption column formed soon after and produced the fallout deposit of Member B. In the following water entered the conduit leading to a new phreatomagmatic phase, with the emplacement of the dilute pyroclastic density currents of Members C to E. The eruption ended with the formation of a pulsating sub-plinian magmatic column generating the fallout deposit of Member F. Lithic clasts and SEM investigations indicate a progressive increase of water-magma interaction during the course of deposition of member C and its decrease from member D to F. Sr-isotopic ratio for crystals and whole-rocks indicates that the magma batch was isotopically homogeneous and deviated its composition during the eruption, towards more radiogenic values in response to magma-water interaction.

## Natural gadolinium discharged from volcanic sources

Falcone E.E.<sup>\*1-2</sup>, Sortino F.<sup>2</sup>, Bellomo S.<sup>2</sup> & Censi P.<sup>1</sup>

1. DISTEM department University of Palermo. 2. Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo.

Corresponding email: [eddaelisa.falcone@unipa.it](mailto:eddaelisa.falcone@unipa.it)

Keywords: Gadolinium anomaly, REE distributions, geochemistry.

Although a large fraction of chemicals is provided from volcanic fluids to the environment (Oppenheimer et al., 2014) only a scarce literature was focused on the Rare Earth elements (REE) release from high temperature fumaroles (Möller et al., 2003; Gilbert & Williams-Jones, 2008; Zelenski et al., 2013). In order to fill this gap, this research was carried out mainly taking in account the REE partitioning during the emissions of fumarolic fluid between newly-forming sublimates and the remaining gas phase. The latter was collected as alkaline condensates according to Sortino et al. (2006). The investigated high temperature fumaroles (95-450°C) occur in several volcanic systems at Vulcano, Aeolian Islands and Phlegrean Fields (Italy), Santorini, Cyclades Islands (Greece), Canary Islands (Spain) and Cape Verde where strong passive emission of fluids occur.

Fumarolic sublimates show higher lanthanide contents, whereas alkaline condensates represent the most volatile fractions of these fluids. The analysis of geochemical behaviour of these elements was investigated studying the features observed in shale-normalised REE patterns (vs. PAAS, Taylor and McLennan, 1995). This analysis indicates that Gd is preferentially partitioned in the vapour phase during the sublimation of less volatile fluid fractions. Consequently, positive Gd anomalies occur in alkaline condensates with respect to coexisting solid sublimates where this effect is less evident. Their amplitudes can be assessed according to the equation:

$$\frac{Gd_n}{Gd^*} = \frac{Gd_n \sqrt{Ho_n}}{\sqrt[3]{Tb_n^2}}$$

(Moller et al., 2007) where n-suffix indicates normalised lanthanide concentrations and Gd\* is the expected normalised Gd concentration according to Tb and Ho contents. Comparing the amplitudes of these anomalies with the temperatures of investigated fumaroles larger Gd/Gd\* values are mainly found in higher temperature fumaroles (450-250°C) in Vulcano ( $1.5 \leq Gd/Gd^* \leq 6.8$ ) and less in lower temperature fumaroles (285-82°C) studied in Phlegrean Fields, Canary and Cape Verde islands ( $1.1 \leq Gd/Gd^* \leq 2.7$ ).

Moreover, comparing the amplitudes of Gd/Gd\* and related HCl/HF ratio values of alkaline condensates a significant positive relationship is observed only in alkaline condensates collected from higher temperature fumaroles ( $T > 200$  °C). This evidence is consistent with a preferential REE complexation via Cl-complexes in vapour phase and can be considered a consequence of nephelauxetic effect. According to this suggestion the growth of positive Gd anomalies is a consequence of changes of the first Gd hydration sphere during the formation of Gd-chloride complexes at higher temperature and does not occur if complexes are formed at temperatures up to 200 °C (Mayanovic et al., 2007).

Being REE-chloride complexes highly soluble species quickly removed from the atmosphere by water droplets, Gd coming from volcanic gas phase could represent a significant component of the geochemical Gd cycle in aqueous media.

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## Compositional changes of erupted lavas and styles of volcanic activity at Mt. Etna during the 2011-2013 period

Giuffrida M.\*<sup>1</sup>, Viccaro M.<sup>1</sup>, Calcagno R.<sup>1</sup>, Garozzo I.<sup>2</sup> & Nicotra E.<sup>1</sup>

1. Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania.

2. Dipartimento di Scienze Geologiche, Università Roma Tre.

Corresponding email: [marisagiuffrida@hotmail.it](mailto:marisagiuffrida@hotmail.it)

Keywords: Etna, magma recharge, paroxysmal activity.

A comprehensive characterization of volcanic rocks related to paroxysmal events developed between January 2011 and April 2013 at Mt. Etna, was here performed through in situ analysis of mineral phases and whole rock geochemistry. The collected dataset provide evidences that magmas feeding the 2011-13 activity preserve a geochemical signature comparable to that of the 2007 erupted products, though with minor differences due to a different evolutionary pattern.

Analysis performed on the main mineralogical phases such as clinopyroxene, plagioclase and olivine showed fluctuations through time of Mg#, An and Fo. Whole rock major and trace elements also display similar compositional changes, which could be accounted for by a transient, pulsating recharge by more basic magma. In order to support this hypothesis, several simulations of magma evolutionary processes were performed by means of MELTS at fixed chemical-physical parameters.

Results point to the superimposition of crystal fractionation and recharge by a more basic magma as the main differentiation processes controlling the composition of the 2011-2013 volcanic products. Composition of the recharging end-member is compatible with that of the most basic magma emitted during the 2007 and the first-emitted products of 2012. Analysis of the erupted volumes of magma, together with petrologic evidences, support the idea that large volumes of non-erupted magma are stored in the intermediate feeding system (2-6 km b.s.l.) after a phase of major magma recharge from the deep portions of the plumbing system (>6 km b.s.l.). The transient recharges from the intermediate level toward the shallow reservoir could be able to trigger paroxysmal activity at the surface.

## Experimental constraints on phase relations in a multilevel magmatic system: the Phlegraean Volcanic District (South Italy) case study

Granati S.F.\*<sup>1</sup>, Perinelli C.<sup>1</sup>, Gaeta M.<sup>1</sup>, Freda C.<sup>2</sup> & D'Antonio M.<sup>3</sup>

1. Dipartimento di Scienze della Terra, Sapienza Università di Roma. 2. Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Roma. 3. Dipartimento di Scienze della Terra, Università Federico II di Napoli.

Corresponding email: [serenafrancesca.granati@uniroma1.it](mailto:serenafrancesca.granati@uniroma1.it)

Keywords: Phlegraean Volcanic District, Experimental Petrology, Phase Relations.

The Phlegraean Volcanic District (PVD) is an active area that hosts about 1,5 million people within its surroundings. This makes the area one of the most dangerous on the Earth. The activity of the PVD (including Campi Flegrei and the islands of Ischia and Procida) produced dramatic explosive events in the Mediterranean area during the last 200 ky, and many studies have been performed to investigate the magmatic differentiation processes responsible of the largely compositionally variable products emitted during PVD activity. However, these studies have mostly followed a petrological and geochemical approach, whereas very few experimental studies have been carried out to understand and constrain origin and evolution of PVD magmas, and only limited to differentiated compositions. Here we present an experimental study conducted on a rock of primitive composition, probably representing the mantle derived parental magmas feeding the PVD, outcropping in the area, a K-basalt from the Solchiaro eruption. This rock has been used as starting material for an experimental study addressed to unravel the differentiation mechanisms acting in the PVD plumbing system. The experiments were performed in a piston-cylinder apparatus at three different pressures, 200, 400 and 800 MPa based on the current knowledge of the PVD plumbing system structure. The ranges of temperature and water concentration investigated were 1050 - 1300 °C and 1-7 wt%, respectively. These experiments allow us to reconstruct the phase relations of Solchiaro K-basalt in the P-T-H<sub>2</sub>O space. At 200 MPa and H<sub>2</sub>O content lower than 4 wt%, olivine is the liquidus phase followed by chromium spinel, clinopyroxene, and finally plagioclase. At 400 MPa and H<sub>2</sub>O lower than 3 wt%, olivine is still the liquidus phase but chromium spinel also occurs; then, clinopyroxene and plagioclase crystallize. Interestingly, at 800 MPa and water content below 1.5 wt%, chromium spinel and clinopyroxene replace olivine as liquidus phases; whereas for water content above 1.5 wt% all the three phases occur on the liquidus. This suggests the equilibrium of primary PVD magmas with a wehrlitic source at pressure corresponding to the crust-mantle boundary. Moreover, our 800 MPa experiments corroborate results from a recent study on melt inclusions constraining the amount of water in the PVD primary magma at values up to 2 wt%. The high pressure experiments, showing olivine on the liquidus only for H<sub>2</sub>O content in the melt above 1.5 wt% suggest that in a magmatic system characterized by water content below 1.5 wt%, the occurrence of olivine as liquidus phase can possibly occur by the increase of XCO<sub>2</sub> in the magma. Experiments to investigate the role of XCO<sub>2</sub> on the phase relations of PVD primitive magmas are in progress.

## Sulfur in alkaline melts: An experimental study

K. Iacovino<sup>1</sup>, Giuli G.\*<sup>2</sup> & Carroll M.<sup>2</sup>

1. Dept. of Geography, University of Cambridge, England. 2. School of Science and Technology, Geology Division, Università di Camerino.

Corresponding email: [gabriele.giuli@unicam.it](mailto:gabriele.giuli@unicam.it)

Keywords: sulphur solubility, phonolite, basanite, eribus.

We present preliminary results of experiments to establish the solubility of sulfur (sulfate and sulfide) in natural alkaline melts (basanite, KI-04; and phonolite, ERE-97018) from Erebus volcano, Antarctica. Melt composition is known to strongly influence S solubility in natural melts, particularly with respect to FeOtot and SiO<sub>2</sub> [Ducea et al.]. Although melt polymerization is thought to have a significant effect on sulfur solubility and speciation, it is likely that a number of other factors, including melt alkali and iron-content, also play a role in controlling sulfur behavior in melts. This experimental study examines the interplay between alkalis, oxygen fugacity, pressure, Fe and S oxidation state, and Fe and S coordination geometries and their effects on S<sup>6+</sup> and S<sup>2-</sup> solubility. Sulfur saturated and undersaturated experiments have been carried out at a range of oxygen fugacities ( $\log fO_2 = -12$  to  $-6$ ) and pressures (1 bar to 1 kb) at superliquidus temperatures (1030 and 1200 °C for phonolite and basanite, respectively). This range of experimental conditions and analyses of the S contents via EPMA and sulfur and iron speciation via XAS will allow S solubility and partitioning to be evaluated with respect to experimental conditions.

Preliminary results indicate a marked increase in total S solubility in evolved phonolite melt relative to primitive basanite at similar T-  $fO_2$  conditions. Experimental data indicate a steep increase in S solubility at highly oxidizing conditions ( $fO_2 = NNO+1.53$ ; ~1000 ppm dissolved S) and minimum solubility at moderately oxidizing conditions ( $fO_2 = QFM+0.23$ ; ~200 ppm dissolved S). The strongly non-linear relationship between S solubility and  $fO_2$  has implications for sulfur degassing at Erebus volcano, whose erupted products indicate a distinct decrease in oxygen fugacity during fluid-magma ascent.

Future experiments at higher pressure and analyses of all experimental products via XAS will elucidate the roles of oxygen fugacity, pressure, Fe and S speciation, in controlling S solubility in basanites and phonolites. Comparisons of our results to data from more polymerized (low-alkali) melts and incorporation of data from an unpublished experimental study of S in phonolite at sub liquidus conditions [D. Moncreiff et al.] will further our understanding of the relation between melt polymerization and S solubility and allow us to characterize the behavior of S in lower temperature systems.

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## On the relationships between tectonics and volcanism in the offshore Capo Vaticano, SE Tyrrhenian Sea, during the Plio-Pleistocene

Loreto M. F.<sup>\*1</sup>, Pepe F.<sup>2</sup>, De Ritis R.<sup>3</sup>, Collura A. M.<sup>2</sup>, Ferrante V.<sup>1</sup>, Italiano F.<sup>4</sup>, Sacchi M.<sup>5</sup>,  
Speranza F.<sup>3</sup> & Tomini I.<sup>6</sup>

1. ISMAR-CCNR U.O.S. Bologna. 2. Dipartimento di Scienze della Terra e del Mare - Università di Palermo  
3. INGV-Roma. 4. INGV-Palermo. 5. IAMC-CNR Napoli. 6. OGS Sgonico – Trieste.

Corresponding email: [filomena.loreto@bo.ismar.cnr.it](mailto:filomena.loreto@bo.ismar.cnr.it)

Keywords: sub-marine volcano, normal faults, Calabria.

High-resolution bathymetry and a grid of single-channel reflection seismic profiles (Sparker and Chirp) were recently recorded in a sector of the upper slope of Capo Vaticano (CV) promontory (Tyrrhenian coast, W Calabria) where forward and inverse modeling of previously acquired aeromagnetic data highlight the presence of a WNW-ESE elongated, 20 km long and 3-5 km wide, magnetized body extending from sea floor to about 3 km below sea level. Magnetic properties of this body are consistent with those of the medium to highly evolved volcanic rocks of the Aeolian Arc (De Ritis et al., 2010).

Offshore promontory, the bathymetry highlights a complex-shape seamount that develops along a WNW direction, orthogonally interrupted by NE-trending ridges (Loreto et al., 2013), the largest of which shows major- and minor-axes of ca. 11 and 2 km, respectively. Summit elevation is ca. 70 m. Several vented fluids points were imaged on top of the seamount by chirp profiles. The largest of which rises from seafloor up to 6/7 m within water column, assuming the acoustic water velocity of 1500 m/s.

Two faults systems associated with extensional faults are mainly observed on seismic profiles. High-angle NW-trending normal faults, SW-dipping, formed along the continental slope connecting the south-west continental shelf of the CV promontory to the Gioia Tauro basin (Pepe et al., 2013). These faults generally have small displacements, up to 40 m, and are sealed by Pleistocene deposits. A NE-trending normal fault, SE-dipping, is also observed on both chirp and sparker profiles. Its length is estimate to be more than 30 km, partially borders the NE-trending ridge intersecting the NW-trending fault. Landward, another NE-trending normal fault affects Pliocene and lower Pleistocene, and is sealed by upper Pleistocene.

The described new geophysical data lead to a re-examination of the magnetic anomaly field interpretation. In fact, the revealed NE-trending ridge encounters the CV NW-SE ridge just where the peak value of the Reduced-to-the-Pole magnetic anomaly lies. Therefore, the inherent source body is emplaced where the maximum fracturing occurs. This suggests highly magnetized material crystallized in a vertical conduit that fed a volcanic system, likely fault-controlled, surrounded by the almost not magnetized rocks of the Gioia and the Paola sedimentary basins and of the Arco Calabro Peloritano units.

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## Magma storage and ascent dynamics of early volcanic manifestations at Salina (Aeolian Islands)

Nicotra E.\*<sup>1</sup>, Viccaro M.<sup>1</sup> & De Rosa R.<sup>2</sup>

1. Dipartimento di Scienze Biologiche, Geologiche e Ambientali - Università di Catania. 2. Dipartimento di Biologia, Ecologia e Scienze della Terra - Università della Calabria.

Corresponding email: [eugenio.nicotra@unict.it](mailto:eugenio.nicotra@unict.it)

Keywords: volcanological evolution, volcano feeding system, salina island.

The Rivi and Capo volcanoes represent the early (240-87 ka; De Rosa et al., 2003; Leocat, 2011) sub-aerial volcanic manifestations at Salina, in the central portion of the Aeolian archipelago. Their lava flows and pyroclastic deposits from strombolian fall-out activity have been here investigated through a multidisciplinary geological-petrological approach. Our geological field survey confirmed that Rivi and Capo volcanoes are part of a unique N50°E aligned volcanic complex, here named Rivi-Capo Volcanic Complex (RCVC). The Capo volcano, which is the most ancient center on the island (from 240 ka; Leocat, 2011), is constituted by three different volcano-stratigraphic Formations. During the deposition of Lower and Middle Capo Formations activity was mainly tectonically-controlled along a NE-SW direction. The last products of Capo volcano (the here-named Upper Capo Formation) are related to a late-stage resumption of volcanic activity at 87 ka (De Rosa et al., 2003). Rivi volcano developed between 160 and 131 ka (Leocat, 2011) and has been divided into two major Formations (Lower and Upper Rivi Formations), separated by a northward-directed sector collapse of the volcanic edifice.

Rock sampling has been stratigraphically constrained and led to reconstruction of the magma feeding system processes through time. Whole rock compositions exhibit a general trend of evolution toward more basic terms within the Capo and the Rivi volcanoes. MELTS simulations and mass balance modeling suggest that the RCVC rocks are the result of fractional crystallization of plagioclase, clinopyroxene and olivine (ca. 45 vol.% of solid removed) from a primary magma. Continuous recharge and mixing by more basic magma coming from the deep portions of the magmatic plumbing system contribute to the final volcanic rock composition. Our textural and microanalytical data on plagioclase and clinopyroxene crystals lead to redrawing of the plumbing system configuration for the RCVC with respect to previous hypotheses. These data allow the definition of a multi-level magmatic storage system with reservoirs at ~20 km and ~4 km of depth below the sea level. When processes of magma differentiation, ascent and storage are considered together with the stratigraphic position of each sample, a history of continuous modification of the RCVC plumbing system can be advanced. Specifically, volcanism could have been characterized by fissure-type eruptions during the early stages and gradually changed later to central-type volcanism.

De Rosa R., Guillou H., Mazzuoli R. & Ventura G. 2003. New unspiked K-Ar ages of volcanic rocks of the central and western sector of the Aeolian Islands: reconstruction of the volcanic ages. *J. Volcanol. Geotherm. Res.*, 120, 161-178.

Leocat E. 2011. Histoire éruptive des volcans du secteur occidental des Iles Eoliennes (Sud de la Mer Tyrrhénienne, Italie) et evolution temporelle du magmatisme. Unpublished PhD thesis, University of Paris 11 Orsay, France.

## Seismic expression of the shallow structure of The Neapolitan Yellow Tuff (NYT) caldera offshore the Campi Flegrei

Sacchi M.\*<sup>1</sup>, Pepe F.<sup>2</sup>, Corradino M.<sup>2</sup>, Insinga D.D.<sup>1</sup> & Molisso F.<sup>1</sup>

1. Istituto per l'Ambiente Marino Costiero (IAMC), CNR, Napoli. 2. Dipartimento di Scienze della Terra e del Mare (DiSTeM), Università di Palermo.

Corresponding email: [marco.sacchi@iamc.cnr.it](mailto:marco.sacchi@iamc.cnr.it)

Keywords: Campi Flegrei, Neapolitan Yellow Tuff, Collapse caldera.

In this study we integrate high-resolution swath bathymetry, single-channel reflection seismic data and gravity core data, to provide new insights into the shallow structure and latest Quaternary to Holocene evolution of the submerged sector of the Neapolitan Yellow Tuff (NYT) caldera (Campi Flegrei) in the Pozzuoli Bay. The new data allow for a reconstruction of the offshore geometry of the NYT caldera collapse – ring fault system, along with the style and timing of deformation of the inner caldera resurgence.

Our interpretation shows that the NYT eruption (~15 ka BP) was associated with a caldera collapse bounded by an inward-dipping ring fault system. The ring fault system consists in a 1-2 km wide fault zone that encircles an inner caldera region ~ 5 km in diameter and is often marked by the occurrence of pore fluids ascending through the fault zone, up to the seafloor, particularly in the western sector of the bay. A shallow magmatic intrusion along the ring fault zone was also detected offshore Bagnoli in the eastern part of the Pozzuoli Bay (Sacchi et al., 2014).

Following the NYT eruption, the inner caldera region underwent significant deformation and resurgence with a maximum cumulative uplift of the offshore structure in the order of 180 m. The net uplift rate of the caldera resurgent dome was ~ 9 - 12 mm/year during the period 15.0 – 6.6 ka BP. The style of deformation of the resurgent structure can be described in terms of a broad doming, accompanied by subordinate brittle deformation, mostly concentrated in a small apical graben at the summit of the resurgent dome (Cole et al., 2005).

Chronostratigraphic calibration of seismic profiles obtained by three tephra layers cored in the Pozzuoli Bay indicates 5 to 25 m of post-Roman differential subsidence and tilting towards ESE of the inner caldera resurgence, as recorded by the drowning of the infralittoral prograding wedge below the present-day storm wave base.

Cole J.W., Milner D.M., Spinks, K.D. 2005. Calderas and caldera structures: a review. *Earth-Science Review*, 69, 1-26.  
Sacchi M., Pepe F., Corradino, M. Insinga D.D., Molisso F. Lubritto C. 2014. The Neapolitan Yellow Tuff caldera offshore the Campi Flegrei: Stratal architecture and kinematic reconstruction during the last 15 ky. *Marine Geology*, 354, 15-33.

## Magmatic underplating and incremental growth of a granite pluton in the Sesia Magmatic System

Sinigo S.\*<sup>1</sup>, Quick J.E.<sup>2</sup> & Demarchi G.<sup>1</sup>

1. Dipartimento di Matematica e Geoscienze, Università di Trieste. 2. Huffington Department of Earth Sciences, Southern Methodist University.

Corresponding email: [sinigois@units.it](mailto:sinigois@units.it)

Keywords: Caldera, Ivrea Verbano, supereruzione.

A virtually complete crustal section in the Sesia Valley of northwest Italy provides a unique opportunity to directly constrain the igneous evolution beneath a continental volcanic field. Capping the section, a bimodal, though mainly rhyolitic, volcanic complex containing a >15-km-diameter caldera is intruded by a granitic cupola segregated from a 7- to 8-km-thick granitic pluton that is rooted in migmatitic paragneiss at mid-crustal levels. At deeper levels, an 8-km-thick gabbroic body, “magmatically underplated” between 17 and 25 Km, intrudes amphibolite- to granulite-facies crustal rocks. Consistent with a cause-and-effect relationship between magmatic underplating in the deep crust and silicic plutonism and volcanism at high crustal levels, SHRIMP U/Pb zircon ages for volcanic, granitic and underplated gabbroic rocks are constrained to a relatively narrow time window of ~290 to ~280 Ma. A Concordia age of  $282 \pm 0.75$  Ma on zircons from the caldera-fill ignimbrite indicates that caldera collapse occurred late in the evolution of this magmatic system. Field relations and geochemistry constrain the thermal history of the Sesia section and the processes of magmatic underplating, crustal anatexis and assimilation, and hybridization during its magmatic evolution. Underplating was accommodated by crustal extension, which is recorded by structures produced by the flow of gabbroic cumulates downward and away from a small magma chamber perched near the top of the intrusion. Heat from the underplated gabbro induced anatexis in country-rock paragneiss, producing granitic melts that migrated higher in the crust. Eu and Ba enrichments,  $\epsilon_{\text{Nd}} < -2.5$ ,  $^{87}\text{Sr}/^{86}\text{Sr} > 0.7075$ , indicate that the parental melt of the underplated gabbro ingested significant amounts of paragneiss previously stripped of a granitic component. The peraluminous composition of granitic and volcanic rocks indicate that melting of metapelitic paragneiss was a contributing source, but  $^{87}\text{Sr}/^{86}\text{Sr}$  values (~ 0.710) are intermediate between the compositions of the paragneiss and the underplated gabbro, indicating that late-stage, residual melts produced by fractional crystallization of the underplated gabbro also contributed to the formation of granite and silicic volcanic rocks. Mass balance computations are consistent with assembly of the granite pluton by mixing of a relatively constant ratio of anatectic and AFC-derived granitic components modulated by thermal buffering in the deep crust by anatexic and AFC processes. Petrographic observations suggest that remelting of the granite pluton contributed to formation of a granitic crystal mush, which may have set the stage for caldera collapse.

## **Timescales of magma storage and ascent at Mt. Etna volcano from plagioclase trace element zoning**

Viccaro M.<sup>\*</sup>, Barca D.<sup>2</sup>, Bohrson W.A.<sup>3</sup>, Giuffrida M.<sup>1</sup>, Nicotra E.<sup>1</sup> & Pitcher B.W.<sup>4</sup>

1. Dipartimento di Scienze Biologiche, Geologiche e Ambientali - Università di Catania 2. Dipartimento di Biologia, Ecologia e Scienze della Terra - Università della Calabria 3. Department of Geological Sciences - Central Washington University 4. College of Earth, Ocean, and Atmospheric Sciences - Oregon State University.

Corresponding email: [m.viccaro@unict.it](mailto:m.viccaro@unict.it)

Keywords: Volcano-tectonics, trace elements, magmatic processes.

How long magma takes to ascend to Earth's surface after storage and how the transfer mechanisms influence the eruptive behaviour are major questions for volcanologists. The use of plagioclase crystals at Mt. Etna volcano, chiefly because it is stable over a wide range of physical-chemical conditions and is sensitive to changes in thermodynamic parameters during its growth in magma storage and transport zones, has recently shown the efficiency of this tool to reconstruct a number of volcanic processes during storage, degassing, and ascent (Viccaro et al., 2010). In this work, textural data and trace element zoning in plagioclase phenocrysts for products of historic (pre-1971 AD) and recent (post-1971 AD) activity of Mt. Etna volcano contributed to addressing these questions for the complex storage and transport system of this volcano. The observed textural characteristics of crystals include near-equilibrium textures (i.e., oscillatory zoning) and textures with variable extent of disequilibrium (patchy zoning, coarse sieve textures and dissolved cores). One of the main differences between crystals of the historic and recent activity is the higher average anorthite content for the post-1971 AD plagioclases, which agrees with the more basic character of the hosting lava. Among the most noticeable variations, recent plagioclases also exhibit higher K, Rb, LREEs and lower Ba abundances than the historic ones, with the largest differences more evident at high anorthite (An) contents. Variations in anorthite content along core-to-rim profiles obtained on crystals with different types of textures for both the historic and recent eruptive periods were evaluated particularly versus Sr/Ba. At comparable average An contents, crystals characterized by oscillatory zoning, which are representative of near-equilibrium crystallization from the magma, display distinct Sr/Ba ratios (~6 in historic and ~17 in recent lavas). We suggest these features are primarily related to recharge of a new, geochemically-distinct magma into the storage and transport system of the volcano since 1971 AD. In addition to distinct trace element and textural characteristics of plagioclase, Sr diffusion calculations for plagioclase suggest that magma residence times are generally shorter for magmas erupted in recent times (i.e., post-1971 AD) compared to those erupted during the historic period. These estimations match well with the enhanced extension rate within the upper 10 km of the crust observed during the last decades, and are also in accordance with the increased eruptive frequency after the 1971 AD eruption.

Viccaro M., Giacomoni P.P., Ferlito C., Cristofolini R. 2010. Dynamics of magma supply at Mt. Etna volcano (Southern Italy) as revealed by textural and compositional features of plagioclase phenocrysts. *Lithos*, 116, 77-91.

## Hydrothermal alteration, fluid entrapment, and paroxysm (Colli Albani Volcano, Italy)

Vignaroli G.\*<sup>1</sup>, Aldega L.<sup>2</sup>, Balsamo F.<sup>3</sup>, Billi A.<sup>4</sup>, De Benedetti A.A.<sup>1</sup>, De Filippis L.<sup>1</sup>, Giordano G.<sup>1</sup> & Rossetti F.<sup>1</sup>

1. Dipartimento di Scienze, Sezione di Geologia, Università Roma Tre. 2. Dipartimento di Scienze della Terra, Sapienza Università di Roma. 3. Dipartimento di Fisica e Scienze della Terra, Università di Parma. 4. Consiglio Nazionale delle Ricerche, IGAG, Roma.

Corresponding email: [gianluca.vignaroli@uniroma3.it](mailto:gianluca.vignaroli@uniroma3.it)

Keywords: hydrothermalism, metasomatism, Colli Albani.

Colli Albani is a quiescent volcano belonging to the Roman Magmatic Province. Several recent and historical hydrothermal manifestations in the Colli Albani area have been connected with CO<sub>2</sub> and other gases accumulation and release during tectonic activity (Funciello & Giordano, 2010; Carapezza & Tarchini, 2007; Chiodini et al., 2012).

A multidisciplinary approach (including outcrop mapping, in situ permeability measurements, minero-petrographic and geochemical analyses) has been applied for understanding what are the main factors controlling gas entrapment and release in the west-southwestern sector of the Colli Albani area, where sulfur and sulfide mineralizations and strongly altered ignimbrites are exposed. The alteration acme corresponds to a narrow sector of active degassing at the top of a buried normal fault that acted as main conduit for magmatic fluid rising. Rock alteration fades away in 2-3 km from the fault and this is typified by the occurrence of localized and selective alteration structures within the ignimbrite succession. Based on the mineralogical assemblage, the steam-heated advanced argillic alteration facies can be attributed both to the fault-proximal and fault-distal domains. Geochemical signature of unaltered/altered rock pairs indicates that element accumulation/depletion is variable within the ignimbrite succession and within the same lithotype, accomplishing for a drastic change in rock petrography and permeability. The progress of the hydrothermal alteration can be framed in a spatio-temporal cyclic process in which mineral precipitation and fracture healing contribute to hydrothermal fluid entrapment and overpressure. The sudden release of hydrothermal fluids may be at the origin of the paroxysmal manifestations that characterized the final phase of the Colli Albani Volcano.

Carapezza M.L. & Tarchini L. 2007. Accidental gas emission from shallow pressurized aquifers at Alban Hills volcano (Rome, Italy): Geochemical evidence of magmatic degassing? *J. Volcanol. Geotherm. Res.*, 165, 5-16.

Chiodini G., Tassi F., Caliro S., Chiarabba C., Vaselli O., Rouwet D. 2012. Time-dependent CO<sub>2</sub> variations in Lake Albano associated with seismic activity. *Bull. Volcanol.* 74, 861-871.

Funciello R. & Giordano G. (Eds.) 2010. The Colli Albani Volcano. Special Publication of IAVCEI, 3. Geol. Soc., London, pp. 400.

## SESSIONE S23

### **Tracing isotopes for tracking processes: advances in radiogenic and stable isotope geochemistry**

*CONVENORS*

*S. Tonarini (CNR-IGG)*

*R. Avanzinelli (Univ. Firenze)*

## The *Ursus spelaeus* lifestyle and feeding behaviour: a tale from Sr isotope studies

Adani T.<sup>1</sup>, Braschi E.\*<sup>2</sup>, Mazza P.<sup>1</sup>, Petrone C.M.<sup>3</sup> & Tommasini S.<sup>1</sup>

1. Dipartimento di Scienze della Terra, Università degli Studi di Firenze. 2. C.N.R., Istituto di Geoscienze e Georisorse, Firenze. 3. The Natural History Museum, Department Earth Sciences, London, UK.

Corresponding email: [leonora.braschi@igg.cnr.it](mailto:leonora.braschi@igg.cnr.it)

Keywords: In situ Sr isotopes, *Ursus spelaeus*'s habitat, fossils bones and teeth

The work presented here is focused on the chemical and isotopic characterization of some fossil remains of *Ursus spelaeus* founded in the Grotta all'Onda cave, at Camaiole (Tuscany, Italy). The principal aim of this study is the reconstruction of the lifestyle and feeding behavior of one of the major mammals living in the region during last interglacial phase. To pursue our purposes we follow a new analytical approach based on the application of *in situ* Sr isotopes on tooth and bones collected by the *Ursus spelaeus*'s skeleton. The idea is to possibly trace and determine the relationship between the animal and the territory in which he lived.

All wet chemical analyses have been carried out using ICP-MS Laser Ablation at the Natural History Museum of London, while microprobe and isotopic analyses have been performed using a Jeol JXA9600 at the Laboratory of Microanalysis of the CNR-IGG in Florence and a Microdrilling device plus Triton Thermal Ionization Mass Spectrometer (TIMS) at the Laboratory of Isotope Geochemistry of the University of Florence, respectively.

Major element analyses establish that bioapatite is more mineralized in enamel than in dentin and bone samples. Trace element analyses show distinct contents between tooth enamel and dentin among all the samples analyzed, with dentin generally enriched in trace elements, such as V, Sr and Ba.

Teeth and bones have variable Sr isotope composition with bones and dentin being less radiogenic than the enamel. The tooth enamel samples (the mineralized portion) can be considered unaffected by diagenetic alteration and, in addition to higher  $^{87}\text{Sr}/^{86}\text{Sr}$ , have also lower Sr/Ca than other organic-rich samples (bones and dentin). The latter have indeed an isotopic composition pointing to that of soils in which they were found, testifying, despite the recent age of the fossil specimens (40 ka), the occurrence of *post mortem* exchange process. The tooth enamel samples can instead be feasibly used to trace the living habitat of the *Ursus spelaeus*, and their Sr isotope signature is consistent with the Triassic carbonate formation (*Calcare Massiccio*) of the Tuscan nappe outcropping in the surrounding of the Grotta all'Onda cave.

Considering major and trace element composition of enamel samples, the only samples not affected by *post mortem* exchange processes, we can gain information on the dietary habits of the studied *Ursus spelaeus*. Given the well-known Ca biopurification process along the trophic chain (soil ® plants ® herbivores ® carnivores), the Sr/Ca and Ba/Ca of enamel samples indicate that the Grotta dell'Onda *Ursus spelaeus* was probably herbivore. This interpretation, however, should be considered carefully and would need to be corroborated by further investigation, by comparing paleontological with geochemical data, taking also into account the soil composition (both trace and isotopes) in which the *Ursus spelaeus* have been found.

## Multiple isotope approach to unravel the sequence of water-rock interaction and hydromagnesite precipitation at Montecastelli (Tuscany)

Boschi C.\*<sup>1</sup>, Baneschi I.<sup>1</sup>, Bedini F.<sup>2</sup>, Chiarantini L.,<sup>1</sup> Dini A.<sup>1</sup> & Perchiazzi N.<sup>2</sup>

1. Istituto di Geoscienze e Georisorse, CNR Pisa. 2. Dipartimento di Scienze della Terra, Università di Pisa.

Corresponding email: [c.boschi@igg.cnr.it](mailto:c.boschi@igg.cnr.it)

Keywords: serpentinite, brucite, CO<sub>2</sub> mineral sequestration.

Atmospheric carbon dioxide is spontaneously sequestered through the weathering and subsequent carbonation of serpentinite outcrops at Montecastelli (Tuscany, Italy). The three selected studied areas consist of: i) serpentinite escarpment close to a spring water; ii) gangue materials dumped in front of the entrance of a serpentinite-hosted copper mine; and iii) the main tunnel of the serpentinite-hosted copper mine. The three sites are characterized by high humidity and the serpentinite rocks appear whitish in color, completely coated by a thin carbonate crust. XRD analyses indicated that precipitated minerals of the carbonate crust are, in different proportion, hydromagnesite, nesquehonite, manasseite, pyroaurite, brugnatellite, very often in association with aragonite. No silica (quartz, opal, chalcedony) has been detected. Serpentinite host rocks do not evidence any pervasive alteration and/or dissolution, with the exception of localized carbonate late veins. In addition, these rocks contain significant amount of brucite, not often recovered in oceanic serpentinites. The emerging waters, sampled in the three areas, have high pH, relatively high TDS (Total Dissolved Solids) and high Mg/Ca molar ratio with respect to the meteoric water, indicating that the chemical compositions are controlled by interaction of rainwater with serpentinite host rocks. Isotopic analyses ( $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ ,  $^{87/86}\text{Sr}$ ) of rainwaters, emerging waters, serpentinites and carbonates highlighted that the carbonates have been precipitated from superficial waters circulating into the serpentinite bodies. Overall, our data point to an on-going rapid uptake of atmospheric CO<sub>2</sub>, triggered by high humidity and presence of magnesium oxide (brucite) into the rocks. At low temperature, brucite dissolves easier than serpentine minerals, as already reported in some occurrences of weathered serpentinites. This natural process introduces new application on the carbon mineralogical sequestration and its study could open new solutions for the environmental sustainability and GHG reduction.

## Dating the lithospheric mantle: A comparison of Re-Os ages in single sulfides and whole-rock in cratonic mantle xenoliths from Somerset Island (Canada)

Bragagni A.\*<sup>1</sup>, Luguet A.<sup>1</sup>, Pearson D.G.<sup>2</sup>, Fonseca R.O.C.<sup>1</sup> & Kjarsgaard B.A.<sup>3</sup>

1. Steinmann Institute, Universitaet Bonn, Germany. 2. Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, Canada. 3. Geological Survey of Canada, Ottawa, Canada.

Corresponding email: [bragagni@uni-bonn.de](mailto:bragagni@uni-bonn.de)

Keywords: lithospheric mantle, Somerset Island, platinum group elements, Os isotopes.

Dating mantle rocks aims at constraining ages of partial melting as well as the possible crust-mantle genetic relationships. The Re-Os isotopic system, based on the radioactive decay of  $^{187}\text{Re}$  into  $^{187}\text{Os}$ , is the chronometer of choice to undertake mantle samples dating. Nevertheless, mantle xenoliths have generally experienced a complex petrological history often consisting in partial melting and later metasomatic overprinting events. However, meaningful chronological constraints on these petrological processes can still be obtained by Re-Os dating of single sulfide grains, the main host-phases of Os in mantle lithologies, whose origin might be related to discrete processes (i.e. metasomatism or mantle melting). Mantle xenoliths from Somerset Island show a large range in Re-Os model ages (2.7-1.3 Ga) correlating with increasingly metasomatism-overprinted HSE signatures. Four mantle peridotites showing representative whole-rock Re-Os model ages and HSE signatures of the full Somerset Island suite were selected to unravel the complex petrological history of the lithospheric mantle root under Somerset. Individual sulfides (down to 20 micron across) were micro-sampled from thick sections, with Os extracted via  $\mu$ -distillation and analyzed by N-TIMS. In three xenoliths, sulfides have preserved Archean Re-Os model ages ( $T_{\text{RD}}$ ) of 2.8 Ga, likely corresponding to the timing of sub continental lithospheric formation. The 2.8 Ga age is not recorded in the whole rock suggesting that sulfides have the ability of preserving the original Os isotopic composition inherited during mantle melting. These 2.8 Ga Re-Os model ages are recorded in primary inclusions in olivine or in inner portion of altered sulfides. The second group of sulfides is characterised by extremely radiogenic Os isotopic composition corresponding to future model ages. Those sulfides are clearly related to later metasomatic processes (e.g. kimberlitic infiltration). The third group of sulfides shows intermediate  $^{187}\text{Os}$  isotopic composition, yielding Re-Os  $T_{\text{RD}}$  ages of 2.0-2.2 Ga and 1.7-1.9. Both age ranges correlate with crustal events having been recorded in Somerset Island as the 2.0 Ga Thelon Orogeny, which marks the collision of the Slave and Rae cratons, and the 1.7 Ga magmatic events characterised by plutonic intrusions. Our findings highlight that mineralogical and textural investigations along with Os isotopic measurements of sulfides provide robust chronological constrains able to unravel the complex petrological evolution of lithospheric mantle roots.

## Cross-study of different isotopic systems in high-pressure ultramafic rocks reveals mass transfer at subduction zones (Cima di Gagnone, Central Alps)

Cannaò E.\*<sup>1</sup>, Agostini S.<sup>2</sup>, Tonarini S.<sup>2</sup> & Scambelluri M.<sup>1</sup>

1. Dipartimento di Scienze della Terra, dell'Ambiente e della Vita - Università di Genova. 2. IGG-CNR Pisa.

Corresponding email: [enrico.cannaò@unige.it](mailto:enrico.cannaò@unige.it)

Keywords: boron isotopes, mass transfer, ultramafic rocks.

The use of isotopes for tracing processes occurring at plate boundaries led to important advancements in understanding the geochemical evolution of the Earth. In particular, across-arc boron (B) isotope variation enabled to define fluid-mediated mass transfer in subduction zones and the genesis of arc lavas. Subsequently, isotopic studies of high-pressure terrains allowed to examine the possible sources of fluids triggering mantle metasomatism and partial melting. Recently, many studies indicate the plate interface as primary site for fluid/rock interaction and element exchange between different subduction reservoirs, with major global implications. To understand interaction between these reservoirs, we examined the lithospheric mélange from Cima di Gagnone (Central Alps; Trommsdorff, 1990). Here, de-serpentinized chlorite harzburgite and garnet peridotite bodies are embedded in metasediments, same as occurs in top-slab melanges (Scambelluri et al., 2014). An original oceanic setting has been established for some chlorite harzburgite lenses enclosing MORB-type eclogite and metaroddingite. The whole rock-suite (peridotite, eclogite, metaroddingite, paraschist) shows low  $\delta^{11}\text{B}$  (-3 to -12 ‰). In a  $d^{11}\text{B}$  vs. B/Nb plot, ultramafic rocks fall on a trend between high-pressure serpentinites (with high B and  $d^{11}\text{B}$  up to 20 ‰) and host metasediments. Coherently with the mélange concept, this points out interaction between the above rock systems that reset the isotopic signature of the ultramafic rocks. This is clearly recorded by the Sr and Pb isotopic composition of ultramafic rocks, whose enrichment in radiogenic Sr and Pb ( $^{87}\text{Sr}/^{86}\text{Sr}=0,7124$ ;  $^{206}\text{Pb}/^{204}\text{Pb}=18,837$ ) indicates fluid-mediated exchange with metasediments. Moreover, metaperidotite enrichment in fluid-mobile elements removed at low-temperature, like As and Sb, suggests that exchange took place since the early stages of subduction. These features provide clues to understand accretion of peridotite and sedimentary materials in plate-interface subduction channels, and related mass transfer from slab-to wedge.

Scambelluri M., Pettko T., Rampone E., Godard M. & Reusser E. 2014. Petrology and Trace Element Budgets of High-pressure Peridotites Indicate Subduction Dehydration of Serpentinized Mantle (Cima di Gagnone, Central Alps, Switzerland). *Journal of Petrology*, 55, 459-498.

Trommsdorff, V. (1990). Metamorphism and tectonics in the Central Alps: The Alpine lithospheric mélange of Cima Lunga and Adula. *Mem. Soc Geol It.*, 45, 39-49.

## Effects of sulphur degassing in komatiite-hosted Ni-PGE ores at Wannaway, Yilgarn Craton, Western Australia

Caruso S.<sup>1</sup>, Moroni M.\*<sup>1</sup>, Fiorentini M.L.<sup>2</sup>, Isaac C.<sup>2</sup>, Barnes S.J.<sup>3</sup>, Wings B.A.<sup>4</sup> & Cliff J.<sup>5</sup>

1. Dipartimento di Scienze della Terra A. Desio, Università degli Studi di Milano. 2. CET/CCFS, The University of Western Australia, Perth, WA, Australia. 3. CSIRO Earth Science and Research Engineering, Perth, WA, Australia. 4. McGill University, Montreal, Quebec, Canada. 5. The University of Western Australia, Perth, WA, Australia.

Corresponding email: [marilena.moroni@unimi.it](mailto:marilena.moroni@unimi.it)

Keywords: komatiite ore, degassing, in-situ sulfur isotopes.

Drillcores of a complete mineralized sequence involving a komatiite-hosted metallic sulfide layer give a unique opportunity for studying the mechanisms of Archean Ni-Fe-PGE metallogeny. The Wannaway Ni-PGE sulfide deposit is located in the Ni-rich Kambalda Domain, Western Australia. The drilled sequence includes a sulfide-rich orebody occurring at the base of a komatiite flow overlying sulfidic black shales and metabasalts with remarkably well preserved, pristine features in spite of low- to mid-metamorphic imprint. In the orebody a basal massive sulfide layer grades to matrix-disseminated facies upwards where sulphides are intergrown with silicates. The ore consists of FeS (pyrrhotite-troilite)-pentlandite assemblage with minor sphalerite, Cr-Fe spinels, and accessory PGE-bearing Ni-Co-Bi-As/Te sulfosalts, chalcopyrite and alabandite. Sulfidic black shales host Fe-Zn-Cu-Pb-Ni sulfides and PGE-rich Ni-Co-Bi-As/Te sulfosalts with distinct chemistry. Significant changes are observed in the primary ore assemblage and phase chemistry with stratigraphy. Such features may correlate with factors involved in the ore genesis: role of wallrocks in S saturation of magma, role of coexisting immiscible S, As and Te liquids in PGE enrichment, and, especially, mechanisms of degassing of volatile components (S, O) during the crystallization of the metallic magma layer. S degassing is recorded in progressive changes in the ore chemistry culminating in the crystallization of a primary, S-poor troilite-sphalerite-pentlandite-alabandite-magnetite assemblage in the degassed upper part of the ore sequence. This study was also the basis for in-situ, ion probe multiple S isotope analyses on dominant Fe-Ni sulfide phases across the whole ore sequence. Plots of  $\delta^{34}\text{S}$  vs.  $\Delta^{33}\text{S}$  compare the effects of mass-dependent ( $\delta^{34}\text{S}$ ) to the mass-independent fractionation index  $\Delta^{33}\text{S}$ , the latter fingerprinting Archean crustal S reservoirs characterized by intense photochemical reactions between S-bearing gases and unshielded cosmic UV rays (Jamieson et al. 2006). Both ore and black shale clusters plot at positive non-zero values of  $\Delta^{33}\text{S}$ , coping with S saturation of magma via assimilation of S-rich sediments. A remarkable feature is the flat  $\Delta^{33}\text{S}$  arrays for both ore Fe sulfide and pentlandite, which are in textural, chemical and isotopic equilibrium. Both phases display shifts in  $\delta^{34}\text{S}$  values related to stratigraphy and chemistry, and testify progressive lowering of  $\delta^{34}\text{S}$  signatures from basal massive ore upwards. Such a trend may correlate with intense isotopically heavy  $\text{SO}_2$  outgassing of the lava (Marini et al. 2011).

Jamieson J.W., Wing B.A., Hannington M.D. 2006. Evaluating isotopic equilibrium among sulfide mineral pairs in Archean ore deposits: case history from the Kidd Creek VMS deposit, Ontario, Canada. *Econ. Geol.*, 101, 1055–1061.  
Marini L., Moretti R., Accornero M. 2011. Sulfur Isotopes in Magmatic-Hydrothermal Systems, Melts, and Magmas. *Rev. Mineralogy & Geochemistry*, 73, 423-492.

## Mo and stable U isotopes as tracers for subduction components in the Quaternary West-Mediterranean potassic and ultrapotassic magmatism

Casalini M.\*<sup>1-2</sup>, Avanzinelli R.<sup>1</sup>, Elliott T.<sup>3</sup>, Tommasini S.<sup>1</sup> & Conticelli S.<sup>1</sup>

1. Dipartimento di Scienze della Terra, Università degli Studi di Firenze. 2. Dipartimento di Scienze della Terra, Università di Pisa. 3. School of Earth Science, University of Bristol (UK).

Corresponding email: [martina.casalini@unifi.it](mailto:martina.casalini@unifi.it)

Keywords: Mo and U stable-isotopes, geochemical tracers, Italian potassic magmatism.

The central-western Mediterranean is one of the most important areas on Earth for studying subduction-related potassic and ultrapotassic magmatism. In a very restricted area, leucite-free (lamproite) and leucite-bearing (kamafugite, leucitite, and plagioleucitite) ultrapotassic rocks have been emplaced and are associated with shoshonites and high-K calc-alkaline volcanic rocks.

Despite their alkaline characteristics, the least evolved Italian ultrapotassic rocks associated with destructive plate margins invariably show a strong depletion of Nb and Ta along with the highest levels of incompatible trace elements ever seen in any volcanic arc. These characteristics are thought to be derived through the recycling of sediments via subduction within the mantle wedge, and their extreme trace element enrichments make them unique for understanding the roles of different subduction-related metasomatic agents (e.g. silico-clastic vs carbonate). In fact, the variable compositions of the sedimentary materials, subducted along the Adriatic slab and transported into the overlying mantle forming a vein network, could explain the distinct geochemical signature of each Italian magmatic region (Avanzinelli et al., 2009).

We propose to investigate this issue considering two stable isotopic systematics that are perceptible to redox condition-related isotopic fractionation. We measured Mo and stable U isotopes with the high-resolution MC-ICP-MS (Neptune), using a double-spike technique, on selected volcanic rocks from three Italian magmatic provinces and representative samples of subducting sediments.

Molybdenum has seven stable isotopes, which have been shown to fractionate during the incorporation into oceanic sediments. Under oxic conditions, Mo adsorbs to particles into the sediment, particularly when Fe-Mn oxides are present, producing lighter isotopic composition ( $\delta^{98}\text{Mo}/^{95}\text{Mo}$ ), whilst is quantitatively removed in anoxic conditions, leaving sediments with a heavier isotopic signature. The recently observed variability in natural  $^{238}\text{U}/^{235}\text{U}$  values (different from the widely used “consensus” value of 137.88) due to isotopic fractionation during the redox transition between the U(IV) and U(VI) oxidation states, produces as well as Mo isotopes, a lighter isotopic composition ( $\delta^{238}\text{U}/^{235}\text{U}$ ) in oxic sediments compared to a heavier composition in anoxic sediments. We interpret those results in order to recognize the U and Mo isotopic signature of sediments, with different lithology and chemical composition, recorded into the selected volcanic rocks, and to set new constraints on the metasomatic agents responsible for the transition from silica oversaturated lamproite-like to strongly silica undersaturated HKS magmas.

Avanzinelli R., Lustrino M., Mattei M., Melluso L., Conticelli S. 2009. Potassic and ultrapotassic magmatism in the circum-Tyrrhenian region: Significance of carbonated pelitic vs. pelitic sediment recycling at destructive plate margins. *Lithos*, 113, 213–227.

## Chromium isotopic signature of naturally Cr (VI) contaminated spring waters from Western Tuscany

Chiarantini L.\*<sup>1-2</sup>, Agostini A.<sup>1</sup>, Baneschi I.<sup>1</sup>, Natali C.<sup>3</sup> & Tonarini S.<sup>1</sup>

1. IGG-CNR, Pisa. 2. Dipartimento di Scienze della Terra, Università di Firenze. 3. Dipartimento di Fisica e Scienze della Terra, Università di Ferrara.

Corresponding email: [laura.chiarantini@gmail.com](mailto:laura.chiarantini@gmail.com)

Keywords: chromium isotopes, serpentinites, spring waters.

Weathering of serpentinites produces soils and sediments with high Cr concentrations. High Cr (VI) contents (up to 50 µg/l) have also been found in some spring waters spilling out from serpentinite bodies that outcrop in Cecina Valley (Western Tuscany). Petrographic and mineralo-chemical analyses of both rocks and soil samples highlight the occurrence of minerals able to release Cr (III) but the scarce presence of Mn-oxides, able to rapidly oxidise Cr(III), implies that local presence of Cr (VI) in waters have to be ascribed to other processes.

With the aim of enhance the understanding of serpentinite rocks weathering processes, and Cr mobility, radiogenic (Sr-Pb) and Cr isotope composition of serpentinites, soils and spring waters coming from Western Tuscany selected sites have been performed.

Sr-Pb isotopes of serpentinites evidence a significant interaction with recent, low-T, waters; all spring waters display Mg-HCO<sub>3</sub> chemical composition but a Sr-Pb isotopic signature suggest low interaction with serpentinite bedrocks. Cr isotopes are generally used to investigate Cr(VI) reduction occurred in contaminated ground waters, during biotic and abiotic processes, which produces a strong positive fractionation of residual unreduced Cr(VI) as well as a powerful tool for to reconstruct the redox state of ancient sea water. Nevertheless, little is know about fractionation effects accompanying Cr (III) oxidation although small positive fractionation has been experimentally demonstrated. The spring waters preliminary investigated for Cr isotopes are strongly positively fractionated ( $\delta^{53}\text{Cr}$  values between +0.5 and +2.6‰) as observed in other naturally Cr (VI) contaminated ground waters (Izbicki et al., 2008). The observed strong positive fractionation can be the result of both Cr oxidation and partial back reduction of soluble Cr (VI). Differently the investigated serpentinite bedrocks display very low  $\delta^{53}\text{Cr}$  values (-0.2 and -0.3‰) compared to those reported in literature for this type of rocks (Farkaš et al., 2013).

Izbicki J.A., Ball J.W., Bullen T.D. & Sutley S.J. 2008. Chromium, chromium isotopes and selected trace elements, western Mojave Desert, USA. *Appl. Geochem.* 23, 1325–1352.

Farkaš J., Chrástný V., Novák M., Čádková E., Pašava J., Chakrabarti R., Jacobsen S.B., Ackerman L. & Bullen T.D. 2013. Chromium isotope variations ( $\delta^{53}\text{Cr}$ ) in mantle-derived sources and their weathering products: Implications for environmental studies and the evolution of  $\delta^{53}\text{Cr}$  in the Earth's mantle over geologic time. *Geochimica et Cosmochimica Acta*, 123, 74–92.

## The hare as a climatic proxy for south-eastern Turkey

Galli E.\* & Iacumin P.

Dipartimento di Fisica e Scienze della Terra "Macedonio Melloni" - Università degli Studi di Parma.

Corresponding email: [elisa.galli.eli@gmail.com](mailto:elisa.galli.eli@gmail.com)

Keywords: Stable isotopes, climate change, Holocene, hare, Turkey.

The study of fossil skeletal remains by stable isotope analysis can give information related to environmental and climatic conditions that may integrate different archeological surveys.

The archeological site of Arslantepe (Malatya, Turkey) represents a very interesting case study. The systematic excavation has been carried out through a stratigraphic approach since the sixties, by University Roma La Sapienza. This allowed analyzing skeletal samples from a time interval between 6000 and 1500 B.P., that was characterized by regional and global climatic changes (Frangipane, 2012).

In the site many faunistic species were found, both domestic and wild. Hare (*Lepus capensis*) is present in every stratigraphic interval. Data in literature show that hares are characterized by an inverse relationship between the relative humidity and the  $\delta^{18}\text{O}$  values of the skeletal phosphate, suggesting the use of hare fossil bones as a record of relative humidity conditions (Delgado Huertas et al., 1995).

Considering the existence of a relation between carbonate  $\delta^{18}\text{O}$  and phosphate  $\delta^{18}\text{O}$  (Iacumin et al., 1996), and the greater easiness in sample preparation, the analyses were performed on the bone carbonate fraction ( $\delta^{18}\text{O}_{\text{carb}}$ ). The  $\delta^{13}\text{C}$  on the carbonate and collagen fraction and the  $\delta^{15}\text{N}$  on collagen were also measured. A significant variation of  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{15}\text{N}_{\text{coll}}$  between different levels was found: a clear positive peak was recorded in level VIA (5300-4950 B.P.), which is in good agreement with the heavy drought that happened in the Mediterranean areas in 5200 B.P. (e.g., Staubwasser & Weiss, 2006).

The obtained results prove that isotopic signals of this species are a good proxy for the reconstruction of the relative variation of humidity in the history of Arslantepe.

Delgado Huertas A., Iacumin P., Stenni B., Sanchez Chillon B. & Longinelli A. 1995. Oxygen isotope variations of phosphate in mammalian bone and tooth enamel. *Geochimica et Cosmochimica Acta*, 59, 4299-4305.

Frangipane M. 2012. Proceedings of the conference "Fifty years of excavations and researches at Arslantepe-Malatya (Turkey). The contribution of La Sapienza University to the study of the earliest centralized societies". Rome, December 5-7, 2011.

Iacumin P., Bocherens H., Mariotti A. & Longinelli A. 1996. Oxygen isotope analyses of coexisting carbonate and phosphate in biogenic apatite: a way to monitor diagenetic alteration of bone phosphate?. *Earth and Planetary Science Letters*, 142, 1-6.

Staubwasser M. & Weiss H. 2006. Holocene climate and cultural evolution in late prehistoric-early historic West Asia. *Quaternary Research*, 66, 372-387.

## The evolution of stable S-isotopes in poly-metamorphosed sulfide deposits from the Italian Western Alps

Giacometti F.\*<sup>1</sup>, Evans K.A.<sup>2</sup>, Rebay G.<sup>1</sup>, Cliff J.<sup>3</sup>, Tomkins A.G.<sup>4</sup>, Rossetti P.<sup>5</sup>, Vaggelli G.<sup>6</sup> & Adams D.<sup>7</sup>

1. Dipartimento di Scienze della Terra e dell'Ambiente, Università degli Studi di Pavia. 2. School of Applied Geology, Curtin University, Perth, Australia. 3. Centre for Microscopy, Characterisation and Analysis, University of Western Australia, Perth, Australia. 4. School of Geosciences, Monash University, Melbourne, Australia. 5. Dipartimento di Scienze della Terra, Università di Torino. 6. CNR, Istituto di Geoscienze e Georisorse, Torino. 7. Department of Earth and Planetary Sciences, Macquarie University, Sydney, Australia.

Corresponding email: [fabio.giacometti@unipv.it](mailto:fabio.giacometti@unipv.it)

Keywords: sulfur isotopes, high pressure metamorphism, fluid-rock interaction.

Devolatilization reactions in subducting slabs produce H<sub>2</sub>O- and CO<sub>2</sub>- dominated fluids which take part in metamorphic reactions and enhance element mobility. Although sulfur is a minor component of subduction-related fluids, it can play an important role in mobilizing normally un-reactive calcophile and siderophile elements (potentially to be released into mantle wedge) and in taking part in oxidation-reduction reactions.

Evidence of fluid-rock interaction, mineral replacements and/or re-crystallization during metamorphism can be recorded by sulfides and give insights on the mobilization of sulfur and metals in subduction related processes.

On this basis, mineralized samples from two ocean floor-related sulfide deposits (Servette and Beth-Ghinivert in the Italian Western Alps), with different HP to greenschists facies poly-metamorphic evolutions, were investigated with a detailed micro-textural and isotopic study by means of in situ analyses of S-isotopes ratios.

In situ  $\delta^{34}\text{S}$  values within individual pyrite and chalcopyrite grains were interpreted combining micro-textural, mineralogical and geochemical analyses which allowed to assess the effectiveness of metamorphism in modifying the isotopic record. Evidence of fractionation of stable sulfur isotopes between sulfides and fluids was utilized as a tool to identify fluid-rock interaction processes and mobilization of sulfur during metamorphism.

Ocean-floor related features are well preserved at Beth-Ghinivert even at the micro-scale and very little metamorphic overprint is recorded by the sulfides mineralization. At Servette evidence of metamorphic textures is widespread and sub-millimeter scale modifications of  $\delta^{34}\text{S}$  values occur, indicating interactions with an infiltrating hydrothermal fluid. However, none of the deposits record diffusive metamorphic re-equilibration at the deposit scale and largely preserve isotopic records and mineralogical features ascribable to ocean-floor metasomatism.

The preservation of pre-Alpine isotopic features is here interpreted as a consequence of negligible fluid/rock interaction (i.e. limited fluid release) and negligible sulfur release during subduction-exhumation metamorphism. As a consequence, the contribution of sulfur to the mobility of calcophile and siderophile elements is minimized to the conditions experienced by the two deposits.

This study evidences the key-role of the amount of circulating fluids and of deformation in determining the isotopic evolution of subducted sulfide deposits and in favoring sulfur release during metamorphism.

## The mantle isotopic printer

Lustrino M.\*<sup>1</sup> & Anderson D.L.<sup>2</sup>

1. Dipartimento di Scienze della Terra, Università di Roma La Sapienza. 2. Seismological Laboratory, California Institute of Technology, Pasadena, USA.

Corresponding email: [michele.lustrino@uniroma1.it](mailto:michele.lustrino@uniroma1.it)

Keywords: isotope geochemistry, mantle, petrology, mantle plumes.

Computer printers can reproduce all the range of colours using a limited number of colours (black, magenta, yellow, cyan). Similarly, the isotopic composition of oceanic basalts and nearly all the continental counterparts can be expressed in terms of very few mantle end-members (the equivalents of the colour reservoirs). The four most important (actually, "most extreme" since some of these are extraordinarily rare) mantle end-members identified by isotope geochemists nearly thirty years ago are DMM or DUM (Depleted MORB Mantle or Depleted Upper Mantle), HiMu (High-Mu, where  $\text{Mu} = 238\text{U}/204\text{Pb}$ ), EM-I and EM-II (Enriched Mantle type I and type II). Other mantle end-members, or components, have been proposed (PHeM, FoZo, LVC, PreMa, EM-III, CMR, LoMu, C, and so on) but these can be considered as less extreme components or mixtures in the geochemical mantle zoo, to mix metaphors.

Various petrogenetic models have been proposed to explain the presence, the abundance, the physical state and the origin of the four principal mantle end-members. Models differ from thermodynamic engines in that the latter must be constrained by thermodynamics, in particular the 2nd Law. All the basic mantle "colours" are present in a relatively restricted area concentrated E of Australia, in the Polynesia-Melanesia-Micronesia region. With the exception of DMM/DUM all the other mantle end-members require the involvement of olivine-poor lithologies. These lithologies have been attributed to recycled upper/lower continental crust rocks, recycled oceanic crust, terrigenous and/or pelagic sediments, kimberlites, carbonatites, sulphides, oxides or simply frozen basaltic melts crystallized at depths. Thermal anomalies are not associated with or required to explain these end-members. A small degree of melting is sometimes invoked to explain absolute trace element contents or the trace element fractionation recorded in submarine to subaerial lavas. Shallow degassing and contamination is implied in noble gas systematics.

It is the shallow anomalies that are responsible for intraplate volcanism. Mantle plumes and a fully convecting mantle are based on assumptions that violate physical, mineralogical and cosmological considerations. Physically realistic Earth models have a thick upper thermal boundary layer, characterized by superadiabatic thermal gradient, with a thickness in the order of 200-250 km. This is sufficient to explain three out of the four mantle colours in terms of shallow mantle dynamics, e.g. plate tectonics. Such a thermodynamically self-consistent model eliminates the need for lower mantle involvement in oceanic basalt petrogenesis and in igneous activity in general. All the isotopic colour cartridges can be placed at shallow depths.

## Origin and evolution of Po river water (Northern Italy): insights from geochemical and isotopic ( $\delta^{18}\text{O}$ - $\delta\text{D}$ ) data

Marchina C.\*<sup>1</sup>, Bianchini G.<sup>1-2</sup>, Claudio Natali C.<sup>1</sup>, Pennisi M.<sup>2</sup>, Colombani N.<sup>3</sup>, Tassinari R.<sup>1</sup> & Knoeller K.<sup>4</sup>

1. Dipartimento di Fisica e Scienze della Terra, Università di Ferrara. 2. Istituto di Geoscienze e Georisorse (IGG), CNR, Pisa. 3. Dipartimento di Scienze della Terra, Università di Roma "La Sapienza". 4. Department Catchment Hydrology, Helmholtz Centre for Environmental Reserach – UFZ, Halle/Saale.

Corresponding email: [mrcchr@unife.it](mailto:mrcchr@unife.it)

Keywords: geochemical data, isotopic data, Po river, Northern Italy.

The Po river is the most important fluvial system of Northern Italy and the related basin, the Padanian Plain, is strongly influenced by urban settlements, as well as by industrial, agricultural and zootechnical activities.

In spite of its importance, systematic geochemical and isotopic investigations of its water are rare, difficultly accessible and never reported for the whole basin scale. The present contribution aims to fill this knowledge gap, reporting a comprehensive data-set including oxygen and hydrogen stable isotopes, as well as major and trace element concentration of dissolved species for 54 Po river water samples collected in different seasons at increasing distance from the spring, i.e. from the upper part of the catchment to the terminal (deltaic) part of the river at the confluence with the Adriatic Sea.

The isotopic compositions demonstrate that the predominant part of the runoff derives from the Alpine sector of the catchment through important tributaries such as Dora Baltea, Ticino, Adda and Tanaro rivers, whereas the contribution of the Apennines tributaries is less important. The geochemical and isotopic compositions show that the Po river water attains a homogeneous composition at ca. 100 km from the spring. The average composition is characterized by  $\delta^{18}\text{O}$  - 9.8‰,  $\delta\text{D}$  - 66.2‰, TDS (Total Dissolved Solids) 268 mg/L, chloride 17 mg/L and by a general Ca-HCO<sub>3</sub> hydrochemical facies, which is maintained for most of the river stream, only varying in the terminal part where the river is diverted in a complex deltaic system affected by more significant evaporation and mixing with saline water evidenced by higher TDS and chloride content (up to 8,198 mg/L and 4,197 mg/L, respectively). A series of geochemical and isotopic maps have been carried out to visualize spatial gradients, which reflect the evolution of the river water composition at progressive distance from the source; more detailed maps were focused on the deltaic part in order to visualize the processes occurring in the transitional zone toward the Adriatic Sea. The data also highlight anthropogenic contributions, mainly represented by significant concentration of nitrate (average 8 mg/L) and possibly arsenic (average 12 µg/L), which have to be monitored to minimize environmental risks. On the whole the data allow the calculation of geochemical fluxes transferred by the river to the sea, and more in general contribute to the definition of a "hydro-archive" which is useful to highlight ongoing variation in the related ecosystems.

## Conservation of $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios in the oenological food chain of “Red” wines to validate their use as geographic tracer

Marchionni S.\*<sup>1</sup>, Bollati A.<sup>2</sup>, Braschi E.<sup>3</sup>, Cifelli F.<sup>2</sup>, Molin P.<sup>2</sup>, Parotto M.<sup>2</sup>, Mattei M.<sup>2</sup>,  
Tommasini S.<sup>1</sup> & Conticelli S.<sup>1-3</sup>

1. Dipartimento di Scienze della Terra, Università degli Studi di Firenze. 2. Dipartimento di Scienze, Università Roma Tre. 3. Istituto di Geoscienze e Georisorse, Consiglio Nazionale delle Ricerche, Firenze.

Corresponding email: [sara.marchionni@unifi.it](mailto:sara.marchionni@unifi.it)

Keywords: Sr isotopes, geographic traceability, wines.

The use of  $^{87}\text{Sr}/^{86}\text{Sr}$  in tracking wine regional provenance was among the most pioneeristic application of isotope geology to other sciences. In most of the cases, however, the analytical uncertainty observed in Sr isotopes analyses of wines from literature is larger than most of the rock/soil isotopic variability, giving strong difficulties in matching data of wines with those from geological substrata of the vineyards. Recently, high-precision analytical method for determining  $^{87}\text{Sr}/^{86}\text{Sr}$  has been provided enabling then the direct comparison between data on wines with those of the geological substrata. Although the use of high precision Sr isotopic measurement, in some case discrepancies have been observed between the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in wine with those of geological material of the substrata of the vineyards. This might be due either to adulteration of the analysed wines or to processes related with the oenological chain from the Sr uptake by the roots of the vine to the winemaking process.

With this contribution we present a detailed study on the distribution of  $^{87}\text{Sr}/^{86}\text{Sr}$  in the complete food-chain of an Italian “Red” wine with the aim of verifying the occurrence of  $^{87}\text{Sr}/^{86}\text{Sr}$  decoupling between the wine and the geological substratum (i.e., rocks). We determined  $^{87}\text{Sr}/^{86}\text{Sr}$  in soil, grape, grape juice (must), and wine on four different farms from the broad “Cesanese” wine region. The “Cesanese” cultivar is a red Italian grape variety that is grown primarily in the Latium district, Central Italy. The “Cesanese” Red wine is produced using 100 % of the homonymous grape and it is regulated and certified through three geographically distinct production areas: the *Cesanese di Affile*, *Cesanese di Olevano* DOC, and *Cesanese del Piglio* DOCG. The selected wineries cover the three distinct DOC areas and they are from a geologically and geochemically well defined region, from which a wide isotopic set of data for volcanic rocks is available.

Our data indicate that all of the wines, musts, and grapes from different vintages have an excellent reproducibility of their Sr isotope composition within each single vineyard, independently from the nature of the substratum, climate, altitude, geomorphology, and water availability. These data also demonstrate that Sr isotopes are not affected by the wine-making process as we obtained the same Sr isotope composition in grape, must, and bottled wine. This evidence indicates a good manufacture practices of the different producers (i.e., without artificially adulterating the wine organoleptic characteristics).

With this study we corroborate and validate the use of  $^{87}\text{Sr}/^{86}\text{Sr}$  as a robust geochemical parameter that, in addition to organoleptic characteristics, is apt to trace the authenticity of the geographic provenance of high-quality red wines of the Consortium of Cesanese, Latium, Italy.

## IMS 1280-HR: a versatile ion microprobe for Geosciences

Peres P.\*<sup>1</sup>, Saliot P.<sup>1</sup> & Lombardi E.<sup>2</sup>

1. AMETEK, Gennevilliers, Franc. 2. AMETEK srl, Robecco sul Naviglio (MI).

Corresponding email: [paula.peres@ametek.com](mailto:paula.peres@ametek.com)

Keywords: sims, geochronology, geochemistry.

SIMS (Secondary Ion Mass Spectrometry) is applied to a variety of applications in Geosciences, because it provides *in situ* measurement of elemental and isotopic composition in selected  $\mu\text{m}$ -size areas of the sample.

The IMS 1280-HR is a large geometry magnetic sector ion microprobe delivering unequalled analytical performance for a wide range of applications: tracking geological processes using stable isotopes, dating minerals, determining the content of trace elements, screening and analyzing large numbers of particles.

High density cesium or oxygen primary ion beam bombardment combined with optimized transmission allow high precision stable isotope studies and analysis of trace elements at high sensitivity (e.g. mandatory for Pb analyses in Zircon). The multicollector system ensures ultimate reproducibility for stable isotope ratio measurements (H, C, O, S, Li, B, Mg...) and significantly increases the throughput of the instrument by reducing the total acquisition time. Thanks to its superior imaging capabilities (both microscope and microprobe), the IMS 1280-HR is capable of mapping the distribution of major, minor and trace elements or isotopes at sub-micron lateral resolution.

Hundreds of scientific papers have been published covering major application fields in geo- and cosmochemistry, geochronology, environmental studies,... A review of recent analytical data obtained with the IMS 1280-HR on different domains will be presented, among which:

Hydrogen / Deuterium analysis in apatite from lunar rocks. The determination of the isotopic signature and amount of lunar water has profound implications for our understanding of the history of the Earth-Moon system.

Oxygen isotope ratio analyses in zircon. O isotopic signatures in zircon are used to infer magmatic and pre-magmatic histories, including the presence of liquid water on the surface of earliest Earth.

Sulfur isotope ratio analyses in olivine-hosted sulphides from ocean island basalts. Basaltic lavas at some oceanic intraplate hotspot volcanoes are thought to sample ancient subducted crustal materials.

Magmatic dating of individual crystals from the Yellowstone supervolcano. U-Pb and U-Th dating measurements combined with oxygen isotope analyses allow to investigate the genesis of voluminous post-caldera rhyolites.

Martian meteorite age using micro-baddeleyite: U-Pb isotopic analyses of resistant micro-baddeleyite ( $\text{ZrO}_2$ ) and host igneous minerals performed in a basaltic Martian meteorite in order to distinguish between the ages of formation and the ages of the impact events (that launched debris towards Earth).

## **SESSIONE S24**

### **Geological risks and geomorphic processes in the Mediterranean area**

#### *CONVENORS*

*L. Martelli (Regione Emilia-Romagna)*

*L. Sandri (INGV, Bologna)*

*J. Selva (INGV, Bologna)*

## Lithologic effects on mountain stream morphodynamics

Abram G.\*<sup>1</sup>, Toro M.<sup>2</sup> & Brardinoni F.<sup>1</sup>

1. DISAT, Università degli Studi di Milano-Bicocca. 2. DICA, Università degli Studi di Trento.

Corresponding email: [geol.gabram@gmail.com](mailto:geol.gabram@gmail.com)

Keywords: Mountain streams, bedload, scaling relations.

In this contribution we aim to characterize the morphology, the hydraulic geometry and the bedload transport of two mountain streams, Rio Val Ussaia (2.3 km<sup>2</sup>) and Rio Tinto (5.5 km<sup>2</sup>), in Val di Sole, Autonomous Province of Trento. The former flows on tonalites of the Adamello batholith, the latter follows the path of a strike-slip active fault and as such flows on highly fractured limestones and marls of the Brenta Dolomites Group. Both streams have been repeatedly overridden by continental Pleistocene glaciations and as such, in places, are covered by thick glacial sediment blankets. The two study streams have identical mean annual precipitation (870 mm) with maxima falling in May and in October-November.

Methods for each study channel include: (i) rapid field surveys along the entire longitudinal profile (i.e., local slope, surficial channel bed texture, channel cross sections); (ii) bedload monitoring in relation to water discharge (from September 2012 to April 2014) of the distalmost channel reaches via release of 329 PIT-tagged clasts (b-axis ranging from 35 mm to 140 mm), whose travel distances were measured after each rainfall event; and (iii) repeated detailed topographic surveys of the thalweg along the monitored channel reaches.

Results show that, regardless of lithology type, bankfull width and depth, as well as D50, D84, bankfull shear stress, and total stream power increase downstream down to the fan apex, where they all start declining rapidly. Even though Rio Tinto basin is over two times larger than Rio Val Ussaia basin, maximum values of bankfull channel cross-sectional variables for the two streams are virtually identical, an indication of substantial water loss in Rio Tinto due to dissolution-driven effects in highly fractured lithologies. Lithology affects the caliber of the mobile bedload fractions in that the D50 and D84 of more resistant tonalite clasts in Rio Val Ussaia are about twice the size of those found in marls and limestone clasts in Rio Tinto.

Bedload monitoring indicates that boulder steps in Rio Val Ussaia are extremely unstable and mobile due to the abundance of till-derived sand. Conversely, in Rio Tinto we observe that the majority of steps are made of jammed, interlocked key stones, stabilized by the presence of a cohesive fine fraction derived from crushed marly limestones. Maximum single displacements of PIT-tagged stones associated with peak flow events in both streams are in the order of hundreds of meters. During the largest recorded event in Rio Tinto, which has exceeded bankfull flow and has formed lateral levees typical of hyper-concentrated transport, PIT-tagged stones have reached the basin outlet travelling distances > 700 m.

## **Giant, slow rock slope deformations in the European Alps: controls, geomorphic impacts and geohazard implications**

Agliardi F.\*, Crosta G. & Zanchi A.

Dipartimento di Scienze dell'Ambiente e del Territorio e di Scienze della Terra, Università degli Studi di Milano-Bicocca.

Corresponding email: [federico.agliardi@unimib.it](mailto:federico.agliardi@unimib.it)

Keywords: Deep-seated gravitational slope deformations, landslides, Alps.

Large rock slope instabilities are widespread in active orogenic belts as the European Alps, with significant geomorphic and geohazard implications. Landslide research has usually focused on large catastrophic landslides (e.g. rockslides/rock avalanches) characterised by high mobility and runout potential. However, several studies have documented the widespread occurrence of giant “non-catastrophic” slope instabilities known as Deep-seated Gravitational Slope Deformations (DSGSD). These long-lasting phenomena are characterised by peculiar morpho-structural evidence and significant interactions with slope forms and engineering structures. Nevertheless, their distribution, mechanisms, evolution, and potential for catastrophic collapse have rarely been systematically analysed.

We investigated general geological and climatic controls on DSGSDs and their links with landscape evolution at the orogen scale by using the first inventory dataset covering the entire European Alps, including over 1000 individual DSGSDs. We quantified the spatial density of DSGSDs, evaluated their distribution with respect to lithology, structures, morphometry, climate-related variables and long-term exhumation, and characterised their activity using remotely-sensed displacement monitoring data. In addition, we investigated the local-scale controls of inherited structures, active tectonics and post-glacial debuttrressing on the mechanisms, onset and potential catastrophic collapse for different case studies in the Central-Eastern Alps, by integrating field surveys, structural analyses, monitoring and numerical modelling.

We showed that DSGSDs in the European Alps are widespread, very long-lasting, and often active phenomena. They preferentially affect high-relief slopes in moderately strong anisotropic rock masses, mostly along structurally-controlled glacial valley sides. DSGSDs undergo significant structural controls at the local to regional scale whereas, at the orogen scale, their distribution and clustering correlate with the long-term exhumation patterns of different orogen sectors. The long-term deformations of DSGSDs effectively adjust post-glacial relief by significantly reducing slope gradient values. Where they are abundant, DSGSDs are thus expected to contribute to long-term denudation. At slope scale, inherited structures (e.g. master fractures and folds) strongly constrain the mechanisms of alpine DSGSDs, which are commonly triggered by postglacial debuttrressing and related processes, locally possibly enhanced by active stress fields and seismicity. Finally, DSGSDs are likely to cause engineering problems related to slow, long-term displacements and rock mass strength degradation, and are often preferential sites for the development of large catastrophic landslides posing significant threats to life and property.

## **Multidisciplinary study of the vulnerability of coastal dune system through the use of abiotic and biotic factors**

Alquini F.\*<sup>1</sup>, Sarti G.<sup>1</sup>, Bini M.<sup>1</sup>, Ribolini R.<sup>1</sup>, Ciccarelli D.<sup>2</sup>, Bertoni D.<sup>3</sup> & Pozzebon A.<sup>4</sup>

1. Dipartimento di Scienze della Terra, Università di Pisa. 2. Dipartimento di Biologia, Università di Pisa  
3. Dipartimento di Fisica e Scienze della Terra, Università di Ferrara. 4. Dipartimento di Ingegneria dell'Informazione, Università di Siena.

Corresponding email: [alquini@gmail.com](mailto:alquini@gmail.com)

Keywords: Coastal dunes, vulnerability, multidisciplinary approach.

Coastal dunes are high dynamic ecosystems and their equilibrium depends on the interaction of many biotic and abiotic factors. They are characterized by a high variety of habitats along with complex ecosystem. Furthermore, coastal dunes act as a barrier to the action of wind and waves allowing the preservation of shore and backshore environments. Multidisciplinary studies provide quantitative tools for assessing the vulnerabilities rates of these systems. The vulnerability of coastal dunes depends on the ability to recovery the dynamic equilibrium in response to a damage event. This study aims to: i) acquire an integrated biotic and abiotic set of data; ii) quantify the relationships among abiotic and biotic factors; iii) identify the vulnerability for each coastal dune sub-environment; iv) verify the reliability and advantages of the applied methodology. The research is running in two pilot sites, but only data from the first site will be presented: Migliarino – San Rossore – Massaciuccoli Regional Park in Italy (Mediterranean Sea) and Acarai National Park in Brazil (Atlantic Ocean). The study allows the acquisition of a dataset including: a) the distribution and coverage of the different plant communities (pioneer annual vegetation, herbaceous dune vegetation which includes embryonic and mobile dunes, and woody dune vegetation), b) the definition of a geomorphological and sedimentological framework integrated geophysical investigation (RTI-DGPS, GPR), c) the analysis of dunes aerial images cyclically-captured by drone flies, d) the monitoring of a set of physical parameters (wave height, wind speed and direction, ground temperature and humidity) by the use of wireless sensor technology. Canonic Correlation Analysis method allows the understanding of the relation occurring between biotic and abiotic factors. The evaluation of the vulnerability classes is based on the United States Geological Survey - USGS (2004). The results of from the two pilot sites can provide indications for a proper management and for efficient plane of interventions.

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## Large boulder deposits along the Maltese coasts

Biolchi S.<sup>1</sup>, Furlani S.<sup>1</sup>, Baldassini N.\*<sup>2</sup>, Antonioli F.<sup>3</sup>, Cucchi F.<sup>1</sup>, Devoto S.<sup>1</sup>, Di Stefano A.<sup>2</sup>, Gambin T.<sup>4</sup>,  
Gauci R.<sup>5</sup>, Monaco C.<sup>2</sup> & Scicchitano G.<sup>6</sup>

1. Dipartimento di Matematica e Geoscienze-Università di Trieste. 2. Dipartimento di Scienze Biologiche, Geologiche e Ambientali-Università degli Studi di Catania. 3. ENEA, Roma. 4. Department of Classic and Archaeology-University of Malta. 5. Department of Geography-University of Malta. 6. Studio Geologi Associati T.S.T., Catania.

Corresponding email: [nbaldas@unict.it](mailto:nbaldas@unict.it)

Keywords: large boulder deposits, storm wave, tsunamis, Malta.

The accumulation of large boulders related to large waves generated by tsunami and extreme storm events have been observed in different areas of the Mediterranean Sea. Along the NE and E low-lying rocky coasts of Malta a tens of large boulder deposits have been observed (Furlani et al., 2011; Mottershead et al., 2014). In the Sicily-Malta channel heavy seas are frequent and are originated by the NE and NW winds. Few severe earthquakes and tsunamis hit historically the Maltese Archipelago, where the seismicity is related mainly to the Malta Escarpment, the Sicily Channel Rift Zone and the Hellenic Arc.

A multidisciplinary study has been carried out on a large boulder deposit located between Armier Bay and Ahrax Point on the NE coast of Malta.

The boulder accumulation is 100 m wide and is located on a gently sloping coast, at an altitude ranging between 0 and 5 m asl. The boulders, metric in size, are made up by limestones and are Miocene in age.

An underwater surveying allowed to describe the submerged scenario, where fresh detachment scarps and isolated boulders can be observed.

Three different hydrodynamic equations (Nott, 2003; Pignatelli et al., 2009; Nandasena et al., 2011) were applied to assess the wave heights required to carry the boulders out of the sea in a joint-bounded scenario. The axis sizes were determined by means of 3D models achieved by digital photogrammetric technique. The rock densities were calculated by field campaigns using N-type Schmidt Hammer. The application of the formula developed by Katz et al. (2000) permitted to correlate sclerometer outputs and limestone densities of boulders.

Moreover Radiocarbon datings were performed on a tens of *Serpulides* samples.

The combination of the hydrodynamic equations and the Radiocarbon outputs suggests that most of the large boulders has been detached and moved by intense storm waves; conversely some of them have been transported by one or more tsunami events.

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## Cluster analysis of HVSR peak datasets to detect geological structures

Capizzi P.\*, Martorana R., Stassi G., D'Alessandro A. & Luzio D.

Dipartimento di Scienze della Terra e del Mare - DiSTeM - Università degli Studi di Palermo.

Corresponding email: [patrizia.capizzi@unipa.it](mailto:patrizia.capizzi@unipa.it)

Keywords: Cluster analysis, HVSR, geological structures.

A modified centroid-based algorithm has been applied to HVSR (Horizontal to Vertical Spectral Ratio) datasets (Nakamura, 2000) acquired for studies of seismic microzoning in various urban centers of Sicilian towns also aimed to obtain detailed reconstruction of the roof of the seismic bedrock (Di Stefano et al. 2014). HVSR data were previously properly processed to extract frequency and amplitude of peaks by a code based on clustering of HVSR curves determined in sliding time windows.

In centroid-based clustering, clusters are represented by a central vector, which may not necessarily be a member of the data set. After fixing the number of clusters, the algorithm finds the cluster centers and assigns each HVSR peak to the cluster, such that the squared distances from the cluster centroid are minimized. Then it calculates the new means to be the centroids in the next step. The algorithm converges to a (local) optimum when the assignments no longer change. There is no guarantee that the global optimum is found using this algorithm.

The proposed algorithm doesn't fix the number of  $k$  clusters and chooses automatically for each  $k$  value the initial centroids from data set. In particular, the UTM coordinates, amplitude and lithology values are the same for all  $k$  initial centroids and corresponding to their average value of all the units to be partitioned. The differentiation on the initial coordinates of the centroids was only based on frequency of the H/V peaks. The distance of each unit from the initial centroids and those obtained after each iteration was calculated as the weighted sum of the Euclidean normalized distances of all the variables considered, UTM coordinates, frequency, amplitude and lithology. The choice of weights has been optimized taking into account, for each  $k$  number of groups, the intra-cluster and inter-cluster variances. Also the choice of the optimal number of  $k$  classes was supported by the analysis of intra-cluster and inter-cluster variances, but basically remains a subjective choice, which is based on priori information and contextual data. The distribution in the frequency domain of H/V peaks obtained using the described centroid-based algorithm for different  $k$  values have been used to reconstruct geological discontinuities and to separate the stratigraphic peaks from those morphological.

In many cases the clustering analysis of HVSR data showed excellent results, allowing to group peaks that can be attributed to the same seismic structures. However, the choice of the partition is strongly linked to the choice of weights for the calculation of the distance and to the geological and stratigraphic knowledge of the area. In other cases, the results showed similar results regardless of a priori choices. The obtained results underline how the most appropriate clustering algorithm for a particular problem often needs to be chosen experimentally.

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## **The evaluation of the intrinsic vulnerability of a superficial aquifer, through the implementation of the sintacs method: the study case of S. Eufemia Lamezia Plain (Calabria - Southern Italy)**

Cuiuli E.\*

Geologo.

Corresponding email: [e.cuiuli@arpacal.it](mailto:e.cuiuli@arpacal.it)

Keywords: S. Eufemia Lamezia Plain, Groundwater, Acquifer, Vulnerability map, SINTACS.

This study aims to evaluate the intrinsic vulnerability of the superficial aquifer underlying the S.E. Lamezia plain (Calabria), located near the homonymous gulf, along the Tyrrhenian coast. The method used in the study is SINTACS (Civita, 1994; De Maio et al., 2001); using, for the representation of the hydrogeological situation and impact, the string of weights Normal Impact which enhances at most the value the depth of groundwater and of unsaturated. At regional scale the plain lying in the Tyrrhenian sector of the Graben of Catanzaro. This is a tectonic structure of regional significance, in the wider geological context of the Calabrian-Peloritani Arc (Amodio Morelli et al., 1976). The study has concretized in the: Groundwater intrinsic vulnerability map of S. E. Lamezia Plain. This last one appears divided into areas with a degree of vulnerability variable from medium to very high, moving from the inner areas of the plain toward the coast. In particular: the medium vulnerability zones are located in the inner areas of the plain, in correspondence of the terraces and alluvial fan deposits, where the depth to groundwater varies from values higher than 30,0 m from ground level (near the hills) up to values including approximately between 5,0 and 10,0 m from the g.l. (in the zones of valley). The high vulnerability zone, located in middle position between the hinterland of the plain and the coast, extends approximately from the central sector to the southern end of the map. This area is characterized by alluvial soils where sand prevails compared to the gravel and silt; the depth of the groundwater varies between 1,0 and 5,0 m from g.l. The elevated vulnerability zone is stretched parallel to the coast. In this zone the surfacing lithotypes are alluvial soils sandy-gravelly and the depth to water table is very low (1,0 - 5,0 m from g.l.). Moreover, in the internal sector of map, there is a small area to elevated vulnerability, formed by alluvial soils gravelly-sandy lightly silty. In this area the water table is attested between 1,0 and 7,0 m about the g.l. The very high vulnerability zone, stretches from N to S, near the coast. Here are alluvial soils, eolian sands and large tracts of ancient dune belt, with groundwater sub-surfacing (0,5/1,0 m - 2,0 m from g.l.). In conclusion, this study aims to give a contribution to the definition the scenarios of potential risk of pollution in the study area, giving back a cartographic product that identifies the most vulnerable areas of the plain.

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## **Landslides induced by fluid release - Sardinian southern margin**

Deiana G.\*, Lecca L., Paliaga E., Todde S. & Orrù P.E.

Dipartimento Scienze Chimiche e Geologiche - Università degli Studi di Cagliari.

Corresponding email: [giacodeiana@tiscali.it](mailto:giacodeiana@tiscali.it)

Keywords: Submarine landslide, debris avalanche, pockmarks.

Study area includes a portion of southern Sardinia continental margin, this sector is characterized by a submarine depositional system divided by Pliocene tectonics into several marginal basins in which arrives sedimentary contributions from various segments of the Continental Shelf (Lecca et al., 1998). The structure of the margin is characterized by the succession of two deformational regimes. The oldest corresponding to a compressive phase of crustal thickening during the Oligocene Miocene, contemporary to the rotation of the Sardo-Corso block and the opening of the Algero-Provençal basin (Mascle et al., 2001).

Based on multibeam data collected during MAGIC (Marine Geohazard along Italian Coasts) surveys, integrating with seismic data acquired during of previous research projects (Progetti Finalizzati CNR, CARG, PRIN and others), have been studied the main gravitational processes in the continental slope of south Sardinia.

South western Sardinia continental margin includes the distal shelf and upper slope in front of San Pietro and Sant'Antioco islands, the Gulf of Palmas and Teulada Cape. Instability areas are represented by canyons headscarp in retrogressive erosion, particularly active are the Toro Canyon heads and the Teulada canyon system which shows evidences of tectonic control. In this area, particularly significant is the complex landslide off the Toro Island which affects a volume of loose sediments of about 7 km<sup>3</sup>; two low-angle landslides that develop off the coast of Cape Teulada affects a volume of 2 km<sup>3</sup>. Areas characterized by fluids emission are home of large pockforms (d > 500) concentrated in the summit area of the most active headscarp, while large fields of pockmarks and mud volcanoes were found on the right side of Teulada Canyon.

Sardinian southern margin includes distal shelf and upper slope of the Gulf of Cagliari and the northernmost part of Ichnusa seamount. Gravitational instability processes are represented by two major landslides located 10 Nm off the city of Cagliari, the landslide body is affected by processes of base scouring due to the migration of the meanders of the Pula Canyon. 10 nautical miles off Punta Zavorra, on an isolated strip of continental shelf were recognized block landslides evolved along the main tectonic features (NW-SE) that give rise to a debris avalanche deposit; gravitational instability occurs at the summit area of the left side of Sant'Elia canyon, where significant creep waves affects surface sediments.

## Case study of the Entella river floodplain (Liguria, Italy): engineering geological mapping for the development of urban areas

Faccini F.<sup>1</sup>, Lazzeri R.\*<sup>1</sup>, Perasso L.<sup>2</sup>, Raso E.<sup>1</sup> & Robbiano A.<sup>2</sup>

1. University of Genoa, Earth Science Department. 2. Geologist consultant.

Corresponding email: [lazzeririccardo@yahoo.it](mailto:lazzeririccardo@yahoo.it)

Keywords: Engineering geology, Geotechnical map, Entella Stream.

The advancement of the engineering geological mapping for a correct management of the Entella River floodplain is of primary importance for a general town planning and a sustainable development of the nearby areas.

This paper presents the case-study of the Entella Stream floodplain including the final catchment area with a total surface of 376 km<sup>2</sup>: the presence of the towns of Lavagna, Chiavari and Cogorno which sum up over 50,000 inhabitants makes this area extremely vulnerable and therefore susceptible to high risk values.

The final sector of the catchment is divided in three zones of different lithology: the first one consists of shales and presents gentle slopes, the second part shows steeper sides made by slates and sandstones, while the last one corresponds to the plain area and it's made up of fluvial and marine deposits.

The Entella Stream floodplain is 4,5 km long and its width ranges between 150 m and 400 m; the stream flow rate during a flooding event is about 3000 m<sup>3</sup>/s and since the 17th century more than 50 critical events have been recorded making it possible to determine a mean recurrence time for overflowing in the lower portion of the Entella basin of about 10 years.

Recent deposits can be identified in the valley floor area corresponding to the actual riverbed of the Entella Stream; present-day terraced alluvial deposits actually give origin to the flat areas along the stream becoming wider in the middle-lower sector; approaching the delta, ancient fluvial terraces represented by small residual lenses on a higher level compared to the actual valley floor can be also identified.

Alluvial fans on the orographic left along the central and southern sectors show a grade range between 2% and 10% while the ones located on the orographic right are less extended and steeper than the previous ones (more than 10%).

From the analysis of the collected data an engineering geomorphological map (scale 1:10,000) has been carried out as well as a lithotechnical sketch of the soils and a hydrogeological sketch of the plain sector in which the soils have been distinguished according to their geotechnical features and their permeability degree.

The whole study area has been involved in a strong urbanization process during the last one hundred years which considerably reduced the hydraulic efficiency of the river. Slopes have also been modified by the ancient practice of building terraces made up of dry-stone walls while the coastal sector has been altered by embankments and artificial cliffs.

Further infrastructural projects such as the extension of existing roads, the enlargement of the Chiavari City stadium and a purification plant close to the Entella stream delta will soon concern this area: an evaluation of the stream catchment main features is therefore needed also to evaluate the present and future anthropic impact.

## **A new interpretation of the large-scale Alpepiana landslide (upper Aveto Valley, Northern Apennines) based on a field survey, gis applications, and integrated monitoring activities**

Lazzeri R.\*<sup>1</sup>, Faccini F.<sup>1</sup> & Robbiano A.<sup>2</sup>

1. University of Genoa, Earth Sciences Department. 2. Geologist consultant.

Corresponding email: [lazzeririccardo@yahoo.it](mailto:lazzeririccardo@yahoo.it)

Keywords: Landslides kinematic, Deep-seated gravitational deformation, Sturla Valley.

This work aims to present the results of geomorphological studies and monitoring activities concerning the landslide of Alpepiana (Aveto Valley) at the boundary of Liguria and Emilia-Romagna.

Alpepiana hamlet was built between 800 m and 1000 m a.s.l. on the foot of a relict slow-flow-type landslide which represents the evolution of a large mass movement that originated from the southern slope of Mt. Oramara.

The landslide presents a lengthened shape extended over 2 km<sup>2</sup> with direction NE-SW in the upper portion and NW-SE in the lower.

Instability phenomena are well known since the Roman period, and the parish church was continually rebuilt due to the movements of the landslide.

The geological setting of the area is characterized by the Ottone Unit (marly limestones epherophic to ophiolitic sandstones and breccias), the Orocco Unit (marly limestones), and the Canetolo Unit (marls and limestones).

Fifteen boreholes have been drilled, and equipped with monitoring instrumentation, consisting of four inclinometers, nine piezometers and two pumping wells. In addition, more than 600 m of seismic refraction have been acquired.

Hydrogeological and geotechnical field tests were carried out, and some laboratory tests were conducted in order to improve our knowledge of the landslide material.

The phenomenon can be classified as a complex-flow type landslide, with a maximum depth of the landslide mass exceeding 40 m in the central portion.

According to geological and geomorphological features, the Alpepiana landslide seems to be a deep-seated gravitational slope deformation.

The observations during the field survey show evident signs of movement, as creep forms in soil at the surface level, and structural damage can be seen in historical and recent buildings. Inclinometric monitoring activity, carried on from 1999 to 2000 and from 2001 to 2002, showed an average velocity of 10 cm/y, highlighting the slip surface's depth, ranging between 15 and 20 m.

The piezometric measurements identified an unconfined aquifer inside the landslide body, whose level doesn't seem to be directly related to rainfall events.

Back analysis carried out on the landslide cross section indicated a residual strength angle of 14°, apparently related to the finer clayey component of the soil; therefore mineralogical XRD analysis was executed, showing a good relation between clay minerals and geotechnical properties.

The government has intervened with drainage and forest management measures: nevertheless the results are not exhaustive, because of the size of the landslide.

This study represents a contribution with the aim of developing the most effective interventions to increase the stability of the slopes involved through a slow kinematic landslide.

## The sinkholes of Rio Marina (Elba Island, Italy): a case of study

Liali G.\*<sup>1</sup>, Algeri G.<sup>1</sup>, Afferri A.<sup>1</sup>, Barletta R.<sup>1</sup>, Benucci C.<sup>2</sup>, Bigio T.<sup>1</sup>, Bonciani F.<sup>1</sup>, Brogna F.N.A.<sup>1</sup>, Carmignani L.<sup>1</sup>, Colonna T.<sup>1</sup>, Guastaldi E.<sup>1</sup>, Massa G.<sup>1</sup>, Muti A.<sup>2</sup>, Pieruccioni D.<sup>1-3</sup>, Trotta M.<sup>1</sup> & Tufarolo E.<sup>1</sup>

1. Università di Siena- CGT Centro di Geotecnologie, San Giovanni Valdarno, Arezzo. 2. A.S.A. S.p.a. - Azienda Servizi Ambientali, Livorno.  
3. Università di Cagliari - Dipartimento di Scienze Chimiche e Geologiche.

Corresponding email: [liali@cgt-spinoff.it](mailto:liali@cgt-spinoff.it)

Keywords: Sinkhole, Subsidence, Elba Island.

This work concerns the multidisciplinary study of the Mulini Valley in the eastern part of Elba Island (municipalities of Rio nell'Elba and Rio Marina, province of Livorno), which affected by sinkhole phenomena since many years. We firstly performed a detailed geological and geomorphological analysis (scale 1:1000) through both aerial photo-interpretation and field survey. After that, we carried on the morphodynamic interpretation of the landscape shapes and the definition of the existence of widespread subsidence processes that have characterized the study area. These processes generated a large depressed area highlighted by geomorphological evidences showing a recall of the river network and a consequent sedimentation toward the center of the depression.

Subsequently, we investigated the geometry of the subsurface by utilizing geophysical techniques: in particular we realized 14 two-dimensional electrical resistivity tomographies, with interelectrode distance ranging between 2 and 10 meters, and 56 passive seismic surveys in single station through a digital tomograph.

The results of these studies allowed us to reconstruct the following sequence of events:

- A sinkhole on "Calcare Cavernoso" formation originated in Middle?-Upper Pleistocene, with a probable stagnation of water and deposition of clays: the groundwater level in this period was approximately localized 20 meters below the present surface level. An important environmental and climatic change occurred in Holocene. It constituted the trigger processes of surface runoff and debris flow phenomena that partially invade the Mulini Valley toward the sea coast at Rio Marina village. So the current stratigraphic succession and morphology of the valley are very recent.

This sequence and the resulting stratigraphy determine the formation of two aquifers:

- A superficial aquifer, exploited by many large dug wells, that is hosted in the Holocene conglomerates and which water level reaches the surface in the rainy season;
- A deep or karst aquifer, exploited by several drilled wells, which is hosted in the "Calcare Cavernoso" formation with the dynamic level measured at about 40 m depth from the surface level.

During the fieldwork local authorities allowed us switched off the pumping in the study area, in order to monitor the dynamic level within karst aquifer. This allowed us to detect the presence of a layer of unsaturated limestone with thickness of about ten meters. So, it can be stated that changes of the deep groundwater level do not interfere with the deep Quaternary deposits. Such fluctuations are not the reason of the subsidence occurred in the Mulini Valley, the causes of which seem to be related rather to the phenomena of filtration from superficial aquifer, resulting in transport of material and triggering of phenomena described in literature as Cover collapse sinkhole or Subsidence sinkhole.

## Why did the slope at Cavargna Valley Sackung (N Italy) start moving? Preliminary results on causative/triggering mechanisms

Livio F.\*<sup>1</sup>, Zerboni A.<sup>2</sup>, Castelletti L.<sup>4</sup>, Tremari M.<sup>5</sup>, Mazzola D.<sup>1</sup> & Amit R.<sup>3</sup>

1. Dipartimento di Scienza ed Alta Tecnologia, Università degli Studi dell'Insubria. 2. Dipartimento di Scienze della Terra "A.Desio", Università degli Studi di Milano. 3. Geological Survey of Israel. 4. Museo Civico di Como 5 – SAP (Società Archeologica S.r.l.).

Corresponding email: [franz.livio@uninsubria.it](mailto:franz.livio@uninsubria.it)

Keywords: Deep Seated Gravitational Slope Deformation (DSGSD), Val Cavargna, triggering mechanism.

Triggering mechanisms and causative processes of Deep Seated Gravitational Slope Deformations (DSGSD) in alpine areas can trigger by several processes such as post-glacial debuttrressing, earthquake-induced ground shaking or co-seismic surface faulting. Distinguishing between climatic and tectonically-driven factors for such slope deformations is challenging, since faults and fracture systems can play both an active and/or passive role in the initiation of slope processes. Nevertheless this issue has major implications both in the reconstruction of the recent evolution of the landscape and in paleoseismological studies.

Here we present a study on a Deep Seated Gravitational Slope Deformation (DSGSD) located in the Cavargna Valley, N Italy. The deformed slope presents a moderate relief with an elevation drop of ca. 650 meters (from 1750 to 1100 m a.s.l.), is characterized by a typical concave-convex profile and shows morpho-features commonly caused by deep-seated slope movements (e.g., Agliardi et al. 2001; Gutierrez-Santolalla et al. 2005). The DSGSD area and its surrounding was not under extensive glaciations conditions. In fact: (i) The main ice cap which covered the alpine valley during Pleistocene reached an elevation of ca. 950 m during Latl Glacial Maximum, (ii) glacial and periglacial erosional features suggest that only small cirque glaciers locally occupied higher elevations, above 1700 m a.s.l. (e.g., Bini et al. 2009).

The study area experienced a considerable regional deformation due to post glacial rebound: an uplift of ca. 90 m, reached mainly between 21 kyr and 13 kyr BP (e.g., Norton & Hampel 2010). The rate of the uplift due to post-glacial isostasy decreases with time and can be considered negligible.

The integrated approach of this study, including morpho-structural analysis, geologic field survey, ERT geophysical survey, a paleoseismological approach applied to the deformed slope, 14C dating and a detailed pedosedimentary analysis on trench infilling enable us to date the onset of the DSGSD to the ca. 2700 BP. We then consider different possible causative/triggering mechanisms, taking into account alternative scenarios consistent with the timing and characteristics of the described slope deformation.

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## Interaction between alluvial and debris flow processes at Vinschgau/Venosta Valley (Italian Alps), revealed by high resolution seismic reflection/refraction profiling

Maraio S.\*<sup>1</sup>, Bruno P.P.G.<sup>2</sup>, Picotti V.<sup>1</sup>, Brardinoni F.<sup>3</sup>, Cucato M.<sup>4</sup> & Mair V.<sup>4</sup>

1. Dipartimento di Scienze Biologiche, Geologiche ed Ambientali, Università di Bologna. 2. INGV, Istituto Nazionale di Geofisica e Vulcanologia, Napoli. 3. Dipartimento di Scienze dell'Ambiente e del Territorio e di Scienze della Terra, Università di Milano Bicocca. 4. Ufficio Geologia e Prove Materiali, Provincia Autonoma di Bolzano, Cardano di Cornedo all'Isarco.

Corresponding email: [stefanomaraio@gmail.com](mailto:stefanomaraio@gmail.com)

Keywords: Debris-flow fan, Vinschgau/Val Venosta, High resolution seismic.

Alluvial and debris-flow fans are common in formerly glaciated mountains, especially where moderate-to-steep tributaries join broad valleys. A cluster of exceptionally large alluvial and debris-flow fans characterize the Vinschgau/Val Venosta, a major relict trough drained by the Etsch/Adige River in the east-central Alps, Italy. In this work, we focus on the Gatria fan, near Laas/Lasa. This sedimentary linkage is one of the largest symmetrical fans in the Alps, it deflects the Adige River to the opposite slope foot, and dominates the valley as an extraordinary half-barrier. Using a high-frequency vibratory source, we acquired and processed a ~4 km long high-resolution seismic reflection profile across a representative transect of Val Venosta, over the Gatria fan, and throughout the Adige valley floor. Our main targets are to study the shallow portion (about 500m deep) of the Gatria debris-flow fan, and examine how this has interacted with the Adige River bed after the Last Glacial Maximum.

Alluvial fan environments, often present significant challenges for high-resolution seismic exploration. A dense wide-aperture geophone array geometry used in the field (see Bruno et al., 2010), allowed a meaningful interaction between refraction and reflection data processing and overcome most of the factors limiting the data quality in those environments. To evaluate the optimal imaging strategy, we compared the Common-Reflection-Surface (CRS) imaging technique with conventional common-depth-point (CDP) reflection processing. The CRS was originally developed as a data-driven and velocity-independent stacking method for producing zero-offset sections with high signal-to-noise ratios, improved resolution, more continuous reflectors, and enhanced images of dipping reflectors stack (see Mann et al., 1999 and references therein). In our case the CRS stack, followed by post-stack depth migration, produced a seismic image more suited for a subsurface interpretation, because the imaged reflectors possess greater coherency and lateral continuity. Seismic reflection images and  $V_p$  velocity models obtained from first-arrival seismic tomography in excellent agreement and delineate:

- (1) the structure and geometry of the buried bedrock along the entire profile;
- (2) the thickness of sediment accumulation, and the valley stratigraphy;
- (3) the seismo-stratigraphic features of the Adige River deposits, which fill the more depressed portion of the valley;
- (4) the internal geometry of debris-flow fan deposits and the interaction between debris flow and fluvial transport processes.

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## Geological modeling of Altavilla Milicia (Sicily) using HVSr data

Martorana R. \*, Capizzi P., Avellone G., Siragusa R., D'Alessandro A. & Luzio D.

Dipartimento di Scienze della Terra e del Mare (DiSTeM) - Università degli Studi di Palermo.

Corresponding email: [raffaele.martorana@unipa.it](mailto:raffaele.martorana@unipa.it)

Keywords: HVSr, ellipticity, shear wave velocity models.

At today the use of inversion of HVSr curves is mainly limited to derive average parameters of the shear wave velocity, although recently they have been used also for a detailed reconstruction of the roof of the seismic bedrock (Di Stefano et al. 2014). Since ambient vibrations may contain waves travelling in all directions, as body waves and Rayleigh and Love waves, a limit of this method lies in the uncertain composition of seismic noise, in the lack of knowledge about the microseismic field and in the subjective choices regarding the data processing. This work aims to verify the potential and limits of the HVSr inversion for the purposes of geological reconstruction of the subsoil in heavy urbanized areas, where few stratigraphic and geophysical constraints are available, and the only information is practically derived from the geological maps. The test site is the area of Altavilla Milicia (Sicily), characterized by outcrops of marine terraces and continental Pleistocene deposits that do not indicate directly the oldest geological formations, which, however, outcrop in the surrounding areas.

Microtremor measurements were carried out on 20 recording points equally spaced of about 300 meters along two alignments: the line P in NW-SE direction near parallel to the coast and the line Q in NNE-SSW direction crossing the town. The HVSr inversion has been carried out using the Neighborhood Algorithm (Wathelet et al. 2004) implemented by the Geopsy software. Because of the lack of boreholes, starting models for inversions were chosen by assigning to each seismic layer ranges of thickness and velocity typical of the lithology expected, as deduced from the geological formations outcropping in the area and from previous geophysical surveys. The 1D seismic models obtained by results of HVSr inversion were correlated and laterally interpolated in order to construct two-dimensional geophysical sections, considering typical seismic velocities for each lithology concerned.

In the study area, the outcropping Plio-Pleistocene clastic succession covers the Numidian Flysch silico-clastic deposits and the substrate related to slope to deep water Imerese Succession. The study area is characterized by a Miocene compression and later Plio-Pleistocene transcurrent and extensional tectonics (Catalano et al. 2013).

The profiles display seismic layers mostly dipping towards N. Profile P (NW-SE-trending) shows displacements whereby seismic layers are abruptly downthrown towards N. This can be interpreted as high angle transcurrent and extensional faults, that downthrow a backlimb of a major fold towards the coast.

Results of this test demonstrate that HVSr inversion can be a valuable method for the reconstruction of the geometry of the main subsurface structures, if supported by the right geological-structural information.

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## The Po Plain Experiment (POPLEX) Field Campaign - Effects of urban sprawl on environmental matrices in northern Italy

Masetti M.<sup>1</sup>, Nghiem S.V.<sup>2</sup>, Sorichetta A.<sup>3</sup>, Stevenazzi S.\*<sup>1</sup>, Bonfanti M.<sup>1</sup>, Conforto A.<sup>1</sup>, Fabbri P.<sup>4</sup>, Filippini M.<sup>5</sup>, Gargini A.<sup>5</sup>, Hall D.<sup>6</sup>, Linard C.<sup>7</sup>, Pola M.<sup>4</sup>, Richter A.<sup>8</sup>, Catani F.<sup>9</sup>, Paloscia S.<sup>10</sup>, Pampaloni P.<sup>10</sup> & Santi E.<sup>10</sup>

1. Dipartimento di Scienze della Terra "Ardito Desio" - Università degli Studi di Milano. 2. Jet Propulsion Laboratory - California Institute of Technology. 3. Department of Geography and Environment - University of Southampton. 4. Dipartimento di Geoscienze - Università degli Studi di Padova. 5. Dipartimento BiGeA - Alma Mater Studiorum Università di Bologna. 6. NASA Goddard Space Flight Center. 7. Université libre de Bruxelles. 8. Institute of Environmental Physics - University of Bremen. 9. Dipartimento di Scienze della Terra - Università degli Studi di Firenze. 10. Istituto di Fisica Applicata - CNR.

Corresponding email: [stefania.stevenazzi@unimi.it](mailto:stefania.stevenazzi@unimi.it)

Keywords: Po Plain, urban changes, satellite data.

The Po Plain Experiment (POPLEX) Field Campaign has been successfully carried out in May 2014 to investigate effects of urban sprawl on environmental matrices across the Po Plain in Italy. It involved 25 participants from 15 institutions in five different countries, supported by remote sensing observations from 12 satellites and data from many in-situ networks, a peculiar characteristic of the study area. POPLEX was conducted effectively to identify and understand impacts of urban characteristics and change on: (a) groundwater resources and management, (b) air quality assessment, and (c) river regime.

Groundwater contamination (Sorichetta et al., 2011), air pollution (Ordóñez et al., 2006) and river regime (Marchetti, 2002) can be impacted by land use type and change in the study area. Thus, it is extremely important to have a temporally and spatially consistent dataset delineating land use changes over time in order to investigate the potential relationship between these changes and the contamination of environmental matrices. Innovative processing of QuikSCAT satellite data with the Dense Sampling Method (DSM) has allowed a successful development of a spatially and temporally consistent dataset capable of identifying urban areas and monitoring annual urban changes, in each pixel of a 1-km grid, for the decade of 2000s (Nghiem et al., 2009).

QuikSCAT-DSM data enabled the identification of a clear direct relationship between urban sprawl and nitrate groundwater contamination in the shallow aquifer with the trends observed in the decadal dataset. Such relationship is independently cross-validated with the spatial pattern of population difference between 2001 and 2011. Air pollution seemed to be less affected by the growth of urban areas, indicating the efficacy of the environmental policies adopted in the last 20 years to improve air quality. Nevertheless, the areas with the most extensive sprawl showed an increase of air pollution along the main roads that can be related to the increase of vehicle commuting distance.

Also observed are a series of effects of land use changes related to specific situations such as the availability of thermal groundwater exploited for tourism, the impact on the environment of industrial plants and of urban sprawling due to the residential and commercial transformation of remediated former industrial sites.

Furthermore, during POPLEX, a series of river sections were selected to calibrate satellite observations for long-term river discharge measurement record with time continuity for the decade 2000s along the Po River. River discharge data will be then used to investigate the effects of land use changes on surface water availability and river regime and thus to forecast future hazard condition related to flood events. As the POPLEX extension, field activities were conducted across the region of Florence in Tuscany to compare and contrast with results in the Po Plain.

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## **Geological models and geotechnical parameters as the essential basis for road design. Emergency operations, planning and maintenance the provincial road no. 108 ("Sulcis Iglesiente", S-W Sardinia, Italy )**

Mureddu A.\*

Provincia di Carbonia Iglesias - Servizio Viabilità - Carbonia (CI).

Corresponding email: [mureddu.alessio@tiscali.it](mailto:mureddu.alessio@tiscali.it)

Keywords: Geological model, Geophisic, Safety levels.

The provincial road no. 108 is of primary importance for the development of communication in the industrial center of Portovesme ( S-W Sardinia), and the highway n. 126 , between the municipalities of Portoscuso and Iglesias in the direction of the chief town, Cagliari. The instability of the entire stretch of road is caused by phenomena of collapse and overturning that periodically occur, also, in relation to the safety of the road, more and serious problems exist due to poor sealing and insufficient bearing capacity of the foundations.

The geological structure of the project area is characterized by the presence of faults, (NW- SE and NNE-SSW), which lead to discards on average no more than 50 meters. The lithostratigraphic structure:

- limestone outcrops and shale belonging to the Paleozoic
- outcrops of volcanics organized in pyroclastic flows
- deposits of Pleistocene age
- Holocene, sand deposits
- Anthropogenic deposits, landfill mining, slope deposits and alluvial

The presence of clay alterations, have brought in a few years to a deep subsidence to the outer limit of the road, led the administration to restrict the roadway with a partial driving ban to safeguard on traffic safety. Following the execution of a detailed geological survey, were made the choices for the investigations, to prepare the accurate geological model.

The province has done so:

- Geophisic electromagnetic relief
- Ground Penetrating Radar
- Relief with Falling Weight Deflectometer
- Laser profilometry of the entire roadway
- Geoelectric relief
- Geological surveys
- Evidence of lift in the hole
- Testing and evaluation of materials lithological unstable

Regarding the problems of the parameters of lift of the superstructure road, from processing of survey data has been possible to model and compute the type and depth of the interventions, which have led to this actions choose:

- demolition and removal of the road surface and, for the most problematic areas, also the foundations of the entire road
- recovery of the substrate of the foundation, for different heights depending on the results of the geophysical tests
- cleaning of the road section in correspondence of the most important subsidence with excavations up to a depth of 3.5 m.
- Placement of drainage and accumulation water structure
- reshaping of the entire road network
- laying of pavement draining.

The programming of a deep and detailed geological relief, the execution of direct and indirect investigations, appropriately targeted at the most problematic areas, allowed, in the medium term, to reach an improvement of the safety parameters concerning the geomorphological risk. The use of "Best Available Technologies" in the planning and design of interventions has allowed us to diversify the work to be performed for the safety total of 10.2 km of road. The use of the acquired data for geological modeling, (in situ investigations, geoelectric prospecting and geo-radar), for geotechnical modeling (in situ surveys, SPT, Hard Falling Weight), and for the design of new roadway, (Hard Falling Weight and laser profilometer), were allowed to bring forward engineering solutions thanks to a fundamental support coming from the modeling of geological and geophysical data. The geophysical surveys, aimed to quantifying the extent of the renovations to be performed on sections of road with important structural deficiencies, will be a basic parameter in the coming years to ensure the maintenance status and the actual residual life of works carried.

## **A new prototype system for MASW2D roadside survey**

Naldi M.\* & Duò E.

TECHGEA Geophysics, Pont-Saint-Martin (AO).

Corresponding email: [info@techgea.eu](mailto:info@techgea.eu)

Keywords: MASW2D, automated data acquisition system, urban survey, geotechnical design.

This paper describes a new prototype system for shallow surface waves seismic survey in urban areas, with an automated MASW2D roadside survey routine. Identification and mapping of soil profile and evaluation of dynamic properties are very important issues in geotechnical design of underground structures in urban area (i.e., new metro lines, large diameter underground utilities for sewage system, etc); moreover, it requires high resolution soil investigation and very low impact on the urban traffic. The new prototype system deals with these issues, with a reduction of survey time (which means less traffic interruption) and a high quality data and resolution degree (due to the high impact energy and the reduction of the typical vibration noise of the urban environment). This system involves the use of an accelerated energy propeller mounted on a pick up truck and a geophones array positioned on a towed land-streamer; the survey is made in a roll-along mode (for the purpose of 2D VS profiling) with a single shot point for each MASW sounding. The optimized mobility and effectiveness of the routine MASW survey has been tested in two urban areas in different traffic conditions and for different objectives. The first case has been applied in a low traffic road to detect collapsed mine cavities in an area with large settlement. The second case has been applied in a quite heavy traffic road to investigate the shallow soil deformation along the main underground water-pipe line. The obtained results demonstrate the efficiency of the entire system in urban environment, with an increased resolution of seismic data.

## Marine slumping risk induced by hyperpycnal flows - Sardinian southern continental margin

Paliaga E.M.\*, Deiana G., Meleddu A., Todde S. & Orrù P.E.

Dipartimento Scienze Chimiche e Geologiche – Università di Cagliari.

Corresponding email: [enricopaliaga@gmail.com](mailto:enricopaliaga@gmail.com)

Keywords: Hyperpycnal flows, Geohazard, Submarine Canyon.

Study area is located on southern Sardinian continental margin whose structural setting is the result of the superimposition of two successive deformational regimes. The first refers to a compressive geodynamic occurred during the Oligocene - Miocene age, contemporary to the Sardinia – Corsica microplate rotation. The southern part of the Sardinian rift, with the superimposed Campidano graben structure continues at sea within the Cagliari gulf, both at the continental shelf level than in the deeper part. The continental shelf reaches a maximum width of about 2 Km and is characterized by sub planar morphology with a slightly steep ground (about 3-4 %). In this area the morphology is strongly controlled by tectonic lineaments which follows the main regional structural features. In particular the western shelf edge and the upper slope are oriented according to an important tectonic feature N130° oriented, resulting in a steep (>40°) fault wall exposure. Have been studied areas susceptible to potential triggering of quick gravitative movements in upper slope. Watercourses present onshore are capable of giving rise to important phenomena of mud-flow and debris-flow, by putting the coastal environment life at risk of abnormal waves back because of the short distance between the shelf edge and the coastline ( $d < 1000\text{m}$ ). In particular, we analyzed the Rio Geremeas hydrographic basin, a steep equilibrium profile water course ( $L = 15\text{ km}$ ,  $H 900\text{ m}$ ) that, in the event of extreme rainfall event could lead to mud flows / debris flow and generate important hyperpycnal flows at sea (Milliman & Syvitski, 1992), similar to what happened on October 2008 in Rio San Girolamo on the western edge of the Campidano Graben and in Sicily (Giampileri) October 2009 (Casalbore et al., 2011). Inside Foxi canyon's headscarp have been detected bedforms characterized by a wave length of dozen of meters and a height of several meters, with the ridge lines arranged approximately perpendicular to maximum slope, this bedforms are called "crescent-shaped bedforms". These forms are generated by the erosion and deposition repetition due to the load of gravitative sedimentary flows (Casalbore et al., 2013).

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## Ten year geomorphological evolution of Zebrù Valley (Italian Central Alps) after the Thurwieser rock avalanche

Riva F.\*, Frattini P., Greggio L., Brardinoni F., Crosta G.B.

University of Milano - Bicocca, Earth and Environmental Sciences, Milano, Italy

Corresponding email: [f.riva22@campus.unimib.it](mailto:f.riva22@campus.unimib.it)

Keywords: Rock Avalanche, geomorphological evolution, remote sensing.

On September 18, 2004, a rock avalanche with an estimated volume of about  $3.8 \text{ M m}^3$  (Riva, 2009) propagated from southern flank of Punta Thurwieser, affecting Marè Valley in upper part of Zebrù Valley, 30 Km East from Bormio, Italian Central Alps. The landslide event deposited a thick debris cover on the pre-landslide morphology up to 2.2 Km from source area (Sosio et al. 2008). In this contribution, we aim at studying role of the rock avalanche on the geomorphological evolution of the valley, specifically in controlling the evolution of the drainage system, the sediment budget and the mass balance of Zebrù glacier. Through Terrestrial Laser Scanner, airborne Lidar and GPS data collected since 2004, it was possible to appreciate and evaluate how such an event was able to modify the landscape and the geomorphology of the valley.

First, the landslide body dammed the Marè river, splitting the original drainage basin into two different sub-units. This caused a different distribution of sediments in the upper part of the valley. Immediately after 2004 rock avalanche, a new creek was carved along the left margin of the landslide, ending in a new alluvial fan located in the Zebrù valley. Debris volume accumulated in this fan between 2003 and 2013 amounts to about  $6000 \text{ m}^3$ .

During normal flow regime, a consistent groundwater flow still occurs within the rock avalanche deposit along the old valley axis; during periods characterized by intense precipitation and snow melting events, the recently developed drainage channel is activated. Thus, the main transport of sediments occurs along the new channel, during periods of high discharge. Within the landslide accumulation, a new channel was formed in central axis of deposit, flowing from the upper part of the accumulation to median portion, where more gentle sector is reached. Here, a sediment trap collects the material eroded by the upper sector of the deposit and by a lateral drainage basin, forming a small plain and two aggrading fans. From this temporary trap, an estimated periglacial sediment denudation rate of  $0.61 \text{ mm/yr}$  was calculated from the lateral basin.

A portion of the Zebrù glacier, that flows from the Mt Zebrù, was mantled with a shallow layer of blocks and finer matrix. This accumulation acted as a thermal insulator, preserving a significant ice volume and building up a steep bound, in the order of 13 m high, between non-covered and covered glacier surface. Glacier volume preserved and mean velocity of ice flow were estimated.

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## **Application of the gravity method for the three-dimensional modeling of the intermountain basins: the cases of Rieti and Leonessa (Central Apennines, Italy)**

Skrame K.\*<sup>1</sup>, Di Filippo M.<sup>1</sup> & Di Nezza M.<sup>2</sup>

1. Dipartimento di Scienze della Terra- Sapienza Università di Roma. 2. INGV - Roma2.

Corresponding email: [klodian.skrame@uniroma1.it](mailto:klodian.skrame@uniroma1.it)

Keywords: Gravity survey, 3D bedrock configuration, Rieti and Leonessa basins.

The intermountain basins represent a typical populated environment where ground motion amplifications can occur owing to the thickness of unconsolidated deposits combined with the complex topography of the carbonate bedrock. An accurate model for the subsurface structure should be obtained to refine the assessment of the earthquake damage potential of the area.

This paper describes the acquisition of gravity data and their analysis and how gravity helped map the thickness of unconsolidated deposits and determine the bedrock configuration of two different intermountain basins: Leonessa plain (hereafter LP) and Rieti plain (hereafter RP).

The LP and the RP, the test areas of this study, are typical intermountain depressions of Center Apennines, related to the Plio-Quaternary extensional tectonic. Both basins are characterized by thick Quaternary fluvial-lacustrine deposits (gravel, sand and clay) overlaying the Meso-Cenozoic pelagic basin deposits.

On the LP, the study involved an area of 52 km<sup>2</sup> occupied by 300 gravity stations. Instead, on the RP, the study area, of 35 km<sup>2</sup>, were occupied by 170 gravity stations, 60 of which were collected during the 1995 gravity survey. The gravity measurements were performed using a LaCoste & Romberg gravimeter mod. D.60 that has a reading resolution and an accuracy of 0.01 mGal. The stations were accurately located with differential GPS (Ashtech Z-Xtreme dual-frequency GPS) that provided centimetric accuracy in elevation. The gravity data resulted from the network adjustment were used to calculate the Bouguer anomaly map. Free air, Bouguer and Terrain corrections were applied to the data. In order to isolate the regional signal different filtering and mathematical functions were tested. The first-degree polynomial expression of the Bouguer anomaly field result to be the most appropriate regional field. Subtracting the regional field from the Bouguer anomaly produced the residual anomaly map.

In order to determine the distribution of the sedimentary infill, a 2D gravity modeling was developed in the region, including three profiles in the case study of LP and six profiles in the case study of RP. A realistic density of the unconsolidated Quaternary deposits (1.75-2,00 g/cm<sup>3</sup> in the case of LP and 2,15 g/cm<sup>3</sup> in the case of RP), a density of 2.50 g/cm<sup>3</sup> for the Travertine and a density of 2.60 g/cm<sup>3</sup> for the Meso-Cenozoic pelagic basin deposits were used to constrain the 2D gravimetric models. The models match quite well with the information determined from a collection of existing well logs and geophysical data.

These models allowed us to reconstruct the geometry of the depression and to evaluate the thickness of the Quaternary sedimentary infilling.

Finally, referring to the obtained paleo-morphology, we were able to reproduce and to define the 3D bedrock configuration of the basins. These 3D models represent a useful starting point for future activities such as microzonation or seismic hazard studies.

## Computation of run-up heights for landslide-generated tsunamis. An attempt of hazard assessment in the North Sicily continental margin

Sulli A.\*, Zizzo E., Albano L.

Dipartimento di Scienze della Terra e del Mare, Università di Palermo.

Corresponding email: [attilio.sulli@unipa.it](mailto:attilio.sulli@unipa.it)

Keywords: tsunamis, run-up, submarine landslide.

The North Sicily continental margin is a very active region located in a transitional area between the Sicilian-Maghrebian Chain to the south and the southern Tyrrhenian Sea to the north. Strong seismicity, active tectonics and volcanism, fluid escape, high sediment supply and widespread mass movements exposed this region to marine geo-hazards, with a potential for tsunami generation (e.g. Messina 1908, Stromboli 2004 events).

In recent years, high resolution swath mapping and high resolution to high penetration seismic reflection profiles have been collected during several oceanographic cruises, in the frame of the MaGIC and CARG projects. Morphobathymetric and geoseismic analysis evidenced the main hazard elements and allowed the production of risk maps.

Available data revealed that one of the most common mechanisms associated with marine geo-hazards is due to submarine mass failure processes, genetically linked to other processes active in this margin (canyon, gas venting, volcanism, tectonic structures, volcanoes, high sedimentation rate).

With the aim to assess the risks linked to landslide-generated anomalous waves we selected two different sectors of the North Sicily continental margin, located in the western (Gulf of Palermo) and eastern (offshore Patti) coasts. These area were selected based on their morphologic, stratigraphic and tectonic setting and for the large amount of morphostructural elements.

The working flow developed through different steps as follows:

- identification and mapping of the main morphobathymetric elements affecting unstable areas;
- characterization and morphometric analysis of landslide scars (ten Brink et al., 2006) selected on the base of their hazard potenzial;
- computation of parameters (wavelength, velocity, amplitude) of landslide-generated anomalous waves (Rahiman and Pettinga, 2006);
- modelling tsunami runup expected by the largest failure volume, breaking on the Sicily coastline, based on Green law relations and solution of the Boussinesq equations (Choi et al., 2006).

In detail, we obtained values of maximum run-up of 6.6-9.1 m for the Gulf of Palermo and 6.3-13.3 m for the Patti offshore. However the obtained values appear to be overvalued because the model foresees a precautionary scenario. Moreover the next step will be the assessment of inundation, taking into account the morphologic features of the coastal area and the roughness, land-use and urbanization of the affected areas, concerning a wider concept of risk assessment.

ten Brink U.S., Geist E.L., Andrews B.D. 2006. Size distribution of submarine landslides and its implication to tsunami hazard in Puerto Rico. *GRL*, 33, L11307.

Choi B.H., Hong S.J., Pelinovsky E. 2006. Distribution of runup heights of the December 26, 2004 tsunami in the Indian Ocean. *GRL*, 33, L13601.

Rahiman T.I.H., Pettinga J.R. 2006. The offshore morphostructure and tsunami sources of the Viti Levu Seismic Zone, southeast Viti Levu, Fiji. *Marine Geology*, 232, 203-225.

## **Developing a spatial vent opening probability map of Somma-Vesuvius caldera**

Tadini A.\*<sup>1-2</sup>, Bisson M.<sup>2</sup>, Cioni R.<sup>1</sup>, Neri A.<sup>2</sup>, Santacroce R.<sup>3</sup>, Bevilacqua A.<sup>2-4</sup> & Flandoli F.<sup>5</sup>

1. Dipartimento di Scienze della Terra, Università di Firenze. 2. Istituto Nazionale di Geofisica e Vulcanologia, Pisa  
3. Dipartimento di Scienze della Terra, Università di Pisa. 4. Scuola Normale Superiore, Pisa. 5. Dipartimento di Matematica, Università di Pisa.

Corresponding email: [alessandro.tadini@pi.ingv.it](mailto:alessandro.tadini@pi.ingv.it)

Keywords: Somma-Vesuvius, vent opening probability map, hazard assesement.

The Somma-Vesuvius volcanic complex has shown in his history a significant variability of eruptive styles associated with a significant spatial variability of the associated vent locations. This is proved by the presence of numerous eccentric vents which fed effusive eruptions and also by the variability of the vent area of the large explosive eruptions that showed a significant shift within the present multi-stage Somma-Vesuvius caldera. Numerical simulations of explosive eruptions with variable vent locations inside the caldera have shown that this variability can have a major effect on the associated hazard, particularly for the threat associated to the occurrence of pyroclastic density currents produced by column collapse. In this work we illustrate some of the activities we have started with the aim of producing a first long-term vent opening probability map for the area of the Somma-Vesuvius caldera. These activities mainly consist in the recognition and collection of key volcano features that can be linked to the spatial distribution of volcanic activity as well as used for their probabilistic treatment. Key variables that have been considered so far include: a) location of Plinian and sub-Plinian volcanic vents; b) location of parasitic cones; c) distribution of faults and fractures; d) type and position of the main subsurface lineaments, as deduced from published geophysical inversions. Locations of Plinian and sub-Plinian volcanic vents have been represented considering their uncertainties based on the available reconstruction of deposits and expert judgment. Parasitic cone locations has been also compiled after a comparative analysis of different bibliographic sources, including geological, geomorphological and topographic maps. Distribution of faults and fractures have been finally derived by integrating data from literature studies and new analysis of different digital terrain models (DTM). All the data have been imported into a GIS-based workspace that allowed to organize, analyze and elaborate different datasets. By assuming that each dataset can contribute to the probability distribution of vent opening through the assignment of appropriate weights (e.g. based on expert elicitation), preliminary vent opening (susceptibility) maps have been produced. Results will be used in the production of more accurate hazard maps of the range of expected explosive phenomena in case of a future reactivation of Somma-Vesuvius.

## Particle tracking via RFID technology to monitor bedload sediment dynamics in mountain streams

Toro M.\*<sup>1</sup>, Fraccarollo L.<sup>1</sup> & Brardinoni F.<sup>2</sup>

1. Dipartimento Ingegneria Civile, Ambientale e Meccanica- Università di Trento. 2. DISAT- Università degli Studi di Milano-Bicocca.

Corresponding email: [luigi.fraccarollo@unitn.it](mailto:luigi.fraccarollo@unitn.it)

Keywords: Bedload monitoring, thresholds of entrainment, step-pool river.

In this contribution we present preliminary results on the monitoring of bedload entrainment and transport in Grigno Creek (90 km<sup>2</sup>), a mountain stream located in Valsugana, Autonomous Province of Trento. In particular, we monitor bedload by means of Radio Frequency Identification (RFID) technology in conjunction with Passive Integrated Transponders (PIT) (e.g., Lamarre et al., 2005) injected into 110 pebble-to-cobble sized tracer stones (b-axis ranging from 30 to 130 mm), which were released in December 2013 along a 100-m channel reach.

Particle tracking is conducted by integrating two complementary antenna types: (i) a portable one, which enables to estimate travel distances of tagged clasts; and (ii) a set of four fixed antennas (25m apart from each other), which allows detecting motion/rest periods of particles, entrainment thresholds and transport velocities.

Particle tracking is combined with on-site high-frequency (i.e., 10 minutes) water stage monitoring. Salt dilution method is seasonally applied to relate flow discharge to water stage. The analysed river reach extends over different morphologic units (steps, pools, glides and boulder-cascades). We are looking to estimate (i) the channel forming discharge; (ii) a quantitative evaluation of specific bedload transport. These information will be associated to the surficial bed texture and bed morphology. Data collected from fixed and mobile antennas will enable to infer statistical information of the trajectories run by tracer ensemble, in particular the step lengths, the total distances and the rest periods.

Lamarre H., MacVicar B., Roy A.G. 2005 Using Passive Integrated Transponder (PIT) tags to investigate sediment transport in gravel-bed rivers. *Journal of Sedimentary Research*, 75, 736-741.

## SESSIONE S25

### **Characterization, modeling and remediation of groundwater resources and contaminated sites**

#### *CONVENORS*

*R. De Franco (CNR-IDPA, Milano)*

*P. Frattini (Univ. Milano Bicocca)*

*A. Gargini (Univ. Bologna)*

*M. Petitta (Univ. Roma La Sapienza)*

*M. Tallini (Univ. Aquila)*

## **Water-rock interaction in the Cimino-Vico volcanoes (central Italy): what we can infer to solve the problem of water supply in naturally arsenic-contaminated area**

Armiento G.<sup>1</sup>, Baiocchi A.\*<sup>2</sup>, Crovato C.<sup>1</sup>, Lotti F.<sup>2</sup>, Nardi E.<sup>1</sup>, Mazzuoli M.<sup>2</sup>, Piscopo V.<sup>2</sup> & Proposito M.<sup>1</sup>

1. ENEA, Laboratorio di Biogeochimica Ambientale, Roma. 2. Dipartimento di Scienze Ecologiche e Biologiche, Università degli Studi della Tuscia, Viterbo.

Corresponding email: [baiocchi@unitus.it](mailto:baiocchi@unitus.it)

Keywords: Volcanic aquifer, Arsenic, Sustainable water management

The volcanoes of central and southern Italy constitute aquifer systems with average yield from 0.005 to 0.02 m<sup>3</sup>/s per km<sup>2</sup>. These aquifers are widely used for drinking water supply, irrigation, industry, water bottling and therapeutic purposes. The type of volcano, hydrostratigraphy and volcano-tectonic settings control the flow in the aquifer systems, originating complex circulations. Waters frequently show different qualities, which strongly influence their possible use for drinkable purposes, especially in relation with the geogenic contamination by arsenic and fluoride. In the Cimino-Vico volcanic areas (central Italy), the occurrence of arsenic in groundwater is well documented. Previous studies show that several factors affect the mobility and distribution of arsenic in groundwater, such as temperature and water chemistry, as well as the regional and local hydrogeological characteristics.

This study examines the relationships between the arsenic content in the rocks and groundwater, considering the complex geological and hydrogeological environment. Based on hydrogeological and hydrochemical investigations, analyses of the arsenic contents in representative rocks constituting the main aquifers were carried out.

Type of aquifer (basal, perched and dome-impounded aquifers), composition of the rocks, hydrostratigraphy, volcano-tectonic setting and related uprising of deep fluids, and hydraulic properties of the different rocks result to be the causes of the heterogeneous arsenic concentration in groundwater (from 1 to 100 µg/L). The waters of the perched aquifers, dome-impounded aquifers and basal aquifer hosted in the acidic lavas and Ignimbrite Cimina show the lower arsenic contents.

New approaches to tap safe drinking water can be inferred from the promising results of the investigations in an area where, at present, the drinkable waters are characterized by geogenic contaminant often exceeding the maximum admissible concentration (10 µg/L).

The case study highlights that the future options for promoting sustainable water management in a naturally contaminated area are strongly conditioned by the knowledge of the geological and hydrogeological environment. From this knowledge some alternative and/or integrative possibilities to the proposed and partly adopted treatment solutions arise.

## Geological 3D model for the design of artificial recharge facilities into the Oued Biskra inféro-flux aquifer (NE Algeria)

Arras C.\*<sup>1-2</sup>, Buttau C.<sup>1</sup>, Carletti A.<sup>1-2</sup>, Funedda A.<sup>1</sup> & Ghiglieri G.<sup>1-2</sup>

1. Dipartimento di Scienze Chimiche e Geologiche, Università degli studi di Cagliari. 2. NRD-Nucleo Ricerca Desertificazione, Università degli Studi di Sassari.

Corresponding email: [cla.arras1@studenti.unica.it](mailto:cla.arras1@studenti.unica.it)

Keywords: NE Algeria, 3D Modelling, aquifer artificial recharge.

North Africa arid regions of Maghreb suffers of dry climatic conditions with erratic behaviour of rainfall in which most part of available superficial waters is lost, providing scarce benefits for households living in villages of such semi-desertic areas.

Oued Biskra watershed (NE Algeria) is one of two study areas implemented in WADIS-MAR demonstration project ([www.wadis-mar.eu](http://www.wadis-mar.eu)) founded by European Commission through SWIM Programme ([www.swim-sm.eu](http://www.swim-sm.eu)). North to the city of Biskra the river bed is imposed on Mio-Plio-Quaternary deposits and the alluvial sediments constitute a phreatic aquifer called inféro-flux (AA.VV., 1980). The aquifer is overexploited for drinking water and irrigation purposes, therefore the aquifer artificial recharge systems were designed in order to increase the sustainable yield of the aquifer and to store water underground when available and to employ it when needed.

Using the software Move (Midland Valley Exploration Ltd.) a preliminary 3D hydro-geological model, based on geological, hydro-geological and sub-surface data, a 30 meters Aster DEM and photo-interpretation, was made to better understand the hydro-geological setting of the inféro-flux aquifer. This study investigated 4 kilometres of the oued Biskra. Through 28 geological cross sections orthogonal to the river bed the 3D model of the alluvial aquifer was reconstructed. It is made up by alluvial deposits, mainly sand and gravel, with thickness that increases from 20 metres in the North to 80 metres in the South. In order to estimate the storativity, from sub-surface data we inferred an effective porosity value of 30%.

Based on the hydro-geological model an aquifer artificial recharge system was designed, consists by:

- 6 dry recharge wells: they will have a diameter ranging from 2 to 3 meters and a depth from 5 to 10, according to local setting of wadi bed and alluvial aquifer. From each well, three buried drainage pipes will depart to maximize the infiltration rates;

- 6 recharge trenches: they will be arrange perpendicular to the flow direction in cascade in a v-shape manner;

- 3 recharge basin: they will permit the infiltration of excess water conducted by buried pipes from the recharge wells. Its shape will be built as an inverted pyramid and built in slightly higher areas of the wadi bed to be sure to not being affected by superficial flow.

Groundwater pollution will be prevent using a “reactive layer”, a palm leaves compost with clay and sand to improve the quality of infiltrating water, that will work as a filter. The evaluation of the artificial recharge yield according the above described system, considering the occurrence of water along the oued for 20 days per year, is 1.5 million cubic metres per year.

WADIS-MAR Project website [www.wadismar.eu](http://www.wadismar.eu)

AA.VV. 1980. Notice explicative de la Carte Hydrogeologique de Biskra au 1/200.000. Ministère de l'Hydraulique Algerienne.

## Geological modelling for hydro-geological purposes in Oum Zessar area (SE Tunisia)

Arras C.\*<sup>1-2</sup>, Cau F.<sup>1</sup>, Buttau C.<sup>1</sup>, Carletti A.<sup>1-2</sup>, Funedda A.<sup>1</sup> & Ghiglieri G.<sup>1-2</sup>

1. Dipartimento di Scienze Chimiche e Geologiche, Università degli studi di Cagliari. 2. NRD-Nucleo Ricerca Desertificazione, Università degli Studi di Sassari.

Corresponding email: [cla.arras1@studenti.unica.it](mailto:cla.arras1@studenti.unica.it)

Keywords: aquifer artificial recharge, 3D hydro-geological modelling, SE Tunisia.

To infer the hydro-geological features of an area wide about 1450 square km in the Saharan Platform we present a 3D hydro-geological model of the Lower Triassic succession in Medenine region (Jeffara plain, SE Tunisia), in order to design an aquifer artificial recharge system for drinking water and irrigation purposes. This region represent one of two study areas implemented in WADIS-MAR demonstration project ([www.wadismar.eu](http://www.wadismar.eu)) founded by European Commission through SWIM Programme ([www.swim-sm.eu](http://www.swim-sm.eu)).

A preliminary geological model was built based on previous geological, hydro-geological data (Yahyaoui, 2007) and remote sensing elaboration. Tectonic and geomorphologic features allow to divide this region into two domains: Jeffara plain and Dahar plateau. The Jeffara Plain represent the footwall of a pre-Cenozoic ENE-dipping fault system that tears apart the Jeffara basin. It consists of a wide sedimentary basin involved in several tectonic events (Gabtni et al., 2009) in which mainly crops out a clastic Cenozoic sequence overlaying a thick Early to Middle Trias succession that generally outcrops along the oued. In the hanging wall of the same fault system, the Dahar plateau occurs. It is a thick Jurassic to Cretaceous carbonate succession representing a fault-bounded structural high that surrounds the Jeffara basin from the South to the West where a Permian succession is well exposed. This geological framework largely influences the various aquifers and the groundwater circulation (Chihi et al., 2013). The lower Triassic succession hosted a strategic aquifer with good quality water for households living in villages and cities of such arid region, up to now overexploited.

The results of the geological model determine the boundaries of the Lower Triassic succession allowing to understanding the hydro-geological conceptual model and to plan an efficacious aquifer artificial recharge system. Based on the collected data and the hydro-geological feasibility, an aquifer artificial recharge system is designed. It consists of dry wells with recharge chambers to catch and infiltrate flash flood waters from the ephemeral streams (ouadi) in 4 intervention sites.

WADIS-MAR Project website [www.wadismar.eu](http://www.wadismar.eu)

Chihi H., Bedir M. & Belayouni H. 2013. Variogram identification aided by a structural framework for improved geometric modeling of faulted reservoirs: Jeffara Basin, Southeastern Tunisia. *Natural Resources Research*, 22(2), 139-161. doi 10.1007/s11053-013-9201-0.

Gabtni H., Jallouli C., Mickus K.L., Zouari H. & Turki M.M. 2009. Deep structure and crustal configuration of the Jeffara basin (Southern Tunisia) based on regional gravity, seismic reflection and borehole data: how to explain a gravity maximum within a large sedimentary basin?. *Journal of Geodynamics*, 47, 142-152.

Yahyaoui H. 2007. Nappes des Grès du Trias Sahel el Ababsa de Médenine, aspects hydrogéologiques et gestion rationnelle des ressources. Internal Report, CRDA Médenine, 27 pp.

## Soil control of trace metals concentration in a photovoltaic power plant project site in Pontina Plain (Center of Italy)

Barbieri M.<sup>1</sup>, Sappa G.\*<sup>2</sup> & Vitale S.<sup>2</sup>

1. Earth Science Department, Sapienza University of Rome. 2. Department of Civil, Building and Environmental Engineering, Sapienza University of Rome.

Corresponding email: [Giuseppe.Sappa@uniroma1.it](mailto:Giuseppe.Sappa@uniroma1.it)

Keywords: soil control, trace metals, Igeo, EF, statistical analysis.

This paper presents preliminary results coming from a survey on the soil contamination of an area located near Latina, Central Italy, where would be built a photovoltaic power plant.

Twenty soil samples were collected for background characterization of sediments coming from this site, located in that part of Pontina Plain, which is very close to Colli Albani Volcanic Region and is made by weathering products of this Volcanic system.

Statistical analysis on chemical data is a fundamental tool, but it isn't sufficient to fully understand and define background conditions that exist at particular sites like this one. Therefore Geoaccumulation Indexes (Muller, 1969) and Enrichment Factors (Forstner & Muller, 1973) have been calculated to assess whether the concentrations observed represents background or contaminated levels

As a matter of fact there are two main sources of trace metals in the soil. The first one is the natural background, which indicates that the trace metal concentration comes from parent rocks, as a result of weathering and water-rock interaction. The second one is anthropogenic contamination, including the application of agrochemicals and the addition of organic amendments, animal manure, mineral fertiliser, and sewage sludge. (Nriagu & Pacyna, 1988)

In soils, generally, more trace metals originate from anthropogenic sources than natural sources. The aims are: to evaluate the geochemical factors that control the distribution pattern of trace elements, to define their natural and/or anthropogenic sources, and to identify the local or anthropogenic sources causing enrichment in the topsoils. (Barbieri et al., 2014)

Statistical analysis indicated that for the Pb the background level exceed the maximum value allowed in soils and it could constitute an anthropogenic component.

Otherwise, the geochemical approach based on Igeo and Ef Factor calculation suggests that the area isn't polluted by this metal. This study shows the importance to evaluate the geochemical factors that control the distribution pattern of trace metals and to define their natural and/or anthropogenic sources.

Barbieri M., Sappa G., Vitale S., Parisse B., Battistel M. 2014. Soil control of trace metals concentrations in landfills: a case study of the largest landfill in Europe, Malagrotta, Rome, *Journal of Geochemical Exploration*, 143,146–154.

Forstner U. & Muller G., 1973. Heavy metal accumulation in river sediments: A response to environmental pollution. *Geoforum*, 4(2), 53–61.

Müller G. 1969. Index of geoaccumulation in sediments of the Rhine River. *Geojournal*, 2, 108–118.

Nriagu J.O., Pacyna J.M. 1988. Quantitative assessment of worldwide contamination of air, water and soils by trace metals. *Nature* 333, 134–139.

## **A stochastic multi-scale approach to study contaminant transport in heterogeneous alluvial sediments**

Bersezio R.<sup>1-2</sup>, Comunian A.\*<sup>1</sup>, De Micheli L.<sup>3</sup>, Felletti F.<sup>1</sup>, Giacobbo F.<sup>3</sup>, Giudici M.<sup>1-2-4</sup>, Lazzati C.<sup>5</sup> & Zappa G.<sup>1</sup>

1. Dipartimento di Scienze della Terra "A. Desio", Università degli Studi di Milano. 2. CNR-IDPA, Milano. 3. Politecnico di Milano. 4. CINFAI, Tolentino (MC). 5. Dipartimento di Fisica, Università degli Studi di Milano.

Corresponding email: [alessandro.comunian@unimi.it](mailto:alessandro.comunian@unimi.it)

Keywords: stochastic simulation, contaminant transport, scaling.

Equiprobable spatial distributions of hydrofacies can be modelled by stochastic simulations, conditioned on field data. Such 3D arrays can be used as input data in numerical models of groundwater flow and contaminant transport, which can be used to assess how the fine scale heterogeneity affects contaminant transport at large scale.

The most common stochastic simulation method is Sequential Indicator Simulation (SISIM). Despite being widely used, SISIM suffers some weaknesses, e.g., in integrating geological information and in reproducing structures with curved shapes. This work deals with a modification of SISIM with a hierarchical approach (HSISIM), which consists in the repeated application of SISIM to perform binary simulations at different hierarchical levels. The advantages of this approach are (1) the possibility of designing a hierarchy based on geological information and (2) the shorter simulation time than for the standard approach, because the time required by SISIM dramatically increases with the number of hydrofacies that are simultaneously simulated.

We illustrate the advantages of the proposed hierarchical method over the standard SISIM using the hydrofacies mapped on the sides of three blocks of glacio-fluvial sediments that were dug in an open air quarry in the Ticino valley (Northern Italy). Each block has a volume of few cubic meters and most of their lateral sides have been analyzed and mapped from the sedimentological point of view with a resolution of 5 cm. From the three field data sets, different ensembles were obtained both with SISIM and with two different HSISIM applications: the first one based on the relative abundance of the hydrofacies; the second one based on geological arguments. Then, the results of the geostatistical simulations were used to perform numerical transport experiments that yielded the statistical distribution of average pore water velocity and effective longitudinal dispersion coefficients at a scale length of the order of 1 m. Finally, these probability distributions were used to predict the fate of toxic and radioactive contaminants over a length scale of 100 m with a 1D stochastic model of solute transport model based on the Kolmogorov-Dmitriev theory in a Montecarlo framework.

The results confirm that a proper estimate of contaminant transport requires a precise reconstruction of the heterogeneity field at the fine scale.

## An aqueduct for Guarani

Brutti P.<sup>1</sup>, Agostini L.\*<sup>2</sup>, Agnelli E.<sup>1</sup>, Righetti M.<sup>3</sup>, Croce S.<sup>4</sup> & Dosserich R.<sup>5</sup>

1 Free Professional. 2. Dipartimento di Geoscienze, Università di Padova. 3 Istituto di Ingegneria, Università di Trento  
4 Caritas Verona. 5 Caritas Camiri (Bolivia).

Corresponding email: [laura.agostini.2@studenti.unipd.it](mailto:laura.agostini.2@studenti.unipd.it)

Keywords: aqueduct, Guarani, tank.

This project, which started in 2009 with the collaboration of local authorities in the South American country, Caritas Bolivia (Camiri) and Caritas Italian (Verona), and some Italian volunteers, aims to build an aqueduct to a small community Guarani which recently has settled in the town of La Junta, or near the confluence of the Rio Grande and the Rio Nanchahuazu. The project itself is part of a broader pattern of views conceived by Father Tarcisio Ciabatti a missionary of Toscana for 40 years in the first person strives to create infrastructure such as water supply, small hospitals and schools, which are able to improve the quality of life of the people Guarani leaving them the opportunity to live in the heart of the Bolivian Chaco, preserving culture and traditions. This project gave birth to the school of environmental health Tekove Katu, which has made available its facilities for the realization of this project. the work in question is an aqueduct that takes advantage of gravity to a height of about 90 meters between source and storage tank. The water is derived by means of an intake water flowing from the Rio Lacayotal, small stream located 20 kilometers south of the village of La Junta. The feed then reaches settlement Guarani Nanchahuazu following the course of the Rio (River which is a tributary of the Rio Lacayotal) crossing it several times until you reach the tank. From here a small network of distribution (the village is less than a mile), which provides the drinking water needs of the entire community.

## **Radioprotection in the groundwater managing**

Carciotto S.B.<sup>1</sup>, Marino M.C.\*<sup>1</sup>, Pennisi A.<sup>2</sup>, Raffa P.<sup>2</sup> & Spartà S.<sup>1</sup>

1. Servizio di Fisica Sanitaria/SPPR - Università degli studi di Catania. 2. SIDRA S.p.A.

Corresponding email: [marinom@unict.it](mailto:marinom@unict.it)

Keywords: Radon, drinking water, radiation safety.

In the context of safeguarding water resources, the radioprotection within the municipal aqueducts is of particular importance, especially if we consider that such aqueducts with their extensive network supply many users.

The aqueduct of Sidra SpA is a practical example. Indeed, since 1967, it has been managing the public services for collection, transportation and distribution of water for civil, irrigation and industrial use in the municipality of Catania and in a neighbouring districts. Furthermore, it supplies "wholesale" water to other distribution systems.

In 2013, the total volume of water injected into the network by Sidra SpA was mc 61.133.535, of which mc 11.688.163 were for domestic use is. In terms of areal extent, the Km of the network are as follows: adduction km. 67.00; distribution Km 895.00.

Since January 2013, the Sidra S.p.A. has entrusted the radioprotection of workers employed in their aqueduct to the Servizio di Fisica Sanitaria/SPPR University of Catania.

In order to protect those who carry out part of their work inside the tunnel, the Servizio di Fisica Sanitaria, complying with the D. Lgs. 230/1995, has organized the radioprotection service and the monitoring of radon gas concentrations in the air inside the aqueduct's tunnels.

At the same time, the "Servizio di Fisica Sanitaria", in accordance with Council Directive 2013/51 Euratom of 22 October 2013, and taking into consideration the elevated levels of radon concentration recorded in the air, is activating the monitoring of radon in the water which from the aqueduct arrives in people's homes, thus extending the radioprotection to the citizens.

Pumping sources are located in the north-eastern side of Etna mount, the extraction is both vertical (pumping wells) and horizontal (culverts). The correlation among the geological structure of the tunnels where the water flows, their morphology and the confined environment, which does not allow the degassing of the water, as well as the comparison between the levels of radon concentration in air and in water, make it possible to assess the impact of radionuclides in the water system. Such upstream oversight assessment can reduce consistently the levels of radon air and water concentrations before the water reaches the end consumer.

The risk of radioactive pollution increases in the aqueducts which develop exclusively through underground galleries, as the outcropping rock and the confined environment generate greater accumulation of ionizing radiation than what happens in the atmosphere, due to the fact that both uranium-thorium, in their decay processes, generate gaseous elements such as Radon and Thoron.

The first means of protection against radionuclides pollution of groundwater resources is the knowledge of the problem through a proper monitoring of the radon gas, providing the basis for the development of a suitable strategy and management of the aquifer.

## Geophysical techniques for hydrological and hydrogeological characterization

Cassiani G.\*

Dipartimento di Geoscienze, Università degli Studi di Padova.

Corresponding email: [giorgio.cassiani@unipd.it](mailto:giorgio.cassiani@unipd.it)

Keywords: Geophysics, Non-invasive, Characterization, Hydrogeophysics.

The characterization of the subsurface from a hydrological point of view requires that the key hydraulic parameters be identified together with the main forcing/boundary conditions. These pieces of information will then contribute towards a correct conceptualization of the system's components and behavior and ultimately towards the construction of mathematical models capable of reproducing the system's behavior and predicting its reaction to future changing conditions. Geophysical techniques can provide a key contribution in this direction. The resulting discipline, named "hydro-geophysics" (Binley et al., 2010) aims for a quantitative use of (geo)physical measurements to constrain and calibrate hydrological models. The conceptual scheme that underlies this technical integration calls for the joint use of geophysical and traditional hydrological data to provide quantitative data for the calibration of a predictive model, and then to identify its relevant key parameters. The advantage of using geophysical data in addition to traditional data is especially in spatial coverage, potentially three-dimensional, which geophysics can provide and that perfectly integrates with the more direct, but generally point-wise, information produced by traditional methods. It should be borne in mind that the geophysical data consists of physical measurements made at the edge of the domain of interest (often at the surface of the ground) but that depend on the distribution of physical parameters within the domain (the soil and subsoil). These physical parameters (e.g. electrical resistivity, electric permittivity, magnetic susceptibility, elastic parameters, etc) are dependent on the physical properties of porous media but also on the state of the interstitial fluids (in varying degrees for different geophysical methods). Therefore from the geophysical data we can get, especially if the measurements are repeated over time, information on: (1) the geometrical structure and geology of the site, i.e. its static characteristics (2) environmental and hydrological dynamics of the site, i.e. time-varying characteristics. Both types of information are integrated in the (static) construction and (dynamic) calibration of a hydrological model (e.g. Deiana et al., 2008; Cassiani et al., 2009). The latter is based on the fact that geophysical data are linkable with good accuracy to the system state change and especially to state variables such as saturation, salt content and temperature. The use of geophysical data in this scheme often use Data Assimilation techniques (e.g. Camporese et al., 2010).

Binley A.M, Cassiani G. & Deiana R. 2010, Hydrogeophysics – Opportunities and Challenges, *Bollettino di Geofisica Teorica ed Applicata*, 51(4), 267-284.

Camporese M., Salandin P., Cassiani G. & Deiana R. 2011. Impact of ERT data inversion uncertainty on the assessment of local hydraulic properties from tracer test experiments, *Water Resources Research*, 47, W12508, doi:10.1029/2011WR010528, 2011.

Cassiani G., Godio A., Stocco S., Villa A., Deiana R., Frattini P., Rossi M. 2009. Monitoring the hydrologic behaviour of steep slopes via time-lapse electrical resistivity tomography, *Near Surface Geophysics*, special issue on Hydrogeophysics – Methods and Processes, 475-486, doi: 10.3997/1873-0604.2009013.

Deiana R., Cassiani G., Villa A., Bagliani A. & Bruno V. 2008. Model calibration of a water injection test in the vadose zone of the Po River plain using GPR cross-hole data, doi: 10.2136/vzj2006.0137 *Vadose Zone Journal*, Feb 25 2008: 215-226.

## Joint hydrogeological and hydrogeophysical inversion for the characterization of subsurface heterogeneity

Cattaneo L.\*<sup>1-2</sup>, Giudici M.<sup>1-2-3</sup> & De Franco R.<sup>2-3</sup>

1. Università degli Studi di Milano, Dipartimento di Scienze della Terra "A. Desio".  
2. CNR-IDPA, Milano. 3. CINFAI, Tolentino (MC).

Corresponding email: [laura.cattaneo1@unimi.it](mailto:laura.cattaneo1@unimi.it)

Keywords: hydrogeophysics, mathematical modeling, joint inversion.

Characterization of subsurface heterogeneity and monitoring groundwater dynamics are of paramount importance to protect groundwater quality and to design remediation plans and can be accomplished by the collection of geoelectrical and hydraulic data and by the joint modeling of the corresponding physical processes. Invasive and expensive direct tools, mostly based on the drilling of piezometers and boreholes and on geotechnical and geognostic surveys, often provide information with accurate vertical resolution, but require horizontal interpolation or correlation. Hydrogeophysics is a useful complementary technique, for both hydrostratigraphic characterization and monitoring. This presentation shows an interpretative tool, that profits from DC geoelectrical and hydraulic measurements, to provide a further step towards this objective. The subsurface is considered to be subdivided in hydro-electrical geobodies, which are regions occupied by geological materials (hydro-electrical facies, HEF) characterized by their geoelectrical and hydrodynamic properties, namely phenomenological laws that relate electrical resistivity and hydraulic conductivity to texture, soil saturation and pore water conductivity, through specific phenomenological parameters for each HEF. The spatial distribution of HEFs can be estimated from a collection of lithological data (e.g., borehole stratigraphic logs), through stochastic simulations that yield ensembles of equiprobable realizations. Two original computer codes, both based on conservative finite differences schemes, have been developed to solve the hydrological (YAGMOD) and the geoelectrical (YAELMOD) forward problems, to obtain the modeled saturation field and the modeled apparent resistivity for given electrode configurations. Using a Monte-Carlo approach, different sets of parameters for the phenomenological laws are introduced into an iterative procedure that repeatedly solves the hydraulic and electrical forward problem for different stress condition of the aquifer, as a basic step to match experimental data (apparent resistivity and hydraulic head) with model outcomes. The distribution of estimated HEF parameters is modified at each step, by the application of an approach based on the Ensemble Kalman filter, with the purpose of minimizing the objective function that quantifies the discrepancy between model outcomes and measured data. Moreover, a sensitivity analysis on both BCs and phenomenological parameters has been conducted, in order to assess the capability of the interpretative tool.

## **Modeling groundwater resource of an alluvial aquifer of Somalia: the Ged Deeble basin**

Cattaneo L.\*<sup>1-2</sup>, Giudici M.<sup>1-2-3</sup> & Petrucci B.<sup>4</sup>

1. Università degli Studi di Milano, Dipartimento di Scienze della Terra "A. Desio". 2. CNR-IDPA, Milano  
3. CINFAI, Tolentino (MC). 4. NGO Africa '70.

Corresponding email: [laura.cattaneo1@unimi.it](mailto:laura.cattaneo1@unimi.it)

Keywords: groundwater resources, mathematical modeling, arid regions.

Water for the city of Hargeisa (Somalia) is supplied by some wells drilled in the alluvial aquifer of the Ged Deeble (GD) basin. The well pumping started in the 1970's and some new wells were drilled later. The water production raised from 6000 m<sup>3</sup>/day in 2003 up to 10400 m<sup>3</sup>/day at the beginning of 2010. This trend reflects in the variation of the water table depth with time. An EU project allowed to perform some exploration activities from 2003 to 2007: a detailed geological survey, a geoelectrical campaign, a series of pumping tests, a continuous monitoring activity prolonged for two years. The data permit a first reconstruction of the basin geometry, of the hydrogeological structure and of the mechanisms of the aquifer recharge. The code YAGMod has been applied to model groundwater flow in the GD basin. Due to great uncertainties on the data, a sensitivity analysis has been conducted to assess which are the most sensitive model parameters. Then, different exploitation scenarios have been examined to verify and try to predict if the future water demand of the city could be satisfied, so that the results of this study could be used to explore and manage water resources. The interpretation of the data and the model calibration give some important suggestions to describe the state of the GD basin. From the geological point of view, the basin could be subdivided in two zones, separated by a strip-shaped area of low permeability. From the hydrological point of view, modelling results support the hypothesis that recharge cannot be limited to rain and wadis infiltration: increasing extraction generates additional recharge sources, that probably come from an underground fracture-fault network in the upstream (southern) area, but from the wide Laas Dhuurre-Damal (LDD) basin which is in contact with the GD basin in the downstream (northern) area. The identification and characterization of the fracture network in the crystalline basement and the potential flow paths could be improved by improve the knowledge of the structural setup of the basin. In this model, incoming flux from fractures is estimated by model calibration. Moreover, a more precise quantification of wadis recharge could be obtained after the extension of the piezometric survey, with a more uniform spatial distribution throughout the whole basin and close to the wadis. With regard to the problems related to water demand, unfortunately it appears that the GD basin alone cannot satisfy the future water demand of the city without a further, more dramatic depletion. However, a shift of the production from the wells in the southern area to those located in the northern one or even in the wider LDD basin could sustain the development of the city.

## Study of the impacts of a former pyrite mine in the territory of Gimigliano (Calabria, Southern Italy)

Cuiuli E., Fòlino Gallo M.\* & Migliorino C.

Dipartimento di Catanzaro – ARPACal.

Corresponding email: [m.folinogallo@arpacal.it](mailto:m.folinogallo@arpacal.it)

Keywords: Environmental Impact, Acid Rock Drainage, Pyrite.

The study aims to determine the environmental impacts deriving from an abandoned mining site located in the NE sector of the *Graben of Catanzaro*, in the territory of Gimigliano (CZ), where it was active a Pyrite quarry managed by Montecatini until 1948. Currently, at the mine site only the working residues, composed of rock fragments ranging in size that constitute the landfill mining, are identifiable. In this context, the greatest impact is the dispersion of potentially toxic elements and the water circulation is the preferential route of dispersion. In particular, the study was initiated after reporting of the presence of a evident whitish coating on the rocks present in the bed of the Patia Creek, a small river which rises just downstream of the mine site and that has caused concern in the local population. After an expeditious radiometric survey which excluded the presence of radiological risk, it was carried out a detailed geological survey to define the lithological structure of the studied area, which is characterized, in outcrop, by *scisti filladici* with darker bands where Pyrite minerals are concentrated. The remains of the rock processing are light, porous and within them it is not recognizable the structure schistose of the parent rock while the Pyrite minerals appear less visible. All this is likely due to the processing phases (extraction of Pyrite) and to the weathering/dissolution processes that the rocks, exposed to exogenous agents, have endured over the years. For the chemical and mineralogical characterization of rock types present and for the understanding of the processes that generated them, seven samples were taken and analyzed by ARPACal laboratories. From the analysis it was found the presence of *Quartz*, *Pyrite*, small quantities of *Sulphides* and *Oxides* and anomalous values of *Arsenic* (max 52 mg/kg). Moreover, to better understand the phenomena of interaction between the water flowing underground and the mining site, chemical analysis were performed on samples of water taken in correspondence of the upstream sources and downstream of the site. The first analysis didn't show particular chemical characteristics, while the latter showed *high acidity* (max pH 4,8), with a strong presence of *Sulfates* (max 504 mg/kg) and *Calcium* (max 135 mg/kg) in addition to discrete levels of *Manganese and Zinc*. About the whitish coating detected on the rock of the Patia Creek, chemical analysis performed on two samples have revealed an high content of *Sulfates* (max 192000 mg/kg) and *Calcium* (max. 3000 mg/kg) showing that the *coating* consists essentially of *Calcium Sulphate*. Therefore the field observations and the analytical results have shown that processes of alteration of *Sulphides*, known in the literature as *Acid Rock Drainage*, are underway at the mine site. They resulted in the acidification of the waters circulating due to the solution of chemical elements (essentially *Sulfates*) that in some environments can reach very high concentrations (whitish coating of Patia Creek).

## **Versilia coastal plain aquifer system: a multidisciplinary approach to define qualitative and quantitative aspects of groundwater resources**

Da Prato S. \*, Doveri M., Ellero A., Lelli M., Masetti G., Menichini M., Nisi B. & Raco B.

IGG-CNR, Pisa.

Corresponding email: [simone.daprato@igg.cnr.it](mailto:simone.daprato@igg.cnr.it)

Keywords: Versilia coastal plain, 3D hydrostructural model, groundwater resources.

Pollution and wrong management of natural resources have led to an increasing attention of the public administration and a development of scientific research in environmental field. Following the Deliberation of the Regional Committee (no 939/2009) in the Tuscany territory, 66 Subterranean Groundwater Bodies (SGBs) were identified by regional Administration, which also promoted their geo-hydrological and geochemical characterization for reaching a better groundwater management.

In this work a multidisciplinary geological-hydrogeological-geochemical approach has been applied to the study of Versilia SGB, that represents one of the major aquifer system of the Tuscany (Menichini, 2012).

The study area is located in the extensional neogenic–quaternary Viareggio Basin, in the inner sector of the Northern Apennines, and it is encompassed from Serchio River (S), Carrara town (N), the Tyrrhenian Sea (W) and Apuan Alps (E).

In the first phase of this study, the geometrical reconstruction of the subsurface geology has been performed through a sequence stratigraphic approach. Sedimentological and micropaleontological analysis of continuously cored boreholes were used as tools for facies definition. Furthermore a stratigraphic logs database allowed a detailed description of the hydrogeological units.

During a second phase a 3D hydrostructural model was achieved by using Aquaveo Software and a computation of the total volume was performed for each hydrogeological unit.

By means of the comparison among the elaborations of the water head and pumping test data and the 3D hydrostructural model, in the third phase the amount of the total water volume stored in the aquifer system was estimate, both in low-flow and high-flow conditions. Moreover, the piezometric surfaces, allowed to individuate the flow pattern and the most exploited zones of the aquifer.

The fourth phase was the hydrogeochemical characterization, through deterministic and geostatistical approach, and through geochemical and isotopic data acquisition and processing.

Main results pointed out that the Versilia SGB is constituted by multilayer aquifer system; a sequence of permeable, gravel and sand layers separated by impermeable silty-clayey deposits.

This multi-layer system behaves similarly to a single-layer aquifer, as suggested by the reconstruction of the piezometric surfaces, owing to both the discontinuous nature of the impermeable deposits and the presence of several boreholes connecting the permeable layers situated at different depths.

The chemical and water isotopes analyses allowed to identify and to characterise the main feeding components of multilayer aquifer system.

The conceptual model is the starting point for flow and transport numerical models, which is a useful tool to define future groundwater management plans.

Menichini M. 2012. A multidisciplinary approach to define the hydrogeological model of aquifer systems in the "Fiume Versilia" catchment and the adjacent coastal plain. Tesi, 341.

## Numerical modeling of groundwater flow in the coastal aquifer system of the Taranto gulf (southern Italy)

De Filippis G.\*<sup>1-2</sup>, Giudici M.<sup>1-2-3</sup>, Negri S.<sup>4</sup>, Margiotta S.<sup>4-5</sup>, Cattaneo L.<sup>2-3</sup> & Vassena C.<sup>2</sup>

1. Consorzio Interuniversitario Nazionale per la Fisica della Atmosfera e delle Idrosfere (CINFAI). 2. Dipartimento di Scienze della Terra "A. Desio" - Università degli Studi di Milano. 3. Istituto per la Dinamica dei Processi Ambientali (IDPA-CNR). 4. Laboratorio di Idrogeofisica e Stratigrafia per i Rischi Naturali, DISTeBa - Università del Salento. 5. Geomod srl - Dipartimento di Scienze dei Materiali, Spin-off of Università del Salento.

Corresponding email: [giovanna.defilippis@unimi.it](mailto:giovanna.defilippis@unimi.it)

Keywords: Salento, coastal aquifers, numerical model.

The Taranto area is among the most sensitive coastal regions of southern Italy to the phenomenon of seawater intrusion, because of the hydrostratigraphic configuration and for the presence of highly water-demanding industrial activities, as it was shown by a preliminary 2D numerical model describing the groundwater flow in the karst aquifer of Salento peninsula, developed by Giudici et al. (2012) at the regional scale and then improved by De Filippis et al. (2013).

In the subprogram of the research project RITMARE (The Italian Research for the Sea) dedicated to the preservation of groundwater quality in Italian coastal aquifers, and in particular in the Taranto area, the CINFAI operative unit provides a contribution to the characterization of groundwater in the area of the Taranto gulf. The specific objectives are:

- the reconstruction of the groundwater dynamic (i.e., the identification of a conceptual model for the aquifer system and the modeling of groundwater flow in a complex multilayered system);
- the characterization of groundwater outflows through submarine and subaerial springs and the water exchanges with the shallow coastal water bodies and the off-shore sea;
- the modeling of seawater intrusion in the coastal aquifer system.

The first objective is achieved through the analysis of hydrostratigraphic reconstructions obtained from different data sets. The hydrostratigraphic setup is merged with maps of land use, hydraulic head maps, data on water extraction and source discharge, in order to identify the conceptual model.

The numerical simulations are conducted with the computer code YAGMod. This code was originally developed to perform 3D groundwater flow simulation with a simplified treatment of unsaturated/saturated conditions under the effects of strong aquifer exploitation and is extended to the case of a variable density flow.

Giudici M., Margiotta S., Mazzone F., Negri S., Vassena C. 2012. Modelling Hydrostratigraphy and groundwater flow of a fractured and karst aquifer in a Mediterranean basin (Salento peninsula, southeastern Italy), *Environmental Earth Sciences*. doi: 10.1007/s12665-012-1631-1

De Filippis G., Giudici M., Margiotta S., Mazzone F., Negri S., Vassena C. 2013. Numerical modeling of the groundwater flow in the fractured and karst aquifer of the Salento peninsula (Southern Italy), *Acque Sotterranee*, 2:17-28. doi: 10.7343/AS-016-013-0040.

## Use of water resources in mountain. The case study of the Montellina Spring

De Luca D. A.<sup>1</sup>, Forno M. G.\*<sup>1</sup>, Gattiglio M.<sup>1</sup>, Gianotti F.<sup>1</sup>, Lasagna M.<sup>1</sup>, Cerino Abdin E.<sup>2</sup> & Dino G.A.<sup>1</sup>

1. Dipartimento di Scienze della Terra, Università degli Studi di Torino. 2. Dipartimento di Ingegneria dell'ambiente, del territorio e delle infrastrutture, Politecnico di Torino.

Corresponding email: [gabriella.forno@unito.it](mailto:gabriella.forno@unito.it)

Keywords: drinking-water spring, geological context, groundwater/surface water relations.

The Montellina Spring (370 m a.s.l.) represents an example of groundwater resource in mountain region. It is a significant source of drinking water located in the right side of the Dora Baltea Valley (Northwestern Italy), SW of Quincinetto town. This spring shows a morphological location along a ridge, 400 m from the Renanchio Torrent in the lower sector of the slope.

The spring was investigated using various methodologies as geological survey, supported by photo interpretation, structural reconstruction, NaCl and fluorescent tracer tests, discharge measurements. This multidisciplinary approach, necessary due to the complex geological setting, is required for the importance of the Montellina Spring. It is interesting in the hydrogeological context of Western Alps for its high discharge, relatively constant over time (average 150 l/s), and for its location outside a fluvial incision and suspended about 40 m above the Dora Baltea valley floor (Lasagna et al. 2013).

According to the geological setting, the hydrogeological reconstruction of the area suggests that the large amount of groundwater in the basin is essentially favoured by a highly fractured bedrock, covered by wide and thick bodies of glacial and gravitational sediments. The emergence of the water along the slope, in the Montellina Spring, is essentially due to a change of permeability between the deep bedrock and the shallow bedrock and/or surficial sediments. The deep bedrock, showing closed fractures and/or fractures filled by glacial deposits, is slightly permeable. The shallow bedrock, strongly loosened as result of gravitational phenomena, and the local gravitational sediments are, on the contrary, highly permeable.

The concentration of water at the spring is due to several reasons. a) The spring is immediately downward a detachment niche, dipping towards the spring, that essentially drains the water connected to the change of permeability in the bedrock. b) It is along an important fracture, that carries a part of the losses of the Renanchio Torrent. c) Finally, it is favored by the visible and buried morphology. Although it is located along a ridge, the spring occurs in a small depression between a moraine and a landslide body. It also can be favored by the likely concave trend of buried base of the landslide.

At last, tracer tests of the Renanchio Torrent water with fluorescent tracer are performed, with a continuous monitoring in the Montellina Spring. The surveys permit to verify and quantify the spring and torrent hydrogeological relationship, suggesting that only a small fraction of stream losses feeds the spring.

Lasagna M., De Luca D.A., Clemente P., Dino G.A., Forno M.G., Gattiglio M., Gianotti F. 2013. Valutazione dell'apporto idrico alla Sorgente Montellina da parte del Torrente Renanchio (Quincinetto, Torino). *Acque Sotterranee - Italian Journal of Groundwater*, 131(2), 75-85.

## The identification of homogeneous hydrochemical areas in the evaluation of natural background levels

Ducci D.\*<sup>1</sup>, Maio V.<sup>2</sup> & Sellerino M.<sup>1</sup>

1. Dipartimento di Ingegneria Civile, Edile e Ambientale (DICEA), Università degli Studi di Napoli. 2. External collaborator.

Corresponding email: [daniela@unina.it](mailto:daniela@unina.it)

Keywords: Hydrogeochemistry, Natural background levels, Campania.

The 'background level' is the concentration of a substance or the value of an indicator in a body of groundwater corresponding to no, or only very minor, anthropogenic alterations to undisturbed conditions" (art 2.5 of the Groundwater Daughter Directive 2006/118/EC). The determination of the NBLs allows the distinction between anthropogenic pollution and natural origin of contamination in a groundwater body (Wendland et al., 2005). The «Groundwater body» is a distinct volume of groundwater within an aquifer or aquifers and its delineation predominantly starts with the identification of geological boundaries, followed by hydrogeological features and topography, taking into account actual and potential utilisation, protection needs, risk potential, economic importance and water management aspects. It is evident that in some cases this definition cannot contemplate the highly diversified hydrogeological environment of the Italian territory.

Under peculiar hydrogeological conditions, e.g. presence of tectonic structures, upwelling of hydrothermal fluids, interactions with other groundwater bodies, the concentrations of certain elements can widely vary, and therefore the differences in groundwater chemistry inside a groundwater body can be remarkable.

In this case, to evaluate the natural background levels and to determine the threshold values (Hinsby et al., 2008), both required by the Groundwater Daughter Directive for the assessment of the chemical status of groundwater bodies in EU Member States, it is necessary to distinguish homogeneous hydrochemical zones within the groundwater body.

This research examines the problem of the identification of these sub-areas and proposes an integrated approach that can be applied, by using statistical elaborations of major, minor and trace elements and the standardized hydrochemical diagrams, in combination with the GIS spatial analysis.

This approach has been applied in four groundwater bodies of the Campania region (Ducci & Sellerino, 2012), encompassing an area of 1380 km<sup>2</sup>, where about 150 groundwater full analyses of the same period are available.

Ducci D. & Sellerino M. 2012. Natural background levels for some ions in groundwater of the Campania region (southern Italy). *Environ. Earth. Sci.*, 67(3), 683-693.

Hinsby K., Condoso de Melo T. & Dahl M. 2008. European case studies supporting the derivation of natural background levels and groundwater threshold values for the protection of dependent ecosystems and human health. *Sci. Total. Environ.*, 401, 1-20.

Wendland F., Hannappel S., Kunkel R., Schenk R., Voigt H.J. & Wolter R. 2005. A procedure to define natural groundwater conditions of groundwater bodies in Germany. *Water Sci. Technol.*, 51(3-4), 249-257.

## Environmental study of Reps sulfide mine dumps, Mirdita District, Northern Albania

Fantone I.\*, Grieco G. & De Capitani L.

Dipartimento di Scienze della Terra "Ardito Desio" - Università degli Studi di Milano

Corresponding email: [irene.fantone@unimi.it](mailto:irene.fantone@unimi.it)

Keywords: Potentially Toxic Elements, tailings, Acid Drainage, sulfides, Mirdita.

The mine and processing site of Reps operated until 1994 in the Fan valley, about 20km NE of Rreshen, Northern Albania. The mine dumps host sulfide-rich tailing materials resulting from the copper concentration processes. These tailing dumps are issues of environmental concern because of their proximity to the river, the presence of acid drainage-producing minerals and the unstable conditions of the piles. The aim of this work is to evaluate the release of potentially toxic elements (PTE) in the local environment through a geochemical survey of the two main piles, respectively named *Reps1* and *Reps2*. We collected 46 solid samples and 17 water samples representative of the upstream flow, drainage and downstream delivery. Analyses have been conducted in order to characterize (i) the mineralogy, grain size and bulk chemical composition of the earthen samples; (ii) the concentration of PTE either in solid materials and waters; (iii) the presence and persistence of acid drainage. The features of the earthen materials have been defined by grain size and bulk elemental (ICP) composition, pH measures and in situ permeability tests. Microscopy, XRD and MPA analyses have also been performed on selected samples. The mineralogical and geochemical analyses have been performed on the granulometric fraction <2mm. The physical and chemical parameters of the water samples have been investigated through pH-Eh measurements and atomic emission spectrometry. The acid drainage production and the neutralising capacity were evaluated for a set of samples through the Acid Base Account (ABA) test. Moreover, we assessed the spatial relations between the geochemical variables using dedicated mapping softwares. The comparison between the pH analyses on solid samples reveals a stronger acidity of the waste materials of the *Reps2* dump (pH=2.4-3.7), with respect to *Reps1* (pH=3.2-4.3). Such a difference is due to a higher content of sulfides in the *Reps2* samples. These contain a mixture of pyrite, marcasite, minor chalcopyrite, sphalerite and enargite, with associated silicates, oxides (Fe and Fe-Mg spinels) and sulphates (gypsum, barite). Secondary phases comprise hydrated Fe-sulfates and hydroxides. The mineralogical composition of these samples is reflected in the average concentration of S (14.9%) and hazardous metals such as Cu (4430 ppm), Zn (1970 ppm), and As (660 ppm). The drainage water samples show very low pH values (2.3-2.7), with respect to the upstream waters (pH=6.7-7.8). This acid character is associated to a high concentration of ions, the highest values being those of Zn (up to 100 ppm), Cu (up to 20 ppm) and Mn (up to 20 ppm). Our preliminary results on the potential acid drainage production include a total H<sub>2</sub>SO<sub>4</sub> release of 588.087t and a predicted buffering time of 230 000 years. Our investigations at Reps show that this site undergoes a general widespread pollution due to the storage of sulfur and PTE-rich fine grained material in strong disequilibrium with the local morphology and adjacent to a main river that works as a collector of highly acid PTE-rich phases drainage water.

## Water quality assessment of the Buna River Protected Landscape, Northern Albania

Garone A.\*<sup>1</sup>, Rossi M.<sup>2</sup>, Nigro A.<sup>1</sup> & Barbieri M.<sup>1</sup>

1. Dipartimento di Scienze della Terra - "Sapienza" Università di Roma. 2. IUCN, Albania.

Corresponding email: [angelica.garone@uniroma1.it](mailto:angelica.garone@uniroma1.it)

Keywords: Albania; geochemistry; water quality.

HydroGeochemistry is an useful tool to improve knowledge on possible effects of natural and anthropogenic disturbance on surface and groundwaters and the function of ecosystems. Groundwater bodies are constantly exposed to different pressures resulting from human activities and the correct management of water resources is very important especially in less development countries where the socio-economic and environmental conditions are particularly critical.

The aim of this study is to analyze the geochemical characteristic of groundwater concerning the Buna River Protected Landscape, Northern Albania. This area, chosen for the International Union for Conservation of Nature project started in 2011, has favored the international cooperation between Italy and Albania, for promote new management methods of protected areas. The project will specifically contribute to the enhancement of local socio-economic conditions through the promotion of alternative sustainable economic activities for local populations residing near or within the selected site.

The Buna River Protected Landscape has several problems: due to the tourism the population of the area increases from 15,000 to 150,000 during the Summer; many municipalities have no water infrastructure and take water from private wells or rivers; the municipalities have neither sewage systems, nor management systems for solid waste; the Buna River waters are contaminated by heavy metals. One geochemical *facies* was found: low salinity Ca-HCO<sub>3</sub> waters. Because of the proximity to the coastline was evaluate the probably seawater intrusion phenomena that can influence the water quality; the study of molar ratios doesn't show highlights of this process in the Buna River Protected Landscape. Furthermore, in some wells was found a NO<sub>3</sub> concentration exceed the standard limits provided to 2006/118/CE.

The water quality assessment and its monitoring are crucial both for the water resource ecological value and for the health of the local population, in order to improve and promote sustainable agriculture and ecotourism as preferred development activities of the area.

Monitoring the water resource is important to preserve and manage compromises natural ecosystem and protect optimal condition for human health. Natural and anthropogenic disturbance can influence the groundwater quality and ecosystem; its life and quality must not exclude from correct management of water resources.

## **Evaluating the feasibility of hydraulic and physical barriers at contaminated sites by means of multicriteria analysis**

Gigliuto A.\*<sup>1</sup> & Rossetto R.<sup>2</sup>

1. AECOM ITALY SRL. 2 Institute of Life Sciences - Scuola Superiore Sant'Anna, Pisa.

Corresponding email: [andrea.gigliuto@aecom.com](mailto:andrea.gigliuto@aecom.com)

Keywords: Hydraulic and physical barriers, multi-criteria analysis, remediation.

The contaminant plume control systems, using pump and treat or hydraulic and physical barriers, is a common practice to contain and reduce solute contaminants in remediation activities. The recent evolution in engineering techniques has also allowed to extend the number of solutions that can be designed and realized. The decision-making process assumes great importance in leading the selection of the best suitable technology for the case study. This process has to take into account technical, economic, social and environmental factors. The aim of the research project was to define a multi-criteria procedure analysis to support the decision making process in the barrier technology selection, taking into account technical, economic, social and environmental factors.

A multi-criteria analysis methodology has been defined to provide a quantitative tool to guide the selection of the best suitable technology concerning a specific case. The methodology was applied to a real case, selected from many case studies, in order to verify the effectiveness of the tool in evaluating the alternative selections and to highlight the differences between the results of the multi-criteria analysis and the real engineers choices. A sensitivity analysis was performed to analyze the influence of each criterion on the final result of the study.

The outcome of the study was the definition of a methodology, based on the principles of multi-criteria analysis, which can support in the contaminant plume control systems decision process.

## **A multidisciplinary approach to model aquifer analogues: from fine scale heterogeneity to large scale flow and transport**

Giudici M.\*<sup>1-2-3</sup>, Bersezio R.<sup>1-2</sup>, Felletti F.<sup>1</sup>, Baratelli F.<sup>1</sup>, Cattaneo L.<sup>1-2</sup>, Cavalli E.<sup>1</sup>, Comunian A.<sup>1</sup>, Dell'Arciprete D.<sup>1</sup>, De Micheli L.<sup>4</sup>, Giacobbo F.<sup>4</sup>, Lazzati C.<sup>5</sup>, Mele M.<sup>1-2</sup>, Parravicini G.<sup>5-6</sup>, Pessina L.<sup>1</sup>, Vassena C.<sup>1</sup> & Zappa G.<sup>1</sup>

1. Dipartimento di Scienze della Terra "A. Desio" - Università degli Studi di Milano. 2. CNR-IDPA – Milano. 3. CINFAI - Tolentino (MC). 4. Politecnico di Milano. 5. Dipartimento di Fisica - Università degli Studi di Milano 6 INFN – Milano.

Corresponding email: [mauro.giudici@unimi.it](mailto:mauro.giudici@unimi.it)

Keywords: heterogeneity, groundwater, alluvial sediments.

“Field virtual aquifers” or “aquifer analogues” are geological bodies which are quite well exposed, so that they can be analyzed with geological, geophysical and hydrogeological surveys, and which can be assumed to be similar to the buried aquifers from the geometrical and lithological point of view. They can be used to build “numerical virtual aquifers”, i.e., 3D arrays of categorical or continuous variables; such arrays describe the spatial distribution of physical properties, share the same statistical properties as the field data and can be used to perform synthetic experiments with numerical flow and transport models. Therefore, virtual aquifers are a tool to understand the effects that fine scale hydrofacies heterogeneity has on solute transport in the subsurface at large scale.

Our research group has developed a multidisciplinary methodology that involves the following steps.

- (a) Collection of field data, e.g.: sedimentological logs directly measured on the outcrops; photographs of the whole outcrop; electrical resistivity ground imaging and ground penetrating radar surveys; infiltration tests to obtain values of  $K$  at saturation to validate the results of upscaling with numerical flow models.
- (b) Hydrostratigraphic description of the aquifer analogues, by GIS-aided processing of field data, merging measured hydrostratigraphic logs with photomosaic and vertical facies maps of the complete exposures and geostatistical interpolation of the surfaces separating the hydrostratigraphic units.
- (c) Laboratory analysis on samples to determine grain-size-distribution and  $K$  of different facies.  $K$  values can be estimated from laboratory measurements on undisturbed samples of fine-grained facies and with phenomenological relationships (Kozeny-Karman's equation) and literature data for the facies, which are difficult to be sampled without introducing strong disturbances of the fabric.
- (d) Geostatistical simulation of the hydrofacies distribution with different techniques: Sequential Indicator Simulation (SISIM) and an original hierarchic approach (HSISIM), Transitional Probability Geostatistical Simulations (T-ProGS), Multiple Point Simulation (MPS).
- (e) Flow modelling and determination of the equivalent conductivity tensor, by 2D or 3D finite difference modelling of groundwater flow under stationary conditions.
- (f) Numerical experiments of 3D convective transport of a non-reactive solute for an average 1D flow and determination of the lagrangian dispersion tensor and of the effective eulerian dispersion coefficients.
- (g) Numerical experiments of 1D large-scale convective transport with stochastic transport models based on the Kolmogorov-Dmitriev theory in a Montecarlo framework.

The presentation will illustrate the developed approach, both from a general perspective and with some specific examples of successful applications to aquifer analogues representative of the hydrostratigraphic features of the alluvial Po plain (Northern Italy).

## Recent trends in groundwater vulnerability assessment to Non-Point sources of contamination

Masetti M.\*

Dipartimento di Scienze della Terra "Ardito Desio", Università degli Studi di Milano.

Corresponding email: [marco.masetti@unimi.it](mailto:marco.masetti@unimi.it)

Keywords: Non-point sources, vulnerability, spatial statistic.

Groundwater resources are worldwide used as a major source of drinking water. The increase use of the resources and the increase of potential Non-Point sources of contamination require the development of strategies and solutions to protect groundwater from these anthropogenic sources. Non-Point Source contaminants, recognized as major contributors to both surface water and groundwater contamination on a global scale (Duda 1993), present significant challenges for groundwater protection. The most efficient tool which help supporting land use development, while protecting groundwater from contamination is represented by groundwater vulnerability assessment (Gogu and Dassargues, 2000). The use of spatial statistical methods has deeply changed the approaches to this topic, highlighting new possibilities both for researches and applications. By reducing subjectivity, statistical models can provide better support and guidance for protective land-use policies and help to identify management objectives and strategies for groundwater protection (Focazio et al. 2002). The use of statistical methods for assessing groundwater vulnerability to contamination from Non-Point Source contaminants represents an effective tool to better determine the factors having the highest influence on groundwater vulnerability, to provide guidelines to interpret their role in influencing vulnerability and to identify the likely important sources of contamination (Sorichetta et al, 2013). The talk explores the main features of spatial statistical techniques through some examples in different hydrogeological contexts (Nolan et al, 2002, Worrall and Besien, 2005, Masetti et al, 2008, Sorichetta et al, 2011). Examples will be focused on: a) how to use groundwater qualitative data to emphasize the role of groundwater monitoring nets; b) the possibilities to use innovative satellite data to keep into account the distribution of non-point sources of contamination; c) the definition of techniques to evaluate results reliability; d) recent proposals to introduce the "time" variable in groundwater vulnerability assessment.

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## Geochemical characterization of groundwater around Municipal Solid Waste landfill

Nigro A.\*<sup>1</sup>, Barbieri M.<sup>1</sup> & Sappa G.<sup>2</sup>

1. Dipartimento di Scienze della Terra - Sapienza Università di Roma. 2. Dipartimento di Ingegneria Civile e Ambientale  
- Sapienza Università di Roma.

Corresponding email: [angela.nigro86@gmail.com](mailto:angela.nigro86@gmail.com)

Keywords: Landfill, geochemistry, groundwater.

In Italy landfills are the most common method of organizing waste disposal as it is simple and economical. About 60% of total waste produced is disposed of in landfills. Landfills have been identified as one of major threats to groundwater resources (Mor et al., 2006). They continue to serve a key function in the waste management system in the less developed countries, although the general trend is to minimize the use of them by new policies of reducing, reusing, recycling, and the development of technologies for composting and residues incineration. Moreover in the last years it increase the importance of the position of the monitoring network on the identification of the pollution process and the protection of the water resources. One of the main problem of management landfill is a possible contamination of groundwater due to leachates. The studied landfill is located in central Italy and it has been working since 1995. It's divided in 3 lots, and it has a capacity more than 2,000,000 cubic meters. The geology of the area is characterized by a Plio-Pleistocene substrate of marine origin formed at the base by clayey-sandy deposits that in the upper part of the formation to pass sands and conglomerates. The oldest deposits are represented by gray-blue clays. The aim of this study is to assess the impact of a Municipal Solid Waste on the surrounding environment using some simple geochemical tools as tracer of anthropogenic contamination. To evaluate the environmental risks of groundwater contamination associated with landfill were analyzed the geochemical characteristics of water surrounding landfill; were define the concentrations of major ions (Ca, Mg, Na, K, Cl, SO<sub>4</sub>, NO<sub>3</sub>, HCO<sub>3</sub>) and trace elements of samples and were evaluate the correlation between these elements. The integrated elaboration of the data allows to obtain information and to make inferences on the influence of the landfill on the contamination of the underground resources. The results show that concentration of some trace elements (Fe, Mn, B and Hg) exceed the threshold concentration of contamination provided by D.lgs 152/2006. The aim of this study is to assess the impact of a Municipal Solid Waste landfill on the environment using some simple geochemical tools as tracer of anthropogenic contamination and it emphasizes the need for constant monitoring of the area, in order to limit its impact on the groundwater resources.

Mor S., Ravindra K., Dahiya R.P. & Chandra A. 2006. Leachate characterization and assessment of groundwater pollution near municipal solid waste landfill site. *Environmental Monitoring and Assessment*, 118, 435–456.

## Remediation procedures of petrol stations: conventional techniques and phytoremediation for reclamation of hydrocarbon based contaminants in the Terni area (Central Italy)

Paglialunga M.\*<sup>1</sup>, Valigi D.<sup>1</sup>, Di Matteo L.<sup>1</sup>, Grigioni P.<sup>2</sup>, Locci D.<sup>2</sup>, Sconocchia A.<sup>3</sup>, Sconocchia P.<sup>3</sup> & Stoico M.<sup>2</sup>

1. Dipartimento di Fisica e Geologia - Università di Perugia. 2. Provincia di Terni, 3. ARPA UMBRIA Dipartimento Provinciale di Terni.

Corresponding email: [marilena\\_paglialunga@libero.it](mailto:marilena_paglialunga@libero.it)

Keywords: Remediation techniques, Petrol Stations, Hydrocarbon Contaminants, Phytoremediation.

Hydrocarbon contaminants – produced by spillages from storage tanks – are some of the hazardous substances detected in soil and groundwater. The petrol stations in Italy are about 3.4 times higher than the European mean (Tabarelli, 2010). According to the Italian guidelines (DLgs 152/2006), threshold concentrations of contamination are more stringent than in other European countries and USA: thus, due to the high number of potential contaminated areas, the cost for characterization plain and for risk analysis is very high. The present work takes as reference the remediation times and technologies of 25 petrol stations located in the Terni area (Central Italy). The maximum value of total petroleum hydrocarbons (TPHs) in the soil matrix was about 1750 g/l while in groundwater a value of about 184 g/l was registered. The statistical analysis of data from reclamation procedures shows that about 15 sites may be considered – in terms of contaminant levels – as reclaimed. Results showed that the reclamation times are between 5 and 10 years (60% of sites) although some of these are characterized by coarse-grained soils, which increase the efficiency of soil reclamation. So long reclamation periods are due mainly to the delivery of the remediation and risk analysis projects by the companies in charge of remediation, and to the delays by the territorial authorities. The soil removal, the Bioventing and the Soil Vapor Extraction are the most widely used technologies for the unsaturated soil, while Pump & Treat (P&T), the Air Sparging and the Multi Phase Extraction are used to reclaim groundwater. Apart of the costs to remove the contaminated soils, the application of conventional technologies has high management costs and - in some cases - led to a stagnation of the overall remediation process. Taking as reference a site where contaminants in groundwater are present since 1998, a mean cost for the management of reclamation by using P&T and recharge wells has been estimated of about 25000 Euro/year in period 2010-2013. In order to reduce costs for removing the contaminated soils, the present study proposes, for some sites, the application of phytoremediation technologies by using the plant species: *Lolium Multififormum*. Although, the phytoremediation of TPHs is still not a proven technology, more in-depth studies on this topic would be useful, because of the low cost and to the low environmental impact of this type of procedure (Collins, 2007). The application of this technique requires a proper evaluation of the soil moisture which has been computed by using the Thornthwaite-Mather method, allowing to define the monthly water to be supplied to the system for an optimal efficiency.

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## **Arsenic contamination in the Upper Valtellina (Central Italian Alps)**

Peña Reyes F.A. \*, Basiricò S., Frattini P., Villa A., Lari S. & Crosta G.B.

Dipartimento di Scienze dell'Ambiente e del Territorio e di Scienze della Terra - Università degli Studi di Milano-Bicocca.

Corresponding email: [fredy.penareyes@unimib.it](mailto:fredy.penareyes@unimib.it)

Keywords: Arsenic, Upper Valtellina, springs hydrochemistry.

Since 1998, a maximum admissible concentration level of Arsenic (As) of 10 µg/L was established by the WHO (World Health Organization), in water for human consumption, because concentrations previously fixed at 50 µg/L revealed not to be safe enough for human health. In Italy, the contamination due to As affects 128 municipalities scattered around the whole country. Natural Arsenic is present in different areas of the Alps with particular rock types like: phyllites, micaschist and Schist. The current research covers an area of 800 km<sup>2</sup> in the Upper Valtellina Valley (UVV - central Italian Alps), including five municipalities: Bormio; Livigno; Valdidentro; Valdisotto and Valfurva, with elevation ranging from 1150 to 3500 m a.s.l. Historical data from 1996 to 2011 on water quality from springs, wells, lakes, rivers and public fountains were obtained and organized in a database for interpretation through GIS and AQUACHEM analysis. Moreover, four sampling campaign were done for one hydrologic year 2012-2013 in 57 springs. In addition, isotopic and whole-rock analysis were completed. The isotopic analysis (Deuterium, Tritium and O<sup>18</sup>) were performed for eleven samples distributed across the areas with higher As concentration in areas with higher As concentration in order to understand the isotopic "age" and the general circulation conditions in the UVV. pH and Redox field measurements were useful to suggest the factors influencing the dominant environments for Arsenic release and speciation. Different chemical analysis were completed in springs, rivers, lakes and wells, in order to characterize the hydrogeochemistry of the UVV area.

Within the research area, both mountain alpine springs with cold temperatures over the year below 10°C and thermal springs are present. The first group presents a dominance of Ca-HCO<sub>3</sub>-SO<sub>4</sub> and Mg-HCO<sub>3</sub>-SO<sub>4</sub> facies, while the thermal springs are Ca-Mg-SO<sub>4</sub>. The Arsenic concentration ranges from 5 to 230 µg/L, with the highest concentrations in the thermal springs. In order to determine the dominant Arsenic species in the springs, speciation on most of the springs were performed finding that in almost 90% of the spring, As (V) was the dominant species.

The study area is characterized by the presence of several small villages or single houses scattered around the area, using water directly from the mountain springs (i.e Plata fraction – Valfurva) with As concentrations over the 10µg/L limit. The application of centralized treatment techniques in those areas is challenging because it would require the extension of the existent aqueduct network. Thus, some simple treatment methods for house scale are proposed based on low-cost distributed systems to be installed at the affected houses.

## **Geochemical characteristics of groundwater in the coastal aquifers of Dar Es Salaam, Tanzania**

Sappa G.\*, Ergul S. & Ferranti F.

DICEA, Department of Civil, Building and Environmental Engineering – Sapienza, University of Rome.

Corresponding email: [giuseppe.sappa@uniroma1.it](mailto:giuseppe.sappa@uniroma1.it)

Keywords: geochemistry, groundwater, coastal aquifer, Tanzania.

In Dar Es Salaam, Tanzania, groundwater is the major source of public domestic water supply and is a vital source for industrial and agricultural uses. Due to a rapid increase in population and climate and land-use changes, the demand for water increases significantly throughout the region. Although groundwater resources are less vulnerable to pollution than surface waters, in many parts of the world people suffer from poor drinking water quality. The variations in water composition are generally controlled by the combination of both anthropogenic activities and natural processes (Chenini & Khmiri, 2009). Groundwater quality in coastal aquifers is largely influenced by climate change, seawater intrusion, human activities and coastal erosion etc. and needs a special attention in terms of monitoring and for sustainable management. In the present study, groundwater chemical data from 72 wells collected during a year of monitoring in Dar es Salaam area and are employed to determine processes that control water chemistry, referring to, especially, to seawater intrusion and climate change (Sappa et al., 2013 a,b). Based on the hydrochemistry, the groundwater was classified into three types: (a) Na-Cl, (b) Ca-Cl, (c) mixed Ca-Na-HCO<sub>3</sub>-Cl and (d) mixed Ca-Mg-Cl-SO<sub>4</sub> and characterized as fresh to brackish water with acidic to alkaline in nature. A Durov diagram plot revealed that the groundwater has been evolved from Ca to HCO<sub>3</sub> recharge water, followed by mixing and reverse ion exchange processes, due to the respective dominance of Na-Cl and Ca-Cl water types. According to Gibbs's diagram plots, evaporation process, chemical weathering of rock forming minerals and seawater intrusion are the major factors controlling water chemistry in this area. The groundwater at many locations in the study area is not suitable for drinking due to its high salinity, which is mainly caused by seawater intrusion and will need to be purified.

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## A revision of the hydrogeological setting of the Cassino plain from Gari to Peccia springs

Saroli M.<sup>1</sup>, Lancia M.\*<sup>1</sup>, Giovinco G.<sup>1</sup>, Albano M.<sup>2</sup> & Petitta M.<sup>3</sup>

1. Università di Cassino e del Lazio Meridionale. 2. INGV-Roma. 3. Sapienza Università di Roma.

Corresponding email: [m.lancia@unicas.it](mailto:m.lancia@unicas.it)

Keywords: Central-Southern Apennines, hydrogeological-modeling, numerical-simulations.

The Cassino plain is located in the end-sector of the Latina Valley, between the Simbruini-Ernici-Cairo Mts. hydrostructure (NW) and the Venafrò Mts. hydrostructure (NE). Both aquifers belong to the Lazio-Abruzzi domain, with limestone ranging from platform to slope facies. Terrigenous sequences as well as late-Quaternary lacustrine and fluvial deposits cover the carbonatic hydrostructures in the low-land areas. After compressional stages related to the chain-growth, extensional tectonic has intensively characterized the investigated area. Along the plain sector, the ridges of Trocchio and Porchio Mts. are made by platform limestone and they are bounded by three normal faults. Two plentiful springs with bicarbonate-calcium features are located at the plain borders: Gari spring (discharge of 13-18 m<sup>3</sup>/s, elevation of 40-30 m a.s.l.) and Peccia spring (discharge of 5 m<sup>3</sup>/s, elevation of 29-25 m a.s.l.). Starting from the 70's the outlining of the two springs recharge-areas has been under discussion. A first conceptual model (Boni & Bono, 1973; Boni et al., 1986) considers both springs as related to the Simbruini-Ernici-Cairo Mts.-Venafrò Mts. hydrostructures. Furthermore the hydrogeological continuity between the springs would be ensured by underground fluxes through Trocchio and Porchio Mts. On the contrary, a second conceptual model (CASMEZ, 1979; Celico, 1979) considers the springs as disconnected; Gari spring would be fed by the Simbruini-Ernici-Cairo Mts. hydrostructure while Peccia springs would be fed by the Venafrò Mt. hydrostructure. Thanks to previous works (CASMEZ, 1979; Celico, 1979; Boni et al., 1986), the gathering of unpublished borehole data (as the Western-Campania Aqueduct prospects), a revised geological and hydrogeological conceptual-model has been proposed. More specifically, compressive tectonic elements at the western side of the Cairo Mt., as well as several klippen have been recognized. Taking into account new data including piezometric surveys, a hydrogeological section has been built, from Gari to Peccia springs. Assuming an equivalent porous media and steady-state conditions, numerical simulations by means of Comsol® and Rocscience® softwares has been carried out, in order to verify the proposed conceptual model and the possible groundwater-flow continuity between the two springs through Trocchio and Porchio Mts.

Boni C.F. & Bono P. 1973. Segnalazione di un gruppo di grandi sorgenti nel bacino del fiume Peccia, affluente del Garigliano. *Geol. Rom.* 12, 227-242.

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## Gaza Coastal Aquifer Modelling for groundwater management

Selmi A.\*<sup>1</sup>, Basiricò S.<sup>1</sup>, Peña Reyes F.A.<sup>1</sup>, Lari S.<sup>1</sup>, Frattini P.<sup>1</sup>, Mogheir Y.<sup>2</sup> & Crosta G.B.<sup>1</sup>

1. Department of Earth and Environmental Sciences, Università degli Studi di Milano Bicocca. 2. Islamic University of Gaza, Gaza City, Palestinian territories.

Corresponding email: [amalraee@gmail.com](mailto:amalraee@gmail.com)

Keywords: Groundwater modelling; Groundwater management; Gaza aquifer.

Groundwater represents a critical issue for the future of Gaza Strip, as it is the main resource available to satisfy the daily water needs. As future population growth will increase the stress upon water supplies, the need for effective water management is greater than ever. This study has the aim of planning a sustainable use of groundwater resources in Gaza Strip through a deep understanding of the hydrologic system and modelling. Firstly, the hydrological budget of Gaza aquifer is calculated for different years (2003 to 2009). A significant deficit between the annual recharge and abstraction is observed. Chemical analyses are carried out to study the salinization process and to identify the salt sources in the aquifer. Results show that groundwater is characterized by Na-Cl-SO<sub>4</sub> and Ca-Mg-HCO<sub>3</sub> facies, and that the occurrence of salinity in different parts of the aquifer is related to the presence of the seawater in the western side, and lateral inflow from the eastern border due to the hydraulic connection with brackish aquifer. The vulnerability of the aquifer to seawater intrusion is assessed by means of GALDIT index method. The resulting vulnerability map can be used as an additional tool to determine areas of potential saltwater intrusion and to identify the favourable zones to artificial recharge.

A 3D finite difference flow model was developed in order to quantify and assess impacts of variable pumping and recharge. Based on the transient model, three different management scenarios were simulated in order to study the impact of pumping rates and additional water resources on the groundwater level in the next 20 years. These scenarios are conceived to support coastal aquifer management plan adopted by Palestinian Water Authority for the control of the seawater intrusion. The results show that the ground water level is strongly influenced by the over pumping: two large depression zones are observed in the northern and southern Strip, and an increase of several meters in groundwater level is observed under the effect of decreasing abstraction rates. Groundwater level significantly rises under the effect of an increasing recharge. Based on these results, recommendations are made regarding optimal solutions to control seawater intrusion in the Gaza aquifer.

Using treated waste water to increase the groundwater level and control the sea water intrusion in the Gaza aquifer appears as the most practical, renewable and suitable solution, since the other options require the use of fresh water resources, which are costly and unpractical in Gaza Strip situation.

## SESSIONE S26

### **Energy and earth resources: geology between renewable, sustainable and conventional energy sources**

#### *CONVENORS*

*A. Zaccone (Regione Lombardia)*

*S. Chiesa (CNR-IDPA, Milano)*

*F. Quattrocchi (INGV)*

*A. Galgaro (Univ. Padova)*

## Geothermalism in the Province of Verona

Agostini L.\*<sup>1</sup>, Galgaro A.<sup>1</sup>, Collareda M.<sup>2</sup>, Castellaccio E.<sup>3</sup> & Dal Degan D.<sup>3</sup>

1. Department of Geosciences, University of Padova. 2. Independent professional of Vicenza. 3. Independent professionals of Verona.

Corresponding email: [laura.agostini.2@studenti.unipd.it](mailto:laura.agostini.2@studenti.unipd.it)

Keywords: thermal springs, geothermalism, district, energy.

The authors, through analysis of several geological, chemical and historical data, studied the thermal waters of the province of Verona and provided new insights and interpretations on the hydrothermalism western of the Veneto, with the ultimate objective of permitting the rational use purpose energy. The preliminary research allowed to define areas of thermal springs divided into two main districts. Now it is possible to distinguish "hot areas" characterized by homogeneous geological and chemical conditions. The first district of the plain Eastern (A) is focused mainly in the neighborhood of Caldiero, but also brings together the towns of Belfiore, Colognola ai Colli, Lavagno, S. Martino Buon Albergo, S. Bonifacio, Zevio, Ronco all'Adige and Arcole. The temperature of the fluid takes on values between 20 ° C and 31 ° C and the peculiar hydrological conditions allow artesiansimo bubbling to the surface. In this area we can see the manifestation of the historical sources as Brentella spring. The second district, called District spa northern plain (B), distinguishes between two different sectors based on hydrogeological conditions: to the east, it includes the towns V.lla Sant'Ambrogio, San Pietro in Cariano, Pescantina while, to the west, thermal fields are found in the moraines of the municipalities of Pastrengo, Lazise, Bardolino, Peschiera d / G. and Castelnuovo d / G. Including also Sirmione (BS) we can see that the temperature of groundwater is decreasing from west (about 70 ° C-Sirmione) to the east (46 ° C-S.A.V.). In Saint Ambrose of V.lla water hot is been found in wells between -60 ÷ -130 m m from ground level while the temperatures vary between a minimum of 20 ° C to 46 ° C (Castellaccio & Zorzin, 2012). In the morainic, however, areas characterized by the presence of hot water at higher temperatures is between the villages of Colà di Lazise, Piovezzano and, especially, at around the same localities with the largest number of deep wells, ranging between -140 m and -240 m from the PC, with temperature values of water ranging from 35 ° C and 52 ° C. Outside the spa districts, considered most important for the discovery of hot water, wells are isolated reports of possible thermal anomaly (20 ° C to 22 ° C). This situation testifies, on one hand the vast extent of the hydrothermal system and, secondly, the existence of complex hydrogeological phenomena. In the context of the Padana Plain and other areas located at the edges of the central and southern Apennines and Calabrian arc-Peloritano exist thermal waters whose genesis is related to circulation of fluids within carbonate structural clusters heated the normal geothermal gradient. The geothermal mapping of the Italian territory for that type of thermal spas shows a potential huge and easily available, which include the areas between Sirmione and the Adige Valley and the wide area around Caldiero. The low enthalpy of Verona spa is therefore a possible important source of energy for public environments (residential, industrial, hospital, sports, etc.), agriculture (greenhouses for vegetables and flowers, drying, pasteurization of milk, hydroponics, etc.) or for breeding (itticoltura of valuable species, incubation of eggs and poultry) or as a result of the presence of hot fluids in a favorable salt content, for the development of wellness centers and balneotherapy.

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Castellaccio E. & Zorzin R. 2012. Le acque calde del territorio veronese. Museo di Storia Naturale di Verona.

## **Borehole Heat Exchanger simulations in aquifer: the borehole grout influence in Thermal Response Test modeling**

Alberti L.\*<sup>1</sup>, Angelotti A.<sup>2</sup>, Antelmi M.<sup>1</sup> & La Licata I.<sup>1</sup>

1. DICA-Politecnico di Milano. 2. D.EN.-Politecnico di Milano.

Corresponding email: [ivana.lalicata@polimi.it](mailto:ivana.lalicata@polimi.it)

Keywords: TRT, Borehole Heat Exchangers, thermal modeling.

Geothermal energy, and especially the use of low enthalpy resources, has a rising importance; ground-coupled heat pump (GCHP) systems have been used increasingly because they are among the cleanest and most energy efficient heating and cooling systems for buildings. Simulation models can be applied for a more effective use of the subsoil for geothermal purposes. In fact they are useful tools for the design of efficient systems which consider also the need to avoid abnormal temperature distributions in soil and aquifers. In the hydrogeology field the Modflow/MT3DMS codes are the most widely used programs to face environmental problems and forecast quantity and quality impacts on groundwater resources. Although Modflow/MT3DMS are used to represent open circuit heat pumps, they had never been used to represent borehole heat exchangers (BHE). Aim of this study is to simulate a Thermal Response Test (TRT) through Modflow/MT3MS codes implementing into the model all the components of a Ground Heat Exchanger system: from the U-shaped BHE to the grout material surrounding it.

For GCHP systems, the TRT is commonly used to determine the heat transport parameters of the subsurface as thermal conductivity and thermal diffusivity. It also allows to determine the BHE thermal resistance which mainly depends on the geometry of the dug area and on the thermal properties of the surrounding grout material.

Starting from a model implemented in a previous work (Angelotti et. al., 2014) Modflow has been used for the simulation of a TRT. Two cases have been analysed and compared: in the first the cells around the BHE are assigned the aquifer parameters while in the second they have been assigned the characteristics of the grout material (hydraulically impermeable but highly conductive from the thermal point of view). A 10-6 m/s groundwater Darcy velocity case is analysed applying a 40 W/m specific heat rate to the fluid circulating into the BHE. Considering the temperature distribution in the ground, the differences between the two simulated cases (with/without-grout) result essentially negligible presenting a maximum value equal to 0.07 °C in the proximity of the BHE (around 20 cm from the centre of the U-pipes). A slightly more relevant difference (0.55°C) in simulated temperature is registered very close to the BHE, into the area occupied by the grout (only 6 cm from the centre of the U-pipes). This is due to the absence of the advective term in the zone where the grout is present and the heat transfer is linked just to conduction term. By the way there are almost no differences in the temperature of the heat-carrier fluid in the two cases (0.02 °C). These results lead to conclude that, simulating a TRT, the effect of the grout is negligible, therefore is advantageous to avoid modeling its geometry and thermal/physical parameters so as to save time and energies in the model implementation phase.

## Thermal characterization of shallow aquifer in the left sector of the Lanzo Fan (Piemonte region) for geothermal applications

Barbero D.\*<sup>1</sup>, De Luca D. A.<sup>1</sup>, Forno M. G.<sup>1</sup>, Lasagna M.<sup>1</sup> & Magnea L.<sup>2</sup>

1. Dipartimento di Scienze della Terra, Università degli Studi di Torino. 2. Dipartimento di Fisica, Università degli Studi di Torino.

Corresponding email: [diego.barbero@unito.it](mailto:diego.barbero@unito.it)

Keywords: Lanzo Fan, thermal characterization of shallow aquifer, low enthalpy.

This research is aimed to profitably accommodate open loop systems that permit the exploitation of low enthalpy geothermal energy. A statistical analysis of the thermometric data of the shallow aquifer is performed, also, for the evaluation of the presence of a “homoeothermic surface”.

Previous studies (Stringari et al., 2009) focused the attention on the thermal mapping of the left sector of Lanzo Fan shallow aquifer. The data were collected to identify the most promising areas for the installation of geothermal probes.

The Lanzo Fan, extended about 300 km<sup>2</sup>, is formed by a very thick villafranchian transitional succession with a thin fluvial quaternary cover (Forno et al., 2009). The villafranchian sediments (Lower Complex of middle Pliocene and Upper Complex of lower Pleistocene) consist of prevalently strongly consolidated silt and sand, hosting productive deep aquifers. The fluvial sediments (five units of middle and upper Pleistocene - Holocene forming five terraced surfaces) consist of gravel 20-40 m thick, hosting a shallow poorly productive aquifer. Gravel sediments have a high clay tenor and a significant Fe oxides cementation, connected with the strong weathering, and thus have a low permeability.

The trend of the piezometric surface follows the topographic surface, with variable hydraulic gradient between 1% in the apex of the fan (NW) and 0.1% in the low sector (SE). The water table depth varies between a few tens of meters in the high terraces, where the direction of flow is predominantly WNW-ESE, and a few meters in the other sectors, where the direction of flow is NW-SE.

The statistical analysis made on spring and autumn thermometric measures (related to the year 2009), collected in environmental monitoring piezometers, allowed us to check the presence of the “homoeothermic surface”, with its depth range. Moreover it permitted to determine an average value of the temperature with its relative experimental uncertainty at the homoeothermic surface. This average value is compatible with the sinusoidal asymptotic behavior connected to seasonal temperature fluctuations found in the subsurface.

The reported reading is in agreement with the solutions of the heat conduction equation in stationary boundary conditions. This method provides a statistically well-defined evaluation of the expected value of the groundwater temperature, at the homeothermic surface, and of the corresponding uncertainty.

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## **Thermo-physical properties of Euganean Hills lithologies (Padua, North-Eastern Italy) related to underground thermal storage feasibility**

Buggiarin S.<sup>1</sup>, Di Sipio E.\*<sup>2</sup>, Galgaro A.<sup>1-2</sup> & Sassi R.<sup>1</sup>

1. Dipartimento di Geoscienze, Università di Padova. 2. IGG-CNR, Padova.

Corresponding email: [raffaele.sassi@unipd.it](mailto:raffaele.sassi@unipd.it)

Keywords: Thermal energy storage, physical thermal parameters, renewable energy, Euganean Hills.

The rapid growth of the world population has put a big problem on conventional energy resources such as fuel, coal and oil, which are estimated to be depleted in a few decades.

These conventional resources are also accused by the excessive production of CO<sub>2</sub> and other harmful gases that lead to climate change issues, such as global warming and the deterioration of the ozone layer (Xu et al., 2013). These serious consequences require people to start considering new models of sustainable development. In particular solar energy is as a pollution-free, inexhaustible and affordable energy resource, has received extensive study and numerous applications throughout the world.

In recent years a considerable progress in renewable energy development has made new energy resources quite competitive with conventional energy in terms of both efficiency and reliability.

The term TES indicates all energy storage technologies (which can be used in combination with other energy sources) to economically buffer variable rates of energy supply and demand (Dincer, 2001). The heat which is stored usually come from solar thermal panel or from other renewable resources (for example a biomass power plant). Also the waste heat from an conventional industrial plant can be used for this purpose. By means of energy storage, intermittentsolar energy is able to not only meet the demands of space heating and domestic water supply but also to offer a high grade heat source all year round regardless of timing or seasonal constraints: in this case it's possible use the excess heat collected in the summer for heat supply during the wintertime (Xu et al., 2013). In this work the preliminary studies voted to support the planning of Underground Thermal energy storage (UTES) systems are considered. In order to properly design this type of systems the knowledge of the main underground thermo-physical parameters is fundamental (Clauser, 2011). In this study, the thermal properties of Euganean Hills (Padua, North-Eastern Italy) main lithologies have been measured, such as thermal conductivity, volumetric heat capacity, thermal diffusivity, density and porosity. A literature research has accompanied the study allowing to compare the experimental results.

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## **Thermo-physical properties of groundwater in sedimentary deposits of Umbria-Marche succession and their role for low enthalpy geothermal plants**

Chicco J.\*<sup>1-2</sup> & Invernizzi C.<sup>1</sup>

1. School of Science and Technology, Geology Division, Università di Camerino. 2. Eureka Project (Regione Marche).

Corresponding email: [jessica.chicco@unicam.it](mailto:jessica.chicco@unicam.it)

Keywords: Geothermal plants, heat transfer, groundwater.

To realize the EU Strategy for Sustainable Development, improving the quality of life on planet Earth of both present and future generations through the use of renewable energy, the geothermal energy plays certainly an important role. In particular, in the last years, the interest towards the exploitation of low enthalpy geothermal resources to produce heating, sanitary warm water and cooling for private and public buildings is notably increased. In this regard, our project is oriented on a detailed knowledge of the subsoil through a multidisciplinary approach (geological, hydrogeological, structural and geophysical data) that permit a correct evaluation of geo-exchange potential of heat at depth, corresponding to specific lithologies. We focus our attention on the seasonal monitoring of the thermo-physical properties of groundwater at depths (temperature and thermal conductivity above all), under different conditions of elevation and morphology, and within specific lithologies, belonging to sedimentary deposits of the Umbria-Marche succession. Information so obtained, together with other parameters taken from literature, are fundamental to acquire the Péclet Number (Pe) (Miranda & Campos, 2004), a dimensionless number used in the study of transport phenomena in fluid flow that permit to know the amount of heat transfer by conduction, and to compare it with the heat transfer by convection. Introducing the Péclet Number (Pe) within the equations that define the heat and mass transfer (Martin, 2011), it is possible to obtain a better knowledge about the processes that rule the geo-exchange of heat in the subsoil (Sonney, 2010). This improves the understanding of the correct amount of thermal energy available for building energy needs, and it is very important in order to favourite a correct use of the resources supported by a technological optimization of low enthalpy geothermal plants.

First results in the studied area show that in fractured limestones with significant groundwater circulation the thermal energy that define the geo-exchange of heat is in the order of 70 W/m, higly different with respect to alluvial deposits.

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## **Site location and planning of Borehole Heat Exchangers using Electrical Resistivity Tomography**

Cuccuru S.\*, Longo V. & Testone V.

Dipartimento di Scienze della Natura e del Territorio - Università di Sassari.

Corresponding email: [scuccuru@uniss.it](mailto:scuccuru@uniss.it)

Keywords: Borehole Heat Exchangers, Geothermal energy, Electrical Resistivity Tomography.

In the present energetic context, where decreases the availability of fossil fuels, exploration and exploitation of renewable energy sources are gaining increasingly importance. Among these, geothermal energy is one of the cleaner source. The low enthalpy geothermal energy is one of the energy sources more widely available and easily exploitable through Borehole Heat Exchangers (BHEs) which use the stable temperature occurring below 10-20 m from the surface level. Within these depths, the stable temperature (which is not affected by seasonal variations) allows the system to extract heat in the winter and pumping heat during the summer. The efficiency of these systems depends on many geological parameters such as stratigraphy and respective thermal conductivity of the rocks close the borehole, porosity, faulting, fractures (and their filling), water content, groundwater presence and geothermal gradient. Informations concerning deep structures and geometric characteristics of faulting zones, need expensive and invasive methods such as drilling wells or digging shafts in order to be investigated. In this study we propose the application of Electrical Resistivity Tomography (ERT), a fast and low-cost method, to identify the areas with geological features suitable to the BHEs systems installation. The ERT technique employs an artificial source of direct electric current injected into the ground via galvanic contact through point electrodes, thus creating stationary current flow in the earth. By measuring potentials at the surface in the vicinity of this current-flow is possible to determine the resistivity of the underground. The resistivity values of rocks change in relation to the porosity, degree of fracturing, water saturation and temperature: all parameters which are also directly responsible to the efficiency of BHEs systems. Different resistivity value in tomography allow therefore to reconstruct indirectly the stratigraphy of the area. Within the same rock formation, also the other features are detectable due to their resistivity values. Positive thermal anomaly in wet conditions, for example, shows lower electrical resistivity respect to their surroundings. Finally, 2D and 3D ERT models could be create in order to reconstruct the structural setting of the area, the fault/fracture pattern and relative water circulation. This is very important in order to improve the efficiency of BHEs systems because water triggers convective movements that improve the removal of the thermal disturbance around the probe.

## **BHE geological hazard on clayey sediments induced by thermal stress**

Dalla Santa G.\*<sup>1</sup>, Galgaro A.<sup>1-2</sup>, Tateo F.<sup>2</sup>, Destro E.<sup>2</sup>, Cola S.<sup>3</sup> & Bassan V.<sup>4</sup>

1. Dipartimento di Geoscienze, Università di Padova. 2. CNR – Institute of Geosciences and Georesources  
3. DICEA (Department of Civil Engineering), University of Padua. 4. Servizio Geologia, Geotermia e Cave, Provincia di Venezia, Venezia Mestre.

Corresponding email: [giorgia.dallasanta@studenti.unipd.it](mailto:giorgia.dallasanta@studenti.unipd.it)

Keywords: borehole heat exchanger; freeze-thaw cycles, Venice thermal sensitivity map.

The heat exchange connected to a BHE field for building conditioning has been shown to alter the natural thermal status of the surrounding subsoil. During winter if the BHE field is undersized, it may be necessary to lower the carrier fluid working temperature below 0°C in order to increase thermal withdrawal from the ground. In this working conditions freezing and subsequent thawing cycles occur in the surrounding subsoil, resulting in an irreversible alteration of the soil texture (Konrad, 1989). This leads to an increase of compressibility (Dashjamts & Altantsetseg, 2011) and vertical permeability (Chamberlain & Gow, 1979) in the normal-consolidated cohesive sediments (Farouki, 1981).

The issue studied is particularly hazardous in dense urbanized areas characterized by abundance of cohesive layers in the stratigraphic sequence, where the lack of external spaces implies that the BHEs have to be bored under or close to the buildings' foundations. In this conditions the BHE induced thermal stress could result in potential risk on the buildings' integrity due to differential settlements. Furthermore, the increased vertical permeability of the BHE surrounding subsoil could constitute a possible hydraulic connection of different aquifers previously separated.

In order to regulate the installation of new BHE fields and their exploitation avoiding the highlighted issues, it is important to identify the areas more suitable for this application. Mapping the territory's geological sensibility to the thermal stress induced by a BHE could be based on the distribution of sensitive cohesive sediments in the subsoil obtained by a new stratigraphic data-base.

The case-study of Venice (Italy) is studied, as representative of a dense urbanized area characterized by a typical geological context of floodplains and transitional environments, rich in cohesive sediments. The thermal response of typical cohesive sediments of the area were tested by means of an expressly made thermally controlled oedometer. The obtained results show an no negligible overall thermally induced irreversible settlement of the tested samples. The effect of the freezing-thawing processes occurs in the first 7-8 cycles, after which there is no more evidence of settlement. Finally, the mapping of thermal sensitivity distribution of the of Venice historical centre is presented.

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## Seasonal heat storage systems in mountain regions: potential and feasibility of a pilot project in the Trento municipality

Di Sipio E.\*<sup>1</sup>, Destro E.<sup>1</sup>, Ruggeri M.<sup>2</sup>, Viesi D.<sup>3</sup>, Sassi R.<sup>2</sup> & Galgaro A.<sup>1-2</sup>

1. Istituto di Geoscienze e Georisorse - IGG-CNR, Padova. 2. Dipartimento di Geoscienze - Università di Padova. 3. Renewable Energies & Environmental Technologies, Fondazione Bruno Kessler, Trento.

Corresponding email: [eloisa.disipio@gmail.com](mailto:eloisa.disipio@gmail.com)

Keywords: thermal energy storage, thermal properties, borehole heat exchangers.

During the last decades, the growing needs for more efficient energy use in buildings due to heating and cooling made the employment of Underground Thermal Energy Storage (UTES) systems increasingly interesting. The possibility to store the waste heat and the excessive heat production in the underground in the warm season to recover it during cold periods enables energy cost saving and environmental protection (Schmidt et al 2004; Paksoy et al 2000). However, the thermal efficiency of storage is strictly dependent on the different geological and environmental conditions characterizing the territory and on the energy requirements of the building. Among others, one of the key priorities for the properly assessment of the heat storage suitability in the underground is the knowledge of the thermal properties of rocks and sediments necessary to quantify the heat storage capability and the potential losses of the system (Clauser 2011a; Clauser 2011b).

For example, in cold regions, such as mountain areas, the amount of energy required for buildings heating during the winter period is very high, while in summer the cooling demand is generally negligible. In this case the integration of borehole heat exchangers (BHE) with solar heating plants allow to store solar heat underground in summer to be used in winter. The seasonal heat storage achieved in this way ensures the system efficiency and the renewability of the heat resource exploited mainly under seasonal cold conditions.

This paper provides an overview of the thermal properties of rocks and sediments in Trento municipality, where a pilot plant using solar energy combined with geothermal heat pumps was designed. Pros and cons associated with the geological, hydrogeological and climatic characteristics of the area are taken into account. The thermal characterization of lithotypes belonging to the main outcropping lithologies provides input data for numerical modeling simulation devoted to analyze the underground thermal behavior related to charging and discharging cycles.

The expected results will constitute an important support, suited to real underground conditions, for UTES plants design and for policy makers taking decisions concerning promotion and control diffusion of the ground heat storage solutions.

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## **Closed-loop heat-exchanging systems in geothermal anomaly areas: a feasibility analysis in the Euganean Thermal Basin, Italy**

Farina Z.\* & Galgaro A.

Dipartimento di Geoscienze, Università di Padova.

Corresponding email: [zeno.farina@gmail.com](mailto:zeno.farina@gmail.com)

Keywords: groundwater modelling, low-enthalpy geothermal energy, thermal impact.

The Euganean Thermal Basin is the most important thermal field in northern Italy. It is located in the Veneto alluvial plain, south-west of Padua, close to the north-eastern edge of the Euganean Hills. Abano Terme is the largest town of the Basin (which includes a few other smaller towns) and is one of the most important thermal and mud-therapeutic resorts and in the world. Its very well structured hotels' system offers hospitality to more than 3 million tourists every year (BIOCE, 2009). Almost every hotel and spa owns a well to extract thermal water at a temperature in the range 60-87°C from the fractured carbonatic bedrock found at a depth of about 150-200 m (Antonelli and Montin, 2003). To preserve this fundamental resource, the local legislation does not allow extracted thermal water to be used for purposes other than therapeutic ones (Dainese, 2002). For this reason, this work analyses the feasibility, potential and sustainability of closed-loop heat-exchangers, also known as Borehole Heat Exchangers (BHE), as they do not require the extraction (and re-injection) of thermal water. By circulating a refrigerant liquid in a closed loop of pipes installed vertically in the ground, there is no fluid exchange between refrigerant and groundwater, but only heat transfer. The refrigerant accumulates heat when in contact with the hot groundwater, and releases it to a receiving body on the surface. Given the anomalous thermal condition and availability in the underground the use of a Ground Source Heat Pump is considered unnecessary and the possibility of employing a free-heating system is investigated. An actual application of such technique is analysed in terms of its thermal impact on underground and groundwater temperature. This impact is the most delicate element for the assessment of ecological sustainability and compatibility with the primary therapeutic use of the thermal fluid and it cannot therefore be impaired. The need to analyse all the physical processes involved in the volume of soil affected by the BHE arises from this issue. Evaluating the impact on environmental underground in the medium to long-term becomes especially important in areas which could host particularly concentrated distribution systems. The analysis is carried out using a finite elements analysis code (FEFlow 6.1), simulating mass and heat transfer inside porous media.

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## Marine georesources of the southern Tyrrhenian Sea: critical elements potential assessed by geochemical data

Funari V.\*<sup>1</sup>, Rovere M.<sup>2</sup>, Gamberi F.<sup>2</sup>, Marani M.<sup>2</sup>, Dinelli E.<sup>1</sup> & Braga R.<sup>1</sup>

1. Dipartimento BiGeA (Sezione Geologia) - Università di Bologna. 2. ISMAR-CNR Bologna.

Corresponding email: [valerio.funari@unibo.it](mailto:valerio.funari@unibo.it)

Keywords: Deep-sea mining, Critical elements, Southern Tyrrhenian Sea.

Critical Elements (CrE), i.e. Be, Co, Ga, Ge, In, Mg, Nb, Sb, Ta, W, the Platinum Group Elements (PGE) and the Rare Earth Elements (REE), have been identified to be essential for Europe due to their high relative economic importance concurrent with their high supply risk. The highest production of CrE is based in non-EU countries and in China in particular (European Commission, 2010). Their availability is increasingly under pressure because of their strategic importance for emerging new and green-energy technologies, such as hybrid cars, energy saving LEDs, electronic devices memories, wind power generators, medical applications.

In the past few years, the development of seafloor exploration technology and novel geochemical and mineralogical results are adding new perspectives to the economic potential of marine georesources. Several submarine geological processes are suggested to be capable of depositing CrE (e.g. Kato et al., 2011). Here we present the preliminary results of XRF and ICP-MS analyses performed on a number of sub-surface (depth < 1 m) seafloor samples collected in the southern Tyrrhenian Sea from different provinces associated with cold seeps and hydrothermal vents at the seabed. We focus on: 1) the determination of geochemical proxies for the CrE occurrence in specific deep-sea settings and 2) the prediction of CrE's potential in the seafloor sediments through colour-shaded concentration maps.

The southern Tyrrhenian seabed shows up to 47 g/kg total CrE. By clustering samples on the basis of the average bulk concentration of the main oxide, we found that Co content is high in iron oxy-hydroxides, while REE are enriched in Al-Si-rich samples. The Ca- and Mn-rich samples appear to be depleted in CrE. Interpolated maps of CrE concentration (IDW algorithm) indicate that the Paola Basin and the Eastern Aeolian Arc show relatively high content of Co and REE, the Palinuro area is high in Mg and precious metals (both with local hot spots of highest concentration). These data will be compared to the typical cut-off grade values used for land-based mining industry.

Seabed mining is still in its infancy with a few companies at present fully engaged in exploring the potential of deep sea resources worldwide, while general skepticism about the real potential of the seabed CrE deposits, coupled with the growing sensibility to environmental protection issues, are increasing. Yet, the global demand could drive further expansion of seabed mining in the near future and any efforts to develop innovative and sustainable exploration and exploitation techniques have to be encouraged among both the scientific community and the industry.

## Geochemical approach for the assessment of Lamezia Terme (Southern Italy) geothermal system

Garone A.\*<sup>1</sup>, Pizzino L.<sup>2</sup>, Sciarra A.<sup>2</sup> & Quattrocchi F.<sup>2</sup>

1. Dipartimento di Scienze della Terra - "Sapienza" Università di Roma. 2. INGV – Roma.

Corresponding email: [angelica.garone@uniroma1.it](mailto:angelica.garone@uniroma1.it)

Keywords: Lamezia Terme; geochemistry; low-enthalpy geothermal system.

Geothermal energy is a constant non-polluting source renewable natural heat that is emitted from within the earth's crust (McGee, 2007). It is used in a variety of diverse applications ranging from small domestic application to massive generation of electricity, which requires steam turbines (Rashid et al., 2012). The type of conversion technologies include dry steam, flash and binary type processes, which depend on the state of the fluid and its temperature (Jaaskelainen, 2010).

This work presents geochemical data collected in the Lamezia Terme area in May 2012, thanks to the adoption of a "local" approach. Three geochemical families were found: *i*) low salinity Ca-HCO<sub>3</sub> waters belonging to shallow hydrological circuits; *ii*) high salinity Ca-SO<sub>4</sub> samples characterizing the thermal waters of Caronte; *iii*) Na-Cl and Na-SO<sub>4</sub> chemistry, typical of interaction with marine sediments.

$\delta^{18}\text{O}$  and  $\delta\text{D}$  point out a common meteoric origin of the sampled waters; all waters are positioned between the Global Meteoric Water Line and the Regional Meteoric Water Line.

Dissolved carbon (i.e. CO<sub>2</sub>) isotopic analysis was carried out to distinguish its different sources. Isotopes point out a biogenic origin of the carbon dioxide for the bulk of the cold groundwaters, while the Caronte thermal waters trend toward the equilibrium with deep carbonates. This process is possible only hypothesizing a slow and deep circulation in the geothermal system, characterized by a prolonged WRI. N<sub>2</sub>, Ar and He distribution supported us to discriminate shallow and deep circuits. Most of the waters are characterized by shallow circulation, while both Caronte thermal waters and Na-SO<sub>4</sub> sample plot towards the crustal end-member due to their high helium content.

The deep temperature was evaluated applying the SO<sub>4</sub>/F<sub>2</sub> geothermometer. A realistic deep temperature, in the range 50-60°C, was estimated, assessing the low enthalpy of the Caronte hydrologic system.

The low-enthalpy geothermal resources are abundant, widely available, easily accessible and their use is believed to be beneficial. In the study area, there are several towns, farms, one of the largest industrial site of Calabria region and an airport. The geothermal resource can be used for domestic heating and/or cooling as well as agricultural, industrial and baths uses. Geothermal energy, with its proven technology and abundant resources, can make a significant contribution towards reducing the emission of greenhouse gases worldwide.

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## Near surface and deep subsurface geochemical monitoring for successful geologic sequestration of carbon dioxide

Kharaka Y.\*<sup>1</sup>, Thordsen J.<sup>1</sup>, Conaway C.<sup>1</sup>, Bullen T.<sup>1</sup>, Cole D.<sup>2</sup> & Phelps T.<sup>3</sup>

1. U.S. Geological Survey Menlo Park California, USA. 2. Ohio State University, School of Earth Sciences Columbus Ohio, USA. 3. Oak Ridge National Laboratory Oak Ridge Tennessee, USA.

Corresponding email: [ykharaka@usgs.gov](mailto:ykharaka@usgs.gov)

Keywords: carbon dioxide, CCS, geochemistry.

Carbon dioxide (CO<sub>2</sub>) capture, transport and sequestration, especially its geologic storage, is now considered one of the necessary options to stabilize atmospheric CO<sub>2</sub> levels and global temperatures at values that are considered acceptable for society and the environment. However, geologically sequestered CO<sub>2</sub> is buoyant, has low viscosity and, when dissolved in brine, becomes reactive to minerals, cements and well pipes. These properties of CO<sub>2</sub> may cause it to leak upward through faults, fracture systems and corroded well pipes, possibly contaminating underground sources of drinking water.

We have participated in several multi-laboratory field experiments to investigate geochemical parameters and methods to monitor the flow of injected CO<sub>2</sub> into deep saline aquifers (e. g., the Frio Brine Pilot, Texas) and into potable shallow groundwater (e.g., the ZERT site, Montana). Geochemical results from the Frio proved powerful tools in: 1- Tracking the successful injection and flow of CO<sub>2</sub> into the Frio sandstones; 2- showing that some of the CO<sub>2</sub> injected into the "C" sandstone leaked as it was detected in the overlying "B" sandstone that is separated from the injection "C" sandstone by 15 m of shale and siltstone; 3- showing mobilization of metals, including Fe ( from 30 to 1100 mg/L), Mn and Pb, and organic compounds (DOC from 5 to 700 mg/L), including BTEX, PAHs, and phenols following CO<sub>2</sub> injection; and 4- showing major changes in chemical and isotopic compositions of formation water , including a dramatic drop in calculated brine pH, (initially from 6.3 to 3.0) and major increases in alkalinity (from 100 to 3000 mg/L as HCO<sub>3</sub>). Geochemical modeling, chemical data and Fe isotopes indicated rapid dissolution of minerals, especially calcite and Fe-oxyhydroxides, and that part of the Fe and metal increases were caused by corrosion of well pipe.

## **Is the Mt. Amiata aquifer made vulnerable by geothermal exploitation?**

La Felice S., Montanari D.\* , Battaglia S., Bertini G., Gianelli G. & Principe C.

Institute of Geosciences and Earth Resources Italian – CNR.

Corresponding email: [domenico.montanari@igg.cnr.it](mailto:domenico.montanari@igg.cnr.it)

Keywords: Geothermal Energy; Aquifer Vulnerability; Volcanic rocks.

The Mt. Amiata (Central Italy) is a Quaternary volcano of silicic to intermediate mainly effusive products from trachydacite to latite composition, whose emplacement occurred about 300 ka ago. The volcanic rocks host a major regional aquifer exploited for the domestic water supply of a populated area. Two geothermal fields are located at the southern limits of the volcanic edifice. The geothermal reservoir is separated from the volcanic aquifer by a thick cover of flysch units (approx. 300 – 600 m), consisting of shale and limestone south, and shale and sandstone north the volcanic edifice. An eventual, aquifer vulnerability could depend on the interaction with the exploited geothermal reservoirs. An exploration well was drilled by the Tuscan regional authority (Regione Toscana) in order to monitor the eventual lowering of the water table of the fresh water aquifer and to gather data for defining a better hydrogeological model. The drill-hole crossed the volcanic sequence, found the water table and reached the flysch substratum. The aim of our scientific work is to find evidence of water-rock interaction in the volcanic rocks, both above and below the present day water table, in order to ascertain an eventual drawdown of the water table. We studied for the first time the sequence drilled by the well in order to investigate the volcanic stratigraphy, the reservoir characteristics, identifying the number and type of fractures, the depth of the piezometric level and the eventual presence of hydrothermal circulation. Therefore it was studied the mineralogy and petrology of the rock samples, the location, type and mineralization of the in-hole fractures. The results are interpreted considering the existing geological, geochemical and hydrogeological data.

The new discovery is that: 1) the water table level is at a depth of 302 m b.g.l. (783 m a.s.l.), in agreement with recent magnetotelluric surveys, and in disagreement with previous hydrogeological models; 2) there is no evidence of present or past interaction with geothermal fluids, the alteration minerals being present only in fractures within the volcanic rocks and indicating fluids of low temperature and low pH due to gas inlets in the volcanic reservoir; 3) the volcanic reservoir is characterized by fracture permeability, as shown by the fracture system along the well.

We conclude that our investigation gathers some pieces of evidence against the hypothesis of an aquifer vulnerability related to the geothermal exploitation.

### **3D Numerical Modeling of a geothermal reservoir: the case of Torre Alfina in central Italy**

Moia F., Colucci F.\*, Guandalini R., Agate G. & Rondena E.

Ricerca sul Sistema Energetico – RSE S.p.A. (MI).

Corresponding email: [francesca.colucci@rse-web.it](mailto:francesca.colucci@rse-web.it)

Keywords: geothermal reservoir, numerical modeling, GeoSIAM.

Geothermal energy is a renewable source that uses the endogenous heat of the Earth to produce energy. It has a great potential for development and can provide a valuable contribution to reduce greenhouse gases emissions.

An important impulse for the production, research and development of geothermal energy has occurred with the issue of Legislative Decree of February 11, 2010 n.22. It has favored the opening of the market to new operators and has encouraged experimentations of pilot plants with reduced environmental impact and with a nominal installed power not exceeding 5 MWe.

An interesting geothermal reservoir has been identified in the area of Torre Alfina. This area is located to the North of Bolsena Lake, at the border between Lazio and Umbria regions.

The geological investigations (Buonasorte et al., 1988) carried out in this area, have shown a medium enthalpy geothermal field, in fact, at the top of the reservoir, the temperature reaches about 140° C. The reservoir has been identified in permeable carbonate formations belonging to the Complex of Tuscan facies. At the top of the reservoir there is a gas cap, predominantly CO<sub>2</sub>, which presents an average thickness of about 100 m. Indeed, the caprock has been identified in the overlying Complexes of Ligurian and internal Austro-alpine facies.

All the available documentation has been carefully analyzed in order to identify the geological-structural and hydrogeological characteristics of the area. These are the basic data to carry out the detailed 3D geological model and the thermo-fluid dynamics numerical simulations of the geothermal field. The numerical modeling has been performed using the Integrated System for GeoModeling Analysis - GeoSIAM (Guandalini & Agate, 2013) realized by RSE.

For numerical modeling a 5 MWe power plant has been considered with two injection and two extraction wells of geothermal fluids. The numerical simulation, for a 30 years life of power plant, has allowed to study the plant feasibility and the conservation of appropriate temperature in the geothermal reservoir. In addition, the model of hydrothermal circulation, the isotherm trends and the CO<sub>2</sub> behavior have been studied as function of thermodynamic conditions.

Buonasorte G., Cataldi R., Ceccarelli A., Costantini A., D'Offizzi S., Lazzarotto A., Ridolfi A., Baldi P., Barelli A., Bertini G., Bertrami R., Calamai A., Cameli G., Corsi R., Dacquino C., Fiordalisi A., Ghezzi A. & Lovari F. 1988. Ricerca ed esplorazione nell'area geotermica di Torre Alfina (Lazio Umbria). Boll. Soc. Geol. It., 107, 265-337.  
Guandalini R. & Agate G. 2013. Revisione ed aggiornamento del Manuale d'uso del Sistema Integrato di Analisi Modellistica (SIAM). Rapporto RSE 13000782, 276 pp.

## **Synergies among CO<sub>2</sub>-CH<sub>4</sub> geological storage and geothermal energy: underground potential evaluation for strategic energy mix plans**

Procesi M., Cantucci B.\*, Buttinelli M. & Quattrocchi F.

Istituto Nazionale di Geofisica e Vulcanologia, Roma.

Corresponding email: [barbara.cantucci@ingv.it](mailto:barbara.cantucci@ingv.it)

Keywords: CCS, CH<sub>4</sub> geological storage, Geothermal energy, Energy mix.

In recent decades, the worldwide demand for energy has been increasing, with an associated rise in CO<sub>2</sub> emissions being observed. The European Commission in 2007 underlined the need to elaborate, at the European level, a Strategic Energy Technology Plan that focused on non-carbon or reduced carbon sources of energy and smart-energy networks, as well as energy efficiency and energy conservation.

A useful step for this planning is the evaluation of the underground potential for different energy applications, such as coal combustion combined with CO<sub>2</sub> geological storage (CCS), CH<sub>4</sub> storage in natural reservoirs (CH<sub>4</sub>-GS) and geothermal energy (GE) exploitation for power generation. The synergies between these technologies can be strategic, especially for densely populated countries, such as Italy.

This work proposes a multidisciplinary approach to develop energy-mix scenarios and to identify areas that are potentially suitable for CCS, CH<sub>4</sub>-GS and GE. The evaluation was performed by revisiting public data, as well as composite logs, seismic lines, geological and fluid geochemical data. Exclusion criteria as well as the presence of geological hazards were also taken into account.

This approach has been initially applied to the Latium Region (Central Italy), because it has one of the highest energy deficits in Italy, but the analysis of other strategic Regions is in progress.

For the Latium Region the storage capacities and geothermal potentials were estimated. Finally, based on the hypothesized energy mix plan, the potential reduction in CO<sub>2</sub> emissions was calculated. Three main scenarios are proposed: (A) a combination of CH<sub>4</sub>-GS with methane as cushion gas and GE; (B) a combination of CH<sub>4</sub>-GS with CO<sub>2</sub> as cushion gas and GE; (C) a combination of CCS and GE. Scenario A results in a reduction of the regional energy deficit that ranges from 21.8% to 45.6%. In Scenario B, the regional energy deficit reduction ranges from 30.8% to 80.7% and the CO<sub>2</sub> emissions reduction ranges from 1.4% to 5.6%, supposing an injection of 20 years. Scenario C shows a decrease in the regional energy deficit that ranges from 15.9% to 22.1%, while the CO<sub>2</sub> emissions reduction ranges from 7.1% to 31.3%, over the same time period.

The proposed scenarios can be useful both for the scientific community to improve the modeling of combined use of the underground resources and for the policymakers and economic managers to define the most reliable energy and CO<sub>2</sub> emissions saving strategies.

## SESSIONE S27

### **Microstructures: characterization, interpretation and modeling as a key to deformation and reaction mechanisms, and technological processes**

#### *CONVENORS*

*L. Mancini (Elettra, Trieste)*

*R. Spiess (Univ. Padova)*

*C. Viti (Univ. Siena)*

*M. Zucali (Univ. Milano)*

## Natural and laboratory compaction band in porous carbonates: a 3D characterization using synchrotron X-ray microtomography

Arzilli F.\*<sup>1</sup>, Cilona A.<sup>2-3</sup>, Mancini L.<sup>1</sup> & Tondi E.<sup>3</sup>

1. Elettra-Sincrotrone Trieste S.C.p.A., Basovizza (TS). 2. Department of Geological and Environmental Sciences, Stanford University, Stanford, CA, United States. 3. School of Science and Technology, Geology Division, Università di Camerino.

Corresponding email: [fabio.arzilli@elettra.eu](mailto:fabio.arzilli@elettra.eu)

Keywords: porous carbonates, compaction bands, porosity, connectivity, X-ray computed microtomography.

Porous carbonates form important reservoirs for water and hydrocarbons. Post-depositional processes (e.g. mechanical) are important to quantify because they may affect the fluid flow properties of reservoirs. Field-based studies (Tondi et al., 2006; Rustichelli et al., 2012) described bed-parallel compaction bands (CBs) within carbonates with a wide range of porosities. These CBs are burial-related structures, which accommodate volumetric strain by grain rotation, grain translation, pore collapse and pressure solution. Cilona et al. (2012) performed triaxial compression experiments, under dry conditions on the porous cretaceous grainstones (the Orfento Formation, in Majella Mountain, Abruzzi), reproducing for the first time CBs in laboratory. In this work, the authors defined the pressure conditions at which natural CBs form and documented the role of Hertzian cracks for grain size and porosity reduction within the CBs.

Here we use a new methodology to characterize the pore networks of natural and laboratory CBs and compare them with the host rock one.

Data were collected using the synchrotron X-ray microtomography technique at the SYRMEP beamline of the Elettra-Sincrotrone Trieste Laboratory (Basovizza (Trieste), Italy). Quantitative analyses of the samples were carried out using the Pore3D software library (Brun et al., 2010). The porosity was calculated from segmented 3D images of deformed and pristine rocks. The process of skeletonization, which provides the number of connected pores within a rock volume, was applied. By analyzing the skeletons we were able to highlight the differences between natural and laboratory CBs, and to investigate how pore connectivity evolves as a function of the deformation.

Preliminary results show that within compaction bands both pore volume and connectivity are reduced in comparison with the undeformed host rock. Natural CB has a lower porosity with respect to the laboratory one. In natural CBs, the contact among granules seem be welded, whereas in the laboratory CBs it shows pores with irregular shape.

Brun F., Mancini L., Kasae P., Favretto S., Dreossi D. & Tromba G. 2010. Pore3D: A software library for quantitative analysis of porous media: Nucl. Instrum. Methods Phys. Res. A, 615, 326-332.

Cilona A., Baud P., Tondi E., Agosta F., Vinciguerra S., Rustichelli A. & Spiers C.J. 2012. Deformation bands in porous carbonate grainstones: field and laboratory observations. J. Struct. Geol., 45, 137-157.

Rustichelli A., Tondi E., Agosta F., Cilona A. & Giorgioni M. 2012. Development and distribution of bed-parallel compaction bands and pressure solution seams in the Bolognana Formation carbonates (Majella Mountain, Italy). J. Struct. Geol., 37, 181-199.

Tondi E., Antonellini M., Aydin A., Marchegiani L. & Cello G. 2006. The role of deformation bands, stylolites and sheared stylolites in fault development in carbonate grainstones of Majella Mountain, Italy. J. Struct. Geol., 28, 376-391.

## **X-ray computed microtomography in geosciences**

Arzilli F.\*

Elettra-Sincrotrone Trieste S.C.p.A., Basovizza (TS)

Corresponding email: [fabio.arzilli@elettra.eu](mailto:fabio.arzilli@elettra.eu)

Keywords: X-ray computed microtomography, X-ray phase-contrast imaging, image processing, rock textures.

X-ray computed microtomography ( $\mu$ -CT) has become an invaluable technique for geologists, with wide applications in various geological disciplines. X-ray  $\mu$ -CT is a non-destructive technique and it is based on both conventional and synchrotron radiation sources (Baker et al., 2012). This technique produces three-dimensional (3D) images of the internal structure of objects, determined by variations in morphology, mass density and/or chemical composition. It is a powerful tool for 3D investigation of several geological materials with spatial resolution at the micro- and submicron- scale. The possibility to visualize and measure textures in 3D is crucial for understanding the processes responsible for the formation of rocks. Therefore, all kind of rocks can be studied and the morphology of unique and precious samples (such as fossils) can be investigated in a non-destructive way.

This contribution provides an introduction to the principles of X-ray  $\mu$ -CT and to the image analysis to study several geologic issues. Furthermore, different factors affecting the image quality and several image processing methods will be discussed.

The use of synchrotron radiation X-ray imaging in geosciences allows to dramatically improve the contrast and spatial resolution compared to conventional sources, allowing to perform highly precise quantitative analyses in rocks. X-ray phase-contrast imaging can also improve the visualization of features with small differences in mass density and chemical composition with respect to the rock matrix, so this technique is crucial to analyze geological samples characterized by several phases.

In this seminar several applications of X-ray  $\mu$ -CT methodologies for the extraction of quantitative information from 3D images of geomaterials will be presented.

Important applications of X-ray  $\mu$ -CT are e.g. the study of bubbles and crystals in volcanic rocks. Several studies of crystallization kinetics were carried out using two-dimensional images (e.g. Arzilli & Carroll, 2013) but recently these processes have been investigated using volumetric datasets. Another example is in the field of structural geology, where X-ray  $\mu$ -CT was employed to study the porosity and connectivity of carbonates and how the localized deformation acts on their structure.

Arzilli F. & Carroll M.R. 2013. Crystallization kinetics of alkali feldspars in cooling and decompression-induced crystallization experiments in trachytic melt. *Contrib. Mineral. Petr.*, 166, 1011-1027.

Baker D.R., Mancini L., Polacci M., Higgins M.D., Gualda G.A.R., Hill R.J. & Rivers M.L. 2012. An introduction to the application of X-ray microtomography to the three-dimensional study of igneous rocks. *Lithos*, 148, 262-276.

## Microstructural characterization of raw and fired sanitary-ware vitreous body by Synchrotron Computed Microtomography

Bernasconi A.<sup>1</sup>, Marinoni N.\*<sup>2</sup>, Lanzarotti R.<sup>3</sup>, Pedersini F.<sup>3</sup>, Mancini L.<sup>4</sup> & Francescon F.<sup>5</sup>

1. European Synchrotron Radiation Facility Grenoble – France. 2. Dipartimento di Scienze della Terra "Ardito Desio" - Università degli Studi di Milano. 3. Dipartimento di Informatica - Università degli Studi di Milano. 4. SYRMEP Group, Sincrotrone Trieste S.C.p.A. 5. Ideal Standard International - C.O.E. - Ceramic Process Technology - Trichiana (BL).

Corresponding email: [nicoletta.marinoni@unimi.it](mailto:nicoletta.marinoni@unimi.it)

Keywords: sanitary-ware ceramic, synchrotron X-ray microtomography, microstructure.

China whiteware products represent a large part of ceramic materials and cover a wide range of applications like tile, dinnerware and sanitary-ware. They are mainly formed by a vitreous body which comes from heating above 1100 C a mixture of clays, fluxing agents (typically feldspar) and fillers (typically quartz), after previous processing like, for example, aging, drying and body preparation (Carty & Senapati, 1998). Phase composition of vitreous body has been widely studied in past and is characterized by a glassy matrix with some crystalline phases like mullite, which forms upon heating, and residual filler (Martin-Marquez et al., 2009). Additionally, a well developed porosity can be present, with consequent implication on some technological properties of the materials like mechanical strength (Braganca & Bergman, 2003).

In the present investigation, four different industrial sanitary-ware compositions have prepared by fixing the “hard” compound (21 % feldspar, 19 % quartz and 6 % China whiteware waste) and by varying the “plastic” compound with four different industrial clay components (one per sample). After casting procedure, half of each sample was saved to investigate the packing of the green body whilst the other half was fired in a muffle furnace at the peak temperature of 1200 C to investigate the porosity of the fired product, for a total of eight samples.

All these eight samples, after previous XRPD characterization, have been investigated by Synchrotron Computed Microtomography at the SYRMEP beamline (Elettra, Trieste) in phase contrast modality.

Data reconstruction have been performed and the microstructure have been evaluated by processing slices with a Matlab written code. In particular, it was possible to focus on voids but also on zircon crystals that come from the 6 % of China whiteware waste, due to their “transmitted” signals which differ from the one of the other phases (i.e. quartz, mullite and glass).

For each sample, it was possible to characterize the volume of voids and zircon in terms of total volume and size distribution in the 10-1000 µm range; moreover, Higgins sphericity index and Flynn diagrams have been determined.

The results have been also compared with mercury porosimeter measurements.

Braganca S.R. & Bergmann C.P. 2003. A view of whitewares mechanical strength and microstructure. *Ceramics International*, 29, 801-806.

Carty W.M. & Senapati U. 1998. Porcelain – Raw Materials, Processing, Phase Evolution, and Mechanical Behaviour. *Journal of American Ceramic Society*, 81(1), 3-20.

Martin-Marquez J., De la Torre A.G., Aranda M.A.G., Rincon J.M. & Romero M. 2009. Evolution with Temperature of Crystalline and Amorphous Phases in Porcelain Stoneware. *Journal of American Ceramic Society*, 92(1), 229-234.

## Comparison of Total Scattering data from gahnite nanocrystals

Confalonieri G.\*<sup>1</sup>, Dapiaggi M.<sup>1</sup>, Sommariva M.<sup>2</sup>, Gateshki M.<sup>2</sup>, Fitch A.N.<sup>3</sup> & Kimber S.J.A.<sup>3</sup>

1. Department of Earth Sciences- University of Milan. 2. PANalytical BV, The Netherlands. 3. ESRF, France.

Corresponding email: [giorgia.confalonieri@unimi.it](mailto:giorgia.confalonieri@unimi.it)

Keywords: PDF, total scattering, nanospinels, synchrotron, in-house diffractometer.

Total scattering technique (X Ray Powder Diffraction) has been used to investigate the structure of nanocrystalline (and possibly disordered) spinel gahnite  $ZnAl_2O_4$ . This experimental method allows to use both the Bragg scattering (used in traditional crystallography) and the diffuse scattering, caused by anything that does not diffuse exactly following the Bragg law (such as defects, local distortions, etc.). High energy incident wave is required and three different instruments have been employed: (i) ID31 high resolution diffractometer at the ESRF (9 line detectors, all with crystal analyzers,  $\lambda=0.3999\text{\AA}$ ), (ii) ID15B high energy beamline at the ESRF with 2D image plate detector (t), ( $\lambda=0.1421\text{\AA}$ ) (iii) PANalytical diffractometer with silver anticathode, with an X'Celerator detector ( $\lambda=0.5608\text{\AA}$ ). In order to compare the three diffraction data sets, the related Pair Distribution Functions (PDFs) are presented. PDFs are functions in which peaks represent the correlations between all pairs of atoms and were obtained with PDFgetX3 (Juhas et al., 2013) that allows to scale, correct, and FT the diffraction data. The same procedure was applied to all data sets subtracting the relevant empty capillary scattering, and correcting and normalizing the data. Different functions for each data set have been calculated changing parameters, such as the background scale, to reduce noise in PDF and optimize the function. The PDFs were visually compared, and then were refined by means of PDFgui (Farrow et al., 2007), using the simplest possible model of a spinel (totally direct, with space group symmetry respected). All the refinements were made exactly in the same way, by refining the same parameters, for the sake of a fair comparison. Small differences in the refined structural parameters could be caused by different instrument's characteristics but also by parameters used in PDF calculation, so attention should be paid to the procedure of PDF attainment from total scattering data.

Farrow C.L., Juhás P., Liu J.W., Bryndin D., Božin E.S., Bloch J., Proffen Th., Billinge S.J.L. 2007. PDFfit2 and PDFgui: computer programs for studying nanostructure in crystals. *J. Phys. Condens. Matter.*, 19, 335219.  
Juhas P., Davis T., Farrow C.L. & Billinge S.J.L. 2013. PDFgetX3: a rapid and highly automatable program for processing powder diffraction data into total scattering pair distribution functions. *J. Appl. Cryst.*, 46, 560-566.

## **Characterization, interpretation and modeling of the present day oceanic crust microstructure by using innovative techniques based on neutron diffraction and X-ray microtomograph**

Fontana E.<sup>1</sup>, Marinoni N.<sup>1</sup>, Zucali M.\*<sup>1-2</sup>, Tartarotti P.<sup>1</sup>, Mancini L.<sup>3</sup>, Brignone V.<sup>1</sup>, Capelli S.<sup>4</sup> & Ouladdiaf B.<sup>4</sup>

1. Università degli Studi di Milano, Dipartimento di Scienze della Terra "A. Desio". 2. IDPA-CNR U.O.S. of Milano.  
3. Elettra-Sincrotrone Trieste S.C.p.A., Basovizza (TS). 4. ILL, Institute Laue-Langevin, Grenoble, France.

Corresponding email: [michele.zucali@unimi.it](mailto:michele.zucali@unimi.it)

Keywords: oceanic crust, neutron, microtomography.

Our understanding of the emplacement kinematics of submarine lavas and dikes is often limited to plan-view geometries of near-axis lava or tectonic windows exposing disrupted portion of oceanic crust. Instead, drilled cores provide in situ access to the intact internal microstructure of submarine rocks. Two innovative methodologies revealing significant constraints on the mechanisms and forces involved in microstructure formation of present day drilled oceanic crust are here presented. These include (1) a neutron diffraction-based analysis for studying an off-axis submarine lava flow and (2) a X-ray microtomography-based analysis for studying the lava-dike transition, both achieved from the drilled oceanic crust of the ODP/IODP-Site 1256 (Cocos Plate).

Quantitative insights into submarine lava microstructures and strong evidence for NW-SE lava flow direction that is parallel to the paleo-ridge axis of the East Pacific Rise, are provided. In situ shear within submarine lavas revealed by composite shape and lattice preferred orientations of minerals, accounts for a dominant laminar non-uniform type flow.

Since porosity and porous shape, as well as permeability strongly affect the physical properties of rocks, namely compressional-wave velocities, the porous shape in basalt from the lava-dike transition has been achieved by synchrotron X-ray microtomography (micro-CT) without requiring any sample preparation. Micro-CT images enhance the phase-contrast between primary (igneous) minerals and alteration minerals now filling the pores. Overall, quantitative data of the volume and shape of the pores (at the sample scale) allow to evaluate the "empty" (effective) porosity or paleo-porosity (pores now filled with secondary minerals) in the investigated basalts, as well as the 3D-pattern of micro-cracks.

For the first time on present day oceanic basement and despite the environmental difficulties in the study of the seafloor under deep water, this work shows that, by using only punctual data deriving from ocean drilling and non-destructive 3D analysis techniques it is possible to obtain detailed microstructural information on distinct stratigraphic basement layers possessing different emplacement mechanisms as well as various post-magmatic evolution.

### 3D distribution of primary melt inclusions in garnets by X-ray microtomography

Parisatto M.<sup>1</sup>, Turina A.<sup>1</sup>, Cesare B.\*<sup>1</sup>, Cruciani G.<sup>2</sup>, Mancini L.<sup>3</sup> & Peruzzo L.<sup>4</sup>

1. Department of Geosciences, University of Padova. 2. Department of Physics and Earth Sciences, University of Ferrara. 3. Elettra - Sincrotrone Trieste S.C.p.A. 4. CNR - Istituto di Geoscienze e Georisorse, Padova.

Corresponding email: [bernardo.cesare@unipd.it](mailto:bernardo.cesare@unipd.it)

Keywords: Garnet, Melt inclusions, Microtomography, garnet, anatexis, melt inclusions, X-ray computed tomography.

Modeling the spatial distribution density of melt inclusions is important to understand the growth and trapping history of peritectic minerals and coexisting fluids/melts during the partial melting of the crust. X-ray computed microtomography (micro-CT) is well suited for this purpose, owing to its three-dimensional (3D) imaging capabilities and non-invasiveness. X-ray micro-CT has been applied here to investigate the 3D distribution of primary melt inclusions in almandine-rich garnets from El Hoyazo (Neogene Volcanic Province, SE Spain). Glassy inclusions are trapped in nearly all mineral phases in metapelitic enclaves found within El Hoyazo dacites and have been extensively analyzed in previous literature (e.g. Acosta-Vigil, 2007; Cesare, 2009).

X-ray micro-CT experiments based on a conventional microfocus source (Dept. of Geosciences, Univ. of Padova) and a synchrotron radiation source (the SYRMEP beamline, Elettra - Sincrotrone Trieste) were carried out on sub- to euhedral garnet crystals (1-5 mm in diameter). Despite the high X-ray absorption of the largest garnets, the internal features of the samples were successfully imaged, with spatial resolutions down to a few microns for synchrotron-based data. A multi-step image analysis procedure, specifically optimized for the investigated samples, was adopted to accurately segment melt inclusions from other non-relevant features within the garnets (e.g. fractures or muscovite crystals) that could not be adequately separated using simple grey values thresholding of tomographic data. This allowed to accurately measure characteristic size and shape parameters of melt inclusions and to calculate their spatial distribution density as a function of radial distance from the centre of the garnets. The 3D spatial distribution of other trapped mineral phases (e.g. monazite, zircon, apatite) was investigated as well, and compared with the distribution of melt inclusions.

Preliminary data analyses revealed the occurrence of a clear peak of melt inclusions density, ranging approximately from 1/3 to 1/2 radial distance from the centre of the distribution, while mineral phases appeared to be more randomly distributed. No evidence of a sharp boundary between inclusion-rich cores and inclusion-free rims was found. The results obtained so far, together with chemical profiles of the garnet composition obtained using SEM-EDS, suggest that the investigated garnets grew in one single event in the presence of anatectic melt, under a constantly decreasing melt supply.

Acosta-Vigil A., Cesare B., London D. & Morgan G.B. 2007. Microstructures and composition of melt inclusions in a crustal anatectic environment: the metapelitic enclaves within El Hoyazo dacites, SE Spain. *Chemical Geology*, 237, 450–465.

Cesare B., Rubatto D. & Gómez-Pugnaire M.T. 2009. Do extrusion ages reflect magma generation processes at depth? An example from SE Spain. *Contributions to Mineralogy and Petrology*, 157, 267–279.

## **Bubble coalescence in magmas: Insights from in-situ high-temperature synchrotron-based X-ray tomographic microscopy**

Pistone M.\*<sup>1-2</sup>, Caricchi L.<sup>3</sup>, Fife J.L.<sup>4</sup>, Mader K.<sup>4-5</sup>, Rust A.<sup>1</sup>, Ulmer P.<sup>2</sup>

1. School of Earth Sciences, University of Bristol, United Kingdom. 2. Institute for Geochemistry and Petrology, Department of Earth Sciences, ETH, Zurich, Switzerland. 3. Department of Mineralogy, University of Geneva, Switzerland. 4. Swiss Light Source, Paul Scherrer Institute, Villigen, Switzerland. 5. Institute for Biomechanical Engineering, ETH-Zurich, Zurich, Switzerland.

Corresponding email: [Mattia.Pistone@bristol.ac.uk](mailto:Mattia.Pistone@bristol.ac.uk)

Keywords: bubbles, volcanoes, synchrotron.

The possibility of removing gas from magma during its rise to the surface decreases the probability of an explosive volcanic eruption to occur. In this respect, bubble coalescence and the achievement of a permeable network play a pivotal role in favouring magma degassing and limiting the explosivity of eruptions. Significant growth and interaction between bubbles occur in natural volcanic systems during ascent of the magma to the surface. Thus, we performed real time, 4D, high-temperature experiments at atmospheric pressure using laser heating and synchrotron-based X-ray tomographic microscopy at the TOMCAT beamline of the Swiss Light Source (SLS). We forced gas exsolution in natural magmas and observed bubble nucleation and growth in situ. The experiments were performed from room temperature up to 1300 K on two different types of crystal-free rhyolitic samples: one vesicle-free obsidian and one obsidian containing pre-existing vesicles. We characterized the main textural variations (bubble volumes, size distributions, shapes, and bulk textures) during the nucleation and growth of bubbles in these highly viscous systems, and tracked the evolution of parameters such as viscosity and overpressure in the foaming samples, which are essential for retrieving information on the processes preceding an eruption from the interpretation of the textures observed in eruptive products. The microstructural features of the starting material, nominally the presence of initial vesicles, strongly influence the dynamics of bubble coalescence. The presence of bubbles in the starting material tends to limit coalescence, therefore increasing the possibility of bubble overpressure. A possible implication of these experiments is that volcanic systems where magma is volatile-saturated already in the subvolcanic reservoir may have a higher tendency to feed explosive volcanic eruptions.

## Image processing of crystallized textures using phase-contrast synchrotron X-ray computed microtomography data

Polacci M.<sup>1</sup>, Arzilli F.<sup>2</sup>, Baker D.R.<sup>3</sup>, Landi P.<sup>1</sup>, Giordano D.<sup>4</sup> & Mancini L.\*<sup>2</sup>

1. Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Pisa. 2. Elettra-Sincrotrone Trieste S.C.p.A., Basovizza (Trieste). 3. Department of Earth and Planetary Sciences - McGill University, Montréal, Canada. 4. Dipartimento di Scienze della Terra - Università di Torino.

Corresponding email: [lucia.mancini@elettra.eu](mailto:lucia.mancini@elettra.eu)

Keywords: X-ray microtomography, image processing, phase-contrast imaging.

X-ray computed microtomography has become a fundamental tool in geosciences to study textures of igneous, metamorphic and sedimentary rocks directly in 3D. This technique is useful to study the vesiculation of pumices (Polacci et al., 2009), but only recently there has been more interest to study the crystallization process using volumetric datasets, where the phases of interest often have similar density. Therefore, image processing for these samples require more sophisticated procedures to separate crystals from silicate glass.

Feldspars are one of the most abundant crystalline phases of igneous rocks, hence their crystallization conditions and abundance are intensely investigated by geologists. Moreover, feldspar is one of the most difficult phases to segment during image analysis, making the separation of feldspars from the silicate glass a challenge.

Here we show that the crystallinity of natural and synthetic rocks could be studied using microtomographic datasets. In this case, a pumice from Stromboli and a synthetic trachyte from the Campi Flegrei were selected in order to separate plagioclases and alkali feldspars from the glass and bubbles.

Data were collected using the propagation-based synchrotron X-ray phase contrast microtomography technique at the SYRMEP beamline of the Elettra-Sincrotrone Trieste Laboratory (Basovizza (Trieste), Italy). Although propagation-based X-ray phase contrast imaging can improve the visualization of weakly absorbing features in a sample, making visible the edge of feldspars, the segmentation of these crystals cannot be directly obtained from the raw phase contrast X-ray images. Phase-retrieval methods are needed for extracting phases of interest (Beltran et al., 2010). A single distance phase-retrieval algorithm (Paganin et al., 2002) was applied to the dataset to improve the contrast between feldspar and glass in the reconstructed images; this allowed us to obtain a better segmentation for microtomographic data where the absorption contrast was too low. Through this technique we are able to isolate feldspars both in natural samples and in synthetic ones, and to perform quantitative analysis of these phases using volumetric datasets. Our preliminary results have demonstrated that phase retrieval processing will be an invaluable tool for geologists to study rock textures.

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## The potential information contained in CPOs: modelling granulite facies quartz pole figures

Spiess R.\*<sup>1</sup>, Faccenda M.<sup>1</sup> & Festa V.<sup>2</sup>

1. Dipartimento di Geoscienze, Università di Padova. 2. Dipartimento Geomineralogico, Università degli Studi di Bari "Aldo Moro".

Corresponding email: [richard.spiess@unipd.it](mailto:richard.spiess@unipd.it)

Keywords: Crystallographic preferred orientation, Modeling CPOs, Granulite facies metamorphism.

The activity of single slip systems during ductile deformation is strongly influenced by the resolved shear stress, the deformation temperature and the strain rate. Pole figures are therefore snap-shots of the deformation conditions of rocks during specific moments of the evolution of orogens and potentially can preserve information on the above mentioned factors. Furthermore, since pole figures vary with changing deformation paths, pure shear and simple shear components of deformation and hence vorticity can be ideally calculated. In order to test which information can be extracted from CPOs, we modelled quartz CPOs using the kinematic model of Kaminski and Ribe (2001, 2002), implemented with quartz slip systems data published by Beata and Ashbee (1969), Lister (1979), Lister and Hobbs (1980). In our contribution we compare numerically modelled CPOs with data measured on granulite facies migmatitic gneisses of Calabria and with published CPOs from the Saxony granulite terrain (Lister and Dornsiepen, 1982).

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## Submarine lava flow direction revealed by neutron diffraction analysis in mineral lattice orientation

Zucali M.<sup>1</sup>, Fontana E.\*<sup>1</sup>, Panseri M.<sup>1</sup>, Tartarotti P.<sup>1</sup>, Capelli S.<sup>2</sup> & Ouladdiaf B.<sup>2</sup>

1. Dipartimento di Scienze della Terra, Università degli Studi di Milano. 2. Institut Laue-Langevin, Grenoble, France.

Corresponding email: [emanuele.fontana@unimi.it](mailto:emanuele.fontana@unimi.it)

Keywords: lava flow, microstructures, neutron diffraction.

Submarine lava flows are the main constituent of young oceanic crust. Studying submarine lava flows is important for understanding the lava eruption and transport mechanisms, either at the ridge axis or off-axis. However, since submarine lava flows are often inaccessible, our knowledge of their internal structure is much less complete than that of better studied subaerial lava flows.

In submarine environment, the most well-known mid-ocean ridge off-axis lava flows occur near fast and superfast spreading ridges, such as the North East Pacific Rise (e.g., Alexander and Macdonald, 1996) and the South East Pacific Rise (e.g., White et al., 2002) as well as ultraslow spreading ridges (e.g., Standish and Sims, 2010). Such lava flows may be important constituent of the ocean crust, since their volumes, although highly variable, may be as high as few tens of km<sup>3</sup> (e.g., White et al., 2002). Therefore, it is of great importance to understand the internal structure of submarine lava flows by in situ techniques, in order to unravel the emplacement mechanisms. The unique opportunity to examine the interior of an in situ and intact lava flow, which is normally inaccessible to seafloor investigations, is by drilling.

An investigation of a submarine lava flow drilled at ODP/IODP Site 1256 is performed by combining three-dimensional (3-D) Lattice Preferred Orientation (LPO) data, obtained by neutron diffraction, with bidimensional (2-D) Shape Preferred Orientation (SPO) data. The main purpose is twofold, i.e., (i) to unravel the transport direction and mechanism of a submarine lava flow by defining the internal microstructure of a drilled section of upper oceanic crust and (ii) to perform a quantitative LPO and SPO study on several ~cm<sup>3</sup> samples from the 1256D lava field discussing the development of different types of fabrics and therefore the dynamics and direction of the lava flow.

This work greatly benefits from neutron diffraction texture analysis, and indeed, this is the first study to present a microstructural analysis of a submarine drilled volcanic body, thus establishing a consistent method for inferring subaqueous lava flow direction on oriented core samples. In particular, our results contribute to the understanding of submarine lava flows that are emplaced off-axis, i.e., at a certain distance, from mid-ocean ridges that, although not uncommon, are still poorly studied.

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## **SESSIONE S28**

### **Active tectonics and seismic potential of the Mediterranean region**

#### *CONVENORS*

*C. Monaco (Univ. Catania)*

*A.M. Michetti (Univ. Insubria)*

*R. Sabadini (Univ. Milano)*

## Quaternary normal faulting along the western side of the Matese Mountains (Central Apennines, Italy). Constraints from field geology and implications for active tectonics

Auciello E.\*<sup>1</sup>, Boncio P.<sup>1</sup>, Dichiarante A.M.<sup>2</sup> & Saroli M.<sup>3</sup>

1. Dipartimento DISPUTer, Università "Gabriele d'Annunzio" di Chieti – Pescara. 2. Department of Earth Sciences, Durham University. 3. Dipartimento di Ingegneria Civile e Meccanica, Università di Cassino e del Lazio Meridionale.

Corresponding email: [e.auciello@unich.it](mailto:e.auciello@unich.it)

Keywords: Earthquakes, Apennine, Matese.

On December 29<sup>th</sup>, 2013 a Mw 5.0 earthquake affected the Matese region, bringing the attention to this high-seismic hazard area. Several strong earthquakes struck this region in the past (346 AD, 848 AD, 1293 M5.8, 1349 M6.6, 1456 M7.2, 1688 M7.0, 1805 M6.6). In spite of this high seismicity, the knowledge on the seismogenic sources is less defined than other seismic areas of Italy. In fact, only two fault systems in northern Matese were associated to strong historical earthquakes: the Isernia-Bojano-Guardiaregia and the Pozzilli – Capriati al Volturno (Aquae Iuliae) normal faults (Di Bucci et al., 2005 cum bibl.; Galli & Naso, 2009). In central and southern Matese there are not constrained active faults, and the seismogenic sources of the 346 AD and 1688 earthquakes are unknown. Moreover, GPS data show high extension rate across the Matese (4-5 mm/a across the Aquae Iuliae and Isernia-Bojano faults; Giuliani et al., 2009).

The GPS data, and the poor geologic knowledge of the region open a number of questions. Is the southern part of the Matese Mts affected by comparable extension rate? If so, which are the most likely active faults able to accommodate this deformation? This work is inspired by these questions and is aimed at understanding the mechanisms which control the transfer of active extension within the Matese Mts.

We present new data for the western side of the Matese Mts, obtained by basic field geology (1:10,000 scale), integrated with active tectonics-oriented photogeology and elementary morphotectonics. The emerging tectonic picture gives insights on the overall segmentation pattern of the normal faults along the western side of the Matese Mts., with implications on the seismogenic potential of the area.

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## Geological and seismological clues for a regionally-extended crustal discontinuity in central-eastern Sicily (Italy)

Barreca G.\*<sup>1</sup>, Scarfi L.<sup>2</sup>, Cannavò F.<sup>2</sup> & Koulakov I.<sup>3</sup>

1. Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania, Sezione di Scienze della Terra. 2. Istituto Nazionale di Geofisica e Vulcanologia, Osservatorio Etneo, Catania. 3. Institute of Petroleum Geology and Geophysics, Novosibirsk, Russia.

Corresponding email: [g.barreca@unict.it](mailto:g.barreca@unict.it)

Keywords: central-eastern Sicily, regional shear zone, dragging precesses, 3-D velocity structure, wave velocity contrast.

An integrated analysis of large scale geological features and seismological data provides clues for a regionally-extended structural discontinuity slicing through all over the central-eastern portion of the Sicilian Fold and Thrust Belt, between the Madonie Mts. range and south of Mt. Etna region. Along this area, major NE-SW trending Mio-Pliocene compressive structures (thrust-top basins and related syncline) are systematically dragged and rotated according to vertical axis until to assume a hook-shape at their terminations. The clockwise sense of rotation of such major structures suggests the occurrence of regional, more than 100 km long, dextral wrench fault zone with a NW-SE direction. More detailed field surveys performed in key sectors (e.g. Madonie Mts. and Mt. Judica region) reveal that this crustal discontinuity consists probably of a wider deformation band that in the near-surface scattered into a series of discrete segments which sometimes overlap to form zone of releasing/restraining stopovers.

The analysis of the seismicity of the studied region helped us to achieve further information about the characteristics of this shear zone. Selected earthquakes (from the CSI 1.1 1981–2002 by Castello et al., 2006, and from Bollettino Sismico 2003-2012, <http://bollettinosismico.rm.ingv.it/index.php>), were used as data source for a simultaneous inversion of a 3-D velocity structure and hypocentre parameters. The obtained velocity images and the foci distribution depict a relevant NW-SE oriented tectonic boundary. This structural element splits a sector of high concentration of earthquakes northwards from a zone with relative paucity of seismicity southward. Further, the possible presence of this major structural discontinuity is emphasized by a strong wave velocity contrast found in central Sicily and visible down to about 30 km of depth.

## The Lipari–Vulcano complex in the geodynamic context of the south-eastern Tyrrhenian sea

Barreca G.\*<sup>1</sup>, Bruno V.<sup>2</sup>, Cultrera F.<sup>1</sup>, Mattia M.<sup>2</sup>, Monaco C.<sup>1</sup> & Scarfi L.<sup>2</sup>

1. Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania, Sezione di Scienze della Terra. 2. Istituto Nazionale di Geofisica e Vulcanologia, Osservatorio Etneo, Catania.

Corresponding email: [g.barreca@unict.it](mailto:g.barreca@unict.it)

Keywords: Tyrrhenian sea, Aeolian islands, lipari-vulcano complex, structural features, stress field, triple junction.

Field, geodetic and seismological data from the Lipari-Vulcano complex (Aeolian Archipelago) allow us to better constrain the geodynamic pattern of this region. Field data consist of structural measurements performed on well exposed fault planes and fractures involving Late Pleistocene volcanic products. The mesostructures are mostly represented by NW-SE striking normal faults with dextral-oblique component of motion. Minor structures are represented by N-S oriented joints and tension gashes widespread over the whole analyzed area and particularly along fumarolized sectors. Analyzed seismological dataset (from 1994 to 2012) is based on earthquakes with magnitude ranging between 1.0 and 4.8. The hypocentres distribution depicts two major alignment corresponding to the NNW–SSE trending Aeolian-Tindari-Letojanni fault system and to the WNW-ESE oriented Sisifo-Alicudi fault system. GPS data analysis displays ~3.0 mm/yr of active shortening between the two islands, with a maximum contraction of about  $1.0 \cdot 10^{-13}$  s<sup>-1</sup>, between La Fossa Caldera and south of Vulcanello. This region is bounded to the north by an area where the maximum values of shear strain rates, of about  $0.7 \cdot 10^{-13}$  s<sup>-1</sup> are observed. This major change occurs in the area south of Vulcanello that is also characterized by a transition in the way of the vertical axis rotation. Moreover, both the islands show a clear subsidence process, as suggested by negative vertical velocity of all GPS stations which exhibit a decrease from about -15 to -7 mm/yr from north to south. The upper Pleistocene transtensional structures and the strong contraction currently occurring between Lipari and Vulcano (considering Vulcanello as a part of Lipari) can be framed in the eastern termination of the Sisifo-Alicudi fault system, at its junction with the northern branch of the Aeolian-Tindari-Letojanni fault system. The former shows strike-slip motion in response to NW-SE oriented regional compression, and it is also characterized by transtensive and transpressive sectors. The latter separates two compartments characterized by different tectonic regimes, a mostly contractional domain to the west and an extensional one to the east. The Lipari-Vulcano complex falls in a sector of the southern Tyrrhenian Sea that, in our opinion, plays the role of a triple junction between Tyrrhenian, Sicilian and Calabrian-Apulian blocks, whose formation can be related to the recent geodynamic reorganization in the south-central Mediterranean area. We observe, in fact, that the cessation of volcanic activity at Ustica (130 ka ago), at Alicudi and Filicudi (30-40 ka ago), the following closure of the volcanic conduits of Salina Island (13 ka ago) and the chemical transition of the volcanic products in Lipari and Vulcano is the magmatic signature of the tectonic inversion occurring in the southern Tyrrhenian domain since the middle Pleistocene.

## Studying and collecting past earthquake environmental effects to properly face future impacts: the 1783 Calabria earthquakes case study

Blumetti A.M.\*<sup>1</sup>, Guerrieri L.<sup>1</sup>, Porfido S.<sup>2</sup> & Michetti A.M.<sup>3</sup>

1. Servizio Geologico d'Italia, ISPRA, Roma. 2. Istituto per l'Ambiente Marino Costiero, CNR, Napoli. 3. Università dell'Insubria.

Corresponding email: [annamaria.blumetti@isprambiente.it](mailto:annamaria.blumetti@isprambiente.it)

Keywords: earthquake environmental effects, seismites, seismic hazard.

Earthquake Environmental Effects (EEE) are the effects caused by an earthquake on natural environment, including surface faulting, regional uplift and subsidence, tsunamis, liquefactions, landslides and ground failure, either directly linked to the earthquake source or provoked by the ground shaking.

Since EEE are a major source of seismic hazards, in addition to ground shaking, the knowledge of the characteristics and spatial distribution of EEE induced by past earthquakes will strongly improve standard seismic hazard assessments.

Nowadays, a significant amount of data about EEEs is available for many earthquakes. However, available information is located in several different sources (scientific papers, historical documents, professional reports), and often difficult to access.

The EEE Catalogue has been promoted with the aim to properly retrieve the available information about EEE at global level and archive it into a unique database, in order to facilitate their use for seismic hazard purposes. Its implementation has been endorsed at global level by INQUA through a WG coordinated by ISPRA - Geological Survey of Italy.

The EEE Catalogue major added value is the possibility to view the scenarios of environmental effects induced by past earthquakes and therefore the most vulnerable areas over the anthropic settlements and infrastructures exposed to this potential source of hazard. To this end, a good location accuracy becomes crucial. Typically, EEEs from recent earthquakes are mapped with good accuracy immediately after the event. Nevertheless, even for some historical earthquakes it is possible to retrieve with very good detail this information.

This is the case of the seismic sequence occurred in Calabria (Southern Italy) in 1783, started with a main shock on 5th February (Intensity 11 MCS;  $M > 7$ ), that caused more than 30.000 casualties and drastically changed the local landscape. This event was followed by other strong earthquakes in the night and during the following days. Particularly, on 6th February, a strong shock triggered in Scilla, along the cliff of the Monte Paci, a huge rock avalanche (5 Mm<sup>3</sup> inland and 3 Mm<sup>3</sup> in the off shore zone), generating a disastrous tsunamis. On 7 February another catastrophic event rocked the Mesima Valley (Intensity 10.5 MCS;  $M = 6.7$ ) followed by another strong event on 28 March, in the Catanzaro Straits ( $I_0 = 11$  MCS,  $M = 7$ ).

The geological effects related to this catastrophic sequence, were studied by Sarconi of the Naples Reale Accademia and published in the *Istoria*, a volume complete of a large atlas of illustrations of many ground effects, such as landslides, liquefaction phenomena and rivers diverted or dammed by landslides. This last phenomenon caused the formation of numerous lakes.

Cotecchia dedicated a monography to "The geomorphogenetic crisis" triggered by the 1783 earthquakes. These Authors studied the Sarconi's report together with other scientific reports and carefully described and mapped many of the coseismic landslides whose trace is still preserved in the landscape, after 200 years. They called these features "seismites" using the term normally used to indicate the characteristic deformation of sediments induced by the seismic shaking, to point out the importance of these features that are often ignored by seismotectonic studies.

The EEE Catalogue allows us to define the impact of the EEEs related to possible future earthquake/tsunami on the present urban texture, pointing out the areas characterized by largest risk.

## Seismic Landscape of the Monferrato Arc

Bonadeo L.<sup>1</sup>, Brunamonte F.<sup>1</sup>, Michetti A.M.\*<sup>1</sup>, Livio F.<sup>1</sup> & Fioraso G.<sup>2</sup>

1. Università degli Studi dell'Insubria, Dipartimento di Scienza e Alta Tecnologia, Como. 2. CNR, Istituto di Geoscienze e Georisorse, Torino.

Corresponding email: [alessandro.michetti@uninsubria.it](mailto:alessandro.michetti@uninsubria.it)

Keywords: Paleoseismology, Po Plain Foredeep, Seismic Landscape, Seismic Hazard.

The Emilia and Lombardia 2012 seismic sequence (two main shocks of Mw ca. 6.0) revamped once again the scientific debate about the seismic hazard posed by Quaternary tectonic structures of the Po Plain foredeep (e.g., Serva, 1990; Boccaletti et al., 2004; Picotti and Pazzaglia, 2008; Michetti et al., 2012; Galli et al., 2012). The W sector of the foredeep represents in particular the area with most controversial interpretation in terms of active tectonics and seismic potential. For instance, in the ITHACA catalogue of capable faults the Monferrato Arc is regarded as a seismogenic structure with potential for surface faulting earthquakes; while in the DISS database the W Lombardia and Piemonte are essentially interpreted as areas lacking any evidence of active faulting and seismic sources with Mw > 5.5. In order to attack this issue, we conducted field investigation, geomorphic analyses and the revision of the large existing database of seismic reflection profiles covering the study area in order to assess the seismic landscape of the Monferrato Arc. Our investigations confirm that the Late Quaternary landscape evolution of the South-Central Piemonte is the result of the interaction between active tectonics and widespread phenomena of river avulsion and piracy, which affected virtually the whole Piemonte and nearby Liguria region. In fact, these dramatic changes in the regional drainage network are controlled by shortening and thrust fault growth, which started during Oligo-Miocene times and is still active with visible deformation rates (Carraro et al., 1995). The development of the Apennines buried thrust fronts since Miocene give rise to the progressive uplift of the Monferrato and Torino Hills, translated above the depositional sequences of the Po Plain foredeep. The continuing deformation and displacement of the surficial deposits up to at least the Mid Pleistocene allow us to regard the buried structures of the Monferrato Arc as potentially capable faults (IAEA, 2010). Therefore, based on the available data, the regional seismotectonic framework for the W Po Plain is comparable with the one already recognized in the Emilia Arc or in the Lombardia-Veneto S Alps (Modena 2012, Brescia 1222, Verona 1117). The seismic landscape of the Monferrato Arc thus includes potential surface faulting earthquakes, with M max in the order of 6.0 – 6.5 (Michetti et al., 2012), and accompanied by considerable liquefaction and earthquake environmental effects.

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## **New features about the Catanzaro Through evolution (Calabria, South Italy) by joining onshore with offshore data**

Brutto F.\*<sup>1</sup>, Muto F.<sup>1</sup>, Loreto M.F.<sup>2</sup>, Tripodi V.<sup>1</sup> & Facchin L.<sup>3</sup>

1. Dipartimento di Biologia, Ecologia e Scienze della Terra (DiBEST)- Università della Calabria, Arcavacata di Rende (CS). 2. Istituto di Scienze Marine (ISMAR – CNR), U.O.S. Bologna. 3. Istituto Nazionale di Oceanografia e di Geofisica Sperimentale - OGS, Sgonico – Trieste.

Corresponding email: [fabrizio.brutto@gmail.com](mailto:fabrizio.brutto@gmail.com)

Keywords: normal fault systems, geodynamics, Calabria.

The Catanzaro Through (CT; South Italy) is a Neogene-Quaternary sedimentary basin developed between the Serre and the Sila massif, located in the central Calabrian Arc.

Since Miocene, the CT experienced different tectonic phases resulting confined by both longitudinal and transversal faults systems. Initially, it was affected by a NW-trending left-lateral strike-slip fault system, arranged in a right-hand en echelon pattern, dissecting an Oligocene-Early Miocene orogenic belt made of Alpine nappes overthrusting the Apennine Chain (Tansi et al., 2007). Later, from Late Pliocene to Early Pleistocene, the Through was affected by normal faults also occurring in the Tyrrhenian basin. As resulting from the distribution of historical seismicity of the area, major events occurred along the NW and NE trending normal faults (Monaco C. & Tortorici L., 2000).

Combining on land geo-structural with marine geophysical data, these last acquired aboard of the R/V OGS-Explora (summer 2010) and aboard of the Bannock (1987) within SE Tyrrhenian Sea, a more detailed analysis of processes affecting the CT over the last 10 My can be performed. Within sedimentary basin, hosted by the CT, we identify three main system faults: 1) WNW-ESE oriented faults with normal and oblique kinematics bordering the northern and southern CT margins. 2) ENE-WSW oriented faults showing normal and right oblique kinematics outcropping to northwestern and southwestern margins of CT. 3) NNE-SSW oriented normal faults, to the western part of the area where displace the Pleistocene deposits of the S. Eufemia plain. These faults represent the propagation, to the north, of the Serre-Mesima normal fault systems. The last likely currently active and related to the main seismogenic sources of major historical earthquakes occurred in the southern crustal block of Calabria.

Forthwith offshore CT the mainly observed tectonic features are represented by the NE-trending normal fault, considered the best candidate as seismogenic source of the 1905 Calabrian earthquake (Loreto et al., 2013), and an ENE-WSW oriented fault system, located within S. Eufemia Gulf which can be considered as the offshore continuation of the on land normal fault system.

Despite the steps forward done improving the knowledge of structural complexity of this area, further studies need to be performed in order to define the role played by the CT in the frame of processes controlling the Quaternary geodynamic of the Calabrian Arc.

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Monaco C. & Tortorici L., 2000. Active faulting in the Calabrian Arc and eastern Sicily. *Journal of Geodyn.* 29, 407–424.

Tansi C., Muto F., Critelli S., Iovine G. 2007. Neogene–Quaternary strike-slip tectonics in the central Calabria Arc (southern Italy). *J. Geodyn.*, v. 43, 397–414.

## Power-law Maxwell rheologies and the interaction between tectonic and seismic deformations

Cambiotti G.\*, Rigamonti S., Splendore R., Marotta A.M. & Sabadini R.

Department of Earth Sciences, University of Milan.

Corresponding email: [gabriele.cambiotti@unimi.it](mailto:gabriele.cambiotti@unimi.it)

Keywords: Rheology, earthquake, tectonic stress, seismic stress.

In a lithosphere where dislocation creep dominates the steady-state flow and the viscosity is stress-dependent, the equilibrium between tectonic stress and strain rate is broken after an earthquake due to the sudden co-seismic stress change. The imbalance between tectonic stress and strain rate manifests itself during the post-seismic phase and, when seismic stress is comparable or smaller than tectonic stress, it affects post-seismic deformation via an effective anisotropy along the principal axes of the tectonic stress tensor. This issue is herein discussed within the framework of post-seismic models based on power-law Maxwell rheologies and, in the limit case of seismic stress much smaller than tectonic stress, we obtain a first-order approximation of the rheology which results into a linear anisotropic Maxwell model and we find that the effective anisotropy is associated to a two-modal relaxation characterized by the Maxwell time and the Maxwell time divided by the power law index. Thus, as far as the steady-state flow within the lithosphere is dominated by dislocation creep, linear isotropic viscoelastic rheologies, like Newtonian Maxwell and Burgers models, represent a severe oversimplification which does not account for the physics of post-seismic deformation. This new physics is discussed characterizing the stress state of the ductile layers of the lithosphere before and after the earthquake for normal, inverse and strike mechanisms and for a variety of continental seismogenic zones and thermal models. We show that the first-order approximation of the power-law Maxwell rheology is valid for a quite wide range of small and moderate earthquakes. The most restrictive upper bounds of the seismic magnitude (which hold for the hottest thermal model here considered, with lithospheric thickness of  $H = 80$  km and surface heat flux of  $Q = 70$  mW/m<sup>2</sup>) occur for normal and inverse earthquakes and are 5.6 or 6.3 for a lower crust of wet diorite or felsic granulite, and 6.5 for a mantle of wet olivine. The upper bounds increase by about 0.3 – 0.4 for strike earthquakes and by more than 1.0 for the cold thermal model ( $H = 200$  km and  $Q = 50$  mW/m<sup>2</sup>).

## Palaeoseismological evidence of the 1570 Ferrara earthquake

Caputo R.\*<sup>1-2</sup> & San Carlo trench Working Group

1. Dipartimento Fisica e Scienze della Terra, Università di Ferrara. 2. Research and Teaching Center for Earthquake Geology, Tynavos, Greece.

Corresponding email: [rcaputo@unife.it](mailto:rcaputo@unife.it)

Keywords: palaeoseismology, liquefaction.

The May 20, 2012 Emilia earthquake ( $M_w = 6.1$ ) produced secondary ground deformation effects, mainly associated with liquefaction phenomena, in several parts of the epicentral region, but particularly concentrated in the western sector of the Ferrara Province. South of San Carlo village, the eastern levee of the palaeo-Reno River was crossed by a system of parallel ground ruptures forming a complex system of overstepping and partly overlapping fractures. Single features were several decameters long, locally showing an extensional kinematics (*i.e.* opening, up to 35 cm) and/or vertical displacements (up to 30 cm). Locally, 1-10 m-wide grabens formed. On the top of the levee, we excavated a 50 m-long and locally 8 m-deep palaeoseismological trench mainly across some fractures where no sand ejection occurred during the 2012 event. In the trench walls, load structures and large slided blocks have been observed along the slope of the palaeo-levee, while in the deeper part of the trench, fluidification structures were detected showing clear mixing phenomena of sandy-silty layers with finer ones. The logs show that the natural levee body is clearly cross-cut by several sand filled dikes almost perpendicular to the trench's walls and at high-to-normal angle with respect to the depositional layering. Dikes were mainly formed as extensional joints characterised by opening up to 10-12 cm. Some dike was reactivated during the 2012 event, with a normal sense of shear and a maximum throw of ca. 15 cm, whereas others, showing a similar kinematics and throw (*ca.* 20 cm), were not visibly affected by the last earthquake. It is worth to note the lack of any ejection from the trenched dikes notwithstanding their opening and the presence of infilling sand at few tens of cm-depth. Moreover, two of the infilled dikes 5-10 cm-thick are clearly truncated upwards at 50-60 cm from the present-day surface. All these evidences document the occurrence of liquefaction phenomena (and the consequent diking) well predating the May 2012 earthquake. Based on a detailed reconstruction of the historical hydrographic network of the area, the affected levee sediments were mainly deposited between the XV and the XVI centuries, therefore constraining the possible time window for the causative event(s). Taking into account the historical catalogue of the period, the proposed magnitudes and the epicentral distances, only the 1570 Ferrara earthquake was able to sufficiently shake the trench site in order to induce the observed liquefaction phenomena.

## The Greek Database of Seismogenic Sources (GreDaSS)

Caputo R.<sup>\*1-3</sup>, Pavlides S.<sup>2-3</sup> & GreDaSS Working Group<sup>4</sup>

1. Dept. of Physics & Earth Sciences, Ferrara University. 2. Department of Geology, Aristotle University of Thessaloniki, Greece. 3. Research and Teaching Centre for Earthquake Geology, Tyrnavos, Greece. 4. the principal scientific contributors are: Sboras. S., Chatzipetros A., Koukouvelas I., Michailidou A., Valkaniotis S., Tarabusi G.

Corresponding email: [rcaputo@unife.it](mailto:rcaputo@unife.it)

Keywords: seismotectonics, seismic hazard, Aegean region.

The Greek Database of Seismogenic Sources (GreDaSS) is a repository of geological, tectonic and active fault data for the Greek territory and its surroundings including sectors of western Anatolia, southern Bulgaria, FYR of Macedonia and Albania. The principal aim of this international project is to create a homogenized framework of all data relevant to the seismotectonics, and especially the seismic hazard assessment, of Greece and its surroundings as well as a common research platform for performing seismic hazard analyses, modelling and scenarios from specific seismogenic structures. GreDaSS represents an on-going project based on the results of decades of investigations by the GreDaSS Working Group and by numerous other researchers working on the active tectonics of the broader Aegean Region. Members of the WG have contributed in several national and European projects like FAUST (Faults as a seismological tool, 1998-2000) and SHARE (Seismic Hazard and Armonization in Europe, 2009-2012). The database is continuously updated by the WG, with the aim of improving its completeness in terms of seismogenic sources analysed and included, but also of enriching and better defining all parametric and ancillary information on each source. GreDaSS is based on the DISS software (version 3.2) provided by the DISS WG (Basili et al., 2008) which is warmly acknowledged. Preliminary and partial versions of GreDaSS have been already presented at previous congresses (Pavlides et al., 2010; Caputo et al., 2012; Sboras et al., 2013), but the whole area and the most recent version of the database will be displayed.

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## **A contribution to earth sciences from localization of the National Repository of LIL Radioactive Waste**

Casale R., Chiaravalli F., Lombardo M., Rosati M. & Ventura G.\*

Sogin S.p.A – Roma.

Corresponding email: [ventura@sogin.it](mailto:ventura@sogin.it)

Keywords: siting, hazard, database.

This article aims to illustrate a new experience in the field of large scale multidisciplinary territorial characterization. The experience is carried out by Sogin that is a State company in charge of the environmental remediation of Italian nuclear sites and of the safe management of radioactive waste. The national law 31/2010 and subsequent amendments appoints Sogin to locate, build and operate a Technology Park, that will include the National low and intermediate level radioactive waste repository. This structure must ensure maximum safety for the population and the environment and will allow for the complete remediation of environmental systems, optimizing time and costs and eliminating the need for temporary storage sites. The Technology Park will support collaboration with research institutions, universities and industrial operators to contribute to a sustainable development of the territory where it will be built.

In the first part, the article illustrates the procedure to identify, within the whole national territory, areas potentially suitable for the localization of the technology park. The large database that has been created for the implementation of CNAPI (map of the potentially suitable areas) is also described. The potentially suitable areas represent parts of the national territory with favorable characteristics to identify sites where safety conditions can be guaranteed and interferences with the activities implemented in the territory can be minimized.

The procedure mentioned above is based on the series of location criteria that have been defined by ISPRA, responsible for the national nuclear regulation and on data suitable to perform the thematic mapping concerning geology, hydrology, hydrogeology, meteorology and climate, seismology, volcanology, geomorphology, subsoil natural resources and nature. Also data about the cultural heritage, planning and legal constraints of the territory are required. These data were collected through a patient and systematic work on the collection and integration carried out with the collaboration of several research institutions. In addition, studies have been developed to fill data gaps and to improve the confidence level on applying the location criteria in relation to seismic hazard land modification due to slow and fast natural processes. These studies, being conducted at national and regional scale have allowed us to analyze natural processes at scales of detail that only infrequently are requested and enabled to give an innovative contribution on interpretation of dynamics of some natural processes.

In the second part, the article discusses the results of data research in archives containing studies never published in full, carried out mostly for the localization of large power plants and pertaining in particular geology and seismology. These studies were conducted in the '70s-'80 for the development of the national energy plan based on that construction of new nuclear power stations. So now, a large amount of "new data" are available for further elaboration. Furthermore a large amount of paper documents has been computerized and is now available in a dedicated database. Moreover, at the national mining office for hydrocarbons and earth resources (UNMIG) of the Ministry of economic development, has been carried out the digitization of a large amount of data and maps. These come from a large study that, in the '60s, was fostered as a basis to revitalize the mining industry nationwide. This knowledge base still provides a valuable effort to earth science, and a public database is now available, containing remarkable in quantity and quality chemical, mineralogical, petrographic and geophysical data. This was achieved by conducting a patient and onerous job of retrieving information from computer storage media that are readable today with great difficulty and carrying out the digitization of microfilm which, thankfully, were made to maintain a copy set aside of the printed material.

## New data on extensional active faults in the Pollino area (Southern Italy)

Cirillo D.\*<sup>1</sup>, Brozzetti F.<sup>1</sup>, Lavecchia G.<sup>1</sup>, de Nardis R.<sup>2</sup> & Cardinali M.<sup>3</sup>

1. DiSPUTer - Università G. d'Annunzio di Chieti. 2. Dipartimento della Protezione Civile, Roma. 3. CNR-IRPI, Perugia.

Corresponding email: [d.cirillo@unich.it](mailto:d.cirillo@unich.it)

Keywords: Quaternary Active Faults, Pollino Earthquakes, Calabria Lucania Boundary.

An updated “Map of the Active Faults” is proposed for the Calabro-Lucano boundary, from the Mercure valley to the Castrovillari basins. This area was affected by a long-lasting seismic sequence (2010-2013) that preceded and followed the  $M_w$  5.2, 26 October 2012 Mormanno earthquake.

Furthermore, its southern part is located inside the well known “Pollino Seismic Gap” where the lacking seismic record contrasts with paleoseismological evidence of strong earthquakes ( $M > 7$ ) documented along the Castrovillari fault.

Our study led to map a number of Quaternary faults some of which were previously undiscovered or strongly underestimated. They are arranged into two conjugate east- and west-dipping sets and their normal to normal-oblique kinematics is compatible with the extensional stress field affecting this portion of the Apennines.

A large number of structural, kinematic and stratigraphic data were collected, in order to characterize in detail the active faults and to define their relationships with other structures that are well known for a long time in the area, as the Pollino, Castrovillari and east-Mercure boundary faults.

A morpho-structural survey allowed, in some cases, to measure the amount of Quaternary throw and to assess the throw-rates associated to the faults.

Field data show that the east-dipping fault-set is characterized by lower dip-angles and gave rise to higher amount of finite extension than the west-dipping one.

The westernmost and oldest structure, is an east-dipping LANF that causes the stratigraphic omission of the whole Jurassic-Cretaceous succession, leading to the abrupt superposition of the Ligurian Frido fm on the Triassic dolostone of the Verbicaro unit. This fault is here interpreted as the regional detachment-fault of the whole system.

However, the clearest evidence of Late Pleistocene-Holocene displacements, as well as of seismogenic activity, was observed along the west-dipping antithetic splays. By integrating the available seismic data (relocated earthquakes) with field mapping and structural survey, the regional-scale geometry of the extensional system was reconstructed.

The reconstructed model is schematized in a geological section that crosses transversely the entire extensional belt from Mt Ciagola to Madonna del Pollino.

It provides preliminary constraints to the subsurface geometry of the main faults and allows to make inferences on their seismogenic potential; finally it suggests some preliminary earthquake-structure association.

In particular, a selection of relocated 2010-2013 earthquakes, suggests that at least two (or maybe three) west-dipping sub-parallel sources were activated during the sequence, and that the westernmost one was probably the source of the Mormanno mainshock.

Based on geological constraints and seismological data, we estimated the geometrical parameters of the main source and its maximum expected earthquake, giving also a plausible explanation of the temporal evolution of the sequence.

## Highly complex fracturing pattern in Southern Tyrrhenian Sea: multiplets triggered by deep fluid circulation

D'Alessandro A.\*<sup>1</sup>, Mangano G.<sup>1</sup>, D'Anna G.<sup>1</sup> & Luzio D.<sup>2</sup>

1. Istituto Nazionale di Geofisica e Vulcanologia, Roma. 2. Università degli Studi di Palermo, Palermo.

Corresponding email: [antonino.dalessandro@ingv.it](mailto:antonino.dalessandro@ingv.it)

Keywords: Southern Tyrrhenian Sea, seismic multiplets, fluid circulation.

The western part of the northern Sicilian offshore is characterized by intense crustal seismic activity that has often generated strong and important seismic sequences, like in September 2002. In the last decade, several hundreds of earthquakes with local magnitudes greater than about 2.2 have been located close to the Palermo 2002 seismogenic volume. The apparent lack of small magnitude earthquakes in the southern Tyrrhenian Sea is a consequence of the on-land station distribution and distance from this offshore area (D'Alessandro et al., 2011a). In 2009, the OBSLab INGV carried out a seismic monitoring experiment lasting 8 months which led to the deployment of an OBS/H (D'Alessandro et al., 2009, 2012) on the epicentral area of the main shock of the Palermo 2002 seismic sequence. The analysis of the recorded signals revealed intense local micro-seismicity (247 events in 8 months) not located by the onshore seismic networks. This local microseismicity has been analysed using an innovative clustering technique that exploits the similarity between the waveforms generated by different events (Adelfio et al., 2012; D'Alessandro et al., 2013;). Sequences of events with low energy, high frequency of occurrence and often containing multiplets, are typical of seismicity produced by the injection of fluids into granitic rocks. The coseismic stress field causes a flow of pore fluid and that this flow is dependent on the pressure gradient and on the permeability of the medium. This phenomenon may produce a change in pore pressure that can decrease the friction on the fault plane and on neighbouring planes, such as to trigger subsequent fault sliding. The local seismic events recorded from the OBS/H are typical of a seismicity generated by a volume characterized by a highly complex fracturing pattern and by an important role in the dynamics of fluid systems that, given the great depth of some multiplets, could come from the mantle.

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## Constraining the slip rates of the Pernicana fault system of Mt. Etna, Italy

D'Amato D.<sup>1</sup>, Pace B.\*<sup>1</sup>, Di Nicola L.<sup>2</sup>, Stuart F.M.<sup>2</sup>, Visini F.<sup>3</sup>, Branca S.<sup>3</sup>, Azzaro R.<sup>3</sup>, Carafa M.<sup>3</sup>, Tanguy J.C.<sup>4</sup>, Condomines M.<sup>5</sup> & Barfod D.N.<sup>2</sup>

1. DiSPUTer, Università "G. d'Annunzio" Chieti-Pescara. 2. Scottish Universities Environmental Research Centre, East Kilbride, United Kingdom. 3. Istituto Nazionale di Geofisica e Vulcanologia. 4. Institut de Physique du Globe de Paris and CNRS, Saint-Maur des Fossés, France. 5. Géosciences Montpellier, Université Montpellier 2 et CNRS, Montpellier, France.

Corresponding email: [b.pace@unich.it](mailto:b.pace@unich.it)

Keywords: Mt. Etna, dating methods, slip rate, Pernicana fault system.

Mount Etna is an active polygenetic basaltic stratovolcano in the north-eastern part of Sicily, Italy. The eastern flank of the volcano is affected by extension and is sliding eastward. While the cause of extension is still disputed, there is general agreement on the surface geometry of the main fault bordering the flanks of the volcano. The E-W oriented Pernicana Fault System (PFS) dominates the NE sector of Mt. Etna. It is characterised by complex kinematics that change along strike from normal to transtensional with oblique left movement, to pure left lateral. It cuts basaltic rocks for 20 km, with scarps up to 80 m high. The aim of this work is to use new determinations of slip rates on the PFS to estimate seismic hazard in the northeast sector of Mt. Etna.

Fault slip rates have been constrained by new age determinations of basaltic lavas that have been cut by the PFS. Cosmogenic <sup>3</sup>He ages have been measured on pyroxene from the Millicucco (1088 ± 108 a) and Due Monti lavas (1101 ± 250 a). These ages have been cross-checked by archaeomagnetic and <sup>226</sup>Ra-<sup>230</sup>Th techniques indicating that these two lava flows were generated by historical eruptions at around 500 AD (Due Monti) and 700 AD (Millicucco) with an uncertainty of no more than 100 years. In addition a combined error-weighted <sup>40</sup>Ar/<sup>39</sup>Ar age of 9900 ± 700 a has been determined for the Pineta di Linguaglossa lava flow. Combining the new lava ages with fault offsets obtained during detailed topographic profiles allows us to determine vertical slip rates from 1.5 mm/a in the western sector to 15 mm/a in the most seismically active central segment, integrated over about 14,000 years (from about 1000 to about 15000 years BP). Horizontal slip rates have been calculated from a numerical model, using a finite-element code and considering mainly the topographic effects, and range from about 2 to about 5 mm/a.

Using these slip rates and assuming a characteristic earthquake behaviour, we calculate that in the central segment of the PFS maximum expected Mw=5.0 recurrence on average every ~70 a in the last 1000 years, up to ~700 a over 15000 years, whereas historical and instrumental records show occurrences of events of magnitude between 3.5 and 4.6 in the last 20 years every ~2 a. This is the first time that long term mean recurrence time estimations have been performed. The results, together with the contemporary data, have obvious implications for fault-based seismic hazard estimations, which use individual seismogenic source parameters to evaluate the expected seismicity rates.

## A review of the Intensity values for the 1743 Salento earthquake

De Lucia M.\*<sup>1</sup>, Alessio G.<sup>1</sup>, Gaudiosi G.<sup>1</sup>, Nappi R.<sup>1</sup>, Porfido S.<sup>2</sup>

1. Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Napoli Osservatorio Vesuviano. 2. CNR IAMC Napoli, Italy.

Corresponding email: [maddalena.delucia@ov.ingv.it](mailto:maddalena.delucia@ov.ingv.it)

Keywords: Salento, historical seismicity, damage evaluation, ESI scale, tsunami.

The area of the Salento peninsula (Apulia, Southern Italy) is considered the stable foreland of the Southern Apennines chain (Cinque et al., 1993), although it has been hit by several low energy and a few high energy earthquakes over the last centuries.

The strongest historical earthquakes in the last 1000 years occurred on September 10, 1087, (Bari,  $I_{max} = VI-VII$ ), on February 20, 1743, (Ionian sea,  $I_{max} = IX$ ), and on October 26, 1826 (Manduria,  $I_{max} = VI-VII$ ) (Guidoboni et al., 2007; Rovida et al., 2011). The instrumental recent seismicity is mainly concentrated in the western sector of the Salento peninsula and in the Strait of Otranto. The maximum recorded event occurred on October, 20, 1974 ( $M_w = 5.0$ , Rovida et al., 2011).

The most severe damage in the Apulian peninsula was caused by the strong historical earthquake of 1743, that was also felt on the western coast of Greece, on the Malta island, in Southern Italy and in some localities of Central and Northern Italy. Heavy damage affected the Salento area, in the towns of Nardò (Lecce), and Francavilla Fontana (Brindisi); in Greece, it was felt in the town of Levkas and in the Ionian Islands. According to Margottini, 1981, Guidoboni et al., 2007, Rovida et al., 2011, the maximum felt intensity was IX MCS in Nardò and Levkas. The casualties were about 180, of which 150 in the town of Nardò. The earthquake is described in a large amount of historical documents and seismic catalogues (Margottini, 1981; Guidoboni et al., 2007, Rovida et al., 2011).

The 1743 earthquake also generated a tsunami, the deposits of which are distributed along the southern Adriatic coastline of Salento (Mastronuzzi et al., 2007). The location and geometry of the seismogenetic source of the  $M_w = 6.9$ , 1743 Salento earthquake is still a subject of scientific debate.

The aim of this study is to review this seismic event in terms of damage evaluation, taking into consideration also the seismically induced ground effects in natural environment, according to the ESI scale 2007 (Michetti et al., 2007, Guerrieri et al., 2012). Moreover it could be better evaluated the seismic potential of the Salento area, currently classified in IV category (Seismic Classification Map of the Italian territory; MPSO4 – Order PCM 3519/2006), despite the considerable damage caused by strong earthquakes occurred not only in the Strait of Otranto, but also in Greece and Albania.

## Seismotectonics of Italy

Dogliani C.\*<sup>1</sup>, Barba S.<sup>2</sup>, Billi A.<sup>3</sup>, Collettini C.<sup>1</sup>, Cuffaro M.<sup>3</sup>, Petricca P.<sup>1</sup>, Riguzzi F.<sup>2</sup>,  
Scrocca D.<sup>3</sup> & Trippetta F.<sup>1</sup>

1. Dipartimento di Scienze della Terra, Università Sapienza. 2. INGV, Roma. 3. IGAG, CNR Roma.

Corresponding email: [carlo.dogliani@uniroma1.it](mailto:carlo.dogliani@uniroma1.it)

Keywords: crustal rheology, fault on-off, earthquake magnitude, seismic volume, seismic hazard.

The seismic hazard and the magnitude of earthquakes is usually interpreted as a function of the length of faults. We suggest that we can go further in relating the energy released by the volume associated to an active fault. In order to test this model, we tried to compute the volume in which the interseismic energy is stored. We first computed the brittle-ductile transition (BDT) and the maximum differential stress expected as a function of the three main tectonic settings (contractional, extensional, strike-slip). Moreover we assume that the fault length is proportional to the velocity gradient detected by GPS. Then we infer the volume confined between a given active fault and its conjugate interseismic band that should form at the BDT (or any another shallower strain partitioning between creeping and un-creeping fault segments). We assume that the coseismic energy release is given by gravitational energy in extensional environments and elastic dissipation in contractional and strike-slip settings. We finally attempt to suggest the maximum expected magnitude of Italy as a function of the involved volumes and the tectonic style. In the extensional settings, the higher magnitudes are obviously expected along the Apennines ridge because the brittle-ductile transition is deeper and therefore the volumes are larger. Moreover, moving along the Apennines strike, the velocity gradients are higher in Southern Italy. Contractional settings are rather located in areas of low topography and the volumes are rather constrained by the depth of the basal decollement, which may be shallower than the BDT in the frontal accretionary prism buried beneath the Po Basin, the western Adriatic, the Ionian Sea and southern Sicily. The result of this study largely confirms the pre-existing seismic hazard maps of Italy, but it suggests that the “volume” rather than the “fault” only approach may give more accurate insights to the seismic study of the country.

## Paleosismological evidence of the 1511 Idrija earthquake along the Colle Villano blind thrust (Friuli, NE Italy)

Faluccci E.<sup>1</sup>, Poli M.E.\*<sup>2</sup>, Galadini F.<sup>1</sup>, Paiero G.<sup>2</sup>, Scardia G.<sup>3</sup> & Zanferrari A.<sup>2</sup>

1. Istituto Nazionale di Geofisica e Vulcanologia, Roma. 2. University of Udine – Dept. of Chemistry, Physics and Environment. 3. Instituto Oceanografico, Universidade de São Paulo, Brazil.

Corresponding email: [eliana.poli@uniud.it](mailto:eliana.poli@uniud.it)

Keywords: paleoseismology, Eastern Southern Alps, Friuli.

New geological, geomorphological, geophysical and paleosismological studies were performed in the eastern corner of the NE Italy (Racchiusana valley, Julian Prealps), where the S-verging polyphase fold and thrust belt of the Eastern Southern Alps joints with the NW-SE trending dextral strike-slip Idrija fault system. The area was hit by destructive earthquakes both historical and instrumental: the 1348 Carinzia (Mw= 7.02), the 1511 Idrija (Mw=6.98) and the 1976 Friuli earthquakes on May (Mw=6.46) and September (Mw=5.98) (Locati et al., 2011). The structural framework of the study area is characterized by a series of WNW-ESE trending, SSW-verging thrusts bordering the hills overlooking the plain or buried under the Upper Pleistocene-Holocene alluvial deposits and probably linked to the NW-SE Borgo Faris dextral strike slip fault that runs at the base of the inner Prealps (Zanferrari et al., 2008). We studied deformational effects of the buried Colle Villano thrust near Magredis village: here surficial geomorphic evidence (drainage anomalies, gentle scarps and back tilted surfaces) were highlighted. The analysis of the seismic industrial lines confirms that the Upper Pleistocene-Holocene deposits are involved in the deformation. In order to characterize the Late Pleistocene-Holocene activity of Colle Villano thrust, paleoseismological investigations were performed. We dug three trenches 1 km to the north of the Magredis village. The analysis of the trench walls allowed identifying deformation events induced by the fault activity. Two subsequent episodes of deformation were distinguished by localised warping (few metres in wave length) of the sedimentary sequences exposed by the excavations and secondary extrados faulting. One event occurred between 544-646 AD (14C  $2\sigma$ ) and 526-624 AD, the other – probably the last one – occurred close to 1485-1604 AD. The last displacement event is chronologically consistent with the 1511 earthquake. This seismic event has been attributed to the activation of Idrija fault by Fitzko et al. (2005). However, no paleoseismological evidence of this has been provided to date. The damage distribution of this event suggests its seismogenic source to be located at the easternmost portion of the Julian Prealps, and our investigations may indicate that the 1511 earthquake could have triggered not only the Idrija fault, but also some segments of the others NW-SE dextral strike slip-systems of the Italian-Slovenian border area.

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## Seismotectonics of the active thrust front in southwestern Sicily: hints on the Belice and Selinunte seismogenic sources

Ferranti L.\*<sup>1</sup>, Guzzetta L.<sup>1</sup>, Pepe F.<sup>2</sup>, Burrato P.<sup>3</sup>, Barreca G.<sup>4</sup>, Mattia M.<sup>5</sup>, Monaco C.<sup>4</sup> & V. Bruno<sup>5</sup>

1. Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse (DiSTAR), Università di Napoli "Federico II". 2. Dipartimento di Scienze della Terra e del Mare, Università di Palermo. 3. Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Roma. 4. Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Sezione di Scienze della Terra, Università di Catania. 5. Istituto Nazionale di Geofisica e Vulcanologia, Osservatorio Etneo - Sezione di Catania.

Corresponding email: [lferrant@unina.it](mailto:lferrant@unina.it)

Keywords: Active thrust system, southwestern Sicily, fault segment parameters, historical earthquakes.

We present a seismotectonic model of the active thrust front in western Sicily, which includes the area hit by the 1968 Belice earthquake sequence. The ~40 km long *South-WEstern Sicilian Thrust* (SWEST) is formed by two aligned albeit non-parallel fault arrays, the *Granitola-Castelevetrano Thrust System* (GCTS) in the west and the *Partanna-Poggioreale Thrust System* (PPTS) in the east.

The ~NE-SW trending, NW-dipping GCTS straddles from the Pelagian coastline to Castelvetro, is ~18 km long and composed of two segments, with the northern, ~12 km long one showing geodetic and geologic evidence of active deformation (Barreca et al., 2014). The segment is marked by a sharp gradient in Differential SAR interferometry (DinSAR and STAMPs) and GPS velocity fields. Geologic evidence include an up to 60 m high, and up to 15° steep scarp, which is the fore-limb of a broad fold involving Lower Pleistocene shore calcarenites, and cm-scale reverse displacement of an ancient road dated as early Bronze-Hellenistic age. Inversion of fault slip-lineation data from structures displacing the archaeological remains yields a ~N110°E shortening axis, consistent with the geodetic shortening direction estimated from GPS differential velocities.

The ~ENE-WSW trending PPTS stretches from Partanna to the macro-seismic area of the 1968 earthquake sequence and is composed of two ~10 km long segments limited by relay ramps. Although geologic and geodetic evidence of deformation are less clear than for the GCTS, we nonetheless observe a gradient in interferometry data for the western segment, and evidence of slow deformation (creep?) in historical to recent (last ~400 yr?) man-made structures.

Integration of geologic, geodetic and seismology data suggests the active folds and thrusts are the uppermost expression of steep (45°) crustal ramps (Monaco et al., 1996) which upthrust the Saccense platform at depth.

Based on macroseismic and seismological evidence (Monaco et al., 1996), we contend that the PPTS was partly activated during the 1968 sequence, and that rupture stopped at the junction with the GCTS. The current geodetic strain accumulation on the GCTS, on the other hand, suggests that the fault array has been significantly loaded, and that its last important co-seismic event could have been caused the 4th–5th century A.D. destruction of Selinunte (Bottari et al., 2009).

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## **The 2013-2014 Matese Massif seismic sequence (Southern Apennine, Italy): a model for the seismogenic structure derived from multidisciplinary investigation**

Ferranti L.<sup>1</sup>, Milano G.<sup>2</sup>, Burrato P.<sup>3</sup>, Cannavò F.<sup>4</sup>, Meccariello M.\*<sup>1</sup> & Palano M.<sup>4</sup>

1. DiSTAR, Università Federico II, Napoli. 2. Osservatorio Vesuviano - INGV, Napoli. 3. INGV, Roma  
4. INGV, Osservatorio Etneo, Catania.

Corresponding email: [melaniamec@hotmail.it](mailto:melaniamec@hotmail.it)

Keywords: Matese Massif, 2013-2014 seismic sequence, seismogenic structure, Southern Apennines.

On December 29, 2013 an ML 5.0 earthquake struck the internal part of the Matese massif, a sector where no evidence of active faulting were recorded so far although it is part of one of the most seismically active sector of Southern Italy. The seismic sequence following the main shock is aligned in between the macroseismic epicentral areas of the destructive Mw 6.6 1349 and Mw 7.0 1688 events.

The epicentral distribution of the sequence depicts an ~11 km long, NNW-SSE trending alignment within the eastern part of the Matese massif. Focii are confined between 10 and 20 km depths with a concentration of events around 17 km. Focal mechanism of the mainshock and those related to three events with  $M_l > 3.0$  show normal dip-slip solutions with NNW-SSE striking planes. These solutions agree with the overall sequence alignment and are consistent with the large scale stress field acting in the Apennine Chain.

The Matese massif is dissected by the NW-SE striking Matese Lake normal fault system. Although the fault array was suspected to have slipped during the Holocene, a clear geomorphic evidence of this activity is lacking. Detailed geologic-structural mapping has shown that the array is formed by discrete strands (the Matese Lake Fault s.s. and the Bocca della Selva Fault in the central and eastern part of the massif, respectively). The spatial distribution of the seismic sequence and fault plane solutions suggest that the surface expression of the seismogenic structure spatially coincides with the eastern segment (Bocca della Selva fault). The pseudo-focal mechanisms computed on the basis of slip-analysis on various strands of the fault are in excellent agreement with the seismological focal solutions.

Analysis of geodetic velocities suggest that, whereas the Matese Lake Fault segment is characterized by strain accumulation at  $0.9 \pm 0.3$  mm/yr, the Bocca della Selva segment shows little geodetic motion. These findings possibly suggest that the Bocca della Selva fault was locked before onset of the seismic sequence.

The geological, seismological, and geodetic constraints have been utilized to propose a model of the seismogenic structure responsible for the 2013-2014 sequence. Upward projection of the causative fault from the observed 17 km hypocentral depth, by using a  $65^\circ$  dipping fault as constrained by surface fault measurements and by the depth elongation of the seismic sequence, intersects the earth surface exactly at the location of the Bocca della Selva fault. The focal volume of the sequence is confined within the crystalline crust of Apulia, which is the lowest tectonic unit of the Apennines fold and thrust belt. Only few events are located at a shallower depth within the carbonate sedimentary cover of Apulia. It appears that seismicity stopped at the top of Apulia and did not interest the Molisan and Matese rootless thrust sheets of the upper part of the Apennines.

## The 2014 seismic sequence in the seismotectonic frame of the Nicaragua depression

Giunta G.<sup>1</sup>, Sulli A.\*<sup>1</sup> & Esposito E.<sup>2</sup>

1. Dipartimento di Scienze della Terra e del Mare, Università di Palermo. 2. IAMC-CNR, Napoli.

Corresponding email: [attilio.sulli@unipa.it](mailto:attilio.sulli@unipa.it)

Keywords: Cocos plate, Caribbean region, earthquake.

A NW-SE oriented seismic sequence with 5.1-6.6  $M_L$ , and NW-SE compressional to alternatively NW-SE right-lateral or NE-SW left-lateral strike-slip focal mechanisms, affected from March 28 to April 14, 2014 the region of Lake Managua (W Nicaragua, Central America), in the volcanic cordillera between Momotombo and Apoyeque. The provisional hypocentral depth ranges from 10 to 135 km. The quakes leaved 1 death, 266 injured, 19 houses destroyed and 1500 damaged.

The Pacific margin of Nicaragua is considered to be an active margin, where oceanic lithosphere of the Cocos plate undergoes fast subduction ( $\sim 73$ -90 mm/y) along the Middle America Trench beneath the Caribbean plate. According to ODP Drillings the frontal wedge of the overriding plate is characterized by a prism of reworked slope sediments underthrusting the igneous forearc wedge. The Benioff zone of the Cocos plate extends to a depth of  $\sim 220$  km beneath the volcanic front in El Salvador, Nicaragua and Costa Rica, with variable dip from Costa Rica ( $32^\circ$ - $40^\circ$ ) to central Nicaragua ( $75^\circ$ - $80^\circ$ ) and northern Nicaragua-Gulf of Fonseca ( $40^\circ$ - $60^\circ$ ).

Onland the most significant structural elements are represented by the Central America volcanic front and the Nicaraguan Depression, parallel to the Pacific coast, with a length greater than 300 km in NW-SE direction, at present revealed by the lakes of Nicaragua and Managua and the Gulf of Fonseca. NE-SW Pliocene extension is the tectonic event likely responsible for the opening of the asymmetric Nicaraguan depression.

Along the volcanic arc, focal mechanisms of shallow crustal seismicity indicates strike-slip motion consistent with either left-lateral north- and northeast-oriented or, alternatively, right-lateral northwest-oriented. These structures are interpreted as due to transform faults induced both by tears in the subducting plate or as a pull-apart system in the frame of a forearc sliver.

In Nicaragua three main tectonic features define the seismogenic zones: Crustal (eleven seismogenic zones, 10-20 km depth and  $M_{max}$  6.4-7.0), Subduction Interface (two zones, 26-70 km depth and  $M_{max}$  7.7-8.2), and Subduction In-Slab (one zone, 61-200 km depth and  $M_{max}$  7.3-7.5). The W Nicaraguan Depression crustal seismogenic zone, that includes the Mateare and the Tiscapa fault system, is associated with catastrophic earthquakes such as the 1972 ( $M_w$  6.2) of Managua.

Based on the chronology of the seismic sequence, focal mechanisms and hypocentral depth, we interpreted the recent activity in Nicaragua as due to a first deep event (65 to 135 km provisional depth), located in the Subduction Interface to Subduction In-Slab seismogenic zones, which reactivated a subsequent shallow sequence (10-15 km provisional depth), located in the Crustal seismogenic zone, according to the NW-SE right-lateral system linked to the Lake Nicaragua-Lake Managua-Gulf of Fonseca pull-apart system or alternatively to the NE-SW left-lateral asymmetric system, conjugate with the NW-SE master faults.

## The ESI macroseismic field for the 1624 AD Argenta earthquake (Po Plain – N Italy): an integrated macroseismic approach to overcome MCS misfittings

Livio F.\*<sup>1</sup>, Michetti A.M.<sup>1</sup>, Ticozzi E.<sup>1</sup> & Porfido S.<sup>2</sup>

1. Dipartimento di Scienza ed Alta Tecnologia, Università degli Studi dell'Insubria, Como. 2. CNR IAMC, Napoli.

Corresponding email: [franz.livio@uninsubria.it](mailto:franz.livio@uninsubria.it)

Keywords: Emilia seismic sequence, ESI Intensity Scale, Argenta earthquake.

The 2012 Emilia seismic sequence (two mainshocks,  $M_w = 5.86$  and  $M_w = 5.66$  on the 20<sup>th</sup> and 29<sup>th</sup> of May, respectively) overclouded the reliability of earthquake parameters derived from MCS Intensity data in the Po Plain. As highlighted for instance by Galli et al. (2012), Intensity-derived Magnitude, calculated through the BOXER 4 algorithm, pointed to a  $M_e = 5.23$ , clearly underestimating the actual energy of the earthquake. Moreover the epicentral Intensity values (Io VII – VIII MCS) are not fitting well with the peak ground acceleration recorded during the sequence (ca. 0.23 – 0.28 g), consistent with a IX MCS instead.

Livio et al. (2012) applied the same calculations on the ESI Intensity data for the 2012 Emilia seismic sequence (e.g., Di Manna et al., 2012), obtaining a better fitting between calculated and recorded Magnitude ( $M_e = 5.86 \pm 0.38$ ) and concluding that best results could be obtained integrating both MCS and ESI databases.

In this work we apply BOXER4 to a new dataset coming from an historical earthquake that hit the eastern Po Plain: the March 19<sup>th</sup>, 1624 Argenta earthquake. Earthquake parameters, recorded in the CPTI11, report for this earthquake a MCS Io = VII – VIII and a derived Magnitude  $M_e = 5.47 \pm 0.49$  (recently revised by Caracciolo et al. 2012).

The epicentral area of this earthquake is characterized by a geological and geomorphological framework similar to the one of the 2012 sequence, and by many environmental effects including liquefactions, collapse of terrains, hydrogeological anomalies and seiches. The ESI Intensity near field is characterized by a wider area occupied by high degrees (in particular by ESI VIII) but is similar to the MCS field in the far field.

For our analysis we used 11 environmental effects, spread over an area of ca. 600 kmq. We integrated them with 17 MCS data points (DMBI catalogue). The calculated derived Magnitude  $M_e = 5.86$ , obtained from the whole dataset, is in line with available empirical relations between epicentral intensity and magnitude in Italy (e.g. CPTI11). This would suggest that, in order to allow comparison between historical and modern strong earthquakes, coseismic environmental effects should be included in the intensity assessment, both in the Po Plain and in other similar areas of the Mediterranean region.

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## The NW sector of the Sicily Channel: geometry and evolution of inverted structural lineaments

Meccariello M.\*<sup>1</sup> Ferranti L.<sup>1</sup> & Pepe F.<sup>2</sup>

1. Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse (DiSTAR), Università di Napoli "Federico II"

2. Dipartimento di Scienze della Terra e del Mare, Università di Palermo.

Corresponding email: [melaniamec@hotmail.it](mailto:melaniamec@hotmail.it)

Keywords: Sicily Channel, MCS profiles, crustal geometries, active deformation.

The 3-D trend of anticline axial planes, fault planes and surfaces has been reconstructed in the offshore area between the Egadi Islands and the Sciacca High from the interpretation of multichannel seismic reflection profiles and well data (available from the VIDEPI project database). In particular, isopach maps generated for the five seismic units of age between Cretaceous and Quaternary allowed highlighting the space-time migration of the tectonic processes. The western portion of the studied area covers the submerged prolongation of the inner sector of the Sicilian-Maghrebian chain, limited in the NW and in the SE by two tectonic lineaments running along the western and eastern margins of the Adventure Bank: the Maghrebian Thrust Front and Adventure Thrust Front, respectively (see Argnani et al., 1986). The eastern portion is characterized by transpressive zones orientated NNE-SSW identifying the Separation Belt that partly corresponds to the foreland area which contains the Gela Nappe Thrust.

Age constraints indicate that contraction related to the Sicilian-Maghrebian fold and thrust belt migrated progressively towards the southeast. The emplacement of the western front is attributable to the Middle-Upper Miocene while that of the eastern front is Plio-Pleistocene. Within this tectonic framework, two tectonic basins were identified on the basis of the different trend, age and evolution. The Adventure foredeep exhibits the maximum thickness of 500 m in correspondence of the Adventure Plateau. Here, the younger Gela foredeep displays minor depth showing a thickness increase towards the Gela Nappe and the Pantelleria graben.

Positive inversion structures form by the Plio-Pleistocene compressional reactivation of preexisting structures limiting the Saccense and Trapanese domains were recognized the offshore sector between Mazara and Sciacca. Moreover, a correlation between the Campobello di Mazara-Castelvetrano alignment as proposed by Barreca et al., 2013, Ferranti et al., this meeting, and the tectonic units recognized in their offshore prolongation has been recognized. Therefore, we propose that in this area contractional tectonics is still active (see also Pepe et al., this meeting), and occurs on high-angle, NW-dipping crustal ramps (Monaco et al., 1996).

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## **Morpho-structural features of extensional basins revealed from aerial photographs interpretation and structural data in the Northern Apennines (Italy)**

Mirabella F.\*<sup>1-2</sup>, Bucci F.<sup>2</sup>, Cardinali M.<sup>2</sup>, Santangelo M.<sup>2</sup> & Guzzetti F.<sup>2</sup>

1. Dipartimento di Fisica e Geologia, Università di Perugia. 2. Istituto di Ricerca per la Protezione Idrogeologica, Perugia.

Corresponding email: [francesco.mirabella@unipg.it](mailto:francesco.mirabella@unipg.it)

Keywords: photogeological interpretation, structural geology, active tectonics.

The investigation of the tectono-sedimentary evolution of fault-controlled extensional basins through the analysis of morpho-structural features and drainage pattern can provide valuable information on the space-time evolution of the active deformation.

We explore this topic in the Quaternary Gualdo Cattaneo and Foligno extensional basins in the Northern Apennines of Italy. Here, extensional tectonics has migrated from West to East since the lower Pleistocene and both GPS and seismological data reveal that the area is presently active. Extension has been accommodated by NW-SE trending normal faults, which have attained mature morphologic and structural features and, nowadays, separate mountain ranges from intermountain basins.

We integrate field structural data with aerial photo-geological interpretation focussing on the Montefalco ridge which topographically separates the Gualdo Cattaneo and Foligno valleys. This ridge represents an inversion of relief being composed of fluvial sands of conglomerates now uplifted more than 200 m above the present day alluvial plain.

Most of the morpho-structural features were identified through the analysis of multi-scale and multi-temporal aerial photographs, identifying the: (i) attitude of fault and bedding traces (i.e. the intersection line between the bedding plane and the topographic surface), (ii) fault-controlled landslides, (iii) pattern of rivers network and (iv) spatial distribution of river terraces.

Data were transferred to obtain a 1:10,000 scale map. The aerial photographs were orthorectified to reduce mapping errors when transferring information from the aerial photographs to the topographic base maps. We exploited the `i.ortho.photo` tool of GRASS GIS, using a 1m resolution orthophoto (available as WMS service) and a 10m resolution DEM (TinItaly). We then exploited a GRASS GIS tool to obtain both bedding and faults attitude starting from the bedding traces and the 10m resolution DEM.

The combined aerial photographs interpretation and field structural geology approach allowed us to detect and map the attitudes of shallow dipping beds pertaining to the fluvio-lacustrine Gualdo Cattaneo Quaternary continental sequence and to understand the deformation pattern of the valley. Field data and aerial photo-geological interpretation of the Montefalco ridge allowed us to map the attitudes of sandy and conglomerates beds of the Montefalco ridge, and to compare the reconstructed geometries with field palaeo-currents data. We then compare our results with the present-day actively subsiding graben of the Foligno valley to the east. Based on our analysis we document the mid-term deformation history controlled by the NE-dipping and SW-dipping structures, which cut the inherited landscape and deform the continental deposits. Recent fault activity has conditioned the rivers pathway and the tectono-sedimentary evolution of their valleys, where fault-controlled subsidence has captured the river courses and produced subsiding plains.

## Quaternary marine terraces and fault activity in the Messina Straits area (southern Italy)

Monaco C.\*, Barreca G., Di Stefano A. & Ristuccia G.

Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Sezione di Scienze della Terra, Università di Catania.

Corresponding email: [cmonaco@unict.it](mailto:cmonaco@unict.it)

Keywords: Fault activity, tectonic uplift, coastal terraces, Messina Straits.

The Straits of Messina area has been affected by strong uplift, which caused the development of spectacular flights of Pleistocene coastal marine terraces. A new detailed mapping of the terraced surfaces has been carried out on both sides of the northern sector of the Straits. In the Calabrian side, a complete sequence of ten fluvial-coastal terraces has been recognized at elevations ranging from 40 to 530 m a.s.l. and dated from 60 to 330 ka. The series is partly displaced by the Pezzo-Scilla and the Cappuccini faults, limiting to the north and south respectively, the structural high of Campo Piale. The Cappuccini fault was characterized by sin-sedimentary activity during the upper Pliocene-lower Pleistocene, then it was sutured by the deposits of the VI terrace order, attributed to the 167 ka marine stand. The Pezzo-Scilla fault is considered still active in its north-eastern sector (Ferranti et al., 2008), whereas on its eastern end it is sutured by the I order terrace, dated at 60 ka. The estimated uplift rates change in time and space in response to the fault activity. They range from 0.8 mm/yr for the period 330-60 ka, on the downthrown block of the Pezzo-Scilla fault, to 2.0 mm/yr (twice the regional component of 1.0 mm/yr estimated by Westaway, 1993) for the period 330-200 ka, on the Campo Piale high. The constant elevation of the I order terrace suggests an uniform uplift rate of 1.4 mm/yr along the Villa San Giovanni coastal area, and a deactivation of the western sector of the Pezzo-Scilla fault in the last 60 ka, even though the offshore activity of segments belonging to the same system is not excluded (Ferranti et al., 2008). In the Sicilian side, six orders of terraces have been recognized on a structural high bounded by the Mortelle fault, to the north and by the Ganzirri fault, to the south. Their inner edges range in elevation from 30 m to 170 m a.s.l., the age attribution varies from 60 to 240 ka. The series is tilted of ~10-15° toward the south, due to the activity of the Mortelle fault. The elevation of inner edges suggests that the uplift process has undergone an acceleration during the late Pleistocene. In fact, we estimated an uplift rate slightly smaller than the regional component for the period 240-80 ka (II-VI order terraces), increased to 1.3 mm/yr in the last 60 ka, as indicated by the I order terrace elevation. Similar rates have been estimated on both side of the Straits by Holocene markers (Antonioli et al., 2006; Scicchitano et al., 2011), probably related to activity of offshore structures.

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## PRIN Project 2010-11 “Active and recent geodynamics of Calabrian Arc and accretionary complex in the Ionian Sea”: new constraints from geological, geodetic and seismological data

Monaco C.\*<sup>3</sup>, Ferranti L.<sup>1</sup>, Mattia M.<sup>2</sup>, Pepe F.<sup>4</sup>, Scarfi L.<sup>2</sup> & PRIN Research Unit

1. DiSTAR - Dipartimento di Scienze della Terra dell’Ambiente e delle Risorse, Università di Napoli Federico II. 2. INGV – Osservatorio Etneo, Catania. 3. Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania. 4. Dipartimento di Scienze della Terra e del Mare, Università di Palermo.

Corresponding email: [cmonaco@unict.it](mailto:cmonaco@unict.it)

Keywords: Active tectonics, Calabrian Arc, Onland and offshore faults, Regional and local deformation sources.

This contribution illustrates the preliminary results of our Research Unit in the PRIN Project 2010-11, which focuses on active and recent geodynamics of Calabrian Arc. The integration of the new geological, geodetic and seismological data supports the inferred recent plate boundary reorganization in the central-southern Mediterranean, where the regional GNNS velocity fields point to a deceleration or cessation of Calabrian Arc migration, and to extension along the axis of the Calabrian Arc, accommodated by normal faulting (e.g. Capo Vaticano and Messina Straits (Aloisi et al., 2012; Pepe et al., 2014; Spampinato et al., 2014). The study of the lateral borders of the Arc revealed that oblique strike-slip displacement has occurred during its southeastwards migration. Active dextral transtension is occurring along the NNW-striking Aeolian-Tindari Letojanni fault system, forming the southern boundary of the Arc. It joins to the north other two boundaries characterized by different tectonic regimes, a contractional belt in the southern Tyrrhenian sea, where a tectonic inversion has occurred since the middle Pleistocene, and the extensional one in northeastern Sicily and western Calabria (Palano et al., 2012; Barreca et al., 2014a). Along the northern boundary of the Arc, the so-called Pollino line (onshore) and Sibari Line (offshore), active deformation has been documented on folds growing above blind oblique thrust ramps extending offshore, controlling the present morphobathymetric pattern (Santoro et al., 2013). Although external to the Calabrian Arc, we also devoted attention to the front of the Maghrebian thrust belt in western Sicily where we presented the first evidence of historical co-seismic deformation on a thrust array running from the Belice area to the Sicily Channel (Barreca et al., 2014b). Morphotectonic analysis and fault numeric modeling of uplifted Pleistocene marine terraces and Holocene paleo-shorelines has documented that most of the uplift along the Calabrian Arc is related to regional processes and the residual to co-seismic displacement on major faults, both transpressional and transtensional, at the borders, and extensional along the chain axis.

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Palano M., Ferranti L., Mattia M., Monaco C., Aloisi M., Bruno V., Cannavò F., Siligato G., 2012. GPS velocity and strain fields in Sicily and southern Calabria, Italy: Updated geodetic constraints on tectonic block interaction in the central Mediterranean. *J. Geophys. Res.*, 117, B07401, doi:10.1029/2012JB009254.

Pepe F., Bertotti G., Ferranti L., Sacchi M., Collura A.M., Passaro S., Sulli A. 2014. Pattern and rate of post-20 ka vertical tectonic motion around the Capo Vaticano Promontory (W Calabria, Italy) based on offshore geomorphological indicators. *Quat. Int.*, 332, 85–98

Spampinato C.R., Ferranti L., Monaco C., Scicchitano G., Antonioli F. 2014. Raised Holocene paleo-shorelines along the Capo Vaticano coast (western Calabria, Italy): Evidence of co-seismic and steady-state deformation. *J. Geodynamics*. Doi:10.1016/J.Jog.2014.03.003.

## High-quality hypocenter locations and waveform-inversion focal mechanisms in the Calabrian Arc subduction zone

Orecchio B.\*<sup>1</sup>, Presti D.<sup>1</sup>, Totaro C.<sup>1</sup>, D'Amico S.<sup>2</sup> & Neri G.<sup>1</sup>

1. Department of Physics and Earth Sciences - University of Messina. 2. Department of Physics - University of Malta – Malta.

Corresponding email: [orecchio@unime.it](mailto:orecchio@unime.it)

Keywords: Seismicity, subducting slab, STEP faults.

Earthquakes shallower than 350 km that occurred in the Calabrian Arc subduction zone between 1997 and 2011 have been located by using 3D velocity structure and both the SIMULPS linearized algorithm (Evans et al., 1994) and the BAYLOC non-linear probabilistic one (Presti et al., 2008). For the same region, the Cut and Paste (Zhu and Helmberger, 1996) waveform inversion method for focal mechanism computation has been applied to recent earthquakes shallower than 70 km. The most accurate solutions so estimated have been joined with focal mechanisms of comparable quality available from literature and official catalogues to obtain a database covering the whole period (1977-2011). Accurate earthquake relocations and focal mechanism estimates performed in the Calabrian Arc subduction zone furnish a new contribution to detection of residual subducting slab and characterization of lithospheric dynamics around it. This seismological contribution to the current, multidisciplinary investigation of one of the most puzzling areas of the Mediterranean region can be summarized in the following three items. First, the new high-quality hypocenter data confirm and refine the location of the residual descending body already revealed beneath southern Calabria by previous local earthquake tomography. Second, earthquake locations and focal mechanism solutions do not indicate any clear trace of STEP (Subduction Transform Edge Propagator; Govers and Wortel, 2005) activity at the lateral edges of the detected descending body, and this matches well with ultraslow trench retreat of 2 mm/yr estimated by GPS data. Third, the crustal strike-slip activity detected along fault zones previously interpreted as shallow expressions of STEP faults in NE Sicily and in NE Calabria seems to reflect reactivation (under a different dynamic source) of old STEP faults relative to an older and wider subduction front, rather than present-day STEP activity. In this scenario, historical normal-faulting seismicity occurring just above the residual subducting slab and consisting of up to M7 events, can be related to shallow deformation of the slab itself pulled down by gravity in a weak-coupling regime due to local, low-velocity plate convergence.

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## Relief vs Hypsometric Integral: new evidence of the Late-Quaternary morphotectonic evolution of northeastern Sicily

Pavano F.\*<sup>1</sup>, Catalano S.<sup>1</sup>, Pazzaglia F.<sup>2</sup>

1. Dipartimento di Scienze Biologiche, Geologiche e Ambientali - Sezione di Scienze della Terra - Università di Catania. 2. Department of Earth and Environmental Sciences, Lehigh University, Bethlehem (PA) USA.

Corresponding email: [francesco.pavano@yahoo.it](mailto:francesco.pavano@yahoo.it)

Keywords: Relief, Hypsometric Integral, north-eastern Sicily.

A morphometric analysis of northeastern Sicily constrains an emerging model of the morphotectonic evolution of this part of the Calabrian Arc. Here we present a morphologic study of the polycyclic summit surface, focusing on the hypsometric integral, contour line density, and relief, constrained by available structural, geodetic (D'Agostino & Selvaggi, 2004) and geophysical data (Gravimetric Chart of Italy; APAT, 2004) that collectively indicate that NE Sicily behaves as a kinematically independent crustal block (PMB - *Peloritani Mobile Block*; Pavano et al., 2012) (Catalano et al., 2009).

The southern boundary of PMB, defined in the morphometric analysis, coincides with geophysical data such as a Bouguer gravity high, consistent with the interpretation of a deep, lithospheric origin. Our morphometric analysis defined two regions of the PMB that have experienced divergent landscape evolution pathways. The landscape of the eastern sector is steep and shows high values of relief and relatively low hypsometric integral values. In contrast, the western sector, is characterised by an almost gentle topography with high values of both relief and hypsometric integral. We suggest that these differences are tectonically driven and rooted in the main geodynamic processes shaping the Calabrian Arc.

During the Plio-Pleistocene ESE-ward migration of the Calabrian Arc, a NE-SW oriented extensional tectonic alignment confined to the east a low relief basin, coincident with the western part of the PMB. Beginning in the middle-Pleistocene (600 ka), the entire PMB experienced rapid tectonic uplift (1.1 mm/a; Catalano et al., 2009), causing both a superposition of fluvial incision on the previously uplifted eastern sector and a new phase of fluvial entrenchment in the western one, starting from an ancient, almost steady, sub-planar topographic surface (Pavano, 2013).

As well as reconstructing the main morphotectonic evolutionary stages of the northeastern Sicily, these analyses also populate a conceptual model that describes changes in the hypsometric integral with respect to the relief, at different stages of landscape evolution.

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- Pavano F. 2013. Late Quaternary deformation of NE Sicily from relief and drainage system analysis. Rend. Online Soc. Geol. It. 29, 134-137.

## Plio-Quaternary tectonic evolution offshore the Capo Vaticano Promontory (W Calabria, Italy)

Pepe F.\*<sup>1</sup> Ferranti L.<sup>2</sup>, Bertotti G.<sup>3</sup>, Monaco C.<sup>4</sup> & Sacchi M.<sup>5</sup>

1. Dipartimento di Scienze della Terra e del Mare, Università di Palermo. 2. Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse (DiSTAR), Università di Napoli "Federico II". 3. Department of GeoSciences and Engineering, Delft University of Technology, The Netherlands. 4. Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Sezione di Scienze della Terra, Università di Catania. 5. Istituto per l'Ambiente Marino Costiero, Consiglio Nazionale delle Ricerche, Napoli.

Corresponding email: [fabrizio.pepe@unipa.it](mailto:fabrizio.pepe@unipa.it)

Keywords: Southern Tyrrhenian Sea, Capo Vaticano, Plio-Quaternary.

We reconstruct the Plio-Quaternary tectono-stratigraphic evolution in the offshore Capo Vaticano (W Calabria, Italy) by integrating data obtained from single- and multi-channel reflection seismic profiles and a reprocessed version of the CROP M2A/III line.

NW-trending, high-angle normal faults, dipping  $\sim 70^\circ$  to the south-west formed along the continental slope connecting the south-west continental shelf of the Capo Vaticano Promontory to the Gioia Tauro Basin (Pepe et al., 2014). Faults generally have small displacements up to 40 m and are sealed by Pleistocene deposits.

West of the Capo Vaticano promontory and in the Gioia Basin, a SE-dipping, normal fault system, more than 32 km long, is recognized. Faults affect lower (?) Pleistocene and are sealed by probably post-0.7 Ma deposits. These faults are here tentatively interpreted as the antithetic faults of major, Late Pliocene to Quaternary, NW-dipping, normal faults, which form the currently active tectonic belt along the Calabrian Arc (e.g. Monaco and Tortorici, 2000; Faccenna et al., 2011).

In the Santa Eufemia Gulf, reverse faults affecting Plio-Quaternary and older sedimentary successions are observed. Faults also offset the seafloor thus indicating their recent activity. A normal fault system has been also inferred on the basis of the present day depth variations of the edges of submerged depositional terraces and associated abrasion platforms, along which a vertical displacement of  $\sim 21$  m during the Late Pleistocene-Holocene has been inferred.

The information derived in offshore the Capo Vaticano Promontory represents an important step towards an accurate 3-D kinematic description of the tectono-stratigraphic evolution of the western (Tyrrhenian) side of the Calabrian Arc orogenic wedge during the Plio-Quaternary.

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Pepe F., Bertotti G., Ferranti L., Sacchi M., Collura A. M., Passaro S., Sulli A. 2014. Pattern and rate of post-20 ka vertical tectonic motion around the Capo Vaticano Promontory (W Calabria, Italy) based on offshore geomorphological indicators. *Quaternary International*, 332, 85-98. <http://dx.doi.org/10.1016/j.quaint.2013.11.012>

Monaco C. & Tortorici L. 2000. Active Faulting in The Calabrian Arc and Eastern Sicily. *Journal Of Geodynamics*, 29, 407-424.

## Architecture and Pliocene to Recent evolution of the offshore prolongation of the Granitola - Castelvetro Thrust System (Sicily Channel)

Pepe F.\*<sup>1</sup>, Ferranti L.<sup>2</sup>, Monaco C.<sup>3</sup> & Meccariello M.<sup>2</sup>

1. Dipartimento di Scienze della Terra e del Mare, Università di Palermo. 2. Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse (DiSTAR), Università di Napoli "Federico II". 3. Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Sezione di Scienze della Terra, Università di Catania.

Corresponding email: [fabrizio.pepe@unipa.it](mailto:fabrizio.pepe@unipa.it)

Keywords: Active tectonics, Sicily channel, Western Sicily.

High-resolution, seismic profiles were recorded in the offshore of Mazara - Punta Granitola with the purpose of reconstructing the architecture and Pliocene to Recent evolution of the south-west prolongation of the Granitola-Castelvetro Thrust System, identified as an active structure possibly related to destructive historical earthquakes (Barreca et al., 2014; Ferranti et al., this meeting).

A number of seismic units were identified. The oldest one is interpreted as representative of the Lower Pliocene pelagic deposits known in the region as Trubi. Lower-middle Pleistocene calcarenites are widespread along the continental shelf (CS) between Mazara del Vallo while their top rapidly deepens moving southeast-ward Capo Granitola. In this area, lower-middle Pleistocene calcarenites are unconformably overlain by the late Pleistocene-Holocene deposits. These latter are thin or absent NW of Punta Granitola along the CS, at water depth less than ~30 m, suggesting that this sector experienced uplift during the Quaternary.

Small scale, NW- and SE-displacing reverse faults are observed along the CS where they cut the lower-middle Pleistocene calcarenites and offset the seafloor. South-eastwards, south-east-verging, reverse faults affect lower-middle Pleistocene calcarenites as well as the late Pleistocene-Holocene layers, suggesting that fault displacement acted during the post-LGM.

Growth folding of Upper Pleistocene-Holocene deposits and thrust faults, predominantly dipping to the NW, affecting Pliocene rocks are observed in the immediate offshore Capo Granitola.

The integration of the new data with those obtained from multi-channel profiles suggests that the active folds and thrusts are the uppermost expression of steep crustal ramps (Monaco et al., 1996; Lavecchia et al., 2007; Meccariello et al., this meeting) which upthrust the Saccense platform at depth.

Barreca G., Bruno V., Cocorullo C., Cultrera F., Ferranti L., Guglielmino F., Guzzetta L., Mattia M., Monaco C., Pepe F. 2014. Geodetic and geological evidence of active tectonics in south-western Sicily (Italy). *Journal of Geodynamics*, <http://dx.doi.org/10.1016/j.jog.2014.03.004>

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Meccariello M., Ferranti L., Pepe F. 2014. The NW sector of the Sicily Channel: geometry and evolution of inverted structural lineaments. This meeting.

## A new hypothesis on the seismogenic source in the Central Apennines axial sector

Pierantoni P.P.\*<sup>1</sup>, Centamore E.<sup>2</sup> & Costa M.<sup>3</sup>

1. Scuola di Scienze e Tecnologie, Sezione Geologia - Università di Camerino. 2. Via Muzio Clementi, 58 - 00193 ROME, Italy.  
3. Via P. Selvelli, 6 - 61032 Fano (PU).

Corresponding email: [pietropaolo.pierantoni@unicam.it](mailto:pietropaolo.pierantoni@unicam.it)

Keywords: Seismicity pattern, Active faults, Seismic profile, Geological setting, Central Apennines.

The April 6<sup>th</sup>, 2009 earthquake that struck the town of L'Aquila and its environs caused hundreds of deaths and severe damage.

This event occurred in the axial Central Apennines, where paleoseismic evidence as well as historic and recent records of earthquakes of moderate to large magnitude attest to ancient and ongoing seismic activity.

This seismicity is combined with extensional processes affecting this sector along a NNW-SSE alignment, obliquely offsetting the main Neogene thrust fronts, while the eastern Adriatic area is characterized by coeval compression.

The Late Pliocene-Quaternary structural pattern of this extensional domain consists of several fault systems: NW-SE, E-W and subordinately NE-SW.

Several faults reactivated pre-existent polyphasic structures, in some places with new tectonic inversion processes; others are newly formed faults. These fault systems are associated intermountain basins filled by continental deposits.

Many researchers hold that the seismogenic faults of the 2009 earthquake are the NW-SE ones of Paganica (South) and Mt Gorzano (North).

In the present work, our interpretation of the seismic section crossing the entire earthquake area (IT-89-01, VIDEPI PROJECT) made it possible to identify the geometry of the deep structures. This knowledge, together with geological and structural data derived by detailed mapping (Carg Project), allowed us to create a deep geo-structural model of the earthquake area.

We have reconstructed the space-time evolution and the kinematics of the seismic sequence in L'Aquila (1/10/2008 - 5/4/2009 for the foreshocks and 6/4/2009 - 30/9/2009 for the aftershocks) using seismological data from the Italian Seismological Instrumental and Parametric Data-Base (ISIDE), provided by the INGV.

Our results point to the following observations:

- a) in the western part of the area, there is a Quaternary NNW-SSE striking negative flower structure, with high-angle NE-dipping deep fault planes (the Celano-Cittareale Fault System - CCFS);
- b) the CCFS has polyphasic activity; in the Early Middle Pleistocene it acted with pure left transcurrent kinematics, favouring the opening of several pull-apart basins. In more recent times, it acted with transtensive or normal kinematics;
- c) hypocentres are located along the NE-dipping fault planes of the deep flowers structures and SW-dipping antithetic fault planes (Paganica and Mt Gorzano Faults);
- d) the CCFS is a continuous structure along the entire seismic sequence area; the Paganica (S) and Mt Gorzano (N) faults are separated by a NE-SW fault caused a NNE-wards shifting of the seismic sequence. Thus the CCFS was the main seismogenic structure and the Paganica and Mt Gorzano faults were activated later;
- e) the CCFS is part of a major system (CAFS) that extends from the Marsica Range (SSE) to Colfiorito (NNW); in the past many important earthquakes affected this belt, so it is possible to consider this system as the main seismogenic source of the Central Apennines axial sector.

## Plate boundary reorganization in the central Mediterranean Sea: the Ionian and Alfeo-Etna fault systems

Polonia A.\*<sup>1</sup>, Torelli L.<sup>2</sup>, Artoni A.<sup>2</sup>, Bortoluzzi G.<sup>1</sup>, Faccenna C.<sup>3</sup>, Ferranti L.<sup>4</sup>, Gasperini L.<sup>1</sup>, Monaco C.<sup>5</sup>,  
Neri G.<sup>6</sup> & Orecchio B.<sup>6</sup>

1. Institute of Marine Sciences (ISMAR-CNR), Bologna. 2. Università di Parma, Dipartimento di Scienze della Terra, Parma. 3. Università Roma TRE, Roma. 4. DiSTAR, University Federico II, Napoli. 5. Università di Catania. 6. Università di Messina.

Corresponding email: [alina.polonia@ismar.cnr.it](mailto:alina.polonia@ismar.cnr.it)

Keywords: Calabrian Arc, Ionian Sea, accretionary wedge, plate boundary, active faults.

The Calabria Arc (CA) is a narrow and arcuate subduction system resulting from the Africa/Eurasia plate convergence and slab rollback. The very slow modern-day plate convergence points to a decrease in subduction efficiency, but underplating may still be active in the central CA where GPS data suggests the outward motion of Calabria relative to Apulia. Shortening is taken up in the accretionary wedge along the outer deformation front and out-of-sequence thrust faults. Transtensive deformation, on the other hand, accounts for margin segmentation and represent the shallow expression of deeply rooted processes at the slab edge. One of these structures is the NNW-SSE trending transtensive fault system located East of the Malta Escarpment close to the Alfeo seamount and reaching the Etna volcano on its northwestern tip (the Alfeo-Etna fault system).

Main margin segmentation occurs along a second NW-SE trending crustal discontinuity delimiting two distinct lobes of the subduction complex that intercepts the Italian coasts close to the Messina Straits region (the Ionian fault system). The Western Lobe (WL) of the subduction complex, offshore Sicily, is a down-dropped and very low tapered (about 1.5°) wedge detaching on the base of the Messinian evaporites. The Eastern Lobe (EL), in front of Central Calabria, shows a more elevated accretionary wedge, steeper topographic slopes, higher deformation rates and a deeper basal detachment. High resolution tomographic maps suggest a strong interplay between structural development and slab dynamics, the WL corresponding to areas where the slab is already detached, while the EL to the region of the CA where the slab is still continuous and penetrating into the mantle.

Newly acquired geophysical data (Urania cruise, October 2013), reveal that the Ionian fault system displays fresh seafloor scarps and mud volcanism suggesting it is an active tectonic structure and a deep fluid/mud conduit. We propose that this discontinuity may represent an incipient plate boundary in the Ionian Sea, connecting the compressive belt in northern Sicily to the Hellenic Arc system and dissecting across strike the whole CA. This deformation zone accommodates differential movements of the Calabrian and the Peloritan portions of CA and can explain the NW-SE extension observed in the Straits of Messina as well as why Calabria has advanced further SE relative to NE Sicily.

## Fault slip-rates on active faults: vital data for seismic hazard mapping

Roberts G.P.<sup>\*1</sup>, Cowie P.A.<sup>2</sup>, Phillips R.<sup>3</sup>, Gregory L.<sup>3</sup>, Faure Walker J.<sup>4</sup>, McCaffrey K.<sup>5</sup>, Papanikolaou I.<sup>6</sup>, Dunai T.<sup>7</sup>, Binnie S.<sup>7</sup>, Freeman S.<sup>8</sup>, Scholz C.<sup>9</sup>, Steer P.<sup>10</sup>, Sammonds P.<sup>4</sup>, Michetti A.<sup>11</sup>, Vittori E.<sup>12</sup>, Wedmore L.<sup>4</sup> & Watson Z.<sup>4</sup>

1. Department of Earth and Planetary Sciences, Birkbeck, University of London, UK. 2. Department of Earth Science, University of Bergen, Bergen, Norway. 3. School of Earth and Environment, University of Leeds, UK. 4. Institute for Risk and Disaster Reduction, University College London, London, UK. 5. Department of Earth Sciences, University of Durham, UK. 6. Laboratory Mineralogy – Geology, Agricultural University of Athens, Greece. 7. Department of Geowissenschaften, Universität zu Köln, Germany. 8. SUERC, East Kilbride, UK. 9. Lamont Doherty Earth Observatory of Columbia University, Palisades, New York, USA. 10. Géosciences Rennes, Université de Rennes 1, CNRS, Rennes, France. 11. Dipartimento Di Scienza Alta Tecnologia, Como. 12. Servizio Geologico d'Italia, ISPRA, Roma.

Corresponding email: [ubfb022@ucl.ac.uk](mailto:ubfb022@ucl.ac.uk)

Keywords: fault slip-rate, active fault, seismic hazard.

Fault slip-rates are not random. When measured over many seismic cycles, slip-rates exhibit spatial variability that correlates with regional constraints from tectonics and/or body forces. When measured over shorter timescales, slip-rates can fluctuate on individual faults as activity migrates along and across strike onto parallel fault sets, evidenced by <sup>36</sup>Cl *in situ* cosmogenic dating. However, slip-rates summed between parallel fault sets maintain the correlation with regional constraints. This talk will give examples of the above from the Italian Apennines, discussing the uncertainties associated with the above statements. It will be argued that fault slip-rates, with their relatively well-understood spatial and temporal behavior, are an under-used resource in seismic hazard mapping.

Firstly, it will be shown that slip-rates measured from offsets of landforms that began to accumulate after the last glacial maximum (15 ±3 ka; these can be converted into strain-rates,  $e$ ) correlate with measurements of long-wavelength topography ( $h$ ), so that  $e \sim h^3$ . This power law dependence of strain-rate on body forces shows that rates of fault slip produced by repeated earthquakes on seismogenic faults near the surface are controlled by viscous flow at depth in shear zones whose rates of viscous slip are driven by body forces. The body forces are long-lived, having developed since uplift and extension began in the Apennines (2-3 Ma), so the pattern of fault slip-rate measured at the surface will be long-lived. This stability of the long-term slip-rate pattern serves (a) as a baseline with which to map seismic hazard, and (b) as a baseline from which to measure slip-rate deviations produced by short-timescale temporal earthquake clustering.

Secondly, we use the slip-rates measured over 15 ±3 ka to drive models of accumulation of <sup>36</sup>Cl on fault planes, comparing these model results with over 300 measurements of <sup>36</sup>Cl from a large number of faults. We use this to study temporal earthquake clustering and migration of fault activity across strike. Much skepticism surrounds interpretations of <sup>36</sup>Cl data, due to the importance of proving that the results are not influenced by local climate/erosion/sedimentation. We present <sup>36</sup>Cl data collected from sites where we have conducted extensive structural mapping, geomorphic mapping with LiDAR, and sub-surface mapping with ground-penetrating radar. These well-constrained sample sites show clear signals of tectonic slip because local climate/erosion/sedimentation can be excluded. We find that some faults exhibit identical <sup>36</sup>Cl concentrations to those predicted by modeling the independent and stable 15 ±3 ka slip-rates. Other faults show <sup>36</sup>Cl concentrations that demonstrate slip-rate variations over time periods much less than 15 kyrs. We show examples where faults have been slipping faster or slower than their 15 ±3 ka rate, for a few thousand years, with faults across strike slowing or quickening their slip to maintain the across-strike sum of slip-rate set by the long-wavelength topography ( $e \sim h^3$ ). The concentration of earthquakes on the NE side of the central Apennines since 1349 A.D., up to and including the 2009 L'Aquila earthquake, was preceded by a pulse of earthquake slip on the SW side of the Apennines, which, itself was preceded by slip concentrated on the NE side of the Apennines in the early Holocene.

We do not yet have the complete story and more work is needed. However, it is argued that we know enough about how earthquake shaking and slip-rates relate to the positions of active faults to use this information to map seismic hazard. Fault slip-rates are an under-used resource in seismic hazard mapping for Italy.

## Merging Geophysics and Space Geodesy for Earthquakes

Sabadini R.\*<sup>1</sup>, Barzaghi R.<sup>2</sup>, Cambiotti G.<sup>1</sup>, Marotta A.M.<sup>1</sup>, Crippa B.<sup>1</sup>, Peresan A.<sup>3</sup> & Panza G.<sup>3</sup>

1. University of Milano. 2. Politecnico of Milano. 3. University of Trieste.

Corresponding email: [roberto.sabadini@unimi.it](mailto:roberto.sabadini@unimi.it)

Keywords: geophysical modelling, space geodesy, seismic hazard.

A novel synergic exploitation of remote sensing and geodetic data from ESA and international space missions, such as ERS, Envisat and Sentinel-1 (SAR-Synthetic Aperture Radar), the satellite gravimetry satellites GOCE and GRACE, and the Global Navigation Satellite Systems (GNSS), jointly with forward and inverse geophysical and seismological models, opens up new perspectives for the evaluation of the seismic potential of strategic seismogenic regions. We focus on the Mediterranean, characterized by moderate magnitude earthquakes, and Asia and Pacific, where large earthquakes occur in China and Japan. The wide spectrum of these new classes of geodetic and remote sensing data (displacements and gravity anomalies in proximity of the seismogenic regions) assimilated into the most advanced physico-mathematical models of the Earth which include the exploitation of globally validated ad hoc algorithms for the analysis of mid term variations (CN and M8), of past and present instrumental seismicity in space and time (earthquake catalogues), will make possible, for the first time, to tackle the physical understanding of earthquake generation. Detection and assimilation in Earth's models of GNSS, SAR and GOCE and GRACE data over month time intervals, reduced to a few days for GNSS and SAR, makes possible to estimate the evolution in time of the stress and deformation over the system of faults in real-time, thus providing information on its seismic potential. We are making a step ahead in the understanding of the physical processes related to earthquakes, from moderate to large ones, and at providing new tools applicable to any chosen seismic area of our planet to mitigate the effects of seismicity in strategic regions of the world, Europe, Asia and Pacific.

## **Crustal structure and fault kinematics between the Aeolian Arc and the Ionian Sea offshore as revealed by earthquake tomography and focal mechanisms stress inversion**

Scarfi L.\*, Barberi G., Musumeci C. & Patanè D.

Istituto Nazionale di Geofisica e Vulcanologia, Osservatorio Etneo, Catania.

Corresponding email: [luciano.scarfi@ct.ingv.it](mailto:luciano.scarfi@ct.ingv.it)

Keywords: Tomography, Faulting Regime, Crustal Stress.

We studied the ongoing tectonics of the region extending between the Aeolian Arc and the Ionian Sea offshore, including the southern Calabria and the north-eastern Sicily, through an in-depth analysis of seismological data. For this area, recent studies have shown a very complex tectonic framework, fragmented into crustal blocks separated by seismically active belts and characterized by neighbouring collisional, subduction and active volcanic (Etna and Aeolian Arc) domains. Contraction affects mainly the western sector with an E-W oriented compressive belt extending from the Aeolian archipelago to the Ustica Island. Conversely, the eastern sector (i.e. NE Sicily and western Calabria) is dominated by Late Quaternary extensional deformation. The definition of the seismogenic sources in this area is a difficult task and a matter of intense debate, mainly because morphological expressions of the faults are not evident, since the terrains traverse make it more difficult to keep track of faulting activity, and because there are difficulties in recognizing geological formations and tectonic structures at the great depth reaching the Tyrrhenian and Ionian Seas. In our study, a selected dataset consisting of more than 4000 small-to moderate-magnitude earthquakes ( $1.0 \leq ML \leq 4.8$ ), collected in two decades by a local seismic network, were used to perform a simultaneous inversion of both 3D velocity structure and earthquake locations, in order to trace the characteristics of the faulting systems. The obtained velocity images and the foci distribution depict relevant structural features at depth. In particular, velocity anomalies and hypocentres highlight some WNW-ESE to NW-SE lineaments between the Aeolian Islands and the Ionian Sea. In addition, the fault plane solutions for the best recorded earthquakes were determined and used to resolve the current local stress fields and to characterize the faulting regime of the main seismogenic sources. The results were combined to achieve a coherent geodynamic scheme and to better characterize the active tectonics of the region.

## Quaternary and active tectonics along the Thyrrenian coast of Sicily and Calabria

Scudero S.\*<sup>1</sup>, De Guidi G.<sup>1</sup>, Caputo R.<sup>2</sup> & Perdicaro V.<sup>1</sup>

1. Dept. of Biological, Geological and Environmental Sciences, University of Catania

2. Dept. of Physics & Earth Sciences, University of Ferrara.

Corresponding email: [salvatore.scudero@gmail.com](mailto:salvatore.scudero@gmail.com)

Keywords: Active faults, Seismotectonics, Calabrian Arc.

Northeastern Sicily and Southern Calabria are among the most tectonically active areas in the whole Mediterranean region. This area was affected by a strong tectonic uplift and by extensional-oblique faulting during Pleistocene.

Here we present the result of new field surveys carried out in this area within the frame of PRIN 2010-11 Project "Active and recent geodynamics of Calabrian Arc and accretionary complex in the Ionian Sea" (responsible C. Monaco). The project aims to provide a more detailed and comprehensive framework of the area.

We performed mesostructural analyses on the Pleistocene terrains that outcrop discontinuously along the northeastern coast of Sicily and southwestern coast of Calabria. The most common features encountered are outcrop scale pure normal (or slightly oblique) shear fractures and extension joint (i.e. purely extensional fractures). Particular attention was given to the crosscutting relationship between the various features.

Results show how the controlling tectonic stresses are not uniformly orientated, rather stress perturbations from the WNW-ESE-oriented extensional direction, are registered both at regional and local scale.

Moreover we improved the mapping of the quaternary faults that are the potentially seismogenic; particular attention was given to the minor structures in the overstepping and overlapping zones between the main lineaments (e.g. Reggio C., Armo S. Eufemia and Scilla faults).

Finally we provide clues for connection at depth for some active faults, suggesting a possible contemporaneous rupture in case of reactivation.

The whole study raise the need of revisiting the seismogenic potential for some faulting system in the Calabrian Arc.

## **Sannio - Matese Mounts (Southern Italy) deformation field from GPS data (2002-2014)**

Sepe V.<sup>\*1</sup>, Brandi G.<sup>2</sup>, Cubellis E.<sup>2</sup>, De Martino P.<sup>2</sup>, Devoti R.<sup>1</sup>, Dolce M.<sup>2</sup>, Esposito A.<sup>1</sup>, Galvani A.<sup>1</sup>,  
Massucci A.<sup>1</sup>, Obrizzo F.<sup>2</sup>, Pietrantonio G.<sup>1</sup>, Riguzzi F.<sup>1</sup> & Tammaro U.<sup>2</sup>

1. Istituto Nazionale di Geofisica e Vulcanologia – Centro Nazionale Terremoti, Roma. 2. Istituto Nazionale di Geofisica e Vulcanologia – Osservatorio Vesuviano, Napoli.

Corresponding email: [vincenzo.sepe@ingv.it](mailto:vincenzo.sepe@ingv.it)

Keywords: Sannio-Matese, GPS, deformation field, Strain rate.

A  $M_L=4.9$  earthquake occurred in the Sannio-Matese area at 18:08 on December 29 2013. The epicenter was located in the “Monti del Matese seismic district”. The epicentral area lies between the small towns of San Gregorio Matese, Cusano Mutri, Gioia Sannitica, Piedimonte Matese, San Potito Sannita in the Caserta province in an area with an high seismic Hazard.

The area was struck by large and destructive earthquakes in the past (1456, 1688, 1702, 1732, 1805,1962) with maximum magnitude up to 7.2.

Past and recent seismicity of the area is generally characterized by both single events and low energy seismic sequences (1885, 1903, 1905, 1990, 1992, 1997). The last sequence occurred on 1997 with the largest event ( $M_D = 4.1$ , 19 March) occurred at the border between the Benevento and Campobasso provinces followed by an intense activity ended only in September of the same year. The epicentral distribution of the 1997 low energy ( $M \leq 4.0$ ) seismic sequence is mainly NE-SW oriented suggesting the activation of anti-Appennine faults.

The December 29 2013 seismic event, is located very close to the 1688 earthquake area. Still open debate is the association of the main event of the sequence and its aftershocks with the seismogenic structures present in the area.

The SAGNET (Southern Apennine Geodetic NETwork) is the Non-permanent GPS network covering the area between the Matese Mounts and the Mainarde–Meta Mountains and consists of 40 3D GPS vertices.

GPS dataset consists of data recorded at non-permanent stations in the time span 2002-2014 and at the Continuous GPS stations (CGPS) of the RING network (managed of INGV) located in the central and southern Apennines regions.

We have calculated the GPS velocity field with permanent and non-permanent stations (with time series of at least 3 surveys). The horizontal velocity field, expressed with respect to a fixed Eurasian plate, shows a good coherence between the velocities field estimated from the SAGNET and CGPS.

In this paper we have evaluated the strain rate in the Sannio-Matese area. Before the earthquake, GPS data analysis showed a decrease in the velocity in the southern sector of Matese Massif (where the December 29 2013 earthquake epicenter will be localized) with respect to the surrounding areas which is also evident from the lower values of the strain rate ranging between  $15 \div 20 \cdot 10^{-9}$  yr<sup>-1</sup>.

Lower GPS Strain rate has been recognized at the end of seismic cycle and appear as a useful tool to point out hazardous seismic areas as already highlighted in the 2009 L'Aquila and in the 2012 Emilia earthquakes.

## Seismicity, active deformation and crustal rheology in the central–eastern Southern Alps (Italy)

Viganò A.\*<sup>1</sup>, Scafidi D.<sup>2</sup>, Ranalli G.<sup>3</sup>, Martin S.<sup>4</sup>, Della Vedova B.<sup>5</sup> & Spallarossa D.<sup>2</sup>

1. Sezione Centro di Ricerche Sismologiche, Istituto Nazionale di Oceanografia e di Geofisica Sperimentale. 2. Dipartimento di Scienze della Terra, dell'Ambiente e della Vita, Università degli Studi di Genova. 3. Department of Earth Sciences and Ottawa-Carleton Geoscience Centre, Carleton University. 4. Dipartimento di Geoscienze, Università degli Studi di Padova. 5. Dipartimento di Ingegneria e Architettura, Università degli Studi di Trieste.

Corresponding email: [alfio.vigano@retesismicatrento.org](mailto:alfio.vigano@retesismicatrento.org)

Keywords: Seismicity relocations, Crustal rheology, Southern Alps.

The central–eastern portion of the Italian Southern Alps (the so-called “Giudicarie deformation zone”), located at the western boundary of the Adriatic microplate, is today characterized by light-to-moderate instrumental seismicity (Viganò et al., 2008). The comparison of earthquake distribution within this area reported by different Seismic Bulletins (PAT, *Provincia Autonoma di Trento*; OGS, *Istituto Nazionale di Oceanografia e di Geofisica Sperimentale*; INGV, *Istituto Nazionale di Geofisica e Vulcanologia*) reveals hypocentral locations with significant differences, in terms of calculated longitude, latitude and depth. This is primarily due to a different coverage of seismic stations and different location procedures between the different networks.

Here we present a revision of the seismic catalog in the period 1994–2007 based on (i) integration of original seismic recordings, (ii) manually-revised phase readings and (iii) improved earthquake relocation procedure. Re-examined local magnitudes are comprised between 1.2 and 5.3. The calculated solutions (396 best-quality seismic events) are obtained using a 3D velocity model from a regionally-calibrated crustal tomography (Viganò et al., 2013). The comparison between the new and standard location procedures shows significant differences both in hypocentral locations and related error uncertainties. The validation of the new procedure is tested by locating a set of 41 quarry blasts occurring in Trentino.

Relocated seismicity is shown on maps and cross-sections, in order to relate earthquake clusters and alignments with faults belonging to the regional Giudicarie, Schio–Vicenza and Valsugana–Montello systems. The study area is subdivided into five contiguous seismotectonics domains, based on information from geology, crustal tomography and seismicity. For each domain a 1D crustal rheological profile is calculated (methodology as in Viganò et al., 2012), assuming simplified lithological stratification and selected geotherms. Rheological results are compared to earthquake distribution in depth and cumulative seismic moment release. A model at the crustal scale is then presented to show where present-day deformation concentrates, in order to consider stress partitioning and active tectonics on regional fault patterns.

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## Seismic, geodetic and geologic scalar moment rates of active faults in the Southern Apennines, Italy

Visini F.<sup>1</sup>, Ferranti L.\*<sup>2</sup>, Pace B.<sup>3</sup>, Palano M.<sup>1</sup> & Cannavò F.<sup>1</sup>

1. Istituto Nazionale di Geofisica e Vulcanologia. 2. DiSTAR, Università degli Studi di Napoli. 3. Università degli Studi di Chieti.

Corresponding email: [lferrant@unina.it](mailto:lferrant@unina.it)

Keywords: Southern Apennines, active faults, Moment rates.

We present here a comparison between scalar moment rates estimated for several seismogenic sources of the Southern Apennines from historical seismicity catalog, space geodesy and geological data.

We build on the geologically-based fault distribution model proposed by Ferranti et al. (2014), which provided geodetic slip rates and a comparison between geodetic accumulation and geologic release moment rates for 32 crustal faults segregated between a western extensional and an eastern strike-slip domain in Southern Italy.

Seismic moment rates have been estimated from the catalog of earthquakes complete for  $M_w > 4.6$  (SHARE European Earthquake Catalogue, available at <http://www.share-eu.org>). To assign earthquake to sources, we developed a weighted-distance probabilistic method, by drawing buffer zones around each source to mimic uncertainties in the location of earthquakes and/or sources. The geodetic moment rates have been obtained, using the Savage and Simpson (1997) formulation, from a combination of continuous (2001.00–2014.00) and episodic (1995.68–2010.79) GNSS observations. The geological moment rates have been estimated, using the Brune (1968) formulation, by taking into account the sources geometries, the known long-term (Pleistocene and/or and Holocene) slip rates and the local average rigidity of the crust.

For most sources we observe an overall agreement between geodetic, geologic and seismic- moment rate. On the other hand, some sources show a seismic moment deficiency that could be released in future ruptures. In other areas, for example along the western margin part of the Apennines, large and diffuse discrepancies (geodetic moment largely greater than the seismic and geologic moment) suggest dominant creeping.

This is the first comparison ever attempted, for a large number of geologically- constrained faults, between rates at different time-scales and coming from different space (depth) layers. Results support the contention that the analyzed time window for seismic moment rates is adequate to carry a comparison with geodetic rates. Combination of geodetic and seismicity analysis may yield important insights on earthquake occurrence rate estimates provided that seismogenic sources are geologically constrained.

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## SESSIONE S29

### **Fault Zones: geometry, architecture, composition, fluid-rock interactions, and their seismic vs. aseismic behavior**

*CONVENORS*

*A. Bistacchi (Univ. Milano Bicocca)*

*C. Collettini (Univ. Roma La Sapienza)*

## **Coseismic ruptures along shallow creeping faults in unconsolidated sediments of the Croton Basin, South Italy: field and experimental data**

Balsamo F.\*<sup>1</sup>, Aldega L.<sup>2</sup>, De Paola N.<sup>3</sup>, Faoro I.<sup>3</sup> & Storti F.<sup>1</sup>

1. NEXT – Natural and Experimental Tectonic Research Group, Department of Physics and Earth Sciences, Parma University. 2. Department of Earth Sciences, Sapienza University of Roma. 3. Rock Mechanics Laboratory, Earth Sciences Department, Durham University, UK.

Corresponding email: [fabrizio.balsamo@unipr.it](mailto:fabrizio.balsamo@unipr.it)

Keywords: Faults, Coseismic signature, creeping.

Large seismic slip occurring along shallow creeping faults in tectonically active areas represents an unsolved paradox, which is largely due to our poor understanding of the mechanics governing creeping faults in unconsolidated granular materials, and to the lack of documented geological evidence showing how coseismic rupturing overprints creep in near-surface conditions. In this work we present field, petrophysical, mineralogical and friction data to characterize the signature of coseismic ruptures propagating along shallow creeping faults affecting forearc sediments of the seismically active Croton Basin, South Italy. Field observations of fault zones show widespread foliated cataclasites in fault cores, locally overprinted by sharp slip surfaces decorated by thin (0.5-1.5 cm) black gouge layers. Compared to foliated cataclasites, black gouges have much lower grain size, porosity and permeability, which may have facilitated slip weakening by thermal fluid pressurization. Black gouges are also characterized by peculiar mineralogical assemblages compatible with high temperatures (180-200°C) due to frictional heating during seismic slip. Foliated cataclasites and black gouges were also produced by laboratory friction experiments performed on host sediments at sub-seismic ( $\leq 0.1$  m/s) and seismic (1 m/s) slip rates, respectively. Black gouges display low friction ( $\mu_f = 0.3$ ) and velocity-weakening behaviour, as opposed to high friction ( $\mu_f = 0.65$ ) and velocity-strengthening behaviour shown by the foliated cataclasites. Our results show that narrow black gouges developed within foliated cataclasites represent a diagnostic marker to recognize episodic seismic slip events in shallow creeping faults. These findings can help understanding the time-space partitioning between aseismic and seismic slip of faults at shallow crustal levels, impacting on seismic hazard evaluation of subduction zones and forearc regions affected by destructive earthquakes and tsunamis.

## The lock-up angle for brittle activation of a phyllosilicate-rich mylonitic fabric: implications for rock strength and failure modes

Bolognesi F.\*<sup>1</sup>, Bistacchi A.<sup>1</sup>, Dobbs M.<sup>2</sup>, Kirkham M.<sup>2</sup> & Vinciguerra S.<sup>2-3</sup>

1. Department of Earth and Environmental Sciences, Bicocca University of Milan. 2. British Geological Survey, Environmental Science Centre, Keyworth, Nottingham, UK. 3. Department of Geology, University of Leicester, UK.

Corresponding email: [f.bolognesi1@campus.unimib.it](mailto:f.bolognesi1@campus.unimib.it)

Keywords: anisotropy, mylonites, phyllosilicate-rich rocks.

One of the possible mechanisms explaining the nucleation and propagation of weak faults showing a non-Andersonian attitude is the mechanical anisotropy of phyllosilicate-rich mylonitic rocks. Here we analyze the mutual orientation of foliation and stress field in the specific case of the Grandes Rousse Massif (France) and discuss the implications in terms of mechanical anisotropy.

The Grandes Rousses Massif is one of the external crystalline massifs in the Helvetic Domain of the French Alps. In the Lac Blanc and Lac Bramant area the chlorite- and mica-schists of the Grandes Rousses massif are characterized by an Alpine brittle deformation developing on an Hercynian mylonitic SCC' fabric. We observe brittle behavior both as Andersonian conjugate shear fractures and as reactivation of the mylonitic fabric. This different behavior is related to the attitude, and particularly to the dip angle, of the mylonitic fabric: Andersonian behavior is associated to areas with a foliation inclination of about 65° whilst reactivation of the mylonitic fabric of about 75°.

Assuming an homogeneous paleostress field, whose reconstruction revealed a strike slip kinematic, we propose that the lock-up angle for reactivation of the Grandes Rousses schists mylonitic foliation falls between these two values, at about 75°. This angle marks the boundary between a domain where the reactivation of preexisting anisotropies is still possible and another one where reactivation is not possible and Andersonian fractures develop. In order to investigate these different failure modes, physical and mechanical properties of representative samples from the Grandes Rousses Massif, collected in undisturbed areas out of the Lac Blanc and Lac Bramant deformation zone, have been tested at the Rock Physics Laboratory of the British Geological Survey, UK. Here we report preliminary results, in terms of physical (density and porosity) and mechanical (point load, uniaxial compressive strength -UCS and elastic moduli) properties. The tests have been performed on samples cored perpendicular and parallel with respect to the foliation planes. UCS and point load tests carried out on samples with foliation planes perpendicular to the load show higher strength and a failure mode characterized by an irregular geometry with a sequence of millimetric segments composed of low-angle steps developed along foliation planes connected by high-angle segments with an Andersonian orientation. Tests on samples with foliation parallel to the loading show a lower strength with a failure mode controlled by the formation of main fractures along the foliation, originating axial splitting, typical outcome of uniaxial tests.

Field observations and laboratory experiments agree upon the role of preexisting anisotropy given by foliation plane in conditioning rock weakness and fracturing behavior and orientation, stressing the competition between an Andersonian and a weaker behavior.

## Deformation mechanisms and fault rocks involving micritic limestones: examples from Corinth rift normal faults

Bussolotto M.<sup>1</sup>, Benedicto A.<sup>2</sup> & Invernizzi C.\*<sup>3</sup>

1. Université Paris Sud Orsay, now Rue Descartes, Villeurbanne 69100, France. 2. Université Paris Sud Orsay, now Areva Canada Resources, Saskatoon, Canada. 3. Scuola di Scienze e Tecnologie, Sezione di Geologia, Università degli Studi di Camerino.

Corresponding email: [chiara.invernizzi@unicam.it](mailto:chiara.invernizzi@unicam.it)

Keywords: non porous carbonate, normal faults, Gulf of Corinth.

3D fault architecture and the development of the internal structure of fault rocks are related to deformation environment and determine fault transmissivity which is connected to the fluid flow in the surface crust. Characterization and understanding of the factors controlling the deformation mechanisms are essential to better understand the interaction between structures and fluid migration. In this sense many studies have been performed on clastic and crystalline rocks, much less on the carbonate rocks.

To better understand deformation mechanisms within normal fault zones developed in nonporous carbonate rocks, and to try to unravel parameters that influence their development, we studied several outcrops selected along different normal faults affecting the Pindus limestones in the southern margin of the Gulf of Corinth (Greece). Deformation mechanisms, their spatial organization and relative chronology, influence of the P/T conditions, lithology and displacement, origin of the fluids and fluid/rock interaction have been unravelled thanks to a multidisciplinary study. Field structural analysis, micro-structural analysis (optical microscope and cathodoluminescence) of calcite sin-kinematic cements, geochemical analyses ( $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ , trace elements) and fluid inclusions microthermometry of cements have been performed.

Results show that: i) displacement doesn't have a prominent role in the deformation of non porous limestones; ii) cumulative displacement within the fault damage zone represents only a small percentage of the total displacement performed on the main fault (~ 5% for the Vela fault, as an example); iii) it may cause a wide range of structures and/or rocks fault; iv) lithology mainly influences the type of fault rocks and its cohesive/non-cohesive nature.

Concerning to depth (in terms of P/T), moving from about 2500 m depth and getting closer to the surface, we observed different deformation mechanisms and variations in fault rock cementation. Distributed deformation, confined (closed) fluid system and completely sealed structures (fault as a barrier) tends to become localized deformation within a fluid system open to the percolation of meteoric water and with structures and fault rocks poorly cemented by a fluid less saturated by dilution with surface water.

The combination of these factors gives to each fault its general features, and in particular controls its petrophysical properties and transmissivity.

## **Structural and paleofluid evolution of a low-angle normal fault: transient permeability, reseal hardening and overpressure build-up**

Clemenzi L.\*<sup>1</sup>, Storti F.<sup>1</sup>, Balsamo F.<sup>1</sup>, Molli G.<sup>2-1</sup>, Ellam R.<sup>3</sup>, Mucchez P.<sup>4</sup> & Swennen R.<sup>4</sup>

1. NEXT - Natural and Experimental Tectonics Research Group - Department of Physics and Earth Sciences "Macedonio Melloni", Università di Parma. 2. Dipartimento di Scienze della Terra, Università di Pisa. 3. SUERC, Rankine Avenue, Scottish Enterprise Technology Park, Scotland, UK. 4. Department of Earth and Environmental Sciences, KU Leuven, Heverlee, Belgium.

Corresponding email: [luca.clemenzi@nemo.unipr.it](mailto:luca.clemenzi@nemo.unipr.it)

Keywords: low-angle normal faults, fault-zone permeability, fracture healing, fluid overpressure.

Classical frictional fault reactivation models indicate that slip along misoriented fault planes is very unlikely. Nevertheless, active or exhumed low-angle normal faults (LANF) have been described in many settings worldwide. This discrepancy is addressed by contrasting models: i) those proposing that LANF result from post-kinematic passive rotation of former high-angle extensional faults; ii) those proposing that specific conditions can promote slip along misoriented fault planes.

In this contribution, we report on results of new investigations on the Tellaro Detachment, a late Miocene LANF exposed in the internal portion of the Northern Apennines thrust wedge. It developed at shallow structural levels within the brittle crust, and mainly affected the non-metamorphic carbonate-dominated Tuscan succession (Late Triassic to early Miocene in age). The three-dimensional geometry of the Tellaro Detachment has been investigated through detailed structural mapping and restoration of the superimposed deformations, while appropriate exposure allowed for accurate damage zone characterization. Pressure-depth conditions and palaeofluid evolution of the fault system have been studied through microstructural, petrographic, fluid inclusion and isotopic analysis of fault rocks such as dolomitic breccias, and dolomite- or calcite-filled veins.

Our results indicate that: i) the main kinematic activity of the Tellaro Detachment occurred between ~ 5 and 2 km depths; ii) major low-angle and subsidiary high-angle faults were active contemporaneously, but the extensional displacement was mostly accommodated by the former; iii) slip along misoriented fault planes was favored by elevated fluid pressures and low-differential stress conditions; iv) the fault system was characterized by transient permeability, possibly due to coseismic slip-related fracturing or post-seismic deformation, followed by slower resealing during interseismic periods. Dilation breccia bodies, tens of m<sup>3</sup> in size, are frequently associated with major low-angle fault segments.

Results presented in this study contribute to support the notions that: i) in a fluid assisted environment, continental crustal thinning can occur for shallow values of fault dip; ii) LANF have a great influence on fluid circulation within the upper crust; iii) transient permeability in detachment faults can alternatively promote fluid mixing or episodic overpressure build-up.

## **Fault zone deformation during exhumation of high-pressure ophiolite: evidence for localised coseismic slip in metasediments?**

Crispini L.\*, Scambelluri M. & Capponi G.

DISTAV - Università di Genova

Corresponding email: [crispini@dipteris.unige.it](mailto:crispini@dipteris.unige.it)

Keywords: Fault zone, pseudotachylyte, metasediment.

This work deals with the study of a pseudotachylyte bearing fault zone at the boundary between eclogite-facies metabasites and metasediments, with greenschist metamorphic overprint. The fault zone is syn- to post-metamorphic with respect to the greenschist facies and it is related to the exhumation of HP-ophiolites of the alpine orogen (Voltri Massif, Western Alps). The studied microstructures developed at the brittle-ductile transition and indicate that seismic and interseismic slip was enhanced by interaction with fluids.

The damaged fault zone is ca. 2 m-thick and is characterized by two black, ultra-finegrained straight and sharp Principal Slip Zones (PSZ), marked by the pseudotachylyte. On the whole, the damage zone shows a variety of fault rocks (mylonite, cataclasite-ultracataclasite, pseudotachylyte and gouge ) with multiple crosscutting relationships.

Within the two main PSZ, pseudotachylyte occurs in 10-20 cm thick layers, in small scale injection veins and in microfractures. In the mafic hanging wall, the PST is recrystallized and does not preserve glass: it shows flow structures with subrounded, embayed and reabsorbed quartz, in a very fine grained matrix composed of isotropic albite+chlorite+quartz+epidote+ titanite, suggesting recrystallization at ca. 270-300° C, 8-10 km of the original glass. The pseudotachylyte shows plastic deformations overprinted by shear bands and fracturing and is intercalated to cataclasite-ultracataclasite foliation.

The matrix of cataclastic layers has the same mineral assemblage as the pseudotachylyte and clasts of recrystallised pseudotachylyte , to indicate polyphase PSZ formation. In the metasedimentary footwall, the original foliation is deflected parallel to the PSZ and is cut by cm-spaced shear bands parallel to PSZ. Deformation propagates in the footwall through mm-thick injections veins, Riedel shear systems and hydrofractures. Pockets of recrystallized PST occur along the pre-existing mylonitic foliation of metasediments.

Worthnote is the occurrence, in the footwall metasediments, of mm-thick bands mainly composed of finely recrystallized calcite coeval with pseudotachylyte production in the hangingwall. The calcite "deformation bands" cut the mylonitic foliation and are mainly composed of fine grained calcite bounded by dissolution seams or ribbons of deformed calcite; they are characterised by subrounded embayed and reabsorbed quartz grains rimmed by new Ca-Mg amphibole and K-feldspar (90-93%K), in dynamic recrystallized calcite 2-10 micron in size and slightly elongated.

Recent friction experiments on calcite-bearing systems reproduce pseudotachylyte structures diagnostic of dynamic calcite recrystallization related to seismic slip in the shallow crust: the features of the calcite bands that we observed suggest that these structures could be considered as diagnostic of localised coseismic slip in metasedimentary rocks.

## Seismic data analysis for source detection of moderate magnitude earthquakes and comparison to geodetic and seismological data: the case of the $M_L$ 5.0 Pollino event of October 25<sup>th</sup> 2012

D'Amico S.\*<sup>1</sup>, Evangelidis C.<sup>2</sup>, Neri G.<sup>3</sup>, Orecchio B.<sup>3</sup> & Totaro C.\*<sup>3</sup>

1. Physics Department, University of Malta, Malta. 2. National Observatory of Athens - Institute of Geodynamics, Athens, Greece. 3. Department of Physics and Earth Sciences, University of Messina.

Corresponding email: [sebdamico@gmail.com](mailto:sebdamico@gmail.com)

Keywords: source detection, moderate magnitude earthquakes, southern Apennines.

In this study we show the rupture details of the  $M_L$  5.0 earthquake that struck the Pollino Mts. area (southern Italy) on October 25<sup>th</sup>, 2012. The region has been affected by an intense seismic sequence of more than 5000 small to moderate earthquakes between 2010 and 2013 (Totaro et al., 2013). We present rupture details of this earthquake derived by back-projecting local recordings from a virtual seismic array (D'Amico et al., 2010). We report the first application of this method for a relatively low magnitude earthquake, showing that it is possible to image the finiteness of source by using data recorded at local distances (within 150 km from the epicenter). Furthermore, we argue that this approach is applicable for studying earthquake sources having a complex and uncertain fault geometry, even for moderate magnitude events. We found that the Pollino earthquake ruptured with a complex behaviour having source time function and earthquake duration of about 10 seconds. Two discrete pulses of energy occurred: the first near the hypocenter and a secondary smaller southwards at 0.9 sec later and 4-5 km shallower. The horizontal distance between these points is about 4 km and the overall distance is about 6 km. We further tested our results by back-projecting synthetic seismograms taking into account for the complete near source wavefield including interference of depth phases, mode conversions, and reverberations. We generated synthetics using an appropriate moment tensor and the same station geometry used with the observed seismograms. Synthetic tests show that both high-frequency sources could be resolved adequately from this station distribution. The results imaging earthquake rupture are robust and they are not much affected by uncertainties in velocity model, has minimal assumptions about fault geometry and no assumptions on rupture kinematics and size are got in consideration. From this point of view it can be considered a step forward in respect to finite fault technique which impose certain constraints in order to regularize the inversion and reduce the number of degrees of freedom. Ideally, both approaches would be combined to give the most robust model of earthquake rupture. We also frame the so obtained information concerning the mainshock rupture process in an overall description of the seismic sequence evolution primarily coming from high-quality earthquake locations and the comparison with geodetic data.

D'Amico S., Koper K. D., Herrmann R. B., Akinci A., Malagnini L. 2010. Imaging the rupture of the Mw 6.3 April 6, 2009 L'Aquila, Italy earthquake using back-projection of teleseismic P-waves. *Geophysical Research Letters*, 37, L03301, doi:10.1029/2009GL042156.

Totaro C., Presti D., Billi A., Gervasi A., Orecchio B., Guerra I., Neri G. 2013. The ongoing seismic sequence at the Pollino Mountains, Italy. *Seism. Res. Lett.*, 84, 6, 955-962, doi: 10.1785/0220120194.

## The internal structure of an exhumed seismogenic fault zone in dolostones (Foiana Fault Zone, Italian Southern Alps)

Fondriest M.\*<sup>1</sup>, Aretusini S.<sup>1</sup>, Di Toro G.<sup>1-2</sup> & Smith S.A.F.<sup>3</sup>

1. Dipartimento di Geoscienze, Università di Padova. 2. Istituto Nazionale di Geofisica e Vulcanologia (INGV), Roma  
3. Department of Geoscience, Otago University, Dunedin, New Zealand.

Corresponding email: [michele.fondriest@studenti.unipd.it](mailto:michele.fondriest@studenti.unipd.it)

Keywords: Fault zone, dolostones, earthquake ruptures.

Fault zones in carbonate rocks (limestones and dolostones) represent significant upper crustal seismogenic sources in several areas worldwide (e.g. L'Aquila 2009 Mw = 6.1 in central Italy). Additionally, fault zones in carbonates often represent favorable structures for the migration and trapping of water, hydrocarbons, and geothermal and mineralizing fluids in the brittle upper crust. Here we describe an exhumed example of a regionally-significant fault zone cutting dolostones.

The Foiana Fault Zone (FFZ) is a major (~ 30 km long) sinistral transpressive fault zone exhumed from depths of 1-2.5 km in the Italian Southern Alps. The fault zone crosscuts Permo-Triassic igneous and sedimentary rocks, the latter including thick sequences of dolostone. At the current exposure level, the FFZ exhibits an increase in cumulative vertical throw in the range of 0.3-1.8 km moving from south to north along fault strike.

The fault zone consists of variably fractured and fragmented dolostones locally cut by networks of small-displacement (<0.5 m) faults containing discrete, highly-reflective (so-called "mirror-like") slip surfaces. The mirror-like slip surfaces are typically embedded within fine-grained gouge layers (maximum clast size of few millimeters) up to a few centimeters thick. Preservation of bedding planes in the fragmented dolostones indicates a lack of significant shear strain. Instead, the fragmented dolostones are affected by in-situ shattering from the centimeter down to the micrometer scale. Similar fracture patterns have been reported in natural and experimental pulverized rocks, the latter produced under dynamic stress wave loading conditions. Moreover mirror-like fault surfaces similar to those found in the FFZ were produced in friction experiments at the deformation conditions expected during seismic slip along the FFZ. Therefore the association of in-situ shattered dolostones and mirror-like fault surfaces might be a potential indicator of seismic rupture propagation.

Detailed field and aerial structural mapping conducted along several well-exposed sections of the fault zone allowed the recognition of significant changes in the structure of the FFZ along strike. In particular, large variations in fault zone thickness (from 100 m in the north to more than 300 m in the south) and changes in mean fault orientation and fault kinematics (from dominant oblique- and strike-slip in the north to dip-slip reverse in the south) were observed, together with the reactivation of preexisting anisotropies (i.e. bedding). Overall, the structure of the FFZ, when considered together with the variable exhumation level along strike, compares favorably to the predicted damage distribution in three-dimensional earthquake rupture simulations on strike-slip faults, as well as the structure of active seismic sources hosted in carbonate rocks as illuminated by seismological techniques.

## Experimental Insights into the Frictional Behavior of Calcite/Talc Binary Mixtures

Giorgetti C.\*<sup>1</sup>, Carpenter B.M.<sup>2</sup> & Collettini C.<sup>1-2</sup>

1. Dipartimento di Scienze della Terra-Sapienza, Università di Roma. 2. INGV, Roma.

Corresponding email: [carolinagiorgetti@libero.it](mailto:carolinagiorgetti@libero.it)

Keywords: friction, healing, talc.

The concentration of talc in active fault zones may have a major influence on the fault's behavior. Field observations of talc in an exhumed low angle normal fault in Italy (Zuccale Fault, Elba Island), where the lithology is dominated by carbonate rocks, has focused our attention on the relationship between the mechanical behavior of the fault and the interaction between two of its main constituents, calcite and talc. We report on laboratory friction experiments in which variable percentages of calcite and talc were tested to better constrain how various amounts of talc can alter a fault's frictional properties.

We sheared different mixtures of talc and calcite as powdered gouges at a constant normal stress of 5 MPa, under saturated conditions and at room temperature. We performed slide-hold-slide tests, 1-3000 seconds, to measure the amount of frictional healing and velocity-stepping tests 0.1-1000  $\mu\text{m/s}$ , to evaluate frictional stability. Experimental samples of slide-hold-slide tests were collected for SEM analysis.

Our results show that the significant reduction in steady-state frictional strength has occurred by 20% talc. Furthermore, we show that the additional of as little as 5% talc is enough to result in a drop of 50% in the rate of frictional healing in comparison to the 100% calcite sample. The velocity-stepping tests show the addition of as little as 5% talc leads to velocity-strengthening behavior. Furthermore, the rate-and-state parameter  $b$  and the healing rate display a similar, decreasing trend with increasing talc content. Finally, we also observe a divergence between the strain to steady state (increasing) and the strain to peak strength (slightly decreasing) as talc content increases. Preliminary SEM microstructural work shows that above 20% talc content, slip localizes in a few, thin, talc-rich shear bands. Below 20% talc, deformation is accommodated by cataclastic flow in a distributed manner.

Our observations of healing and of velocity-dependent frictional behavior indicate that, in faults where talc and calcite are present, a low concentration of talc is enough to strongly modify the gouge's frictional properties. Specifically, low amounts of talc, even originating in a random fashion, are enough to greatly decrease the amount of frictional healing in these faults, and thus the fault's ability to sustain future stress drops.

## Fault development model for the extensional fault system in the lower eastern flank of Mt. Etna

Gudmunsson A.<sup>1</sup>, De Guidi G.<sup>2</sup> & Scudero S.\*<sup>1</sup>

1. Dept. of Earth Sciences, Royal Holloway, University of London, UK. 2. Dept. of Biological, Geological and Environmental Sciences, University of Catania.

Corresponding email: [salvatore.scudero@gmail.com](mailto:salvatore.scudero@gmail.com)

Keywords: fault zones, co-seismic rupture, fault evolution, Etna.

The lower eastern flank of Mt. Etna (Sicily, Italy) is affected by a system of east-dipping normal faults that belongs to a larger extensional belt running roughly N–S for about 370 km and is consistent with the WNW–ESE regional extension. These fault segments cut the volcanic succession forming very clear fault escarpments. The Late Pleistocene to Holocene vertical slip rate ranges from 1 to 2 mm per year.

Following an earthquake in a fault zone, the co-seismic rupture length and the slip are commonly measured. Similarly, in a structural analysis of major faults, the total fault length and displacement are measured when possible. It is well known that, generally, typical rupture length - slip ratios are generally orders of magnitude larger than typical fault length-displacement ratios. So far, however, most of the measured co-seismic ruptures and faults have been from different areas and commonly hosted by rocks of widely different mechanical properties (which have strong effects on these ratios).

In this paper we provide a unique set of new data on length-displacement (and coseismic rupture length-slip) ratios from the faulting system of Mt. Etna. The most important feature of this dataset is that all the displacements and slips occur in the same fault zones, and that these fault zones dissect rocks (mostly Holocene lava flows) of essentially uniform mechanical properties. This means that the scaling relations (the datasets) are free of random variations due to differences in (a) mechanical properties and (b) stress regimes - variations that are common in other datasets. Using the slip/displacement-length scaling relations, both for faults and co-seismic ruptures, together with data from the literature and analytical and numerical models, we provide a general growth model for faults. The presented data consist in length-displacement ratios from 7 fault zones and 19 co-seismic rupture lengths-slips mostly from the same fault zones. For the co-seismic ruptures, the average length is 3657 m, the average slip 0.31 m, and the average length-slip ratio 19595. For the faults, the average length is 6341 m, the average displacement 73 m, and the average length-displacement ratio 130. Thus, the average rupture-slip ratio is about 150-times larger than the length-displacement ratio. We propose that the differences between the length-slip and the length-displacement ratios can be partly explained by dynamic Young's modulus of fault zone being  $10^{1-2}$ -times greater than its static modulus. In this model, the dynamic modulus controls the length-slip ratios whereas the static modulus controls the length-displacement ratio. We suggest that the common aseismic slip in fault zones is partly due to adjustment of the short-term seismogenic length-slip ratios to the long-term length-displacement ratios. Fault displacement is here regarded as analogous to plastic flow, in which case the long-term displacement can be very large so long as sufficient shear stress concentrates in the fault.

Concluding, this model accounts for the difference in the slip/displacement-length scaling relations between co-seismic ruptures and faults and also explains slow earthquakes and aseismic slip, features that are now known to be very common in active fault zones.

## **Investigation of aseismic monitoring of near surface fracture systems by examining S-wave diffraction and interference spectral signature for geo-environmental hazard prognosis in coastal areas**

Hassan B.\*<sup>1</sup>, Butt S.<sup>1</sup> & Hurich C.<sup>2</sup>

1. Faculty of Engineering and Applied Science - Memorial University of Newfoundland. 2. Department of Earth Sciences - Memorial University of Newfoundland.

Corresponding email: [p94bh@mun.ca](mailto:p94bh@mun.ca)

Keywords: Coastal fracture monitoring, S-wave diffraction in faults, Geo-environmental hazard prognosis.

Seismic and aseismic characterization/monitoring of coastal near surface parallel or near parallel complex fracture systems, especially vertical, using S-waves assumes a progressive salience. Such fractures may, locally and regionally, cause both seawater intrusion in coastal aquifers and geo-hazards. Most of United States and Canadian private and public service, and strategic infrastructures, being coasts proximal, are exposed to such dormant geological and environmental hazards. European coastal aquifers are highly susceptible to seawater intrusion with long tortuous coastlines and complex geology. The associated faulted and fractured near surface bedrock formations and outcrops make coastal areas geo-hazard vulnerable, too. Italy has a unique history of seismic and aseismic geo-hazards, dictated by a complex geology, inseparable from lifestyle. Wave action and seawater intrusion has affected groundwater and degraded jointed rocky coastal cliffs by affecting their shear strength. With loss of property and life, a long term aesthetic and economic loss is also sensible. Aseismic monitoring of complex fractures can help assess and predict their seismic, geological and hydrological behavior to avoid associated hazards. In case of near surface ordered vertical fracture systems, analyzing diffraction caused interferometric spectral effects due to S-wave polarized propagation characteristics, with S-wave surveys, can reliably help describe their direction, density and compliance response. This was established in extended results of a laboratory study where a sediment specimen (108mm x 65mm x 65mm) with five equally separated parallel interfaces was through transmitted by ultrasonic S-waves along the fractures or specimen long axis. Cyclical load i.e., loading-unloading 0-900 kg, applied perpendicular to fracture planes was incremented in nine steps, and 1 MHz ultrasonic source and receiver, attached mirroring at specimen ends, were rotated together 0° through 360° in 30° increments for multi azimuth acquisition at each loading step (Hassan et al., 2013). Response bandwidth spectral analyses persistently showed preserved patterns of displacement amplitude loss correlatable to geometrical effects of the ordered fracture set. Fractures acted as virtual ultrasonic source apertures, grating comparable effect, creating size and position dictated alternate bright and dim spectral patterns. Frequency dependence but stress and azimuth independence of such pattern was evident compared to other azimuth and stress variation controlled amplitude effects, observed. Analyses hence vouch for a reliable architectural and mechanistic fracture prognosis, qualified by principles of diffraction/ interference of waves and frequency restricted frame work of ray theory.

Hassan B., Butt S. & Hurich C. 2013. An experimental study of ultrasonic Swave polarization by transmission through fractured porous media. 26<sup>th</sup> Annual Meeting, SAGEEP, Expanded Abstract, 1-7.

## Aseismic creep of mafic fault rocks at the brittle-viscous transition – an experimental study

Marti S.\*<sup>1</sup>, Heilbronner R.<sup>1</sup> & Stünitz H.<sup>2</sup>

1. Department of Environmental Sciences, Geological Institute Basel University, Switzerland. 2. Department of Geology, Tromsø University, Norway.

Corresponding email: [sina.marti@unibas.ch](mailto:sina.marti@unibas.ch)

Keywords: Mafic fault rock, brittle-viscous transition, experiments.

We present an experimental study to investigate the behaviour of fault-zones at deeper crustal levels within mafic rocks. Experiments are performed using a Griggs-type deformation apparatus with solid confining medium at confining pressures ( $P_c$ ) = 0.5 GPa, 1 GPa and 1.5 GPa, temperatures ( $T$ ) between 300 and 800 °C, and aseismic but ‘fast’ displacement rates of  $10^{(-8)}$  m/s. As sample material we use a powder, grain size < 125  $\mu$ m, produced from a natural diabase (composition ~ 56% plagioclase, 41% pyroxene, 3% accessories). 0.18 wt% H<sub>2</sub>O is added. At the elevated  $P_c$ , the fault rock is able to deform at high displacement rates without abrupt failure (bulk shear strain up to  $\gamma = 4$ ) even at  $T$  as low as 300 °C. Differential stresses are high, in the range > 400 MPa, up to 2 GPa. For all experiments, we observe a negative strength dependence with increasing  $T$  and a positive strength dependence with increasing  $P_c$ . Thus, the mechanical data indicates that over 300 – 800 °C and 0.5 to 1.5 GPa  $P_c$ , both brittle and viscous mechanisms measurably contribute to the rheology.

The microstructures can be classified into a lower  $T$  type ( $T \leq 600$  °C) and a higher  $T$  type ( $T \geq 700$  °C,  $P_c \geq 1$  GPa). At lower  $T$ , a foliation develops due to cataclastic flow and most of the shear strain partitions into 2 to 3 shear bands (SBs) in Riedel-shear (R, R', Y) orientations. These SBs are characterized by a strong deflection of foliation, compositional layering, flow structures and an amorphous appearance. Where strain markers can be traced, strain often exceeds a  $\gamma$  of 10. In the higher  $T$  type, cataclastic structures are less prominent, however most of the strain localizes into distributed SBs. The growth of new plagioclase and pyroxene grains is observed, as well as amphibole as a reaction product. At 800 °C, amphiboles occur abundantly, overgrowing pyroxenes and precipitating along plagioclase grain boundaries. SBs are characterized by a homogeneous mixture of amphibole and plagioclase (+ zoisite). Grain sizes in these zones are small, in the range of a few  $\mu$ m.

The deformation mechanism within the SBs at lower  $T$  is not yet fully understood. Flow-structures within them indicate a viscous deformation mechanism (see also Pec et al. 2012), which can explain the negative  $T$  dependence of strength from 300 to 500 °C. For higher  $T$  experiments (especially from 800 °C on), it is suggested from the homogeneous mixture of amphibole + plagioclase (+ zoisite), that granular flow and dissolution-precipitation are the main strain accommodating mechanisms within SBs.

Despite the abundant growth of amphibole at 800 °C, we did not find a correlation between localization and reaction, which might indicate that the microstructure developed at 800 °C needs a brittle precursor for initiation. This is supported by the observation that SBs are thinner in higher  $P_c$  experiments.

Pec M., Stünitz H., Heilbronner R., Drury M., de Capitani C. 2012. Origin of pseudotachylites in slow creep experiments. *Earth and Planetary Science Letters*, 355, 299-310.

## Frictional and mineralogical properties of fault rocks from the Tohoku-Oki megathrust: insights from samples recovered during IODP Expedition 343 (J-FAST)

Mitterpergher S.\*<sup>1</sup>, Smith S.A.F.<sup>2</sup>, Remitti F.<sup>1</sup>, Gualtieri A.<sup>1</sup> & Di Toro G.<sup>3</sup>

1. Dipartimento di Scienze Chimiche e Geologiche - Università di Modena e Reggio Emilia. 2. Geology Department, University of Otago, Dunedin, New Zealand. 3. Dipartimento di Geoscienze, Università degli Studi di Padova

Corresponding email: [silvia.mitterpergher@gmail.com](mailto:silvia.mitterpergher@gmail.com)

Keywords: J-Fast, clay-rich gouge, friction experiments.

The IODP Expedition 343 Japan-FAST (J-FAST) successfully located and drilled the thin ( $\sim 3 \text{ m s}^{-1}$ , for total displacements  $< 1 \text{ m}$ ). Experiments were performed “room-dry” (40-60% humidity, 8.5 -12.5 MPa normal stress) or “water-dampened” (0.5 ml distilled water, 3.5 MPa normal stress). We characterized the mineralogy and microstructures of pre and post-experiment material by quantitative X Ray Powder Diffraction (XRPD), Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM).

The starting material is composed of smectite (beidellite, 53.9 wt.%), illite/mica (15.4 wt.%), quartz (9.6 wt.%), K-feldspar (7.6 wt.%) plagioclase (7.4 wt.%), kaolinite (4.9 wt.%) and amorphous material (2.3 wt.%, close to the detection threshold of 2%). At all investigated slip velocities, water-dampened gouges have peak and steady state frictional strengths (0.04-1, 0.25 0.1  $\text{m s}^{-1}$  ( $\mu$  All deformed gouges contain a greater amorphous fraction (4 – 15.4 wt.%) than the starting material. The amount of amorphous material is not correlated with the estimated frictional heat flux. Deformed water-dampened gouges display homogeneous internal texture, lacking foliation or systematically organized fracture sets. Room-dry gouges deformed at low slip velocities are pervasively foliated (P foliation) and cut by a series of shear bands lying either sub-parallel (Y) or at low angles to gouge layer boundaries (R). At high slip velocities, room-dry gouges contain a weak and heterogeneously developed P foliation and a single, prominent Y shear.

Velocity strengthening at intermediate slip velocities in room dry gouges, as well as a pronounced peak friction at high slip velocities, represents an energy barrier to seismic rupture propagation. The lack of such a barrier in water-dampened conditions is compatible with propagation of the Tohoku-Oki rupture in wet sediments to the trench, and also with large coseismic slip at shallow depths. Additionally, the low friction measured in water-dampened gouges is consistent with the small thermal anomaly measured along the plate boundary fault.

The amorphous material was likely produced by mechanical milling, and did not cause dynamic weakening. The homogeneous microstructures of water-dampened gouges at both slow and high slip velocities might suggest gouge fluidization. In contrast, room-dry gouges display microstructures typical of frictionally sheared clay gouge.

## Field and microstructural characterization of Low-angle normal fault (LANF) hosted in dolomitic rock (Southern Apennine, Italy)

Novellino R.\*<sup>1</sup>, Prosser G.<sup>2</sup>, F. Agosta F.<sup>2</sup> & Tavarnelli E.<sup>1</sup>

1. Dipartimento di Scienze Fisiche, della Terra e Ambientali, Università degli Studi di Siena

2. Dipartimento di Scienze Geologiche, Università della Basilicata, Potenza.

Corresponding email: [novellino.rocco@unisi.it](mailto:novellino.rocco@unisi.it)

Keywords: Low-Angle Normal Faults, deformation mechanisms, dolomitic rock.

Low-Angle Normal Faults (LANFs) consist of shallowly-dipping extensional structures that require the activation of strain weakening mechanisms to allow slip. In this view, detailed structural and microstructural analyses represents an effective tool to understand these processes. In this light, the Lucanian Apennine chain represent a natural laboratory in which LANFs can be extensively mapped and accurately investigated at both meso- and micro-scale.

Here we present the preliminary results of a multi-scale investigation carried out along a LANF hosted in Triassic dolomitic rocks of Agri Valley, aimed at documenting the fault zone architecture and, hence, deciphering the operating deformation mechanisms.

The study fault zone (SLANF) shows a dip-slip kinematics (Strike: N130-170; dip-angle: 20°-38° toward NE) and represents a second order structural element within a several m-thick shear zone. The fault architecture includes a fault core made up of a Principal Slip Surface (PSS) encompassed by 10's of cm-thick cataclastic rock at the hanging-wall (Hfc) and dolomitic gouge at the footwall.

The footwall damage zone consists of m-thick highly-fractured dolomitic rocks that include secondary slip surfaces.

The observation of Hfc polished hand-samples, shows different Cataclastic Layers (CLs) which grade from ultracataclasite, that localize next to PSS, to protocataclasite. Individual CLs are characterized by undulated and band-protrusion boundaries. Usually, a distinct-CL (DCL), few mm-thick localize along the PSS. Locally, R-like shear structures occur along low-mature CLs suggesting a top-to-NE normal sense of movement.

Detailed microstructural analyses are consistent with the CLs being made up of dolomite survivor clasts embedded in a fine-grained matrix and calcite cement. Locally, clast-cortex aggregates are observed within low-cemented layers.

Ultracataclastic veins characterized by clast comminution, observed in proximity of the PSS. It seems likely that these veins originated as R-shear fractures and were subsequently filled by calcite cement. The most striking microstructures are observed within DCL. This layer is bounded by two sharp slip surfaces and contain different sub-layers which are characterized by few rounded dolomitic clasts and abundant angular reworked clasts. Generally, sub-layers are characterized by undulate boundaries and protrusions forming an overall fluid-like structure. Sub-vertical calcite veins intersect DCL, showing either crosscutting or abutting relationship with sub-layers and bounded slip-surfaces.

Detailed structural analysis suggests that deformation along the SLANF was mainly accommodated by cataclastic processes. Microstructural observations indicate localized processes of core-fluidization, which may have triggered weakening processes. Furthermore, different vein generations and diffuse cementation by calcite, suggest that the SLANF has played a key role for fluids migration during and after the deformation processes.

## The southern edge of the Tyrrhenian subduction zone (NE Sicily): a multidisciplinary approach reveals different rheologic behaviour

Palano M.<sup>1</sup>, Schiavone D.<sup>2</sup>, Loddo M.<sup>2</sup>, Neri M.<sup>1</sup>, Presti D.\*<sup>3</sup>, Quarto R.<sup>2</sup>, Totaro C.<sup>3</sup> & Neri G.<sup>3</sup>

1. Istituto Nazionale di Geofisica e Vulcanologia, Osservatorio Etneo - Sezione di Catania. 2. Dipartimento di Geologia e Geofisica, Università di Bari. 3. Dipartimento di Fisica e Scienze della Terra, Università di Messina.

Corresponding email: [dpresti@unime.it](mailto:dpresti@unime.it)

Keywords: subduction edge, geophysical techniques, Calabro-Peloritan Arc.

A multidisciplinary dataset based on gravimetric, magnetotelluric, seismic, geodetic and structural observations has been used to provide an improved picture of shallow structure and dynamics at the southern edge of the Tyrrhenian subduction zone. Nowadays, the Central Mediterranean basin is dominated by the geodynamic processes related to the convergence between African and Eurasian plates. In W-Sicily crustal shortening occurs along thrusts whose fronts are laterally dislocated by transfer crustal zones (Billi et al., 2007), while in NE-Sicily and S-Calabria the occurrence of crustal extension is controlled by the subduction and SE-ward rollback of the Ionian crust underneath the Calabro-Peloritan Arc (Neri et al., 2012). The different deformation pattern of these two adjacent domains is accommodated by the right Aeolian-Tindari-Letojanni strike-slip fault system located in NE-Sicily and characterized by still unclear tectonic at its southern tip (Billi et al., 2006; De Guidi et al., 2013). In correspondence of the Aeolian-Tindari-Letojanni Fault (ATLF) system and surrounding areas, we identify two main crustal domains characterized by different P-waves velocity and density patterns in the depth interval of 0-20 km. The former, comprising NE-Sicily and S-Calabria, shows high  $V_p$ /density values while the latter, enclosing the southern sector of investigated area, is characterized by low  $V_p$ /density values. The transition between the two domains spatially agrees with a right-lateral shear zone formed by the Taormina Line, the ATLF and associated structures. Within this shear zone, a large amount of the deformation/seismicity is concentrated along ATLF. Data comparison suggests a possible different rheological behaviour of the crust in the study area. At finer scale the northern and central segments of ATLF seem to be characterized by a fragile response while its southern segment seems to show a plastic behaviour.

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Billi A., Presti D., Faccenna C., Neri G., Orecchio B. 2007. Seismotectonics of the Nubia plate compressive margin in the south-Tyrrhenian region, Italy: clues for subduction inception. *J Geophys. Res.*, 112:B08302.

De Guidi G., Lanzafame G., Palano M., Puglisi G., Scaltrito A., Scarfi L. 2013. Multidisciplinary study of the Tindari Fault (Sicily, Italy) separating ongoing contractional and extensional compartments along the active Africa-Eurasia convergent boundary. *Tectonophysics*, 588, 1-17.

Neri G., Marotta A.M., Orecchio B., Presti D., Totaro C., Barzaghi R., Borghi A. 2012. How lithospheric subduction changes along the Calabrian Arc in southern Italy: Geophysical evidences. *Int. J. Earth Sci.*, 101, 1949-1969.

## Textures of cohesive carbonate fault rocks in the San Benedetto-Gioia dei Marsi (Fucino, central Italy) shear zone

Scafa M.<sup>1-2</sup>, Pace B.\*<sup>1</sup>, Iezzi G.<sup>2-3</sup> & Merico A.<sup>1-2</sup>

1. DiSPUTer, Università G. d'Annunzio, Chieti. 2. Dipartimento di Ingegneria & Geologia, Università G. d'Annunzio, Chieti. 3. Istituto Nazionale di Geofisica e Vulcanologia, Roma, Italy.

Corresponding email: [b.pace@unich.it](mailto:b.pace@unich.it)

Keywords: carbonate fault rock, texture, image analysis, grain-size distribution, D-value.

The San Benedetto–Gioia dei Marsi active normal fault, responsible of the large 1915 earthquake (Mw 7.0), is located along the eastern boarder of the Fucino Plain (central Italy). The tectonic area has been extensively investigated, but textural features of these carbonate rocks are still poorly characterised, especially those of cohesive carbonate on fault rock planes. Thereby, we have sampled five oriented cohesive carbonate rock samples on three fault surfaces well exposed inside the Venere quarry. The about 100 m width shear zone, consists of fault planes, cohesive rocks and loose gouge.

We quantified the textural parameters using mesoscopic (scanner) and optical microscopy images. For each sample, we prepared polished rock sample surfaces (few dm<sup>2</sup>) and thin sections (35 cm<sup>2</sup>) by cutting the rocks normally to their fault planes. We analysed textural features in the first cm away from the fault planes. Tectonic grains or particles with a size dimensions > 2 mm and < 2 mm, identified on scanner and optical microscopy images respectively, were re-drawn on slides. The re-drawn grains were investigated by image analysis, i.e. the area, aspect ratio and long plus short axes of equal-area ellipses of grains. Absolute and relative abundances of grain sizes were re-calculated by considering the area of images.

The relative abundance of grain sizes evidences that these fault rocks are cataclastics. However, the main fault is characterised by a higher amount of large grain (> 2 mm) and by a lower amount of relative tiny (< 2 mm) grains; in turn, the other fault core samples inside the shear zone are richer in tiny grains. Moreover, couple of rock samples on the same fault shows differences in grain size distribution along strike.

The grain- or particle-size distributions for each fault sample were calculated by the classical log  $d$  vs. log  $N$  plot, where  $d$  is the size dimension of grains and  $N$  their counts. The obtained D-values (“fractal dimensions”) are about 1.5 and 1.7 for the two samples on the main fault, whereas are 1.9, 2.3 and 1.9 for the three samples on the other two fault planes. These D-values are very similar to those measured on the loose gouge samples analysed on the coaxial Serrone fault (Billi, 2007), only few km away from the studied fault.

Therefore, in the limit of our considered range, grain size distribution data measured on 2D images of cohesive rock samples are consistent with those measured on loose (gouge) samples and can be properly used to unravel peculiarity of their fault planes and variation inside a brittle shear zone. Finally, our grain size distributions suggest that comminution increases moving away from the main fault and varies along the shear zone strike.

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## **Geometry and kinematics from a WSW–trending dextral transfer zone: the Tre Monti fault (Central Apennines)**

Smeraglia L.\*<sup>1</sup>, Doglioni C.<sup>1</sup>, Carminati E.<sup>1</sup> & Billi A.<sup>2</sup>

1. Dipartimento di Scienze della Terra, Sapienza Università di Roma. 2. IGAG, Consiglio Nazionale delle Ricerche, Roma.

Corresponding email: [luca.smeraglia@uniroma1.it](mailto:luca.smeraglia@uniroma1.it)

Keywords: Fault geometry, Transfer zone, Central Apennines.

The Central Apennines are characterized by a direction of maximum stretching oriented NE-SW. Despite this extension is mostly accommodated by normal slip on NW-trending fault segments, several faults have different orientation. In this study we present a detailed structural and geological survey to define the kinematics and architecture of an exhumed fault zone in Mesozoic carbonates, the WSW–trending and 8 km long Tre Monti–Celano fault zone, both by field and remote sensed methods (e.g. satellite pictures, aerial images, digital earth model). The Tre Monti–Celano fault zone is the northern boundary of the Fucino Basin, an intramontane half-graben filled by Plio–Quaternary alluvial and lacustrine deposits located in the central part of the Apennines chain, which was formed in Upper Pliocene and in Quaternary time by the extensional tectonic activity. The main fault plane consists of SSE-dipping normal fault cutting lower to middle Cretaceous limestone in the footwall and upper Pliocene to middle Pleistocene lacustrine deposits and subaerial slope debris in the hangingwall. Kinematics indicators, fracture orientation, and geometry of fault splays along the fault zone recorded mainly dextral transtension movement. The main fault is splitted into smaller segments (from 700 m up to 2 km in length) arranged with dextral en-echelon geometry. Inversion of kinematics indicators on fault segments oriented respectively ENE-WSW, NE-SW and NNE-SSW indicate a direction of maximum extension oriented NE-SW, accordingly to the direction of the maximum regional extension. These data suggest that the Tre Monti fault zone acted as a dextral transfer zone between two left-stepping major normal faults, oriented NW–SE and characterized by normal or slightly dextral oblique slip: the Venere-Serrone Fault in the south-east and the Velino fault in the north-west. Detailed mapping along the fault zone allowed to recognize different types of fault rocks generated by different lithologies involved in deformation and different amount of fault displacements. Further work will focus on a microstructural-mineralogical and geochemical characterization of natural fault rock samples to understand the mechanism of deformation and the role of fluid within these processes.

## Fine-scale structure and kinematics of the 2010-2013 Pollino seismic swarm in the southernmost Apennines: setting the stage for post-orogenic extensional tectonics

Totaro C.\*<sup>1</sup>, Seeber L.<sup>2</sup>, Waldhauser F.<sup>2</sup>, Steckler M.<sup>2</sup>, Gervasi A.<sup>3-4</sup>, Guerra I.<sup>4</sup>, Orecchio B.<sup>1</sup>,  
Presti D.<sup>1</sup> & Valoroso L.<sup>3</sup>

1. Dipartimento di Fisica e Scienze della Terra, Università di Messina. 2. Lamont-Doherty Earth Observatory, Palisades, New York, USA. 3. Istituto Nazionale di Geofisica e Vulcanologia, Centro Nazionale Terremoti, Roma. 4. Dipartimento di Fisica, Università della Calabria, Arcavacata di Rende (CS).

Corresponding email: [ctotaro@unime.it](mailto:ctotaro@unime.it)

Keywords: Seismic swarm, southern Apennines, high-precision hypocenter locations.

We present an high-resolution analysis of the space-time evolution of the seismic activity between 2010 and 2013 in the Pollino Mts. region, lying in the junction area between the Calabrian forearc and the southern Apennines domains, southern Italy (Presti et al., 2013). In this region, already proposed as a possible seismic gap (i.e., Cinti et al., 2002), a swarm of thousands of small to moderate earthquakes reaching a maximum magnitude of  $M_L$  5.0 started in spring 2010 (Totaro et al., 2013). The source volume of the swarm is confined within the Apennine thrust allochthon (Steckler et al., 2008). We first obtained high-precision relative hypocenter locations by applying a double difference location method (hypoDD), then we refined hypocentral locations by using relative arrival times measured by waveform cross-correlation (Waldhauser & Ellsworth, 2000; Waldhauser & Schaff, 2008). Earthquake spatial and temporal distribution analysis, detection of clusters of similar earthquakes jointly evaluated with high quality focal mechanisms and surface geology allow us to highlight important aspects of the mechanical behaviour of major and minor faults in the Pollino area. The 3D patterns of hypocenters and focal mechanisms consistently image an about 10-km long NNW-striking and west-dipping fault zone between 5 and 10 km of depth, with predominantly extensional kinematics. At finer scale, these data show fault dip decreasing and secondary faulting increasing from north to south, thus defining a southern and northern segment of the main fault. This geometry leads to the hypothesis of steep seismogenic normal faults rooted into more regional shallow-dipping detachments inherited from the pre-existing Apennine thrust tectonics.

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## SESSIONE S30

### **Field mapping, remote sensing and geomatics: modern tools for the construction and quantitative analysis of geological model in Italy and the Mediterranean region**

#### *CONVENORS*

*S. Catalano (Univ. Catania)*

*C. D'Ambrogi (Servizio Geologico-ISPRA Roma)*

*S. Zanchetta (Univ. Milano Bicocca)*

*J. Wasowski (CNR-IRPI, Bari)*

*A. Tamburini (TRE-Telerilevamento Europa srl)*

*A. Corsini (Univ. Modena e Reggio Emilia)*

## **Geological mapping in the digital age: implications of the availability of new digital tools on the process of geological surveying and hints on the education of a new generation of field geologists**

Berra F.\*

Università degli Studi di Milano, Dipartimento di Scienze della Terra "A. Desio".

Corresponding email: [fabrizio.berra@unimi.it](mailto:fabrizio.berra@unimi.it)

Keywords: Geological mapping, CARG project, 3d modelling.

Geological mapping typically requires a 3D approach that, until the last decades, was based upon graphical representation of the geological objects mostly consisting of geological cross-sections or static perspective views. The evolution of digital handling of geological data by GIS systems and of 3D elaboration and visualization software packages represents a major opportunity a) to review the way geological field data are collected, stored and processed and b) to rethink the way field mapping is taught.

This rapid technological improvement at first forced the field geologists to get acquainted with GIS software packages, producing two major results: 1) the definition of a shared, more coherent and logical classification of the geological objects and 2) the creation of databases that can be used for complex elaborations and integrations with different sets of data. A major impulse on this evolution was played in Italy by the CARG project, that for the first time introduced the digital storage of field geological data at a national scale, involving a large number of geologists. Despite some problems, the CARG project promoted the education of the field geologist toward a new way of collecting, classifying and storing of the field data. The existence of a digital data base, even if up to now not freely available to the geological community, allowed the experimental production of 3D models from surface geological data at different scale and resolution.

This major innovation unfortunately was stopped by the suspension of the government loan more than 10 years ago. This grievous political decision for the geological community (with the admirable exception of a few administrations that anticipated the funds to complete the projects on their districts) had two major consequences: 1) the population of the national digital database halted and 2) teams of field geologists that were becoming expert in this new way of handling geological data stopped their work and, consequently, a wealth of experience was wasted.

Despite in Italy an efficient process promoting the awareness of geologists toward the use of digital tools (up to the use of computers directly during the field survey) was stopped, this new approach needs to be considered fundamental for geological mapping from now on. This consideration opens the necessity for rethinking the classical way of teaching field mapping, both in the academia and at a professional level: the use of digital tools needs to become a part of the educational process, but without substituting the classical field training that remains the base of the education of every field geologist.

This would be surely more efficient when the CARG project will be (hopefully) funded again, so that the new generation of field geologist will be able to test directly the quality of their preparation, further adding indications on how to improve their education.

## A new subduction-related foliation trajectory map in the Southern Sesia-Lanzo Zone

Cantù M.<sup>1</sup>, Zucali M.<sup>\*2-3</sup> & Spalla M.I.<sup>2-3</sup>

1. Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia. 2. Dipartimento di Scienze della Terra "A. Desio", Università degli Studi di Milano. 3. CNR, IDPA, Milano, Italia.

Corresponding email: [michele.zucali@unimi.it](mailto:michele.zucali@unimi.it)

Keywords: form surface map, subducted continental crust, Western Alps.

We present a new foliation trajectory map of the contact between two metamorphic complexes of the Sesia-Lanzo Zone (SLZ), namely the Eclogitic Micaschists Complex (EMC) and the Rocca Canavese thrust sheet (RCT), and the ultramafic Lanzo Massif.

In the southern SLZ the metamorphic complex of RCT (Pognante, 1989 a; Pognante, 1989b) has been recognised, on the ground of its strongly contrasted Alpine metamorphic evolution, characterized by a P-climax recorded under very low temperature conditions at intermediate pressure, with respect to the EMC where the dominant imprint is recorded under eclogite facies conditions. The boundaries between the two complexes and the Lanzo Massif is marked by mylonitic bands (Spalla & Zulbati, 2003).

A multi-scale structural analysis has been performed at 1:5000 scale and several details at 1:500. The result is the reconstruction of a superposed grid of metamorphic foliations allowing the regional scale correlation of structural and metamorphic stages. The micro-structural investigation has been used to identify mineral assemblages marking successive fabrics in each rock type, characterizing the two complexes, and to acquire details on relative chronology of structural imprints and associated metamorphic environments in which they developed.

Such data are reported at the map scale as superimposed foliation trajectories characterized by relative chronology and different colors have been used to distinguish the associated mineral assemblages, fundamental to unravel the metamorphic environment (and therefore geodynamic scenario) in which successive fabrics developed.

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## Proximal remote sensing technique for 3D mapping using UAS aerial system

Cara S., Fiori M. & Matzuzzi C.\*

Istituto di Geologia Ambientale e Geoingegneria. I.G.A.G., CNR, Cagliari.

Corresponding email: [c.matzuzzi@cnr.it](mailto:c.matzuzzi@cnr.it)

Keywords: UAS, Photogrammetry, Proximal Sensing.

The characterization of degraded areas by 3D modeling is mainly conditioned by accurate survey and mapping. In this paper we discuss a method based on proximal sensing photogrammetry technique, to obtain detailed photogrammetric survey by means of an Unmanned Aerial Systems (UAS). This technique allows to collect high definition digital images and generate very dense point clouds for DSM elaboration. In the field of Photogrammetry and Remote Sensing (PaRS; Colomina & Molina, 2014) the acquisition based on UAS platforms allows to perform low-cost survey with reliability and safety, obtaining a better information on morphologically complex landforms and better accuracy of 3D models. The UAS system used for this purpose is a multirotor drone equipped with two high resolution digital camera and 28mm fixed focal lens. The proximal sensing survey is performed at different flight heights (from 5 to 50m), according to the needed ground resolution (GSD), in order to generate DSM by the combination of different photogrammetric shots at consistent resolutions. This reduces errors of digital models due to interpolation, especially in presence of strong steepness, giving a more detailed DSM. After the definition of these parameters the flight is planned by waypoints, according to the photogrammetry rules: longitudinal overlap >70% and cross-overlap >=50%. The flight is monitored with a Ground Control Stations (GCS) using the MkTool software (HiSystems GmbH, 2014), to remotely control the telemetry data in real time. The flight planning is a very important phase, especially when the surfaces that have to be reproduced show different characteristics, strong steepness and different exposition to the incident light. To maximize the acquisition efficiency of the photogrammetric shots we use an experimental gimbal hosting two digital cameras, synchronized with a triggered time-lapse and respectively oriented to a vertical and oblique angle. In this way we can drastically reduce the acquisition time, the costs of the survey and enhance the accuracy, especially in presence of strong surface asperity and vegetation coverage. The resulting digital models could highlight with more details the degradation processes taking place that otherwise could not be properly identified and quantified. This method is particularly designed to characterize abandoned mining areas, allowing to investigate erosion phenomena also into a GIS environment, monitoring the evolution of degradation.

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## Geological map of the eastern flank of Mount Etna (1:25.000 scale)

Catalano S.\*<sup>1</sup>, Pavano F.<sup>1</sup>, Romagnoli G.<sup>1</sup>, Sturiale G.<sup>1</sup>, Torrisi A.<sup>2</sup> & Tortorici G.<sup>1</sup>

1. Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Sezione di Scienze della Terra Università di Catania. 2. Regione Sicilia – Dipartimento Regionale di Protezione Civile, Servizio Regionale per la Provincia di Catania.

Corresponding email: [catalano@unict.it](mailto:catalano@unict.it)

Keywords: Geological map, Mount Etna, lava horizon.

The geological map of the eastern flank of Mount Etna (1:25.000 scale) was implemented using a methodological approach that provided the constrains useful to reconstruct the buried 3D geometry of the geological horizons starting from the interpretation of the surface data. This approach can be applied in the lower eastern flank of the volcano, where the volcanic products alternate with epiclastic deposits extending in the whole studied area. These deposits have been referred to the rapid erosion of ancient volcanic edifices, particularly intense during the climate changes coinciding with major deglaciations accompanying the sea-level rises, starting from the Tyrrhenian Age. The epiclastic deposits have been, thus, considered as new geo-chronological markers which evidence the erosional surfaces modelled on the older volcanic products. These markers allow us to identify the different overlapping volcano-stratigraphic units and to correlate stratigraphic successions cropping out in different sectors of the volcano. The analyzed series are represented by lava flows characterized by a limited areal extension, a preferential elongation parallel to the flow direction and by a great variability of thickness and geometry, on the basis of the distance from the eruptive centers. Usually, different lava flows emitted by the same eruptive center overlap each other near the point of emission, while they place alongside in the distal areas. This implies that lava horizons emitted in the same time interval give rise to thick vertical successions in the central areas of the edifice, while in the distal areas they forms a thin volcanic cover that, mainly canalized along the morphological depressions, often conceal the pre-existing palaeo-topography. This is the reason why in the peripheral areas of Mt Etna the volcanic successions can be used to reconstruct the buried morphology of the substratum that they overlay: thin and incomplete successions indicates the presence of buried morphological highs, while thicker and more complete successions represent the filling of valleys. The depth of the valleys is related to their age that can be inferred from the epiclastic deposits extending beneath the volcanic products. Therefore, the geological map of the eastern flank of Mount Etna can be considered an example of a new interpretation of the stratigraphy of the volcano useful to better reconstruct the buried 3D geometry from the surface data and to correlate the volcanic series to the stratigraphic sequences cumulated into different environments (i.e. marine terraces).

## The first level of the seismic microzonation in volcanic areas: the case of Mount Etna

Catalano S.<sup>1</sup>, Pavano F.<sup>1</sup>, Romagnoli G.\*<sup>1</sup>, Torrisi A.<sup>2</sup> & Tortorici G.<sup>1</sup>

1. Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Sezione di Scienze della Terra, Università di Catania. 2. Regione Sicilia, Dipartimento Regionale di Protezione Civile, Servizio Regionale per la Provincia di Catania.

Corresponding email: [g.romagnoli@unict.it](mailto:g.romagnoli@unict.it).

Keywords: Seismic microzonation, Mount Etna, lava flow.

The studies carried out, during the first level of the seismic microzonation, for several urban areas of Mt. Etna have emphasized the problems related to the use of the definitions enounced in the “*Indirizzi e criteri per la microzonazione sismica*” (Working Group MS, 2008) and in the supplement of the “*Ingegneria Sismica*” (Dolce et al., 2011) to volcanic terrains. In this volcanic environment, in fact, the lithostratigraphic successions are characterized by an alternation of hard (lava banks) and soft (scoriae and volcanoclastic deposits) terrains, with repeated seismic wave velocities inversions measured in a vertical direction. In more detail, terrains with  $V_s > 800$  m/s, that would identify the presence of seismic bedrock, often overlay soft cover terrains characterized by lower  $V_s$ . These phenomena give rise to several uncertainties related to both the evaluation of the depth of the seismic bedrock and the ascription of lava horizons as geological substratum rather than cover terrains. Indeed, in the “Standard di rappresentazione e archiviazione informatica-Versione 2.0beta-II” the classification of lava flow is not provided. It is noteworthy that the volcanic terrains of Mt. Etna rest on a thick marly-clay substratum in which the seismic bedrock would be located. Moreover, the rapid accumulation of lavas above manifold palaeo-topography (i.e. buried valleys, buried terraced slopes) produced different sub-surficial 3D geometries, causing the sudden change of the lithological arrangement and of the mechanical parameters of the terrains along both vertical and horizontal direction. In this study, the representative case history of the above mentioned issues, raised during the first level seismic microzonation studies of the volcanic areas of Mt. Etna (i.e. Aci Castello and Trecastagni villages, and Catania town), are considered. On the basis of the experience acquired, new elements for representation and registration of volcanic products in the “Standard di rappresentazione e archiviazione informatica-Versione 2.0beta-II” have been proposed: 1) lava cover (made of one or more lava flows), 2) lava fan, 3) buried marine abrasion platform, 4) buried volcanoclastic edifice, 5) lava flow boundary. These examples, even if implemented the standards of representation, would require a further analysis in the aim of future more detailed levels of studies.

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Gruppo di lavoro MS 2008. *Indirizzi e Criteri per la Microzonazione Sismica*. 3° Vol. e DVD.

## Mesozoic architecture and tectono-sedimentary evolution of the Mt. Cosce sector (Narni Ridge, Central Apennines, Italy)

Cipriani A.\* & Santantonio M.

"Sapienza" Università di Roma, Dipartimento di Scienze della Terra

Corresponding email: [angelo.cipriani@uniroma1.it](mailto:angelo.cipriani@uniroma1.it)

Keywords: Narni Ridge, Early Cretaceous Tectonics, Mesozoic paleogeography vs. Neogene geodynamic evolution.

Previously unreported stratigraphic-structural features have been identified during a geological mapping project (1:10.000 scale) in the southernmost part of the Amelia-Narni Range (Central Apennines, Italy). The study area exhibits a Meso-Cenozoic succession of the Umbria-Marche-Sabina type, with a Jurassic structural high at Mt. Cosce, flanked to the west and north by basins. While the footwall-block top condensed deposits are not preserved due to tectonics and modern erosion, the marginal escarpments are observed locally. These are marked by the onlap of basin-fill deposits, by sparse pockets of fossiliferous condensed deposits unconformably resting on the Early Jurassic substrate (Calcare Massiccio) (epiescarpment deposits), and by a peculiar diagenetic feature (silicification) at the contacts between the shallow water Calcare Massiccio Fm. and the silica-rich basinal lithologies. The silicification process also affects the huge C. Massiccio olistoliths (up to 1 km longer axis; Mt. Mandrione) embedded in the basinal successions flanking the structural high. The main stratigraphic feature discovered in this area is a sedimentary breccia (Mt. Cosce Breccia) resting through an angular unconformity on the footwall-block C. Massiccio. The breccia is a chaotic deposit with clasts of C. Massiccio, of Jurassic basinal formations and of condensed pelagites, also with white pebbly mudstones bearing calpionellids and radiolarians (Maiolica Fm.). The lack of lithoclasts younger than the earliest Cretaceous, the absence of calpionellids, and the presence of *Hedbergella* sp. in the matrix all suggest an Hauterivian-Barremian age for the deposit. Field relationships and geometries suggest that the breccia is a syntectonic deposit, marking an Early Cretaceous rejuvenation of the western margin of the Jurassic Mt. Cosce High. During the Miocene shortening, the Mt. Cosce horst-block was dissected by the Narni Thrust, becoming a part of its hangingwall, while the N-dipping Jurassic paleoescarpment acted as NE-striking lateral ramp. The NE-dipping forelimb of the thrust overrides an overturned footwall syncline with a thin Jurassic basinal succession (Configni-Vasciano). Our cross-sections suggest a modest shortening (few 100's of metres), unlike previous interpretations (layer-cake models) where larger displacements were implied. The C. Massiccio olistoliths could locally develop shear contacts with the embedding units, due to the contrasting mechanical behavior of the two lithologies when subjected to folding. Last, Pliocene extensional faults apparently exploited the strikes of the rotated pre-orogenic margins.

## Structural mapping of the Ivozio Complex, Sesia-Lanzo Zone Italian Western Alps

Delleani F.\*<sup>1</sup>, Rebay G.<sup>2</sup>, Zucali M.<sup>1-3</sup> & Spalla M.I.<sup>1-3</sup>

1. Università degli Studi di Milano, Dipartimento di Scienze della Terra "A. Desio". 2. Università di Pavia, Dipartimento di Scienze della Terra e dell'Ambiente. 3. IDPA-CNR U.O.S. Milano.

Corresponding email: [francesco.delleani@hotmail.it](mailto:francesco.delleani@hotmail.it)

Keywords: form surface maps, Austroalpine Domain, subducted continental crust.

The Ivozio metagabbroic Complex is mainly known for the occurrence of spectacular Alpine Lws porphyroblasts, widely replaced by Ky and Ep (Pognante et al., 1980; Zucali & Spalla, 2011; Delleani, 2013). Due to the strong tectonic significance of Lws-bearing rocks, often described in the subducted oceanic lithosphere but only occasionally in the continental crust, discrimination between prograde and retrograde Lws crystallization is crucial to individuate highly depressed geothermal gradients and their extent during the subduction process. Here this has been possible with the support of a detailed multiscale structural analysis, integrated with petrological analysis and data on the whole rock compositions of the protoliths from the layered complex.

The results of the 1:20 to 1:100 scale survey of the outcrop contours and structural elements have been represented in a petro-structural map at the 1:1.000 scale and on enlargements at 1:20, 1:50, 1:100 and 1:200 scale of the most significant structural features. This map allows the prompt correlation of structural fabrics and metamorphic assemblages in the subducted-exhumed polyphased tectonites and facilitates the distinction of the pre-Alpine protoliths. The lithostratigraphic configuration of the Ivozio metagabbros is therefore inferred and the main boundaries with their country rocks have been represented on a drift and solid map and on significant cross-sections. Superposed structural elements, such as foliations, axes, axial planes, shear zones and veins are distinguished on the basis of their relative age and the relative associated metamorphic minerals have been specified. This representation technique conveys a dynamic visualization of the complex structural framework together with an immediate perception of the thermal regimes that characterized the deformation history.

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## **Transgressive and tectonically-reworked contacts in a late orogenic basin: the case of the Tertiary Piedmont Basin in the Sassello area (Ligurian Alps, Italy)**

Federico L.\*, Crispini L., Dabove G.M., Piazza M. & Capponi G.

Dipartimento di Scienze della Terra dell'Ambiente e della Vita, Università di Genova.

Corresponding email: [federico@dipteris.unige.it](mailto:federico@dipteris.unige.it)

Keywords: Tertiary Piedmont Basin, stratigraphic contact, thrust tectonics.

The Tertiary Piedmont Basin (TPB) is a syn-tectonic Neoalpine–Apennine basin filled by an upper Eocene–upper Miocene sedimentary succession, having an inner position with respect to the arcuate belt of the Western and Ligurian Alps, in northwestern Italy.

The TPB is transgressive on the collisional stack of tectonic units resulting from the main alpine orogenic deformation phases. In the study area it encompasses upper Eocene (?) continental breccia (Costa Cravara Breccia), Oligocene continental to transitional conglomerate and sandstone (Molare Fm.), and upper Oligocene – lower Miocene (?) pelites (Rocchetta-Monesiglio Fm.).

The early stage of sedimentation of TPB records a pre-transgressive to transgressive phase, characterized by the deposition of alluvial fan and fan delta conglomerates and sandstones, and by reef limestones and sandstones of very shallow marine environment. Locally, primary transgressive contacts with the metamorphic substrate are preserved and evidence of fault-controlled deposition are observable.

The late-alpine/apennine tectonics, related to the Corsica - Sardinia block rotation, caused the backfolding and backthrusting of the alpine units towards NE. Above such units the TPB evolved as a piggy-back basin, affected by Aquitanian–Burdigalian top-to the E-NE long-wavelength open folds, in places evolving into thrust faults, that locally placed the metamorphic basement onto the TPB sediments.

During the Pliocene, a new set of mainly extensional/transensional faults formed in the framework of the opening of the Ligurian Sea. This caused uplift of the metamorphic bedrock and erosion, so that most of outcrops of the TPB rocks in Liguria are erosional remnants of a once much more continuous sedimentary cover.

In this work, we focus on a triangular-shaped area of TPB in the Sassello surroundings (central Liguria), where we collected new stratigraphic and structural observations during the geological mapping of the "212-Spigno Monferrato" quadrangle (Regione Liguria cartographic project). We present an original geological map at the 1:20,000 scale, and we describe the different types of contacts between the TPB and the metamorphic rocks emphasizing on their tectonic and regional significance in the geodynamic evolution of the Ligurian Alps.

## **Compressive deformational styles in the external units of the southern Apennines: field examples from the Sheet 407 San Bartolomeo in Galdo area (southern Italy)**

Festa V., Gallicchio S.\*, Moretti M., Rapisardi L. & Tropeano M.

Dipartimento di Scienze della Terra e Geoambientali - Università degli Studi di Bari "Aldo Moro".

Corresponding email: [salvatore.gallicchio@uniba.it](mailto:salvatore.gallicchio@uniba.it)

Keywords: Shortening, thrust, folding.

The geological survey of the Sheet 407 "San Bartolomeo in Galdo", scale 1: 50.0000 (CARG project), allowed us to analyze the specific structural features that involve the main tectono-stratigraphic units cropping out in the Daunia area of the southern Apennines. In this area, the sector to the front of the chain is built, from west to east by two tectono-stratigraphic units: the Fortore Unit, below, and the Daunia Unit, above. Outcrops of both units offer the opportunity to observe a variety of styles of deformation related to the Upper Miocene – Lower Pleistocene horizontal shortening.

At the outcrop scale, the Lower Cretaceous to Lower Miocene clayey stratigraphic successions (i.e., Argille Variegate and Flysch Rosso Fms) in the lower part of the two units are characterized by disharmonic and close to tight folds. This folding developed due to rheological differences within both units, where the incompetent clayey successions were squeezed and adapted to the geometry imposed by the above most competent beds.

Toward the top of the Fortore Unit, the Lower Miocene to Upper Tortonian stratigraphic successions, each dominated by turbidite arenaceous sediments (i.e. Tufiti di Tusa, Flysch Numidico and Flysch di San Bartolomeo Fms), locally show isopach open folds with upright to inclined axial surfaces, due to buckling. This mechanism was favored by the considerable thickness (up to ca. 10 m) reached by several arenaceous portions.

Toward the top of the Daunia Unit, instead, the Upper Burdigalian - Lower Tortonian marls and calcareous turbidites, belonging to the Flysch di Faeto Fm., generally exhibit chevron-type close folds, with upright to inclined axial surfaces. This folding occurred due to flexural slip mechanism, which was favored by both the relatively thin thickness (up to 1 m) of the calcareous beds and the widespread clayey interlayers.

At the map scale, fault-propagation folds affected especially the Daunia Unit, which often shows overturned strata dipping in the same direction of the neighboring tectonic contacts. In addition, fault-bend folds seem to be the most suitable style of thrusting of the Fortore Unit, since generally there is no evidence of overturned strata, and regular monoclines dipping as the tectonic contacts characterize large sectors of the map.

Along the main thrusts, the two tectono-stratigraphic units were involved in a top-to-the-foreland tectonic transport. Parallely, minor thrusts and back-thrusts branched off from the main thrusts: it should be noted that a back-thrust locally overturned the contact between the two main tectono-stratigraphic units.

Finally, an out-of-sequence thrust, cropping out along the boundary between the higher morphologic part of the chain and the Plio-Pleistocene foredeep domain, cross-cut the previous compressional structures and accommodated the latter stages of shortening.

## **Po evolution during centuries in Pavia's area through historical maps using GIS analysis: identification of homogeneous segments and evolutive cycles evidences**

Finotelli F.\*<sup>1</sup>, Guerrieri E.<sup>2</sup>, Marchesi L.<sup>2</sup> & Vercesi P.L.<sup>3</sup>

1. Servizi di Geo-ingegneria e Progettazione SGP srl, Pavia. 2. Geologo. 3. Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia.

Corresponding email: [ffino@libero.it](mailto:ffino@libero.it)

Keywords: Po river, historical maps, fluvial geomorphology.

The evolution of Po river during last centuries in Pavia's area has been reconstructed by research and analysis of historical maps with GIS. Thanks to archival research was discovered a 1853-1857's survey in the form of a valuable watercolour painting. Only known through textual mentions, this map is the missing piece of the famous series of the nineteenth-century maps Carte del corso del Fiume Po, which consists of the already recently reproduced 1821's and 1874's surveys. The 1853-1857's map is highly relevant for the definition of river morphological evolution and for Po cartography history. The reliability of 17th century maps has been evaluated using GIS by means of a differentiated transformational processes taking into consideration the age and the original accuracy of the maps. Analysing the problems related to the use and validation of historical maps (especially older examples), we selected the most defining attributes of the river bed and organised them in chronological order, before in a relative way and then in an absolute way, according to geo-morphological criteria (evaluation of erosion patterns, meanders). The study allow to review the absolute chronology of the Po river bed represented in historical maps, defined by previous authors mainly basing on maps edition year, and to show the frequent mapping of river by coping it from preceding maps. The result of the reach is a detailed map of the last three centuries' evolution of Po river in Pavia's area. The map reveals parts with different evolutive patterns, where since Middle age the meandering zone's width has been modified by human interventions. This anthropic conditioning has been more or less effective in different areas, also as a result of neotectonics. In addition, the integrated analysis of cartographic, textual and photographic documents led to draw an original map representing the activity periods of preserved paleomeanders and the main natural and artificial meander cutoffs. The detailed analysis of two typical fluvial morphologies (the peninsula at Ticino-Po confluence and the old meanders system near Belgioioso) allowed to identify 4 main evolutive cycles since 1600. Every cycle is marked by distinguishing geomorphological features (kind of forms, morphometric indexes, migration rate) and they are separated by traumatic events (floods, meander cutoffs, effective human interventions). Then has been possible to conjecture the future development of these areas.

## Mapping structures and associated mineral parageneses in HP calcschists from the Italian Western Alps: the Beth-Ghinivert area

Giacometti F.\* & Rebay G.

Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia.

Corresponding email: [fabio.giacometti@unipv.it](mailto:fabio.giacometti@unipv.it)

Keywords: Schistes Lustrés, poly-metamorphic evolution, blueschists facies.

The *Schistes Lustrés* of the Piedmont Zone (Penninic domain) record a poly-metamorphic evolution under high-P/low-T to greenschists facies conditions associated with subduction-exhumation processes. These units consist of calcschists containing metre up to kilometre-sized blocks of mafic to ultramafic ophiolitic bodies.

At Beth-Ghinivert (Chisone Valley), metabasites (meta-gabbros, glaucophanites and prasinites) associated with pyrite-rich mineralizations, are scattered in the calcschists.

A detailed structural and petrological study was performed to determine the metamorphic evolution of this area by unravelling the superposed structures at both meso- and micro- scales and by identifying the associated mineral assemblages.

The record of three deformation-recrystallization events, was recognised in calcschists and metabasites and only rare pre-metamorphic features are preserved in less deformed domains:

- the D1 event is characterized by isoclinal folding of pre-metamorphic surfaces and formation of a S1 axial-plane cleavage. These features are intensively obliterated by the successive tectono-metamorphic events and are only locally recognizable.
- the D2 event produced closed to isoclinal folds and the associated S2 axial-plane foliation which is the main schistosity observable in the field.
- the D3 event produced open to close folds, locally associated with a S3 axial-plane crenulation cleavage.

Epidote-blueschists facies mineral relics occur in both S1 and S2 foliations whereas D3 is associated with greenschists facies parageneses.

In glaucophanites the syn-D1 mineral assemblage consists of blue amphibole, phengite, chlorite, epidote, albite, quartz, minor titanite and sulphides (pyrite and subordinate chalcopyrite). The syn-D2 paragenesis is similar to the D1 described above but minerals have different compositions, reflecting a change in the P-T conditions.

D1 and D2 parageneses consist of quartz, phengite, chloritoid, calcite ± epidote + albite ± chlorite in metapelites, with variations in the mineral composition as observed for the metabasites.

The D3 parageneses, locally associated with a crenulation cleavage, consist of chlorite + muscovite-rich phengite + calcite + quartz in metapelites and chlorite + albite + epidote + actinolite + calcite in metabasites.

Combining structural and petrological information allowed to distinguish volumes which preserve different degrees of re-equilibration and therefore record different moments of the metamorphic evolution. The existence of such volumes can be related to distinct mechanisms which influence the metamorphic evolution and preservation of mineral assemblages and structures, such as deformation and presence of fluids.

## **An assessment of S-waves potential for integrated geotechnical and geohydrological characterization and monitoring of near surface unconsolidated sediments for hazard prevention**

Hassan B\*.<sup>1</sup>, Butt S.<sup>1</sup> & Hurich C.<sup>2</sup>

1. Faculty of Engineering - Memorial University of Newfoundland. 2. Department of Earth Sciences - Memorial University of Newfoundland.

Corresponding email: [p94bh@mun.ca](mailto:p94bh@mun.ca)

Keywords: Integrated S-wave analysis, Near surface characterization, Geohydrological monitoring.

Urban affluence globally, has generated geo-environmentally hazardous effluence specifically in Mediterranean region and Italy as highlighted in recent initiatives. Release of non-aqueous toxins into near surface alone is multifaceted problem. They need to be located and characterized/monitored for containment from ground water aquifers, from sea and/or remedial measures. Their geotechnical effects upon host sediments/bedrock competence given functioning of the associated existing and/or planned infrastructure is critical too. Justifiably relevant is the case of brackish water/brine intrusion/release. S-waves in intergraded surveys can reliably address such complex near surface monitoring problems. Their unique propagation and polarization character given frequency content, assures broader range of responsiveness for smaller property variations. Illuminating horizons of acoustic blindness signify efficacy of S-wave resolving power. Their peculiar response of density variation affected apparent pore pressure change and viscosity variation affected diffraction pattern due to a viscosity structure translates into corresponding anisotropic velocity variation and amplitude effects. These effects facilitate a precise assessment and delineation of the intricate complex of subsurface strength, structure and hydrological process. In due relevance, extended results of an integrated laboratory scale monitoring/imaging of fluid-displacement process, oil with brine at fully saturated constant head controlled conditions, through an analogue of .5mm spherical glass beads packed in a vertical transparent PVC tube i.e., 45cm x 5.09cm, simulating unconsolidated sediments, are reported. Three tests with invading fluid flow rates of 4, 10 and 55 L/d, were performed till breakthrough. S-wave results confirm initial correlation/analyses of ultrasonic P-wave and DC resistance data (Hassan et al., 2014), acquired integrated with S-wave data, providing new insights. Highest velocity in brine saturation, lower in mixed interface and lowest in oil saturation, is distinctive for three fluid saturations in all tests. S-wave amplitudes albeit are lowest magnitude in mixed-zone while higher for the brine saturation compared to that of oil saturation. S-wave velocity not only allows fix three specific saturations spatiotemporally, density variation controlled pore pressure effect upon sediment frame rigidity and strength is also deducible. Flow rate and viscosity dependence of flow morphology i.e., interface deformation/plumes, is resolvable in smaller time widows from amplitude magnitude variation and diffraction related patterns. S-wave potential in addressing near surface problems exacting holistic geotechnical and geohydrological characterization is so evident.

Hassan B., Butt S. & Hurich C. 2014. Results of a laboratory study highlighting the potential of integrated P-wave and electrical methods application in near-surface, 27<sup>th</sup> Annual Meeting, SAGEEP, 422-433.

## The Geological Map of Sicily

Lentini F.\* & Carbone S.

Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università degli Studi di Catania.

Corresponding email: [lentinif38@gmail.com](mailto:lentinif38@gmail.com)

Keywords: Sicily, Geological Mapping, Tectonics, Geodynamics.

The 1:250.000 scale Geological Map of Sicily at present day is the only document containing the main geological features of the entire Island on the base of numerous surveys carried out as research projects; many of these maps have been subsequently updated thanks to the surveys produced by the CARG project and those carried out after the CROP-Mare project. The map will be attached to the v. 96 of the Descriptive Memories of the Geological Map of Italy published by ISPRA, which will be a collection of data carried out by the authors.

In central Mediterranean some structural domains are recognizable: the foreland domain is represented by the Apulian Block and the Pelagian Block, separated by the oceanic crust of the Ionian Basin, the Orogenic Domain is characterized by a system of chains, extending from the Apennines through Calabria-Peloritani Arc (CPA), to Sicily and North Africa. This orogenic belt is located between the old oceanic crust of the Ionian basin, partially consumed, and the new oceanic crust of the Tyrrhenian basin.

The Orogenic Domain is composed of three superimposed tectonic belts, the External Thrust System (ETS), the Apenninic-Maghrebian Chain (AMC) and the Calabride Chain (CC). The ETS, named here Pelagian-Sicilian Thrust Belt, has been generated by the detachment of the internal sedimentary cover of the flexured sector of the foreland simultaneously with the opening of the Tyrrhenian basin; the AMC originated by the imbrication of the sedimentary sequences belonging both to the oceanic crust-type sectors (Tethys and Ionian basins) and to the continental-type crust sectors (Panormide carbonate platforms). The CC is thought as the product of the delamination of the European margin. The innermost domain is characterized by the Tyrrhenian Basin and the Corsica-Sardinia Block.

The distribution of the crusts in the central Mediterranean shows the close connection between the geodynamic evolution of the orogenic belt and the crustal thickness (Lentini et al., 2006). It is evident that the subduction mainly concerned sectors of oceanic crust and, when the latter are consumed, a collision originated between continental blocks and the subduction displaced toward other sectors characterized by oceanic crust. Currently, the only recognizable subduction is that of the Ionian oceanic crust beneath the CPA; while a collisional stage has been recognized to the west along the southern margin of the Tyrrhenian Basin.

The expression is the South Tyrrhenian Fault System, composed of NW-SE oriented en-échelon dextral transcurrent faults, which are well evident in the Geological Map of Sicily.

Lentini F., Carbone S. & Guarnieri P. 2006. Collisional and post-collisional tectonics of the Apenninic-Maghrebian Orogen (Southern Italy). In: Dilek Y. & Pavlides S. Eds., *Postcollisional Tectonics and Magmatism in the Mediterranean Region and Asia*. Geol. Soc. of America., Special Paper 409, 57-81.

## **Remote sensing techniques for the investigation of terrestrial planets: a multisensors and highly integrated approach for the 3D geological mapping**

Marinangeli L.\*<sup>1</sup>, L. Pompilio L.<sup>1</sup> & Pondrelli M.<sup>2</sup>

1. TeleLab-DiSPUTer, Università G. d'Annunzio, Chieti. 2. IRSPS, Università G. d'Annunzio, Pescara.

Corresponding email: [lucia.marinangeli@unich.it](mailto:lucia.marinangeli@unich.it)

Keywords: planetary geology, remote sensing, multispectral instrument.

The space exploration strongly increased in the last decades due to the huge progresses in the field of space technology both at spacecraft and scientific instrument level. A large number of space missions addressed the Solar System planetary bodies. They are mainly remote sensing missions from satellite platforms but a number of rovers and landers for in situ measurements have been employed mostly for Mars. Planetary bodies can be investigated using the same principles and techniques of data analysis used on Earth studies from remote, since the whole dataset is geolocated in space and time. Geomatics allows the geospatial information to be collected, modelled and interpreted according to the several natural phenomena involved. This process is even more challenging when the spatial data come from unknown planetary surfaces, which are only observable from remote. We show some examples of the geological modelling of planetary surfaces using an highly integrated multisensors and georefered dataset.

Mars and the Moon have been the object of several missions, because they are pretty close to the Earth and almost atmosphereless bodies. This latter characteristic allows very spectacular images to be acquired wit a limited amount of pre-processing. On the other hands, planets covered by a dense atmosphere such as Venus and Titan, have been unveiled by radar SAR instruments showing a variety of landforms and crustal processes.

Radar sensors can be used for the observation of the subsurface as well. Spectacular data of the Martian subsurface have been acquired by two italian-led radar instruments, MARSIS and SHARAD allowing a 3D view of the upper 3-5 km of the crustal stratigraphy.

The employment of multi- and hyper-spectral cameras also allows the compositional features at the surface to be unraveled. High quality altimetric measurements are achieved with either laser or radar altimeter. 3D surface reconstruction of planetary surface is an important tool to let the geologist to perform "field work" on other planet.

In conclusion, the interpretation of evolutionary geological processes of extraterrestrial bodies strongly improved in the last decade thanks also to geomatics and data processing techniques.

## Dust storm monitoring with MODIS data on the Multan region (Pakistan)

Melis M.T.<sup>\*1-2</sup>, Locci F.<sup>1</sup>, Dessi F.<sup>3</sup> & Vuillermoz E.<sup>2</sup>

1. Dipartimento Scienze Chimiche e Geologiche, Università di Cagliari. 2. Ev-K2 CNR, Bergamo. 3. CNR-ISAC UOS Torino.

Corresponding email: [titimelis@unica.it](mailto:titimelis@unica.it)

Keywords: MODIS, dust storm, Multan-Pakistan.

Dust storm is a complex process influenced by the interaction of earth-atmosphere system, mainly caused by high wind speed, bared soil and dry air condition. It often takes place in arid and semi-arid areas caused usually by dry and cold front, resulting in ascending airflows and in turn raising dust to upper levels of atmosphere (Omidvar K. and Khosravi Y 2012). In recent years, the frequency of dust storm is rising causing more impact on the climate change over regional and global scale due to its interaction with the solar and terrestrial radiative fields (Shi and Zao, 2003).

Since the 1970s, scientists have succeeded in identifying the outbreaks of dust storms from satellite images by use of two different techniques, the VIR (visible and near-infrared) and the TIR (thermal infrared) window technique. It has been shown that the TIR technique has the distinct advantage in detecting dust storms over high albedo surfaces and in night-times (Zhang P. et al., 2006).

Multan City is a city in the Punjab Province of Pakistan and capital of Multan District, located in the southern part of the province on the east bank of the Chenab River. Multan city is famous not only for its history but also for its blinding dust storms. These dust storms occur mainly between May and June due to a moving western disturbance over the northern areas of Pakistan.

To monitor dust storm in the Multan area MODIS data has been used. MODIS senses the Earth's entire surface in 36 spectral bands, spanning from the visible (0.415  $\mu\text{m}$ ) to the infrared (14.235  $\mu\text{m}$ ) regions of the spectrum with spatial resolutions of 1 km, 500 m, and 250 m at nadir respectively. MODIS data were acquired from NASA DB web service.

The data were georeferenced and reprojected to correct the Bow Tie effect.

When the dust storm happens, lots of dusts particles get together to form a dust cloud. The thick dust layer can absorb and reflect surface radiation and solar radiation, emitting and radiating at the same time, so the values of sensors change (Ochirkhuyag and Solmon, 2008). Among the 36 channels of MODIS, the visible and near infrared channels are used to measure objects reflection while the thermal infrared channels are used to measure objects brightness temperature.

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Omidvar K., Khosravi Y. 2012. Synoptic Survey and Analysis of Sand Storms in Yazd-Ardakan Plain, World Applied Sciences Journal 19(2): 198-204.

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Zhang Peng, Nai-meng Lu, Xiu-qing Hu, Chao-hua Dong. 2006. Identification and physical retrieval of dust storm using three MODIS thermal IR channels. Global and Planetary Change 52 (2006) 197-206.

## **Structural and petrological field mapping techniques in regions characterized by plastic to brittle transition during exhumation process: an example from the Aspromonte Massif nappe-like edifice**

Ortolano G. <sup>\*1</sup>, Cirrincione R. <sup>1</sup>, Zappalà L. <sup>1</sup>, Condorelli A. <sup>1</sup>, Romagnoli G. <sup>1</sup>, Tortorici G. <sup>1</sup>, Tripodi V. <sup>2</sup> & Visalli. R. <sup>1</sup>

1. Dipartimento di Scienze Biologiche Geologiche ed Ambientali – Università di Catania. 2. Dipartimento di Biologia, Ecologia e Scienze della Terra – Università della Calabria.

Corresponding email: [ortolano@unict.it](mailto:ortolano@unict.it)

Keywords: Gis-based geological mapping, Structural and petrological data, Calabria, GeoSciML.

Geological mapping of nappe-like edifice composed by metamorphic basement slices overlying by suturing sedimentary covers requires the possibility to handle multi-disciplinary and multi-scale geological dataset from the outcrop- up to the thin section-scale and beyond in order to permit the interaction between meso-structural data with micro-analytical investigations. In this complex geological framework, characterized by rocks which recorded a geological exhumation history traced by a plastic to brittle transition, it is necessary to produce field-related geological data enabling to manage pluri-geothematic interactive data set, possibly organized within an interoperable data management infrastructure.

In this view, in the last years, the geo-science community begin to be increasingly concerned to a geological information modeling based on a structured framework of the geological domain on continuity and compatibility between output generated by different systems, implementing a real interoperability among heterogeneous software platforms. This have been widely developed by IUGS (International Union of Geological Sciences) through the GeoSciML (Geoscience Markup Language) (Laxton, 2010).

In this context, this work purposes an example of field-mapping of an area located in the eastern sector of the Aspromonte Massif (southern Calabria), characterized by an Alpine-Apennine nappe-like structure consisting of three stacked crystalline basement units (i.e. Madonna di Polsi, Aspromonte-Peloritani and Stilo Units), partly sutured by syn- to late-tectonic deposition of the silicic-clastic terrigenous sequence of the Stilo-Capo D'Orlando Formation (SCOF), covered in turn by the back-thrusting (Tripodi et al., 2013) or re-sedimentation (Cavazza and Barone, 2010), of a clay rich mélange (i.e. the Varicolori Clays).

The proposed database infrastructure is essentially based on the last INSPIRE (Infrastructure for Spatial Information in the European Community) guidelines in terms of syntax and logical relations, integrated by the FGDC-GDS (Federal Geographic Data Committee - Geological Data Subcommittee) (<http://www.fgdc.gov>) map symbols, everything to ensure as far as possible, the interoperability of geospatial data, useful to develop new platforms of data sharing.

Cavazza W., Barone M. 2010. Large-scale sedimentary recycling of tectonic mélange in a forearc setting: The ionian basin (Oligocene-Quaternary, southern Italy) *Bulletin of the Geological Society of America*, 122 (11-12), 1932-1949.

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Tripodi V., Muto F. & Critelli S. 2013, Structural style and tectono-stratigraphic evolution of the Neogene–Quaternary Siderno Basin, southern Calabrian Arc, Italy. *International Geology Review*, v. 4, pp 468-481.

## Geological seabed and habitat mapping on SW Sardinia continental shelf

Paliaga E.M. \*, Deiana G., Todde S. & Orrù P.E.

Dipartimento Scienze Chimiche e Geologiche, Università di Cagliari.

Corresponding email: [enricopaliaga@gmail.com](mailto:enricopaliaga@gmail.com)

Keywords: Georeferenced habitat maps; 3D modelling; Geomorphology.

Study area is located on south-western Sardinian continental shelf, several miles off San Pietro island. The structural setting of this continental margin is the result of the superimposition of two successive deformational regimes. The first refers to a compressive geodynamic phase of crustal thickening occurred during the Oligocene - Miocene age, contemporary to the Sardinia – Corsica microplate rotation. The second, more recent, is associated with the Tyrrhenian spreading stage (Masce et al., 2001). DTM obtained from the “MaGIC” (Marine Geohazard along Italian Coasts) project MBES dataset (2009 and 2010 cruises, R/V *Universitatis*) and geological survey conducted in the CARG project framework, allowed us to study main features of the area. The continental shelf is characterized by an irregular morphology with large outcrops of the Oligo-Miocene volcanic-sedimentary succession, bounded on the South-West by the shelf edge situated at -180m. The limit between inner and outer shelf is represented by an array of cliffs engraved in the volcanic substrate. The proximal area is characterized by large mesas, cuestas and other typically volcanic morphotypes such as calderas, necks and mega-dykes, separated by deep incisions often filled by coarse sediments of both bioclastic and terrigenous origin. The distal area, slightly sloping (0,6° - 0,8° degrees), is filled at the basis by the Miocene sedimentary series and by the prograding Plio Pleistocene succession (Lecca, 2000).

A geomorphological analysis of these elements on a huge amount of data, performed in GIS environment, provided a guideline to plan the further ROV survey, as data obtained through Multibeam echosounder were used to create different maps where ROV transects are reported in respect to:

- Three-dimensional georeferenced shaded relief maps of investigated sites;
- Slope of the substrata.
- Aspect maps of sea bottom related to bottom currents.
- Profile curvature, which describes the rate of change of slope along a profile in the surface and may be useful to highlight convex and concave slopes across the DTM (Wilson et al., 2007)

Geological hypothesis calibration and biological data on coralligenous assemblages were collected by researchers during a Remotely Operated Vehicle survey (ROV “Pollux”) carried out onboard the R/V *Astrea* during Autumn 2011 & 2013.

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## **First results of a 3D geological model in northern Latium to support the assessment of conventional and unconventional geothermal resources**

Petracchini L.\*<sup>1</sup>, Scrocca D.<sup>1</sup>, Spagnesi S.<sup>1</sup> & Minelli F.<sup>2</sup>

1. Consiglio Nazionale delle Ricerche, IGAG, Roma. 2. Università Sapienza, Roma.

Corresponding email: [lorenzo.petracchini@igag.cnr.it](mailto:lorenzo.petracchini@igag.cnr.it)

Keywords: Latium Region, 3D model, geothermal resources.

Italy, after over one century from the first geothermal energy production, has still a relevant unexploited geothermal potential, in particular in the peri-Tyrrhenian regions of Tuscany and Latium. According to the Ministry of Economic Development of Italy an increase in submitted exploration applications and in awarded exploration permits has been observed in the last years. It is worth to note that 23 exploration applications in Italy (data referred at the end of 2013) out of 38 are within Latium.

To promote this promising resource, to support public authorities, and to facilitate private investments, the Italian National Research Council has started the "Geothermal Atlas project". The main aim of the project is to update and organize all the relevant data (geological, geophysical, geochemical, hydrogeological etc.) aiming to characterize and to re-evaluate conventional and unconventional geothermal resources for electricity generation in the central-southern regions of Italy.

The present work shows the first results of an integrated review of the available data in the northern sector of Latium Region in order to reconstruct the 3D subsurface geological model. More than 80 wells, several geological profiles, geological and geophysical maps, hydrogeological and geochemical data have been all collected and analyzed. The 3D model has been generated according to the different thermal conductivity properties of the sedimentary sequences to define the principal lithothermal units.

The future step of this work is to integrate this 3D model with the known hydrogeological system in the Latium region, and to analyzed the effects of the fault network on fluid circulation.

## **Database conceptual design and geological field work**

Piana F.\*

CNR, Istituto di Geoscienze e Georisorse - Unità di Torino.

Corresponding email: [f.piana@csg.to.cnr.it](mailto:f.piana@csg.to.cnr.it)

Keywords: geological mapping, geological database, geological conceptual models.

Databases are one of the two fundamental constitutive parts of modern geological data sets and maps, being the other one represented by geometric-spatial features in a georeference system.

The increasing use of GIS technologies in Earth Sciences can lead scientists and technicians to plan geological investigations and/or mapping (for a given knowledge domain or geological object) starting firstly from the definition of the conceptual model and the related database design.

Database designing prior to the effective beginning of the research activities can have important effects on knowledge paths and conceptualizations performed by researchers as individuals, as well as on the mutual understanding between the members of a research group or a field-work staff.

Cost-benefit analysis is thus due for these instances both as regard the quality of the scientific results and the amount of consumed time.

Furthermore, managing of great amount of georeferenced data should be driven in a way proper for sharing information to a wide range of geological data end-users, such as infrastructures designers, decision makers and human communities. Geological maps and related database should play a crucial role in getting geo-environmental information available (WebGIS, WMS geo-portals) as well as to ensure retraceability of data and interpretation upon which environmental political decisions are taken.

Working experiences from geological mapping projects in some locations of Alpine-Maghrebide area, in the frame of both pure and applied researches are illustrated to allow discussion on the above described issues.

## Interpretation of the urban areas subsidence detected by multitemporal DInSAR: the Cassino test site

Saroli M.<sup>1</sup>, Albano M.<sup>2</sup>, Polcari M.\*<sup>2</sup>, Montuori A.<sup>2</sup>, Tolomei C.<sup>2</sup>, Lancia M.<sup>1</sup>, Moro M.<sup>2</sup>,  
Modoni G.<sup>1</sup> & Stramondo S.<sup>2</sup>

1. Dipartimento di Ingegneria Civile e Meccanica - Università degli studi di Cassino e del Lazio meridionale. 2. Istituto Nazionale di Geofisica e Vulcanologia, Roma.

Corresponding email: [marco.polcari@ingv.it](mailto:marco.polcari@ingv.it)

Keywords: SAR Interferometry, Subsidence, Groundwater.

Cassino municipality is located in a plio-pleistocenic basin, delimited by Latina Valley at SW, Cairo-Monteccasino Mt. at NW, and Venafrian Mt. at NE. Two structural lines that behave as cinematic release delimit the area, i.e. the Ortona-Roccamonfina and Val Roveto Atina Caserta line. The latter passes through the eastern margin of the basin and is an active fault in the segment between Sant Elia and San Pietro Infine. Stratigraphic sequence belongs to the Latium-Abruzzi platform, two thousand meter of dolostone and limestone. Platform is covered by tortonian post-collisional arenaceous and clayey deposits followed by piggy-back sequence. The plio-pleistocenic filling has an epi-continental and continental origin with loose gravels, loose sands and pudding stones on the bottom of a lacustrine series. Lacustrine environment is due to the volcanic edifice construction through the obstruction of Latina Valley. The thickness of the lacustrine deposit can reach even 80-100m. The hydrogeological conditions of the area are characterized by the presence of a multilayered surficial phreatic aquifer consisting of Plio-Quaternary deposits, which overlaps a deep confined carbonatic aquifer. The delivery of the carbonatic acquifer is represented by the Gari springs ( $Q= 15-20$  m<sup>3</sup>/s). The geological and hydrogeological conditions are predisposing to natural and anthropogenic subsidence. The aim of the present work is to investigate the natural and/or anthropic subsidence characterizing the alluvial valleys of central Italy, focusing the attention on the Cassino plain. In order to investigate slow surface displacements characterizing the selected plain, the Differential Interferometric Synthetic Aperture Radar (DInSAR) technique is applied to a dataset of 35 Envisat SAR images, acquired along descending orbit and spanning from September 2003 to August 2010. A Multi-baseline and multi-temporal approach is used to retrieve information about the mean velocity displacements and time series over the selected test area.

The velocity map shows areas affected by subsidence rate of about 1.5 mm/year very limited to the Cassino plain and this result is further confirmed by the analysis of time series extracted by some points in the plain. The latter analysis is both compared to a detailed geological and geotechnical investigation about the lithostratigraphy of the alluvial sediments in the Cassino plain, and then combined with a temporal reconstruction of the city expansion over the alluvial valley. This analysis allows depicting the main factors controlling the observed subsidence, i.e. the in situ effective stress conditions, the compressibility and viscous characteristics of the loaded soils, the thickness of the compressible stratum and the entity of loading.

## Seismotectonic and landslides map of the Crati graben at scale 1:50.000 (Calabria, Southern Italy)

Tansi C.\*<sup>1</sup>, Folino Gallo M.<sup>2</sup>, Muto F.<sup>3</sup>, Magnelli D.<sup>1</sup>, Perrotta P.<sup>1</sup>, Russo L.<sup>1</sup> & Critelli S.<sup>3</sup>

<sup>1</sup> Italian National Research Council – Research Institute for Geo-Hydrological Protection (CNR- IRPI). <sup>2</sup> ARPACAL, Regional Agency for Environmental Protection of Calabria, Catanzaro Lido (CZ). <sup>3</sup> DiBEST, Department of Biology, Ecology and Earth Sciences, University of Calabria.

Corresponding email: [carlotansi@libero.it](mailto:carlotansi@libero.it)

Keywords: recent and active tectonics, landslides, GIS.

Through a scientific collaboration between the Italian National Research Council – Research Institute for Geo-Hydrological Protection (CNR-IRPI) and the Province of Cosenza, in the light of two years of work, has been updated in detail the framework of hydrogeological risk areas and have been mapped the main active and recent faults, together with the instrumental and historical seismicity, of the Crati Graben. The graben is located in the northern side of Calabrian Arc (southern Italy).

The areas at risk from landslides hazard, and the active/recent faults, have been identified and classified, originally in detail scale (1:5.000) and, finally, represented at 1:50.000 scale.

The research has been carried out, by aerial photographic and satellite image interpretation, and field surveys, led to the identification the areas in which they occurred geo-hydrological instability phenomena - many of which destructive - caused by extreme meteorological events that characterized the winter seasons 2008-2012. Analysis involved a significant round of urban areas, as well as facilities and infrastructure of strategic importance (schools, hospitals and stata and provincial roads). Overall have been identified 2690 landslides of which, 1575 slides, 232 flows, 185 complex landslides, 655 landsliding zones, 43 intense erosion areas.

The area was also characterized by a geo-structural point of view, through macro-and meso-structural studies. In particular, measurements of structural data comprise orientations of 567 fault planes with slickensides, gathered from 52 measure stations located along the main faults.

The Crati graben is mainly controlled by extensional N-S striking faults and WNW-ESE transcurrent faults, in its northern and southern extremity. From a morphological point of view the faults are characterized by a remarkable freshness. The comparison of the data showed a good correlation between tectonic structures and areas affected by landslides.

The recent and active faults were compared with the historical and instrumental seismicity, in order to identify the main seismogenic structures.

The analysis of seismological, geo-structural and geomorphological was performed in a Geographic Information System environment (we used the software Quantum GIS), through different steps that have allowed for the structuring of a database for different types of data, spatial analysis information and their interpretation. The data were geo-referenced in UTM (Universal Transverse Mercator) with WGS84 Datum.

In the final analysis we obtained a complete and updated knowledge framework of risk conditions of the whole province, where the risk areas are hierarchized according to the destructive potential of landslides and floods. This document is therefore a useful reference in planning and priority in the design of interventions for the safety of slopes and waterways.

## The Western Alps ophiolites and their cover rocks. A case study from the St. Marcel Valley (Aosta)

Tartarotti P.\*<sup>1</sup>, Martin S.<sup>2</sup>, Monopoli B.<sup>3</sup>, Benciolini L.<sup>4</sup> & Schiavo A.†

1. Dipartimento di Scienze della Terra "A. Desio" - Università degli Studi di Milano. 2. Dipartimento di Geoscienze - Università di Padova. 3. Land Technology & Services S.r.l. 4. Dipartimento di Chimica, Fisica e Ambiente, sezione Georisorse e Territorio - Università di Udine.

Corresponding email: [paola.tartarotti@unimi.it](mailto:paola.tartarotti@unimi.it)

Keywords: Western Alps, ophiolite, metasediments.

The Aosta Valley ophiolites and related sediments pertain to the Piemonte Nappe, i.e. the fossil lithosphere of the Mesozoic Tethyan ocean sandwiched between the Penninic and Austroalpine continental domains. In the St. Marcel Valley (Aosta), ophiolites and sediments have been metamorphosed under HP conditions during subduction in Eocene (Dal Piaz et al., 2001), and partly retrogressed to greenschist-facies conditions during exhumation. Three main units were recognized: the Fontillon-Servette unit made of glaucophanite, eclogite, metagabbro, and chloritoid-rich chloriteschist and talcschist hosting Cu-Fe mineralizations (Martin et al., 2008); the Mt. Roux-Mt. Corquet unit made of metagabbro, quartzites, marble, and calcschists; the Plan Ruè-Grand Avert unit made of metabasalt with relict pillow structures, Mn-quartzite, marble, and calcschists. The metaophiolites are tectonically overthrust by the Austroalpine Mt. Emilius klippe both showing a similar eclogitic imprint of Eocene age (Dal Piaz et al., 2001). A new 1:10.000 scale geological map, integrated with detailed lithostratigraphic sections, reveals that the metasedimentary cover is made of three rock types represented by quartzites, marbles, and calcschists. Quartzites include Mn-rich quartzite commonly characterized by pink to yellow and black colours, white and mica-poor quartzite, and grey fine-grained mica-rich quartzite. Marbles consist of grey fine-grained marble; yellowish coarse-grained garnet-rich marble, and micaceous marble. Calcschists include black micaceous and graphite-rich calcschist; carbonate-rich calcschist, and dm-to m-thick marble layers alternating with carbonaceous schists. This sequence is interpreted as deriving from original radiolarian chert, limestone, and flysch-type sediments covering the ophiolitic basement and is comparable to the cover of the Ligurian ophiolites consisting of radiolarian cherts, Calpionella limestone, and "Palombini shale" (Cortesogno et al., 1987). Differently from most Aosta Valley ophiolites dominated by lower crust and mantle rocks, here ophiolites represent the shallowest part of the Tethyan oceanic lithosphere created not far from the ridge axis where the formation of hydrothermal vents was facilitated.

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## Remote sensing analysis of the Laguna Blanca basin in the Central Andean Plateau (Catamarca, Argentina)

Traforti A.\*, Massironi M. & Zampieri D.

Dipartimento di Geoscienze, Università degli studi di Padova.

Corresponding email: [anna.traforti@yahoo.it](mailto:anna.traforti@yahoo.it)

Keywords: remote sensing, geological mapping, ASTER, Andean Plateau, SAM classification, spectral signatures.

Satellite remote sensing is extensively used for geological mapping, especially in arid regions. In this work, images from multispectral sensor (ASTER and Landsat 7 ETM+) and medium resolution Digital Elevation Models (SRTM and ASTER GDEM) were used to map the Laguna Blanca area (26°35'S-66°49'W). This sector of the southern-central Andes is localized in the Argentina region of Catamarca, along the south-eastern margin of the Puna plateau. The study area is characterized by a low grade metamorphic Precambrian basement, intruded by Ordovician granitoids. These rocks are unconformably covered by a volcano-sedimentary sequence of Miocene age, followed by volcanic and volcanoclastic rocks of Upper Miocene to Plio-Pleistocene age. All these units are cut by two systems of major faults, locally characterized by wide damage zones (15-20 m). The geological mapping was carried out using ASTER image on visible and near infrared (VNIR) and shortwave infrared (SWIR) bands and field checks. On the base of field and petrographic knowledge of the outcropping lithologies, we were able to detect the principal lithological contacts using false color composites, band ratios (BR), relative absorption band-depths (RBD) and spectral angle mapper supervised classifications (SAM). High-resolution spectral signatures of samples collected in the field were of fundamental importance to define specific elaborations of ASTER images. In particular, the spectral data of each lithology were obtained using a Varian-Cary 5000R spectrophotometer (with wavelength range from 0.35µm to 2.5µm and 1nm sampling step). The high-resolution spectral signatures were resampled at the ASTER sensor resolution and used to identify the ASTER bands for BR and RBD elaborations. They were also applied for SAM supervised classification, but in this case spectral signature retrieved from specific Region of Interest (ROI), directly derived from the ASTER image, were much more effective in lithology discrimination. The detection of the principal tectonic lineaments in the study area were enabled by image sharpening of Landsat 7 ETM+ images and hill shades of medium resolution DEMs. In particular, the identification of two prominent fault zones were realized by SAM supervised classification on ASTER images. In this case the SAM classification based on high-resolution spectral signatures of samples collected in the field from faults cores was very effective. The spectral signatures were collected using a Field-Pro spectrophotometer (with wavelength range from 0.35µm to 2.5µm and 1nm sampling step) and resampled at the ASTER sensor resolution.

The results of this work confirm the good support for the geological mapping given by the analysis of multispectral remotely sensed images (ASTER and Landsat 7 ETM+) and DTMs (SRTM and ASTER GDEM) and define the SAM supervised classification on ASTER image as a possible way to identify prominent fault zones on the base of the spectral signatures of fault-rock gouges.

## **Sequential constraints in the stratigraphy of terraced marine deposits of the Metaponto area (Geological Sheet 508 "Policoro", Basilicata, Southern Italy)**

Tropeano M.\*<sup>1</sup>, Cilumbriello A.<sup>1</sup>, Gallicchio S.<sup>1</sup>, Grippa A.<sup>2</sup>, Longhitano S.G.<sup>3</sup> & Sabato L.<sup>1</sup>

1. Dipartimento di Scienze della Terra e Geoambientali, Università degli Studi di Bari "A. Moro". 2. School of Geosciences, Department of Geology and Petroleum Geology, University of Aberdeen. 3. Dipartimento di Scienze, Università della Basilicata, Potenza.

Corresponding email: [marcello.tropeano@uniba.it](mailto:marcello.tropeano@uniba.it)

Keywords: Terraced marine deposits, Metaponto Coastal Plain, Quaternary.

Landwards of the Metaponto Coastal Plain in Basilicata (Southern Italy), the hinterland of the Gulf of Taranto is characterized by the presence of a series of depositional marine terraces developed since middle Pleistocene. It is generally accepted that each depositional marine terrace represents a coastal sedimentary wedge developed during a relative highstand of the sea level in a context of regional uplift. The most recent of these coastal wedge is still prograding, and its upper part (late Holocene) corresponds to the Metaponto Coastal Plain.

The Sheet 508 "Policoro" of the new geological map of Italy comprises sectors of the lowermost (and youngermost) of these terraces and a large sector of the coastal plain too. During the geological survey, a detailed sedimentologic and stratigraphic study was carried out on both outcropping and drilled successions. On the base of sharp/erosional contacts between different facies, vertical stacking of several shallowing upward coastal sequences (cycles), and stratigraphic (physical) correlations between the measured sections, it has been observed that the terraced marine-deposits cropping out in the Metaponto area record several high-frequency relative sea-level changes, each of which cannot be simply linked to a terraced surface. According to chronostratigraphic data, and following a sequence-stratigraphy approach, some of these cycles may be correlated to substages of the MIS (Marine Isotope Stage) curve. Moreover, a coastal wedge buried below the present-day Metaponto Coastal Plain and deeply dissected by incised valleys was found at a depth between -20 and -40 meters respect to the present sea level and was tentatively attributed to the MIS 3. Thanks to resonance properties of the subsurface, the buried landscape was obtained in a 3D visualization, highlighting location and shape of incised valleys and interfluvial areas (top of the remnants of the MIS 3 coastal wedge) during the LGM (Last Glacial Maximum).

In conclusion, the number of sea-level oscillations locally recorded below each terraced surface (comprising the present-day coastal plain) suggests that studies based only on geomorphological evidences are not sufficient to describe the complex interaction between regional uplift and middle-late Quaternary relative sea-level changes.

## Mapping relationships between deformation, magmatism and metamorphism in the Biella and Traversella plutons (Western Italian Alps)

Zanoni D.\*<sup>1</sup>, Gosso G.<sup>1-2</sup> & Spalla M.I.<sup>1-2</sup>

1. Università degli Studi di Milano - Dipartimento di Scienze della Terra "A. Desio". 2. CNR-IDPA, Milano.

Corresponding email: [davide.zanoni@unimi.it](mailto:davide.zanoni@unimi.it)

Keywords: Biella and Traversella plutons, from surface maps, Alpine Oligocene magmatism.

Structural and petrographic maps are the indispensable data display to unravel the interplay of processes active during the evolution of geodynamic environments that ultimately forge the lithosphere of orogenic belts. This work presents a mapping method addressed to show relationships between deformation, magmatism and metamorphism necessary to explore mechanical and thermal processes on going during magma intrusion and to unravel crustal levels and geodynamic scenarios of magma emplacement. The focus is on the Oligocene intrusive stocks (Zanoni et al., 2010) emplaced in the continental HP Sesia Lanzo Zone (SLZ) in the western Austroalpine domain. Structural and petrological data, obtained at 1:5,000 scale, were synthesised and represented in maps at the original scale or 1:10,000 scale. Objective and interpretative maps contain lithostratigraphic, structural (orientation of successive fabric elements, foliation trajectories) and petrological data (mineral support of tectonic, mylonitic and coronitic fabrics). Timing relationships of magma intrusion and deformation are unravelled by analysis of orientation data and structural overprints and represented by from surface maps. Being the SLZ rocks analysed in the contact aureole, where pre-intrusive mineral assemblages are variably affected by contact metamorphism, the correlation of ductile structures relies on geometrical criteria (e.g. Williams, 1985) and take into account also mineral assemblages defining superposed fabrics (e.g. Spalla et al., 2005; Hobbs et al., 2010) only where the contact metamorphism is weak. Mesostructural analysis, integrated by reiterated microstructural analysis, makes possible representing the degree of reaction progress during contact metamorphism, on the ground of contact mineral modal amount.

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## **SESSIONE S31**

### **Geodynamics of the Alpine orogenic systems: from surface processes to deep dynamics**

*CONVENORS*

*G. Capponi (Univ. Genova)*

*M. Malusà (Univ. Milano Bicocca)*

*G. Prosser (Univ. Basilicata)*

## **New structural data for pre-Tyrrhenian thrust tectonics in the Mesozoic carbonate units of Eastern Sardinia**

Arragoni S.\*, Cianfarra P., Maggi M. & Salvini F.

Dipartimento di Scienze, sezione di Geologia, Università degli Studi di Roma Tre

Corresponding email: [simone.arragoni@uniroma3.it](mailto:simone.arragoni@uniroma3.it)

Keywords: pre-Tyrrhenian thrusting, Eastern Sardinia, Mesozoic carbonates.

New structural data collected in the Tacchi and Golfo di Orosei regions provide further constraints for thrust tectonics in the Mesozoic carbonate units outcropping in Eastern Sardinia.

These units consist of shallow water carbonate deposits of middle Jurassic-lower Cretaceous age (Costamagna and Barca, 2004) and show analogies with the Southern Apennine carbonate platforms, although the Sardinian units are characterized by a more continental affinity in their lowermost portions.

Two structural styles have been recognized moving from south to north.

In the southern sector (Tacchi area) these sequences lay sub-horizontally on top of lower Jurassic continental deposits (Genna Selole formation). This initial stratigraphic contact is locally reused as regional thrustings. Secondary structures (duplexes) and deformation style are typical of thrust faulting in a flat-over-flat geometry at the lower detachment (younger on older thrusting). A general top-to-the-west transport can be recognized by brittle kinematic indicators (synthetic and antithetic cleavage shear planes) and slickenlines.

In the northern sector (Golfo di Orosei) the carbonate units rest directly on top of the Paleozoic basement. This contact is usually preserved showing subordered (late) deformation. The structural setting in this area is characterized by E-dipping monoclines separated by sub-horizontal sectors. Locally, low-angle reverse faults are observed within the carbonate units in a ramp-on-flat geometry, evidenced by asymmetric N-S folding observed in the western forelimbs.

Transpressive faulting postdates the thrusting and is chronologically constrained by the Cuccuru 'e Flores conglomerates, a syn/post-tectonic unit made of shallow water carbonate and basement clasts of uncertain age (Lutetian or Oligocene-Aquitainian, Oggiano et al 2009 and references therein).

In both sectors, NE-SW strike-slip faults related to the Sardinia-Corsica block rotation during Miocene time (Oggiano et al., 2009) postdate compressive structures.

Cross-cutting relation and syn-tectonic deposits allow to propose an Eocene-Oligocene age for the thrust tectonics.

The found structural style shows analogies with sectors of the Latium-Abruzzi fold-and-thrust belt, where a Cretaceous-over-Jurassic thrust is present (Simbruini Mts.) and locally the hangingwalls are topped by continental-to-lacustrine deposits of uncertain Miocene age.

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Oggiano G., Funedda A., Carmignani L. & Pasci S. 2009. The Sardinia-Corsica microplate and its role in the Northern Apennine Geodynamics: new insights from the Tertiary intraplate strike-slip tectonics of Sardinia. Boll. Soc. Geol. It., 128 (2), 527-539.

## Understanding *mélange* and *mélange*-forming processes: new constraints for the tectonic evolution of the Alpine orogenic system

Festa A.\*<sup>1</sup>, Pini G.A.<sup>2</sup>, Dilek Y.<sup>3</sup>, Ogata K.<sup>4</sup>, Balestro G.<sup>1</sup> & Tartarotti P.<sup>5</sup>

1. Dipartimento di Scienze della Terra, Università di Torino. 2. Dipartimento di Matematica e Geoscienze, Università di Trieste. 3. Department of Geology and Environmental Earth Science, Miami University, Oxford - OH, USA. 4. Dipartimento di Fisica e Scienze della Terra "Macedonio Melloni", Università di Parma. 5. Dipartimento di Scienze della Terra, Università di Milano.

Corresponding email: [andrea.festa@unito.it](mailto:andrea.festa@unito.it)

Keywords: *Mélanges*, Broken Formations, Apennines, Alps, convergent plate margins.

Chaotic rock units with block-in-matrix structure, commonly known as *mélanges* and broken formations, are one of the hallmarks of the Alpine orogenic system and of many exhumed convergent plate margins throughout the world. They commonly form in different tectonic settings and structural levels during the evolution of convergent plate margins, reflecting a close relationship between the active processes (tectonic, sedimentary and diapiric), and the physical and mechanical conditions experienced by rocks. Hence, systematic and process-oriented, inter-disciplinary studies of these units may provide much-needed information about the evolution of the Alpine orogenic system and convergent plate margins in general.

The relationships between the final block-in-matrix structure and the processes of their formation commonly are, however, obscure and controversial, because of the complex and seemingly chaotic nature. The overlap of shearing, tectonic mixing, and metamorphic recrystallization lead to the reworking and change of the initial block-in-matrix structures formed by different processes (e.g., sedimentary or diapiric), and to the formation of polygenetic *mélange*. In this framework, block-in-matrix units formed by sedimentary processes may result very difficult-to non-distinguishable when placed in settings such as, for example, accretionary wedges or in a subduction channels or after a complete cycle from subduction to collision, exhumation and intra-continental deformation.

We present here different examples of block-in-matrix bodies from the Alpine orogenic system, showing that at shallower structural levels, *mélange*-forming processes commonly operate in complex and mutual interactions, hence in partial superposition and rarely in isolation. In the geological record of *mélanges* we commonly observe as the best-preserved evidence the artifacts of the last and/or more pervasive process. In most cases, the latter is consistent with tectonics, although sedimentary and/or diapiric-derived structures still characterize notably examples. We show here a comparative analysis of on-land exhumed examples of *mélanges* and tectonic environments where *mélange*-forming processes are currently operating. Main types of deformational mode leading to *mélange* formation include extensional, strike-slip, convergent margin/collisional tectonics, and intra-continental deformation.

We discuss:

- (1) possible relationships between various *mélange* types and their tectonic setting of formation;
- (2) contribution of mass-transport versus contractional tectonic deformation processes at the onset of *mélange* formation
- (3) nature of the "continuum" and transition from broken formations to true tectonic *mélanges*.

## Deep controls on Foreland Basin System evolution along the Sicily Thrust Belt

Gasparo Morticelli M.\*, Valenti V., Catalano R., Sulli A., Agate M., Avellone G., Albanese C. & Basilone L.

Dipartimento di Scienze della Terra e del Mare, Università di Palermo.

Corresponding email: [mauro.agate@unipa.it](mailto:mauro.agate@unipa.it)

Keywords: Wedge-top basin, Syn-sedimentary tectonics, restoration, Sicily.

The palinspastic restoration of the Sicilian crustal geological cross section (Catalano et al., 2013) points out two subsequent main thrust (MT1 and MT2) active during the Neogene tectonic evolution as well as the decrease of slip and shortening rate estimated for MT2 with respect to MT1 early main thrust. During orogenic building, syn-tectonic deposits are accumulated inside wedge-top-basin that grow on top of thrust sheets. Sedimentary and stratigraphic features of wedge-top basin change through time following fold and thrust belt evolution. Neogene-Quaternary syn-tectonic successions (terrigenous, evaporitic, hemipelagic and shallow water deposits) extensively crop-out, in more or less wide wedge-top-basins, above the Sicilian Fold and Thrust Belt (Gugliotta et al., 2014 with references therein).

These deposits can be grouped in three main sedimentary successions characterized by basal unconformity surface on deformed substrate (thrust wedge) that, also, represent the depositional interface of coeval wedge-top and foredeep basins: i) middle-late Miocene terrigenous, deep-water succession, accommodated on top of accreted Numidian Flysch nappes; ii) late Miocene deepening upwards succession unconformably covering the inner sector of the FTB constituted by thrusting of Meso-Cenozoic deep-water succession (Sicilide, Imerese and Sicanian Units); iii) Upper Pliocene – Quaternary shallow water succession unconformably covering (in the outer sector of the FTB) a tectonic pile (Gela Thrust System) made by thrusting of the former syn-tectonic succession. Tectono-sedimentary evolution of these basin was controlled by the deepening of the structural levels that were active during fold and thrust belt growth. A crucial change was recorded by the wedge-top depozone during late Pliocene-Pleistocene, when a deeper thrust plain (MT2), cut and thickened the crystalline basement (in the inner sector of the FTB), evolving the thrusting model from thin to thick skinned. As consequence of the involvement of the basement in the Sicilian FTB, and of increased orogenic deep load, the foreland basin system recorded a narrowing of the foredeep:

- during late Tortonian – early Pliocene, regional lithofacies distribution accounts for a wide foredeep that included the present day Iblean Plateau and its offshore;

- following the involvement of the basement and consequent increased orogenic load, the foredeep narrowed up to present day wideness, confined between the deformed outermost units of the GTS, to the NW, and the outcrop of the carbonate successions of the Iblean foreland, to the SE.

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## **Pre-Tyrrhenian tectonic evolution in the Mesozoic carbonate units of Eastern Sardinia from 3D (2D + t) modeling**

Maggi M.\*, Cianfarra P., Arragoni S. & Salvini F.

Dipartimento di Scienze, Sezione Geologia, Università degli Studi Roma Tre.

Corresponding email: [matteo.maggi@uniroma3.it](mailto:matteo.maggi@uniroma3.it)

Keywords: Tertiary thrust tectonics, Eastern Sardinia, balanced cross-section.

Cenozoic tectonics in Sardinia include the effects of the rotation of the Sardinia-Corsica block during Oligocene and the later opening of the Tyrrhenian sea starting from lower Miocene (Oggiano et al., 2009 and references therein). These produced extensional faulting in the south-western sector and strike-slip-to-oblique faulting in the Ogliastra and Golfo di Orosei regions, where Mesozoic shallow water carbonates outcrop (Costamagna and Barca, 2004 and references therein). New structural data and the observed geometry show the presence of dip-slip compressive tectonics and thrusting involving the Mesozoic carbonates and their basement prior to the development of the strike-slip faulting.

In this presentation these new structural observations are integrated with the available geological and geophysical datasets allowed to produce a preliminary balanced and admissible cross section to reconstruct the tectonic evolution of eastern Sardinia prior to the opening of the Tyrrhenian basin.

This tectonics event has been preliminary analyzed to allow the preparation of a 3D (2D + time) evolutionary model. The section trajectory has been selected parallel to the tectonic transport direction, around E-W with a westward vergence (top-to-the-W).

The model shows the emplacement of a thrust tectonic event with thin-skin geometry and involving Cretaceous-over-Jurassic thrusting ("younger-on-older" tectonics) that represents basal flat décollements, best visible in the Tacchi region. Slices of basement are locally involved in the thrusting and have been recognized in the ramp-to-flat sector (Golfo di Orosei region).

Results show the presence of a widespread thrusting event that affected the eastern sector of Sardinia in Eocene-Oligocene time. The modelled tectonics style confirmed the thin-skin geometry and is characterized by décollements at different depths, including the J-K boundary. Similar geometry have been described in the early tectonic evolution of the Latium-Abruzzi sector.

Costamagna L.G. & Barca S. 2004. Stratigrafia, analisi di facies, paleogeografia ed inquadramento regionale della successione giurassica dell'area dei Tacchi (Sardegna Orientale). *Boll. Soc. Geol. It.*, 123, 477-495, 8 ff.

Oggiano G., Funedda A., Carmignani L. & Pasci S. 2009. The Sardinia-Corsica microplate and its role in the Northern Apennine Geodynamics: new insights from the Tertiary intraplate strike-slip tectonics of Sardinia. *Boll. Soc. Geol. It.*, 128(2), 527-539.

## Zircon (U-Th)/He dating of the Penninic basal thrust emplacement

Maino M.\*<sup>1</sup>, Stuart F.<sup>2</sup>, Ceriani A.<sup>1-3</sup>, Decarlis A.<sup>4</sup>, Di Giulio A.<sup>1</sup>, Seno S.<sup>1</sup>, & Setti M.<sup>1</sup>

1. Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia. 2. Isotope Geosciences Unit, SUERC, Scottish Enterprise and Technology Park, East Kilbride, UK. 3. The Petroleum Institute, Abu Dhabi, United Arab Emirates. 4. IPGS/EOST, Strasbourg, France.

Corresponding email: [matteo.maino@unipv.it](mailto:matteo.maino@unipv.it)

Keywords: Alps, thrust, Thermochronometry, zircon (U-Th)/He dating, Helminthoid Flysch.

We presents new zircons (U–Th)/He (ZHe) ages from the thrust fault damage zone and surrounding wall rocks to determine the emplacement age of the southernmost segment of the Penninic basal thrust. Thermochronometry is integrated with X-ray diffraction analysis of clay minerals (illite crystallinity) and fluid inclusion microthermometry on vein-filling minerals to constrain the temperature conditions of the damage zone and the wall rocks during thrusting. This approach has been applied to the basal thrust of the Helminthoid Flysch, which represents the tectonic front of the European Alps accretionary wedge. Zircons selected for He dating are from Early Cretaceous arkosic sandstones the base of which has been involved into the thrust zone.

ZHe ages of the fault rocks are completely reset ( $28.8 \pm 3.4$  to  $33.8 \pm 4.0$  Ma) while the wall rock samples show pre-depositional inherited ages ( $117.4 \pm 14$  to  $158.7 \pm 18.9$  Ma). Thermal constraints support warmer conditions ( $\sim 220$ - $300^\circ\text{C}$ ) within the fault damage zone respect to the wall rocks ( $< \sim 200^\circ\text{C}$ ), with the presence of a transition zone corresponding to a gradual increase of ZHe ages at progressive distance from the top of the fault damage zone.

These results are in excellent agreement with the available independent geological and thermochronometric constraints that support early Oligocene movement of the basal thrust of the Helminthoid Flysch. Our results underscore, for the first time, the validity of ZHe technique as a reliable thermochronometer to dating brittle faults developed into shallow crustal levels ( $< 6$ - $7$  km) on geological timescales.

## Oblique subduction and size of the accretionary prism: insight from 3D numerical modeling

Malatesta C.\*<sup>1</sup>, Gerya T.<sup>2</sup>, Crispini L.<sup>1</sup>, Federico L.<sup>1</sup> & Capponi G.<sup>1</sup>

1. DISTAV, Università di Genova. 2. Institute of Geophysics, Swiss Federal Institute of Technology (ETH-Zurich), Switzerland.

Corresponding email: [cristina.malatesta@unige.it](mailto:cristina.malatesta@unige.it)

Keywords: Sediments lateral migration, oblique subduction, 3D numerical models.

A great number of subduction zones on Earth derive from the oblique convergence between plates. These processes affect margins thousands of kilometers-long and sometimes oblique subduction zones delimit entire continents (i.e. Chile margin).

Using 3D numerical simulations, we investigated geodynamic processes and morphologies occurring along the same plate margins at these particular subduction settings. The models that we defined are based on thermo-mechanical equations solved with finite differences method and marker-in-cell techniques combined with a multigrid approach. An intraoceanic subduction 100-km far from the continental margin is represented in our reference model (Malatesta et al., 2013). We considered a layered oceanic crust with a 5-km-thick layer of gabbro overlain by a 3-km-thick layer of basalt. A 1-km-thick sediment cover seals the sequence. The convergence rate of plates is about 3 cm/yr; the oblique convergence is obtained using velocity vectors that are applied on the lateral boundaries of the model and form an angle of 45° with the initial starting point of subduction (weak zone in the lithosphere).

Sediments are carried into the trench soon after convergence initiation and they are later buried into the subduction zone. According to the trench-parallel component of subduction velocity, a certain amount of sediments migrates laterally in the accretionary prism and along the slab at different depths. This lateral tectonic migration is testified by velocity vectors that have modules comparable to the plate convergence rate. Sediments move till they reach a "barrier": lateral boundaries in our models are in fact not permeable to material transit and they do not allow sediments to pass through them. Therefore the material starts to accumulate against the boundary and locally widen the accretionary prism. This ongoing mechanism produces the variation of morphology and geometry of the accretionary prism along trench-strike and the gradual transition from a sediment-poor to a sediment-rich margin along the same subduction zone. We moreover noticed that greater degrees of obliquity of the subduction zone, or higher rate of plate convergence, sharpen the along-trench variations of the accretionary prism size.

Heterogeneous accretionary prisms occur at several oblique subduction zones around the world (i.e. southern Ryukyu, Hikurangi, Sumatra and New Britain). We think that the lateral tectonic migration of sediments could be one of the possible mechanisms that contribute to determine the varying sediment amount in these prisms, and that in these cases the physical barriers stopping the tectonic migration could be sites of arc-continent/continent-continent collision or strong curvature of the trench.

Malatesta C., Gerya T., Crispini L., Federico L. & Capponi G. 2013. Oblique subduction modelling indicates along-trench tectonic transport of sediments. *Nat. Commun.*, 4, 2456, DOI:10.1038/ncomms3456.

## From ductile to brittle behavior in blueschist-facies mylonite: implications for deformation processes in subduction zones

Malatesta C., Federico L.\*, Crispini L. & Capponi G.

Dipartimento di Scienze della Terra dell'Ambiente e della Vita, Università di Genova.

Corresponding email: [federico@dipteris.unige.it](mailto:federico@dipteris.unige.it)

Keywords: subduction zone, ductile and brittle deformation, blueschist facies metamorphism.

Progressive evolution from ductile to brittle deformation has been observed in a mylonite outcrop at the contact between two metaophiolitic high pressure units of the Alps (the eclogitic Voltri Unit and the blueschist Montenotte Unit; Ligurian Alps, NW Italy). The transition between the different deformation regimes occurs at constant HP-LT metamorphic conditions, i.e. in the blueschist facies within the same structural level.

The mylonite is a fine grained metabasite with a MORB-type geochemical affinity. The main mylonitic foliation is defined by alternate compositional layers consisting either of: *i*) Mg-riebeckite/glaucophane, *or ii*) clinozoisite/Fe-epidote + Mg-riebeckite/glaucophane + sphene + white mica + albite + oxydes, *or iii*) white mica + albite. Along the mylonitic foliation, pseudomorphs of Mg-riebeckite + Fe-epidote + albite (replacing older pyroxene) occur with glaucophane fringes.

The mylonitic foliation is deformed by multiple isoclinal, non-cylindrical folds with the axial plane foliation still coincident with the mylonitic foliation. Such folds are deformed by a symmetric chocolate tablet foliation boudinage. In the boudin necks Na-amphibole or Na-amphibole + quartz infill occurs, and along the contact between the boudins and the surrounding foliation, we observed Fe-epidote crystals and pseudomorphs of fine-grained white mica, possibly on former lawsonite. All the above observations indicate that all the described structures developed during a progressive deformation at blueschist facies metamorphic conditions.

Two sets of blueschist-facies veins cut the mylonite, either containing glaucophane + minor Fe-epidote and sphene or glaucophane + quartz + white mica + apatite; their orientation is consistent with the same 3D strain field of the foliation boudinage.

The brittle deformation is focused in some limited horizons and pods, where the vein network becomes more pervasive and the boudins are progressively disrupted up to brecciation. Such breccia is characterized by clasts with size ranging from less than 1 cm to some cm. Clasts are cemented by abundant interclast synkinematic Na-amphibole and display internal rotation, testified by the variability of attitude of mylonitic foliation planes in the different fragments.

Our observations demonstrate a transition from ductile folding to boudinage, to vein development and brecciation, and thus point to a transition from ductile to brittle deformation in a progressive way, at substantially constant PT conditions (blueschist facies), and in an overall unchanged kinematic framework. These processes are assisted by apparently large fluid availability.

We discuss the possible mechanisms of brittle failure, the role and origin of the fluids responsible for the brecciation at high pressure conditions and the implications for fluid-assisted deformative processes, active inside subduction zones.

## **The Roisan-Cignana Shear Zone (Dent Blanche Tectonic System, Western Alps): from the Permian lithospheric thinning to the Alpine subduction and collision**

Manzotti P.\*<sup>1</sup>, Zucali M.<sup>2</sup>, Ballèvre M.<sup>1</sup>, Robyr M.<sup>3</sup> & Engi M.<sup>3</sup>

<sup>1</sup> Géosciences Rennes, Université de Rennes 1, France. <sup>2</sup> Dipartimento di Scienze della Terra "Ardito Desio", Università degli Studi di Milano.  
<sup>3</sup> Institute of Geological Sciences, University of Bern, Suisse.

Corresponding email: [paola.manzotti@univ-rennes1.fr](mailto:paola.manzotti@univ-rennes1.fr)

Keywords: shear zone, Dent Blanche, Western Alps.

The Dent Blanche Tectonic System (DBTS) is a composite thrust sheet derived from the previously thinned passive Adriatic continental margin. A kilometric high-strain zone, the Roisan-Cignana Shear Zone (RCSZ) defines the major tectonic boundary within the DBTS (Manzotti et al., 2014) and separates it into two subunits, the Dent Blanche s.s. nappe to the northwest and the Mont Mary nappe to the southeast. Within this shear zone, tectonic slices of Mesozoic and pre-Alpine meta-sediments (Manzotti et al., 2012) became amalgamated with continental basement rocks of the Adriatic margin. The occurrence of high pressure assemblages along the contact between these tectonic slices indicates that the amalgamation occurred prior to or during the subduction process, at an early stage of the Alpine orogenic cycle. Detailed mapping (Manzotti, 2011), petrographic and structural analysis show that the Roisan-Cignana Shear Zone results from several superimposed Alpine structural and metamorphic stages. Subduction of the continental fragments is recorded by blueschist-facies deformation, whereas the Alpine collision is reflected by a greenschist facies overprint associated with the development of large-scale open folds. The post-nappe evolution comprises the development of low-angle brittle faults, followed by large-scale folding and finally brittle extensional faults.

The RCSZ shows that fragments of continental crust had been torn off the passive continental margin prior to continental collision, thus recording the entire history of the orogenic cycle. The role of preceding Permo-Triassic lithospheric thinning, Jurassic rifting, and tectonic erosion processes in controlling the removal of crustal fragments from the reactivated passive continental margin is discussed. Results of this study constrain the temporal sequence of the tectono-metamorphic processes involved in the assembly of the DBTS, but they also show limits on the interpretation. In particular it remains difficult to judge to what extent pre-collisional rifting at the Adriatic continental margin preconditioned the efficiency of convergent processes, i.e. accretion, subduction, and orogenic exhumation.

Manzotti P., Zucali M., Ballèvre M., Robyr M., Engi M. 2014. Geometry and kinematics of the Roisan-Cignana Shear Zone, and the orogenic evolution of the Dent Blanche Tectonic System (Western Alps). *Swiss J. Geosciences*, 107, doi:10.1007/s00015-014-0157-9.

Manzotti P., Rubatto D., Darling J., Zucali M., Cenko-Tok B., Engi M. 2012. From Permo-Triassic lithospheric thinning to Jurassic rifting at the Adriatic margin: petrological and geochronological record in Valtournenche (Western Italian Alps). *Lithos*, 146-147, 276-292.

Manzotti P. 2011. Petro-structural map of the Dent Blanche tectonic system between Valpelline and Valtournenche valleys, Western Italian Alps. *J. Maps*, 7, 340-352.

## Out of sequence thrust in the inner zone of northern Apennines: insight from Elba island nappe stack

Massa G.\*<sup>1</sup>, Musumeci G.<sup>2</sup>, Pieruccioni D.<sup>1-3</sup> & Mazzarini F.<sup>4</sup>

1. CGT Centro di GeoTecnologie, Università di Siena, Italy. 2. Dipartimento di Scienze della Terra, Università di Pisa. 3. Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari. 4. Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Pisa.

Corresponding email: [massa2@unisi.it](mailto:massa2@unisi.it)

Keywords: Elba Island, out-of-sequence thrusting, "Serie Ridotta".

The feature of central-eastern Elba island nappe stack is a anomalous tectonic repetition of Tuscan and Ligurian units thrust sheets in the nappe stack due to slice of Tuscan nappe sequence (Complex III, Trevisan, 1950) tectonically sandwiched between two thrust sheets of Ligurian units. The Complex III is made up of the Rio Marina Unit (Deschamps et al., 1983) and the tectonically reduced Tuscan Nappe sequence. The latter sequence is made up of Mesozoic carbonate formations, tectonically overlain by Scaglia Fm. that at the map scale discordantly rests above the Jurassic formations, and Rio Marina Unit. This structural setting is consistent with the "Serie ridotta", interpreted as the result of Middle Miocene extension of the chain.

The nappe stack is folded in a NW-SE striking kilometre-scale antiformal tight fold continuously exposed along the eastern Elba coastline from Ortano to the north of Rio Marina. The antiform is characterized by a gently N-NW plunging axis and an eastward vergence with a shallowly westward dipping axial plane surface. Southward Rio Marina the antiform inverted thinned limb is cross cut by a tectonic contact. The serpentinites slice at the top of the Acquadolce Unit appear under this tectonic contact. Field evidences and borehole data show that the antiform is in turn cross-cut by the Zuccale Fault, and by high angle normal and strike-slip faults. The eastward vergent antiform refolded the early nappe stack leading to the unusual tectonic interfingering of the Tuscan and Ligurian Units. Thus the lower serpentinite slice, cropping out below the Tuscan derived metamorphic and sedimentary units of Complex III, corresponds to the laminated inverted limb of antiform, successively affected by the contact metamorphism related to Porto Azzuro pluton emplacement.

Age of post nappe folding deformation is bracketed between the age of the folded "Serie Ridotta" (Late Langhian, 13 Ma) and the emplacement of intrusive rocks dated in the central-eastern Elba as being from the Messinian (7-6 Ma).

Therefore, the anomalous tectonic repetition of Tuscan and Ligurian units thrust sheets in the eastern Elba nappe stack gives evidence of Middle-Late Miocene out-of-sequence thrusting postdating nappe stack and predating granite emplacement and upper crustal extension (Late Miocene-Pliocene). We suggest that collisional tectonics in the inner zone of northern Apennines was polyphased with early stacking of tectonic units followed by out of sequence thrust predating the eastward shifting of the thrust front towards the external zone during late Miocene-Pliocene.

Deschamps Y., Dagallier G., Macaudière J., Marignac C., Moine B. & Saupé F. 1983. Le gisement de pyrite-hématite de valle Giove (Rio Marina, Ile d'Elbe, Italie), Partie 1. Schweiz. Mineral. Petrogr. Mitt., 63, 149-165.

Trevisan L. 1950. L'Elba orientale e la sua tettonica di scivolamento per gravità. Mem. Ist. Geol. Univ. Padova, 16, 5-39.

## The geodynamic evolution of the Intra-Pontide suture zone, Central Turkey: evidence from the ophiolite bearing Arkot Dağ Mélange

Pandolfi L.\*<sup>1-2</sup>, Göncüoğlu M.C.<sup>3</sup>, Marroni M.<sup>1-2</sup>, Ellero A.<sup>2</sup>, Ottria G.<sup>2</sup>, Catanzariti R.<sup>2</sup>, Tekin U.K.<sup>4</sup> & Sayit K.<sup>3-5</sup>

1. Dipartimento di Scienze della Terra, Università di Pisa. 2. Istituto di Geoscienze e Georisorse, CNR, Pisa. 3. Department of Geological Engineering, Middle East Technical University, Ankara, Turkey. 4. Department of Geological Engineering, Hacettepe University, Ankara, Turkey. 5. Department of Geological Sciences, San Diego State University, USA.

Corresponding email: [pandolfi@dst.unipi.it](mailto:pandolfi@dst.unipi.it)

Keywords: Arkot Dağ Mélange, geochemistry, Radiolaria, obduction, Intra-Pontide suture zone.

The geological setting of Turkey can be described as an assemblage of continental terranes separated by ophiolite-bearing suture zones that mark the areas where the Paleotethyan and Neotethyan oceanic basins were destroyed. In northern Turkey, one of the most important suture zones is represented by the Intra-Pontide one consisting of an east-west trending belt of deformed and/or metamorphic units located at the boundary between the Istanbul-Zonguldak terrane to the north and the Sakarya terrane to the south. These units can be regarded as issued from the Intra-Pontide domain, whose geodynamic history is still a matter of debate.

Along the Akpınar-Araç-Bayramoren geotraverse, located in central Turkey, an ophiolite-bearing mélangé, known as the Arkot Dağ Mélange, is well-exposed along the Intra-Pontide suture zone. The Arkot Dağ Mélange can be described as a Late Santonian chaotic sedimentary deposit consisting of an up to 1000-m-thick succession of slide-blocks of different sizes and lithologies enclosed in a sedimentary matrix consisting of shales, coarse-grained arenites, pebbly mudstones and pebbly sandstones. The slide-blocks, from a few meters to hectometers in size, are represented by metamorphic rocks (mainly micaschists and gneisses), by ophiolites (peridotites, gabbros, IAT and BAB basalts and cherts) and by sedimentary rocks (cherts, neritic and pelagic limestone, marly limestone and ophiolite-bearing turbidites). The youngest age among the slide-blocks has been provided by the ophiolite-bearing turbidites where a late Coniacian nannofossil assemblage has been found. The cherts have provided a wide range of ages from the Middle Trias to Late Cretaceous, whereas the fossils found in the limestone indicate Late Jurassic to Early Cretaceous ages. The matrix of the Arkot Dağ Mélange, even if unaffected by metamorphism, shows deformations represented by multiple meters-thick cataclastic shear zones at the boundaries of the mélangé slices or inside of them. According to its features, the source area of the Arkot Dağ Mélange was most likely a stack of continental and oceanic thrust sheets emplaced in the Late Cretaceous onto a continental margin. The data collected from the different slide-blocks suggest that the Intra-Pontide domain was characterised by an oceanic basin opened at the latest in the Early Jurassic. The opening of the Intra-Pontide oceanic basin was followed by the development of a subduction zone with a subsequent opening of suprasubduction oceanic basin in the Middle Jurassic – Early Cretaceous. The convergence in this suprasubduction oceanic basin started at the Early/Late Cretaceous boundary by an obduction process, whereas its final closure can be regarded as Late Paleocene.

## The continental crust of the Austroalpine Domain: the record of multiple rejuvenation of an orogenic scar

Spalla M.I.\*<sup>1-2</sup>, Delleani F.<sup>1</sup>, Marotta A.M.<sup>1</sup>, Rebay G.<sup>3</sup>, Regorda A.<sup>1</sup>, Roda M.<sup>4</sup>, Salvi F.<sup>5</sup>, Zanoni D.<sup>1</sup>, Zucali M.<sup>1-2</sup> & Gosso G.<sup>1-2</sup>

1. Università degli Studi di Milano, Dipartimento di Scienze della Terra "A. Desio". 2. IDPA-CNR, Milano. 3. Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia. 4. Universiteit Utrecht, Fac. of Geosciences, Utrecht, The Netherlands. 5. Eni E&P Division, San Donato Milanese.

Corresponding email: [iole.spalla@unimi.it](mailto:iole.spalla@unimi.it)

Keywords: pre-Alpine rifting, Alpine subduction, geophysical modeling.

In the Alpine continental crust structural, metamorphic, sedimentary and igneous signatures indicate that orogenic scars are weak lithospheric zones of recurring tectonic and metamorphic rejuvenation during successive convergent and divergent plate dynamics. Fortunately, the overprint related to Alpine subduction and collision in the Austroalpine domain has not completely erased the markers of the transition from Variscan convergence to Permian – Triassic lithospheric thinning, making this domain a key repository to investigate the recycling of passive margins in subduction environments. Due to the fact that subduction–collision zones are characterized by the amalgamation and disaggregation of lithospheric slices, in these domains the determination of contours for thermally and structurally characterized units is crucial to accurately exploit the rock memory (i), and define the variations in sizes of crustal slices involved in the dynamic evolution of an active margin (ii). The dimensions of these structural entities evolve over time and can be reconstructed using the structural and metamorphic evolution of the basement rocks as tracers. These tectono-metamorphic units (TMUs) represent discrete portions of the orogenic crust influenced by a sequence of metamorphic and textural changes and their translational trajectories and shape changes can be derived from a joint reconstruction of quantitative P-T-d-t paths. This analytical approach offers the opportunity to test the physical compatibilities of the interconnected variables constraining numerical modelling, such as density, viscosity, and heat transfer, with structural, petrologic and geochronological data. Comparison between modelling predictions and natural data, obtained by this analytical approach, helped to solve longstanding ambiguities on the pre-Alpine and Alpine geodynamic evolution of Central and Western Austroalpine units and to explore the crustal levels of protolith derivation.

## The Cimmerian accretionary wedge of Anarak: a Variscan subduction complex in Central Iran

Zanchi A.\*<sup>1</sup>, Malaspina N.<sup>1</sup>, Zanchetta S.<sup>1</sup>, Berra F.<sup>2</sup>, Benciolini L.<sup>3</sup>, Martin L.<sup>4</sup>, Bergomi M.<sup>1</sup>, Cavallo A.<sup>1</sup>, Javadi H.R.<sup>5</sup> & Kouhpeyma M.<sup>5</sup>

1. Department of Earth and Environmental Sciences, Milano-Bicocca University. 2. Dipartimento di Scienze della Terra "A.Desio", Università degli Studi di Milano. 3. Dipartimento di Fisica, Chimica e Ambiente, Università degli Studi di Udine. 4. Dipartimento di Geoscienze, Università degli Studi di Padova. 5. Geological Survey of Iran, Azadi Square, Meraj Avenue, Tehran, Iran.

Corresponding email: [andrea.zanchi@unimib.it](mailto:andrea.zanchi@unimib.it)

Keywords: Central Iran, accretionary wedge, blueschist.

The Iran microplate is part of the Cimmerian blocks which rifted off Gondwana in the Early Permian and collided with the Southern Eurasian margin in the Late Triassic due to the closure of the Palaeotethys ocean. The presence of several ophiolite belts in Iran dating between Late Palaeozoic to Triassic poses several questions on the possible existence of various sutures marking the closure of the Palaeotethys ocean between Eurasia and Iran. Late Palaeozoic complexes with a Carboniferous "Variscan" age have been also described in N Iran, along the Alborz range, and in NE Iran, along the Late Triassic Palaeotethys suture, and they are generally related to the Late Palaeozoic evolution of the southern Eurasian margin, consisting of a mosaic of small continental blocks. In this general frame, the Anarak Metamorphic Complex (AMC), located in Central Iran, presently far from the pre-Late Triassic suture zones, is still an open problem. Detailed structural, petrographic and geochemical analyses have been carried out in these last years through the DARIUS PROGRAMME and an Italian PRIN. The AMC, which consists of several metamorphic units including dismembered "ophiolites", displays different tectono-metamorphic evolutions. The Morghab and Chah Gorbek complexes, mainly consisting of metapelites associated with metabasites and thick marble layers display a M1 metamorphism characterized by blueschist relicts along the S1 foliation in the former, and greenschist assemblages in the latter. They share a similar D2 deformational and M2 metamorphic history showing a prograde metamorphism with syn- to post-kinematic growth of blueschist facies phase assemblages. Prograde metamorphism characterized by the syn- to post-D2 growth of sodic amphibole has been recognized also in marbles at the contact between this unit and serpentinites. Evidence of HP/LT metamorphism also occur in Mg-riebeckite-bearing metapillow lavas and serpentinites, which are characterized by the coexistence of lizardite with antigorite. Structural analyses showed that the Chah Gorbek and Morghab units and the "ophiolites" have been tectonically coupled within an accretionary wedge before the D2 folding stage. The other units of the AMC lack evidence of HP metamorphism around Anarak, especially the Lakh Marble, a large thrust sheet that occupies the uppermost structural position in the AMC. Available radiometric ages of undeformed trondhjemites intruding the wedge, as well as our new data constrain the subduction event at the end of the Carboniferous, before 290 Ma. These data suggest that the AMC may be part of an allochthonous crustal fragment being part of the Variscan belt developed along the southern Eurasian margin before the Cimmerian collision of Iran. Subsequent deformational events occurring during the Mesozoic and the Cenozoic, up to the Miocene, dismembered the original structure of the wedge accompanying its displacement to the present day position.

## The record of the transition from Variscan collision to continental break-up in the Permian conglomerates of Central Southern Alps

Zanoni D.<sup>1</sup>, Spalla M.I.<sup>1-2</sup> & Gosso G.\*<sup>1-2</sup>

1. Università degli Studi di Milano, Dipartimento di Scienze della Terra "A. Desio", Milano. 2. CNR-IDPA, Milano.

Corresponding email: [guido.gosso@unimi.it](mailto:guido.gosso@unimi.it)

Keywords: tectono-metamorphic units, sediment provenance, lithospheric thinning, Pangea break-up.

The central Southalpine domain exposes a Variscan crystalline basement bearing different tectono-metamorphic evolutions (Spalla et al., 2014 and references therein). During late to post-Variscan times the orogenic crust has been thinned with development of intermontane strike slip basins in the context of a dextral shear zone within Pangea supercontinent (e.g. Bertoluzza & Perotti, 1997; Muttoni et al., 2003; Cassinis et al., 2012). These basins gathered Lower Permian volcanics and erosional deposits during thinning of the Variscan orogenic crust. Conglomerates containing dm- to m-sized metamorphic clasts are interbedded with these erosional deposits. Microstructural and petrological analysis on clasts of the Dosso dei Galli Conglomerate (Val Trompia basin), Pizzo del Diavolo Formation (central Orobic basin), and Ponteranica Formation (western Orobic basin) conglomerates allows reconstructing the PT evolution of the tectono-metamorphic units exposed to erosion during Lower Permian times. The comparison of the PT evolutions preserved in the clasts with the PTdt evolution inferred in the surrounding basements indicate that these basins were fed by erosion of same type of tectono-metamorphic units presently exposed in the central sector of the Southern Alps (Spalla et al., 2009; Zanoni et al., 2010). The westward increase of the  $T_{max}$  conditions inferred from clasts of these different deposits and decrease of conglomerate ages suggest a westward rejuvenation of tectonic units exhumation and a thinning of the continental crust heralding the Neo-Tethys opening.

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## **LPO of metamorphic tectonites of the Eclogite Micaschists Complex (Sesia-Lanzo Zone, Austroalpine domain, Western Alps, Italy) as indicators of strain partition during alpine subduction**

Zucali M.\*<sup>1</sup>, Vho A.<sup>2</sup>, Chateigner D.<sup>3</sup>, Lutterotti L.<sup>3</sup> & Ouladdiaf B.<sup>4</sup>

<sup>1</sup> Department of Earth Sciences, Università degli Studi di Milano, Via Mangiagalli 34, Milano, Italy. <sup>2</sup> Università degli Studi Milano-Bicocca <sup>3</sup> CRISMAT-ENSICAEN and IUT-Caen, Université de Caen Basse-Normandie, campus 2, 6, Bd. M. Juin 14050 Caen, France <sup>4</sup> Institut Laue-Langevin 6, Rue Jules Horowitz, B.P.156, 38042 Grenoble Cedex 9, France.

Corresponding email: [Michele.Zucali@unimi.it](mailto:Michele.Zucali@unimi.it)

Keywords: LPO, subduction, strain partitioning.

We present a study of microstructures and lattice preferred orientation (LPO) of the Eclogite Micaschists Complex (EMC) metapelites and metabasites. The EMC is part to the Sesia-Lanzo Zone of the Austroalpine domain of the Western Alps (Italy). The Sesia-Lanzo Zone records the alpine subduction as penetrative superimposed foliations, developed under eclogite facies conditions and marked by millimetre- to centimetre-size aggregates. The microstructural analysis revealed a multi-stage evolution: i) pre-S1 mm-thin aggregate of quartz, white mica and rutile as inclusions within S1 garnet porphyroblasts; ii) S1 millimetre foliation defined by white mica and garnet; iii) D2 folding produces a axial planar foliation S2 marked by white mica, rutile, glaucophane, omphacite and locally aggregates of garnet; iv) D3 is associated with the reactivation of S2 and the growth of chlorite and green biotite or produces shear planes cutting the S2 foliation and marked by re-crystallized quartz and white mica.

The LPO analysis was carried out using original diffraction data collected at the Institut Laue-Langevin (Grenoble) and processed using the Maud software package (Material Analysis Using Diffraction). The LPO of white mica is characterized by (001) pole to planes distributions close to a cluster at high angle to S2 while poles to (010) and (100) describe girdle close to the S2 foliation. Quartz distributions describe girdle of (100) and (110) poles close to the foliation plane with maxima close to the macroscopic lineation; (001) and (011) poles to planes describe two clusters close to the normal to the S2 foliation. Several samples, even still displaying broadly same LPO features are also characterised by LPO of quartz more close to a single crystal distribution, likely indicating a contribution of static recrystallization process. We suggest to use LPO as additional tool to infer various scale strain partitioning where mesoscopic evidence are lacking.

## **SESSIONE S32**

### **Geodynamic modeling at different structural levels: comparison between natural data and model predictions**

*CONVENORS*

*G. Corti (IGG-CNR, Firenze)*

*A.M. Marotta (Univ. Milano)*

*F. Storti (Univ. Parma)*

## **Magma-induced axial subsidence during final-stage rifting: implications for the formation of seaward dipping reflectors**

Agostini A.\*<sup>1</sup>, Corti G.<sup>2</sup>, Keir D.<sup>3</sup>, Van Wijk J.<sup>4</sup>, Bastow I.D.<sup>5</sup>, Ebinger C.<sup>6</sup> & Ranalli G.<sup>7</sup>

1. Dipartimento di Scienze della Terra, Università degli Studi di Firenze. 2. Consiglio Nazionale delle Ricerche, Istituto di Geoscienze e Georisorse. 3. National Oceanography Centre Southampton, University of Southampton, United Kingdom. 4. Earth and Environmental Science Department, New Mexico Tech, Socorro, USA. 5. Department of Earth Science and Engineering, Imperial College London, United Kingdom. 6. Department of Earth Sciences, University of Rochester, New York, USA. 7. Department of Earth Sciences and Ottawa-Carleton Geoscience Centre, Carleton University, Ottawa, Canada.

Corresponding email: [giacomo.corti@igg.cnr.it](mailto:giacomo.corti@igg.cnr.it)

Keywords: continental rifting, magma intrusion, plate flexure.

A consensus is now emerging from continental rifts and rifted margins worldwide that significant extension can be accommodated by magma intrusion prior to the development of a new ocean basin. Despite this, the influence of loading from magma intrusion, lava extrusion and sedimentation on plate flexure and resultant subsidence of the basin is poorly understood. In this paper we address this issue by using 3D flexural models, constrained by geological/geophysical data from the Main Ethiopian Rift and the Afar depression in East Africa, to analyse the influence of loading from magma intrusion, lava extrusion and sedimentation on plate flexure and resultant subsidence of the basin. Model results show that axial mafic intrusions in the crust are able to cause significant downward flexure of the extending lithosphere and that the amount of subsidence increases substantially when the plate is weak during the final stages of continental breakup. This process causes tilting of basaltic flows towards the centre of the rift axis causing them to dip towards the eventual new ocean basin when breakup occurs, as recorded by seaward dipping reflector sequences (SDRs) at volcanic passive margins worldwide.

## Strain localization during compression of a laterally heterogeneous continental lithosphere

Calignano E.\*<sup>1</sup>, Sokoutis D.<sup>1-2</sup> & Willingshofer E.<sup>1</sup>

1. Faculty of Geosciences, Department of Earth Sciences, Utrecht University. 2. Department of Geosciences, University of Oslo, Norway.

Corresponding email: [E.Calignano@uu.nl](mailto:E.Calignano@uu.nl)

Keywords: analogue modelling, lithosphere heterogeneity, strain localization.

First order large scale stress fields, associated with active plate tectonic processes, interact with lateral heterogeneities in the lithosphere and generate strain redistribution (Zoback, 1992). Despite the strength of the continental lithosphere is mainly controlled by its depth dependent rheological structure, continents are often the product of the assemblage of domains that suffered different tectonic processes, resulting in lateral changes in composition and thermal structure (Ranalli, 1997; Audet & Burgmann, 2011).

Numerous modelling studies investigated the localization of deformation in compressional settings in case of lithospheric weak zones flanked by stronger domains (Cruden et al., 2006; Cerca et al., 2004; Willingshofer et al., 2005).

We present a series of lithospheric-scale analogue models designed to investigate strain redistribution resulting from the presence of a stronger rheological heterogeneity embedded in a weak lithosphere. Among the investigated parameters, convergence velocity and thickness of the upper brittle mantle are varied, both playing an important role in the crust-mantle coupling. Furthermore, we examined different orientations of the rheological boundaries with respect to the convergence direction, since reactivated lithosphere heterogeneities are often observed to strike oblique with respect to the main horizontal stress field.

Preliminary experimental results indicate that the presence of a strong lithospheric domain induces strong localization of deformation at the rheological boundaries, with associated high relief build-up. Strain rate governs the geometry of the deep lithospheric structure, as well as the dip direction of the main underthrusting plane.

The presented results provide valuable insight for strain localization in collisional settings under various rheological and geometrical configurations.

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## **Magnetorheological fluids as new materials for sandbox analogue experiments**

Cavozzi C.\*<sup>1</sup>, Storti F.<sup>1</sup>, Nestola Y.<sup>1</sup>, Salvi F.<sup>2</sup> & Davoli G.<sup>2</sup>

1. NEXT – Natural and Experimental Tectonics Research Group, Dipartimento di Fisica e Scienze della Terra “Macedonio Melloni”, Università degli Studi di Parma, Italy. 2. Eni E&P, San Donato Milanese (MI), Italy.

Corresponding email: [cristian.cavozzi@unipr.it](mailto:cristian.cavozzi@unipr.it)

Keywords: analogue modelling, new materials, MR magnetoreological fluid.

Since about two centuries, analogue modelling has been proved to provide effective support to research in many geological subject areas including geodynamics, tectonics, tectonic geomorphology, structural geology, and volcanology. During such a long time period, different analogue materials and experimental techniques have been developed to improve our modelling capability. Following this trend, in this contribution, we report on a first attempt to use magnetorheological (MR) fluids as analogue materials for simulating the behavior of mobile décollement layers that change their mechanical properties during deformation. For this purpose, we designed a specific sandbox that includes the possibility of quickly applying and removing a magnetic field below a MR fluid layer, in order to induce an instantaneous change from a frictional to a viscous behavior in the basal décollement material. To test the effectiveness of the new experimental technique, we performed experiments simulating gravitational gliding and sediment progradation above a basal mobile shale layer, using experimental set-ups very similar to previously published models where the basal décollement rheology was controlled by pressurized air injection from the base. The close similarity between results obtained with the two very different experimental techniques indicates that our pilot study of MR fluids as analogue materials deserves further research for optimizing their applicability to the simulation of geological processes in the laboratory.

## **Modeling the long-term mechanical behaviour of the Barreirinhas Basin Deepwater Fold and Thrust Belt (Brazil)**

Cruciani F.\*<sup>1</sup>, Manconi A.<sup>2</sup> & Barchi M.R.<sup>1</sup>

1. Dipartimento di Fisica e Geologia, Università di Perugia. 2. IRPI-CNR, Torino.

Corresponding email: [fra.c85@hotmail.it](mailto:fra.c85@hotmail.it)

Keywords: Barreirinhas Basin, deepwater fold and thrust belt, numerical modeling.

Gravity-driven deepwater fold and thrust belts (DW-FTBs) are extensional-compressional linked systems, quite widespread at continental passive margins. These giant-scale structures, which involve most or the entire sedimentary sequence, may be active for tens of millions of years. The Brazilian Atlantic margin is affected both by salt and shale tectonics, therefore it is an excellent site for recognize and understand the mechanical processes which driving the onset and evolution of these geological features. In this work, we have investigated the shale décollement DW-FTB of the Barreirinhas Basin (BB), where the post-rift sedimentary sequence, up to 5 km thick, has been involved in two separate, overprinted deformation phases; the first, short-lived, that occurred in the Upper Cretaceous, and the latter, long-lived, that covered most of the Cenozoic time. The overall structure consists in a bowl-shaped geometry, with listric normal faults updip and a frontal thrust ramp downdip, detached over a common decollément surface. The frontal thrust gives rise to a large related anticline fold, whose crest crops out at the sea-bottom. From the onshore extensional to the offshore compressional domain, the thrust belt is about 50 km wide, and it extends for 70 km along-strike. Palinspastic restorations have shown that the highest deformation rate, accounting for about 80% of the net strain, occurred in the last 10 m.y., following a rearrangement of the paleo Amazon River drainage system. The rather simple geometry, combined with the relative small size, make the BB DW-FTB particularly suitable for numerical simulations aimed to investigate its long-term mechanical behaviour. We set up a 2D fluid dynamic analysis by considering a Finite Element Method (FEM) environment, to understand whether the Cenozoic evolution of the BB DW-FTB can be reproduced by considering a simplified Newtonian viscous flow or it is controlled by a more complex rheology, which might include the effect of additional parameters such as internal friction, cohesive strength and pore-fluid pressure at the basal detachment. To this purpose, we have reconstructed a schematic geometrical model of the margin, and we have simulated the overburden through time, by considering densities and viscosities as physical input parameters for the geological materials, and gravity as the only driving force.

## **Patterns of seismic anisotropy around subduction zones: predictions by numerical modelling, comparison with observations and implications for subduction-induced mantle flow**

Faccenda M.\*

Dipartimento di Geoscienze - Università di Padova.

Corresponding email: [manuele.faccenda@gmail.com](mailto:manuele.faccenda@gmail.com)

Keywords: numerical modeling, seismic anisotropy, strain-induced LPO, subduction zone.

Subduction zones are convergent margins where the rigid lithosphere sinks into the Earth's viscous mantle inducing complex 3D flow patterns. Seismic anisotropy generated by strain-induced lattice/crystal preferred orientation (LPO/CPO) of intrinsically anisotropic minerals is commonly used to study flow in the mantle and its relations with plate motions.

We computed the upper mantle fabric due to strain-induced LPO in 3D mechanical models of dynamic subduction. Overall, strong fabrics develop in the upper mantle around the subduction zone. The distribution of the fabric in the mantle depends on the distribution and amount of the deformation, and not on the rate at which the slab subducts. As a consequence, distinctive fabric patterns are formed in the upper mantle below, aside and above the slab.

Subsequently, seismogram synthetics of teleseismic waves propagating sub-vertically were computed to estimate SKS splitting patterns that are controlled by the anisotropy in the upper mantle. Results are comparable with observations from different subduction settings (i.e., Cascadia, Calabira, Aegean), yielding a strong constrain on the recent dynamics of these convergent margins.

## **Subduction and mantle dynamics in the Mediterranean: data, modelling and perspectives**

Faccenna C.\*<sup>1</sup>, Becker T.<sup>2</sup> & Funicello F.<sup>1</sup>

1. Dipartimento di Scienze Università Roma TRE. 2. Department of Earth Sciences, University of Southern California.

Corresponding email: [faccenna@uniroma3.it](mailto:faccenna@uniroma3.it)

Keywords: Subduction, Mediterranean, modeling.

Subduction represents the main tectonic driving process in the Central Mediterranean. A large amount of geophysical and geological studies now provide constraints on the geometry of the subduction zones and on the present and past kinematics of the trench. However, important questions concerning the dynamic causes of the morphologically complex subduction process are still unsolved and contrasting models have been proposed so far. Here, we will review the available data and discuss modelling concerning subduction processes in the Central Mediterranean.

## **What drives microplate motion and deformation in the northeastern Caribbean plate boundary region?**

Govers R.\*, van Benthem S. & Wortel R.

Department of Earth Sciences, Faculty of Geosciences, Utrecht University, Utrecht, The Netherlands.

Corresponding email: [r.govers@uu.nl](mailto:r.govers@uu.nl)

Keywords: Caribbean plate boundary zone, Finite element models, Slab Edge Push.

The north Caribbean plate boundary zone is a broad deformation zone with several fault systems and tectonic blocks that move with different velocities. The indentation by the Bahamas Platform (the "Bahamas collision") is generally invoked as a cause of this fragmentation.

On the basis of upper mantle structure we propose that a second driver of deformation may be the western edge of the south-dipping slab along the northern Caribbean plate boundary; the westward motion of this slab edge results in a push on the Caribbean plate further west. We refer to this second mechanism for deformation as "Slab Edge Push".

The motion of the North America plate relative to the Caribbean plate causes both drivers to migrate from east to west. Bahamas collision and Slab Edge Push have been operating simultaneously since the Miocene. The question is: What is the relative importance of the two mechanisms? We use mechanical finite element models that represent the two mechanisms from the Late Oligocene (30 Ma) to the Present. For the Present, both models successfully reproduce observed deformation, implying that both models are viable. Back in time the Slab Edge Push mechanism better reproduces observations.

Neither mechanism successfully reproduces the observed Miocene counter-clockwise rotation of Puerto Rico. We use this rotation to tune a final model that includes fractional contributions of both mechanisms. We find that the Slab Edge Push was the dominant driver of deformation in the north Caribbean plate boundary zone since 30 Ma.

## **A new high-resolution isochron map for the Central Atlantic region since the early Oligocene**

Macchiavelli C.\*, Schettino A. & Turco E.

School of Science and Technology, Geology Division, University of Camerino.

Corresponding email: [chiara.macchiavelli@unicam.it](mailto:chiara.macchiavelli@unicam.it)

Keywords: central Atlantic, marine magnetic anomalies, plate reconstructions.

Although the kinematics associated with the opening of the central Atlantic ocean after the break-up of Pangaea has been the subject of several studies since the late 1960s, there are still open problems and debated solutions to the tectonic evolution of this area. In particular, it has been proposed that an independent Moroccan plate existed in the central Atlantic during the Oligocene and the early Miocene (Schettino & Turco, 2009). In this view, the Atlas mountain belt would represent a giant dextral transpressional flower structure and not an Alpine belt associated with N-S convergence. We derive a detailed chronological picture of North America – northwest Africa plate motions since 33 Ma through a re-examination of marine magnetic anomalies and fracture zone trends. We estimate best-fitting finite rotations and realistic uncertainties from anomaly 13 (33.1 Ma – early Rupelian) to anomaly 2A (2.58 Ma - Pliocene). A total of 858 ship tracks from the NGDC GEODAS database were analysed in the area comprised between the Fifteen-Twenty FZ and the Azores triple junction. The data quality was assessed through the examination of Kp indices. In particular, magnetic data collected during strongly disturbed days ( $Kp > 5$ ) were filtered away. From each ship track, one or more segments were extracted and projected onto profile lines having a unique strike with respect to the magnetized prisms. Finally, the magnetic data were high-pass filtered to remove long-wavelength features. A new advanced software tool for the analysis and interpretation of the anomalies was developed in order to improve the reliability of magnetic anomaly identifications. The main result of this work is a new detailed isochron map of the central Atlantic for the time interval 33.1 – 2.58 Ma (early Rupelian - Pliocene). We defined new stage boundaries on the basis of spreading rate variations or changes in the fracture zone trends. Our analysis shows that there is not a unique consistent system of isochrons in the eastern central Atlantic, as a consequence of the formation of the Moroccan plate during the Oligocene.

Schettino A. & Turco E. 2009. Breakup of Pangaea and plate kinematics of the central Atlantic and Atlas regions, *Geophys. J. Int.*, 110, 1078-1097.

## Coupling and tectonic erosion of plates at oblique subduction zones: hints from numerical modeling

Malatesta C.\*<sup>1</sup>, Gerya T.<sup>2</sup>, Crispini L.<sup>1</sup>, Federico L.<sup>1</sup>, Scambelluri M.<sup>1</sup> & Capponi G.<sup>1</sup>

1. DISTAV, Università di Genova. 2. Institute of Geophysics, Swiss Federal Institute of Technology (ETH-Zurich), Switzerland.

Corresponding email: [cristina.malatesta@unige.it](mailto:cristina.malatesta@unige.it)

Keywords: Upper plate erosion, interplate coupling, oblique subduction.

Convergent plate-margins undergo strong stresses which, on a geological timescale, induce permanent “long-term deformations” in the upper plate. Long-term deformation differs from the dominantly elastic “short-term deformation” that occur at human timescale in direct association with earthquakes.

Considering an oblique plate convergence, long-term deformations and the behaviour of the upper-plate margin can vary along the trench. To analyze the mechanisms and processes acting at oblique subduction zones we produced 3D numerical simulations. Our models are based on thermo-mechanical equations solved with finite differences method and marker-in-cell techniques combined with a multigrid approach. The reference model (Malatesta et al., 2013) simulates an intraoceanic subduction 100-km far from the continental margin; the oceanic crust is layered with a 5-km-thick layer of gabbro overlain by a 3-km-thick layer of basalt. A 1-km-thick sediment caps the sequence. The velocity vectors that produce the oblique convergence are applied on the lateral boundaries of the model and form an angle of 45° with the initial starting point of subduction (weak zone in the lithosphere). The plates move with a total velocity of about 3 cm/yr. A few million years after subduction initiation the upper plate margin reacts in different ways moving along the trench-axis: i) at sediment-poor sectors of the trench, where the sediment infill is scarce, the upper plate records an initial “short-term” shallow coupling with the downgoing slab and starts to bend; no remarkable amount of upper plate crust is eroded and buried; hereafter this sector of the overriding plate is definitely decoupled from the slab; ii) if the amount of trench sediment increases, the upper plate couples with the downgoing plate and is dragged coherently downwards following the trench-parallel direction of convergence; iii) at sediment-rich sectors of the trench the upper plate is instead incorporated as slivers inside the serpentinite channel that forms above the slab.

In order to highlight the possible role of the lithosphere structure (layered or “heterogeneous”) and of fluids released from the subducting slab on plate coupling and erosion of the upper plate, we finally compared our reference model with another 3D simulation. The initial setup of this simulation differs from the one of the reference model only for the type of lithosphere used: an oceanic heterogeneous lithosphere made of abyssal serpentinite, gabbro as lenses inside serpentinite, with a discontinuous basaltic layer overlain by a sedimentary cover.

Malatesta C., Gerya T., Crispini L., Federico L. & Capponi G. 2013. Oblique subduction modelling indicates along-trench tectonic transport of sediments. *Nat. Commun.*, 4, 2456, DOI:10.1038/ncomms3456.

### **3D mechanical structure of the lithosphere below the Alps and the role of gravitational body forces in the regional present-day stress field**

Marotta A.M. & Splendore R.\*

Dipartimento di Scienze della Terra "Ardito Desio", Università degli Studi Milano.

Corresponding email: [raffaele.splendore@gmail.com](mailto:raffaele.splendore@gmail.com)

Keywords: Alps, Stress propagation, Lithosphere rheology, Gravitational body forces.

The present study aims to investigate how the tectonic compression due to Africa-Eurasia convergence is transmitted up to Central Europe via a thermo-mechanical model, in which a high-resolution rheological analysis is performed in the surroundings of the Alpine domain and the predicted heterogeneous lithosphere strength is accounted for to reproduce the surface strain pattern.

Our rheological analysis reveals a strongly heterogeneous lithosphere strength that is characterised by steep strength gradients across the Periadriatic Lineament and the occurrence of non-competent crustal layers located below the northern Alps, where the upper crust controls the total lithosphere strength.

When the predicted lithosphere strength is included within a spherical thin sheet model to investigate the propagation of the tectonic compression due to Africa-Eurasia convergence toward Central Europe, our analysis supports the hypothesis that the N-S compressive stress dominates the gravitational body forces in the Southern Alps up to the Periadriatic Lineament, which defines an abrupt transition from the strong mantle belonging to the Adriatic lithosphere to the softer mantle below the Eastern Alps and is mechanically decoupled from the relatively stronger upper crust, thus preventing stress transmission toward the surface. Thus, in the Eastern Alps, the transmitted S-N compression would remain lower than the E-W extensional stress induced at crustal levels by the body gravitational forces associated with thick crustal layers.

## **Thermo-mechanical numerical model of the transition from continental rifting to oceanization: the transition from Permian-Triassic thinning to oceanisation in the alpine chain**

Marotta A.M.\*<sup>1</sup>, Conte K.<sup>1</sup>, Roda M.<sup>2</sup> & Spalla M.I.<sup>1-3</sup>

1. Department of Earth Sciences "Ardito Desio", Università degli Studi di Milano. 2. Universiteit Utrecht, Fac. of Geosciences, The Netherlands. 3. CNR-IDPA, Milano.

Corresponding email: [anna.maria.marotta@unimi.it](mailto:anna.maria.marotta@unimi.it)

Keywords: Continental rifting, Oceanization, 2D Thermo-mechanical numerical model.

The transition from continental rifting to oceanization has been investigated by mean of a 2D thermo-mechanical numerical model in which the formation of oceanic crust and serpentinite, due to the hydration of the uprising peridotite, as been implemented.

Model predictions have been compared with natural data related to the Permian-Triassic thinning affecting the continental lithosphere of the Alpine domain, in order to identify which portions of the present Alpine belt, preserving the imprints of Permian-Triassic high temperature (HT) metamorphism, is compatible, in terms of lithostratigraphy and tectono-metamorphic evolution, with a lithospheric extension preceding the opening of the Ligure-Piemontese oceanic basin. The HT Permian-Triassic metamorphic re-equilibration overprints an inherited tectonic and metamorphic setting consequent to the Variscan subduction and collision, making the Alps a key case history to explore mechanisms responsible for the re-activation of orogenic scars.

Our comparative analysis supports the thesis that the lithospheric extension preceding the opening of the Alpine Tethys did not start on a stable continental lithosphere, but developed by recycling part of the old Variscan collisional suture.

## **Role of extensional strain-rate on lithosphere necking architecture during continental rifting**

Nestola Y.\*, Storti F. & Cavozi C.

NEXT – Natural and Experimental Tectonics Research Group, Dipartimento di Fisica e Scienze della Terra “Macedonio Melloni”,  
Università degli Studi di Parma.

Corresponding email: [yago.nestola@unipr.it](mailto:yago.nestola@unipr.it)

Keywords: Rifting, Divergence-rate, Analogue modeling.

The evolution of lithosphere necking is a fundamental parameter controlling the structural architecture and thermal-state of rifted margin. Among others, parameters such as extensional strain-rate and thermal layering of the lithosphere exert a fundamental control on necking shape and evolution. Despite a large number of analogue and numerical modelling studies on lithosphere extension are available in the literature, a quantitative description of lithosphere necking evolution is still lacking.

We simulated by physical models the progression of lithosphere thinning and necking during orthogonal rifting at different extensional strain-rates. Our models involve a continental 4-layer mechanical lithosphere, which rests on a glucose syrup asthenosphere. Both the topography and the lithosphere base were monitored by time-lapse laser scanning. At the end of deformation, we remove each of the four layers and acquired the surface shape of the underlying ones by laser scanning. This technical approach allowed us to quantify the evolution in space and time of the thinning factors for the crust, mantle, and lithosphere as a whole. Laser-scanning monitoring provided also a detailed picture of the neck shape evolution, which shows a strong dependency on the strain-rate. At low strain-rates, necking is “boxed” with steep flanks and a flat-lying roof. Few deep basins develop at surface. At high strain-rates, more distributed thinning occurs isolating portions of less deformed mantle. A more distributed deformation affects the model topography. Despite large differences in shape, the aspect ratio (height/amplitude) of the necks converge towards very similar values at the end of the experiments.

The significant differences and evolutionary pathways produced by the plate divergence rate on the lithosphere necking profile, suggest that this parameter can exert a fundamental control on the time and space distribution of heat flow during rifting. Following up on this we can speculate on the location and timing of synrift magmatism, which is expected to be preferentially produced on one shoulder for slow plate divergence rate, and more widely distributed and delayed at fast divergence rates.

## Anatomy of the Ligurian Tethys: a geodynamic model based on field/laboratory studies and numerical/analogue modeling

Piccardo G.B.\*

Corresponding email: [giovanni.b.piccardo@gmail.com](mailto:giovanni.b.piccardo@gmail.com)

Keywords: Ligurian Tethys, field/laboratory studies, numerical/analogue modeling.

The geodynamic model for passive rifting in the Europe-Adria system and opening of Ligurian Tethys is based on: i) Present knowledge on tectonic and magmatic processes recorded in mantle peridotites of the Alpine-Apennine ophiolites; ii) Results of numerical and analogue modeling of lithosphere passive rifting; iii) Feedback between natural data and experimental results.

### **A-magmatic passive rifting: Melt-free shear zones**

Early Iherzolite shear zones show syntectonic ol-opx-cpx-sp assemblage equilibrated at T about 1000°C. Thermodynamically-based numerical models evidence that, during extension, *porosity localization bands* and *strain localization bands*, and strong localizations, are formed in strongly strain-dependent materials.

### **Magmatic passive rifting: Melt porous flow infiltration, magmatic shear zones.**

Asthenosphere melting, melt infiltration and melt/peridotite interaction. Porosity bands enhanced melt localization/infiltration and were transformed into granular harzburgite bands. Rising melts attained silica-saturation, because of reactive dissolution of pyroxenes.

Modeling of magma dynamics and tectonic processes, such as rifting, report that the porosity observed in experiments would weaken the lithosphere and promote localization of deformation.

### **Melt thermal advection: Rheological changes induced in the axial lithosphere.**

Melt thermal advection increased temperatures from 1000°C up to 1300°C, in the axial zone. Numerical modeling evidenced that melt thermal advection of hot liquids result in significant decrease in total lithospheric strength (TLS), from 10 to 1 TN m<sup>-1</sup> as orders of magnitude. At shallow levels, heat loss by conduction prevailed on thermal advection and rising melts underwent stagnation within, and impregnation of the shallow lithosphere, forming plagioclase-enriched peridotites.

### **Geodynamic relevance of the weakened/softened axial mantle wedge.**

Analogue models, focusing on the latest stages of extension of the Ligurian Tethys, evidence the axial localization of the weakened lithospheric mantle (WLM). Melt infiltration has a destabilizing effect on the mantle lithosphere even of cratonic keels.

### **Asthenosphere active upwelling: transition from passive to active rifting.**

Analogue models evidence the active upwelling of the deep asthenosphere within the WLM, The softened/weakened/hot axial lithospheric zone is, accordingly, the preferential way for active upwelling of the deeper/hotter asthenosphere between the future continental margins.

Extension makes transition from passive to active rifting.

The proposed model is characterized by:

- **Passive a-magmatic rifting;**
- **Asthenosphere melting and magmatic rifting;**
- **Melt infiltration through the mantle lithosphere;**
- **Melt thermal advection to shallow lithospheric levels;**
- **Rheological change of the axial lithosphere;**
- **Active asthenosphere upwelling and transition from passive to active rifting;**
- **Continental break-up and establishment of a ridge-type thermal regime.**

## **2D numerical study of the effects of mantle hydration and viscous heating on the dynamics of the wedge area within an ocean/continent subduction complex: the case study of Variscan crust in the Alpine domain**

Regorda A.\*<sup>1</sup>, Marotta A.M.<sup>1</sup>, Spalla M.I.<sup>1</sup>, Roda M.<sup>2</sup> & Rebay G.<sup>3</sup>

1. Dipartimento di Scienze della Terra, Università degli Studi di Milano. 2. Faculty of Geosciences - Universiteit Utrecht. 3. Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia.

Corresponding email: [alessandro.regorda@unimi.it](mailto:alessandro.regorda@unimi.it)

Keywords: Mantle hydration and viscous heating, Numerical modeling, ocean/continent subduction.

The geodynamics of a convergent ocean/continent margin, evolving from subduction to continental collision, was analyzed by means of a 2D finite element thermo-mechanical model, in which the physics of the crust-mantle system is described by the equations for continuity, conservation of momentum and conservation of energy. A viscous behavior for the whole system and density and viscosity depending from both temperature and composition are assumed. Different values of convergence velocities, 3, 5 and 8 cm/yr, have been used, as representative of slow, medium and fast subductions.

Our analysis is particularly focused on the effects of viscous heating and mantle hydration on the dynamics in the wedge area. The results support that both mechanisms induce the development of short wavelength convective cells in the wedge area that favor the exhumation of subducted crustal material since the early stages of the subduction. Model predictions, in terms of pressure, temperature, lithology and age, have been compared with the structural, petrological and age natural data from the Variscan crust of the Alpine domain.

## Understanding rifting processes using analogue modeling

Trippanera D.\*<sup>1</sup>, Ruch J.<sup>2</sup>, Acocella V.<sup>1</sup>, Lamarra D.<sup>1</sup> & Rivalta E.<sup>3</sup>

1. Dipartimento di Scienze - Università Roma Tre. 2. King Abdullah University of Science and Technology (KAUST), Thuwal, Saudi Arabia.  
3. GFZ, Potsdam, Germany.

Corresponding email: [daniele.trippanera@uniroma3.it](mailto:daniele.trippanera@uniroma3.it)

Keywords: analogue modeling, dike intrusions, rift.

The mechanisms of plate motions along divergent plate boundaries and the role of magmatic and tectonic forces are still matter of animate discussion. Spreading centers that accommodate the extension along plate boundaries are formed by a central volcano, flanked by elongated along axis rift zones composed of eruptive fissures, graben, and normal faulting. Typical examples are the Neo-volcanic Zone in Iceland or the Main Ethiopian Rift (MER). Geodetic observations (e.g. InSAR, GPS) show that major episodes of normal faulting are associated to rifting episodes taking place along the spreading centers. These are intimately related to dike intrusions, in both continental rifts and mid-ocean ridge systems. Large episodes of rifting usually last from few weeks to few years and produce extension of up to several meters. However, the influence of the magma on the geometry of the rift zones and its temporal evolution remains unclear. Moreover, geodetic and seismic data allow observing only an instantaneous time frame of longer rifting processes, in terms of geological times.

The aim of this work is to address these questions using analogue models of dike intrusions and therefore to understand: 1) if dikes are able to generate the overall long-term surface deformation observed on the field along rift zones and 2) how the diking process can eventually affect the rift formation and its evolution. The analogue modeling consists of simulating a natural process by means of a scaled physical model in the laboratory. The analogue material properties have to correctly simulate the rheological behavior of the natural rocks, respecting their geometric, kinematic and dynamic similarities. The main advantage of the analogue modeling is to observe the entire process from its beginning to its mature stage. Moreover, it allows investigating the different parameters acting in that process.

In order to quantify the deformation induced by dike intrusions, the experiments have been monitored by a laser scanner and by cameras from both top and side views, respectively.

The laser scanner (sub-millimeter resolution) allows measuring the vertical displacement during the experiment. We also used the Particle Image Velocimetry (PIV) technique to further analyze the horizontal displacement (image cross-correlation approach), both at the surface and from the experiment side. The main results show that the pattern of the surface deformation and the geometry of the brittle failures mainly depends on the intrusion depth and its geometry. The deformation observed in the models has then been compared with that of natural cases (dike intrusions and rifting episodes). The geometries of the faults observed in the experiments are compatible with features observed along large eruptive fissures (e.g. Laki, Iceland) and along spreading centers and central volcanoes (Krafla, Reykjanes in Iceland; MER in Ethiopia; Hawaii).

## SESSIONE S33

### **Planetary Geology: frontiers of geological exploration, modeling and understanding**

#### *CONVENORS*

*M. Massironi (Univ. Padova)*

*A.M. Fioretti (IGG-CNR, Padova)*

*M. Prondelli (Univ. Chieti)*

*F. De Blasio (Univ. Milano Bicocca)*

## Aeolian Activity in Herschel Crater, Mars

Cardinale M.\*<sup>1</sup>, Silvestro S.<sup>2-3</sup>, Vaz D.A.<sup>4-5</sup>, Michaels T.<sup>3</sup> & Marinangeli L.<sup>1</sup>

1. Laboratorio di Telerilevamento e Planetologia, Dipartimento di Scienze Psicologiche, Umanistiche e della Terra, Università G. D'Annunzio. 2. INAF, Osservatorio Astronomico di Capodimonte, Napoli. 3. Carl Sagan Center, SETI Institute, Mountain View, USA. 4. CGUC, Observatório Astronómico da Universidade de Coimbra, Coimbra, Portugal. 5. CERENA, Instituto Superior Técnico, Lisboa, Portugal.

Corresponding email: [marco.cardinale@unich.it](mailto:marco.cardinale@unich.it)

Keywords: Large Dark Dunes; Aeolian Processes; Herschel crater.

In this report, we present a study of a large dark dune field in Herschel Crater, a 300-km-diameter impact basin located close to the martian equator (14.4°S, 130°E).

We quantify the movement of the aeolian bed forms (ripples and dunes) using the High Resolution Imaging Science Experiment (HiRISE) datasets [1]. Dunes are migrating at the rate of ~0.45 meters per Martian year, while ripples are moving at the rate of ~1.46 meters per Martian year.

Both ripples and dunes are migrating toward the south, suggesting dominant winds blowing from the north to the south.

Furthermore, with the aid of the Mars Regional Atmospheric Modeling System (MRAMS) [2, 3] we compare the ripples and dunes morphologies and migrations with the modeled wind stresses and directions.

The modeled winds blow from the North and from the East seasonally, the interaction of these two wind regimes within the dune field might explain the complex pattern of the ripples while the modeled winds toward the south are in agreement with the observed ripple and dune migrations toward the south.

These results are congruous with the recent observations of ripple and dune migration in Gale Crater [4], the landing site of the NASA Mars Science Laboratory (MSL) rover, which is about 80 km to the NE. Our results confirm that this region of Mars is particularly active from an aeolian point of view.

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## A peculiar spectral unit in the Southern Amazonian Polar Layered Deposits

Carli C.\*<sup>1</sup>, Carrozzo F.G.<sup>1</sup>, Altieri F.<sup>1</sup>, Giacomini L.<sup>2</sup> & Bellucci G.<sup>1</sup>

1. IAPS, INAF. 2. CISAS, Università di Padova.

Corresponding email: [cristian.carli@iaps.inaf.it](mailto:cristian.carli@iaps.inaf.it)

Keywords: South Polar Deposits, Spectral classification, Mars.

South Polar regions were geologically mapped by Tanaka and Scott (1987). Several works followed and discussed the evolution of the South Polar Deposits revealing different geological units: i) Noachian crater terrains, ii) Dorsa Argentea Formation, characterized by smooth deposits and large irregular pits of Hesperian age, and iii) Amazonian polar layered deposits and polar ice deposits (Apl and Api, respectively). In particular the Apl deposits are characterized by alternating dark and light lithologies in a smooth, medium albedo material with sparse craters (Milkovich et al., 2002). Recently, thanks to the use of spectral parameters associated to mafic absorption around 1  $\mu\text{m}$ , Carrozzo et al. (2012) highlighted how a portion of these deposits can be clearly differentiated from a spectroscopical point of view. In particular, the 1  $\mu\text{m}$  band integral, the reflectance peak at 0.685  $\mu\text{m}$  and the 0.8/1.0  $\mu\text{m}$  reflectance ratio allowed to consider this area as different in composition from the surrounding Apl terrains, and spectrally similar to some craters dominated by dark dunes. This region was considered as a new spectral unit enriched in pyroxene content (Carrozzo et al., 2013). We have considered the spectral features from this region of interest and preliminary mapped it using the Spectral Angle Mapper (Kruse et al., 1993) supervised classifier to OMEGA mosaic of successive Solar longitude (Ls). The results evidence that this portion of the Apl area is the only region spectrally mapped, confirming that it is peculiar from a spectroscopical point of view compared to the rest of the South Polar region. Here, we'll show morphological and spectroscopical characteristics of this region to better address the characteristic of this smooth region and understand its possible formation and evolution.

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## Particle sizes influence on the retrieving optical constant of silicates on planetary regolith in the VNIR by Hapke model

Carli C.\*<sup>1</sup>, Serventi G.<sup>2</sup>, Ciarniello M.<sup>1</sup>, Capaccioni F.<sup>1</sup> & Sgavetti M.<sup>2</sup>

1. IAPS-INAF. 2. Dipartimento di Fisica e Scienze della Terra, Università di Parma.

Corresponding email: [cristian.carli@iaps.inaf.it](mailto:cristian.carli@iaps.inaf.it)

Keywords: Reflectance spectroscopy, Optical Constants, Hapke model.

Regoliths of inner planets are characterized by silicate materials, rocks and particulates, at different grain sizes. Visible and Near-Infrared (VNIR, ~0.4-2.5  $\mu\text{m}$ ) spectroscopy is an important tool to explore their mineralogical composition. Several techniques can be used to identify and quantify the mineral phases, like radiative transfer model. Optical constants can be retrieved from reflectance spectra applying this model (e.g. Hapke model; Hapke, 1993). Moreover, the particle sizes of an individual component and its distribution are important factors which influence the retrieving of the optical constants from Hapke modeling. Several papers (e.g. Lucey, 1998; Warrel and Davidson, 2010) approach the retrieving of silicate optical constants from reflectance spectra applying radiative transfer models considering measurements of a mineralogical component at multiple narrow size range. Otherwise, few papers discussed the application of this method for wider size ranges considering the effective size distribution. Recently, Carli et al. (2014) shows how the particle size distribution strongly affect the retrieved imaginary part ( $k$ ). Here we present a preliminary systematic application of the Hapke model to different silicates to better constrain the particle size influence. We have measured spectra of different pyroxene, olivine and plagioclase at several narrow particle size ranges (250-224, 224-200, 200-180, 180-150, 150-125, 125-100, 100-75, 75-50, and 50-20  $\mu\text{m}$ ) and wider weighed particle size ranges (e.g. delta size ca. 100 $\mu\text{m}$ ) of which we retrieved the optical constants and fitted the particle size as single average value and as distribution of multiple size components.

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## Radioactive decay as a second-order kinetics transformation process. Consequences on radiometric dating

Cavazzini G.\*

IGG-CNR Padova

Corresponding email: [giancarlo.cavazzini@igg.cnr.it](mailto:giancarlo.cavazzini@igg.cnr.it)

Keywords: Radioactive decay, Second-order kinetics, Solar activity, Decay constant, Apparent age, True age.

The exponential law with negative exponent which describes the change over time in the number of atomic systems of the radio-active species is derived from the observed change over time in the respective rates of decay, and interpreted in terms of first-order kinetics. However, this law cannot describe the change over time in the number of intrinsically-unstable systems, because after an infinite time-span of observation systems still survive unchanged.

Instead, the exponential law adequately describes the change over time in the number of systems which transform due to interaction with external physical entities. The atomic systems we presently call 'radio-active' are actually 'radio-activated', the observed change in the rate of decay of 'radio-active' nuclides is more adequately interpreted and discussed in terms of second-order kinetics, and the decay constant  $\lambda$  of a 'radio-active' species contains information about the concentration of the activating species. This line of reasoning is supported by recent interpretations of experimental data which suggest the existence of a relationship between solar activity and distance and the rate of decay of beta- and alpha-emitting radio-active nuclides (Jenkins & Fischbach, 2009; Jenkins et al., 2012).

It can be reasonably hypothesized that the sun changed its activity over the geological time. In this case a change in the value of the decay constants of the 'radio-active' nuclides occurred over time. A radio-activated nuclide is not characterized by a 'decay constant'  $\lambda$ , but by a 'decay parameter'  $\lambda$ , and we can calculate the effect of the change in  $\lambda$  over time on the age values of geological systems we calculate by using parent-daughter 'radio-active' nuclide systematics. The age values we calculate using the value of  $\lambda$  we measure nowadays are always apparent ages, and if the value of  $\lambda$  decreased monotonically over the geological time, the deviation of the apparent age from the true age of a geological system increases with the true age of the system.

Moreover, since the apparent age of a geological system we obtain by using a parent-daughter radio-active systematics depends not only on the true age of the system but also on the change in the value of the decay parameter of the parent nuclide over the true age time-span, and since the change in the value of the decay parameter depends on the change in the activity of the respective star, coeval geological systems on planets orbiting around different stars generally have different apparent age, and cannot be correlated.

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## Capabilities of the SHARAD instrument to detect subsurface features on Mars: an example of possible buried outflow morphologies in Elysium Planitia

Colantuono L.<sup>1</sup>, Baliva A.<sup>1</sup>, Guallini L.\*<sup>1</sup>, Marinangeli L.<sup>1</sup>, Mastrogiuseppe M.<sup>2</sup>, Cassenti F.<sup>2</sup> & Seu R.<sup>2</sup>

1. Laboratorio di Telerilevamento e Planetologia, Dipartimento di Scienze Umanistiche Psicologiche e del Territorio, Università d'Annunzio. 2. Dipartimento di Scienza e Tecnica dell'Informazione e Comunicazione, Università La Sapienza, Roma.

Corresponding email: [guallini@irsps.unich.it](mailto:guallini@irsps.unich.it)

Keywords: Mars, Outflow Channels, Marte Vallis, Elysium Planitia, SHARAD.

Most part of the channels systems on Mars surface are attributed to the outflow of water, released from the subsurface (e.g. Baker & Milton; Pacifici et al., 2007; Andrews-Hanna & Phillips, 2007). In the present work, we analyze Elysium Planitia region, in which is present a broad and young outflow channel system (Marte Vallis). Recent studies (Morgan et al., 2013) identified also in the subsurface of Marte Vallis several anastomosing channel formed around streamlined islands, later eroded and buried by lava flows (Jaeger et al., 2010; Leverington et al., 2011). Using available radargrams from the SHallow RADar (SHARAD) (Seu et al., 2004) on board the Mars Reconnaissance Orbiter, we analyzed possible geological structures in the subsurface of Cerberus Tholi, about 500 km East of Marte Vallis. In several of them, we identified reflectors with concave-upward morphology intersecting the surface. We interpret these reflectors as possible facies boundaries. The concave-upward features are up to some hundreds of kilometers wide in section view and have an estimated depth up to one hundred meters. In some cases, the material within the concave-upward morphologies has a diverse response (lower power reflection) to the radar signal than the surrounding terrains. Also, it is possible to observe a "stair-stepped" profile of some reflectors at their two termini. On the basis of their locations, we speculate that these geological features can be part of the Marte Vallis outflow channel system. However, it is not clear if we are observing possible depositional basins (i.e. paleolakes) or fluvial channels. Also, the symmetrical "stair-stepped" profile suggest possible terraces and, thus, more than one erosional episode. Further analysis is still ongoing.

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## **Landslides in Valles Marineris and other locations of Mars: a new database and examination of morphologies in relation to the deposition environment**

De Blasio F.V.\*, Crosta G.B., Valbuzzi E. & Frattini P.

Dept. of Earth and Environmental Sciences, University of Milano Bicocca.

Corresponding email: [fabio.deblasio@unimib.it](mailto:fabio.deblasio@unimib.it)

Keywords: Mars, Valles Marineris, Landslides.

In recent years, there has been much interest about landslides on planetary bodies other than the Earth. On Mars, landslides are often extremely well preserved after billions of years, so that they may shed light on ancient times where the hydrologic regime was likely much different from present.

Many Martian landslides punctuate the wallslopes of the 4,000-kilometers long, 8,000 meters high equatorial gorge of Valles Marineris. We have collected data for a large number of these landslides on a database and attempted a classification based not only on similarities with terrestrial events, but also on characteristics that may be informative of the environment of deposition. Landslides on Mars present a series of peculiar features such as the nearly vertical collapse close to the scarp, the extreme thinning, long runout in the distal part. We present some conceptual and numerical approaches to understand the dynamics of these landslides that may help infer the conditions at the moment of flow. It is found that the presence of ice could explain some of the morphologies and run-out of these landslides, but stress that exposed ice like in a modern glacier may be problematic.

## Quantitative 2D and 3D modeling of a ancient Gilbert-type fan delta in Shalbatana Vallis, Mars: paleoclimatic and paleohydrologic implications

Di Achille G.\*<sup>1</sup>, Longhitano S.G.<sup>2</sup>, Ferranti L.<sup>3</sup>, Hutton E.W.H.<sup>4</sup>, Kettner A.<sup>4</sup> & Rossi A.P.<sup>5</sup>

1. Istituto Nazionale di Astrofisica, Osservatorio Astronomico di Collurania, Teramo. 2. Università degli Studi della Basilicata, Dipartimento di Scienze, Potenza. 3. Università di Napoli "Federico II", Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Napoli. 4. University of Colorado, Institute of Arctic and Alpine Research, Boulder, CO, USA. 5. Jacobs University Bremen, Bremen, Germany.

Corresponding email: [diachille@oa-teramo.inaf.it](mailto:diachille@oa-teramo.inaf.it)

Keywords: Quantitative sedimentology, 2D and 3D fan-delta modeling, paleohydrology.

We reconstructed the paleohydrology and sedimentology of a ancient (3.4 Ga) martian Gilbert-type fan delta using a 2D and 3D basin-filling model (Sedflux 2.0, Hutton and Syvitski, 2008). Forward simulations were implemented to reproduce the observational evidence of a ~10 km<sup>3</sup> fluvio-lacustrine deposit having a maximum width of about 12 km and a 7 km mean radius formed within a 450-m-deep lake along Shalbatana Vallis. Using high-resolution imagery and stereo-derived topography from remote sensing datasets we inferred the majority of the model input parameters, bathymetry and morphometric properties of both the sedimentary basin and the deposits (e.g. area, height and especially volume and thickness of the sediments within the deltas). Likewise, average hydrologic and sedimentologic inputs for the simulations were inferred by using the morphometric characteristics of the latest active distributary channels (i.e. width, depth, and slope) as determined from imagery and topographic data. Particularly, paleoflow velocities and water discharges were derived using the Darcy-Weisbach equation, which allows to determine the paleohydrology of the channels from a series of parameters including width, depth, and slope of flow, friction factors and median grain sizes (D<sub>50</sub>). The latter granulometric sizes and their relative proportions were derived from (a) typical terrestrial ranges and from (b) measurements performed from microscopic images on martian alluvial sediments investigated by the Mars Science Laboratory rover at Gale crater (Williams et al., 2013). Sediment discharges were calculated using terrestrial bedload and suspended sediment transport predictors (e.g. Van Rijn and Ribberink equations) modified for application to martian flows. Finally, model runs were finished when the sediment volume transported and deposited through the simulation would match that of the actual deposits. Assuming continuous water and sediment discharges in stillstand conditions, the minimum formation timescales for the main fan-delta are from 400 to over 1000 years depending on the considered range of input parameters. Although this latter scenario (continuous and constant peak discharges) is rather questionable from a paleoclimatic point of view, it could be compatible with the hypothesis of episodic climatic optima produced by regional factors, like for example impact craters, volcanism, or tectonics and associated persistent hydrological activity. Therefore, our results suggest that martian deltas might have not been exclusively formed during extended epochs of clement climatic conditions and thus that they do not necessarily imply the occurrence of favorable and durable conditions for life.

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## Geomorphology and sedimentology of an unnamed ancient fluvial system in the Acidalia region of Mars

Di Achille G.\*<sup>1</sup>, Salese F.<sup>2</sup> & Ori G.G.<sup>2-3</sup>

1. Istituto Nazionale di Astrofisica, Osservatorio Astronomico di Collurania, Teramo. 2. International Research School of Planetary Sciences, Pescara.  
3. Ibn Battuta Centre, Université Cadi Ayyad, Marrakech, Morocco.

Corresponding email: [diachille@oa-teramo.inaf.it](mailto:diachille@oa-teramo.inaf.it)

Keywords: Fluvial system, lake, delta, Mars.

Using mainly High Resolution Stereo Camera (HRSC) image and topography mosaics we investigated a nearly 300-km-long valley system located westward of Idaeus Fossae in the Acidalia region of Mars. The valley apparently originates from a subsided area developed on the ejecta of a relatively fresh crater and extends eastwards trending approximately in E-W direction before terminating in one of the depressions of Idaeus Fossae. The valley floor is mainly characterized by the occurrence of well-preserved braided and anabranching channel systems locally forming extensive meandering patterns. After about 80 km from the apparent source area the valley drains into a ~20-km-diameter unnamed crater forming a deltaic deposit whose front lies at about 1800-1820 m below the martian datum. The deltaic deposit is about 8-km-long and morphologically resembles the Jezero delta (Fassett and Head, 2005), showing a well-developed distributary pattern with evidence of channel switching on the delta plain. The floor of the crater-lake is not incised by the main valley, however a breach area along the eastern crater rim consists of two spillover channels at about the same elevation of the crater inlet (-1820 m). These latter channels connect the crater lake to the eastward portion of the valley continuing towards Idaeus Fossae with its anastomosing channels. The HRSC topography of the crater lake shows that the elevation of delta front (an indicator of the lake main water level) is consistent with that of the valley inlet and outlets at B1 (i.e. -1820 m), thus suggesting that the lake reached its equilibrium state at this level acting as a bypass between the western and eastern portions of the main valley. Moreover, the lack of incision on the crater lake floor suggests that (a) the lake was relatively stable with limited water level fluctuations only responsible for the partial delta entrenchment and channel avulsion on the delta plain and that (b) the overall lake retreat was enough fast to prevent the erosion of the crater floor and significant entrenchment of the delta. Finally, after exiting the open crater lake the main valley continues to the east after breaching two N-S oriented ridges through other two breaching-spillover area characterized by the occurrence of deep scours at the base of the breached ridges. The studied system is particularly interesting since it might have been generated by regional mechanisms like for example impact related groundwater ice melting as suggested by the presence of the subsided region (likely due to subsurface volume loss) on the crater ejecta where is located the source region of the valley system. This hypothesis is also supported by the fact that both the latter depression and the valley seem to postdate the crater ejecta based on cross-cutting relationships.

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## New augite geothermometer for nakhlites

Domeneghetti M.C.\*<sup>1</sup>, Alvaro M.<sup>2</sup>, Fioretti A.M.<sup>3</sup>, Cámara F.<sup>4-5</sup> & Marinangeli L.<sup>6</sup>

1. Dipartimento di Scienze della Terra e dell' Ambiente, Università degli Studi di Pavia. 2. Dipartimento di Geoscienze, Università degli Studi di Padova. 3. Istituto di Geoscienze e Georisorse CNR, UOS di Padova. 4. Dipartimento di Scienze della Terra, Università di Torino. 5. CrisDi, Interdepartmental Centre for the Research and Development of Crystallography, Torino. 6. Int'l Research School of Planetary Sciences, Università G. d'Annunzio, Chieti.

Corresponding email: [chiara.domeneghetti@unipv.it](mailto:chiara.domeneghetti@unipv.it)

Keywords: augite, closure temperature, Martian nakhlite, single crystal X-ray diffraction, thermal history.

Nakhlites, together with shergottites and chassignites constitute the “SNC” group of Martian meteorites. MIL 03346 is a nakhlite, that was found at Miller Range, in Antarctica and is mainly composed of clinopyroxene (79%), with minor olivine (1%), and 20% vitrophyric intercumulus material (McBride et al., 2005; Treiman, 2005). The clinopyroxene is augite with a homogeneous core ( $\text{En}_{36}\text{Fs}_{24}\text{Wo}_{40}$ ) and an iron-enriched rim ( $\text{En}_8\text{Fs}_{64}\text{Wo}_{28}$ ).

Since the first modern petrologic studies of Nakhla, the nakhlite group of meteorites has been interpreted as augite-rich cumulate igneous rocks, derived from basaltic magma, that erupted onto the surface of Mars (Bunch and Reid, 1975; Reid and Bunch, 1975). However, the relative low closure temperature ( $T_c$ ) of ca. 500 ( $\pm 100$ )°C calculated for MIL 03346 by Domeneghetti et al (2013) with the available geothermometer (Brizi et al, 2000) would imply a slow cooling rate that is in disagreement with the petrologic evidence for an origin from a fast cooled lava flow.

Ex-situ annealing experiments combined with high-resolution single-crystal X-ray diffraction (HR-SC-XRD) on crystals from MIL 03346 clearly showed that the degree of order remained unchanged at 600°C thus suggesting that the actual  $T_c$  is close to this temperature. Therefore, we undertook an *ex situ* annealing experiments combined with HR-SC-XRD at 600, 700, 800 and 900 °C until the equilibrium in the intracrystalline  $\text{Fe}^{2+}$ -Mg exchange is reached. The experiments have been performed on two crystals from exactly the same fragment of MIL 03346 sample in order to calibrate a new geothermometer for augites from Martian nakhlites:

$$\ln k_D = -4421(\pm 561)/T(\text{K}) + 1.46(\pm 0.52) \quad (R^2=0.988), \text{ where } k_D = [(\text{Fe}^{2+}_{\text{M1}})(\text{Mg}_{\text{M2}}) / (\text{Fe}^{2+}_{\text{M2}})(\text{Mg}_{\text{M1}})].$$

Applying this new equation to MIL 03346 the closure temperature resulted to be 605(84)°C about 100°C higher than that calculated with previously available calibration (i.e. Brizi et al. 2000). However, this closure temperature is still lower than expected based on petrologic evidences and suggests that MIL 03346 clinopyroxene bears record of a thermal event that postdates, or is superimposed on, the natural cooling path of the host lava flow.

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## **Landslides in Valles Marineris, Mas, and their possible triggering mechanism**

Frattini P.\*<sup>1</sup>, Crosta G.B.<sup>1</sup>, De Blasio F.V.<sup>1</sup>, Castellanza R.<sup>1</sup> & Uti S.<sup>2</sup>

1 Dept. of Earth and Environmental Sciences, University of Milano Bicocca. 2 School of Engineering, University of Warwick, Coventry UK.

Corresponding email: [paolo.frattini@unimib.it](mailto:paolo.frattini@unimib.it)

Keywords: Valles Marineris, Landslides, Crater damage zone.

Slope stability and landslide size-frequency analysis on Earth has been at the focus of research of disaster prevention for decades. On Mars, several landslides can be observed in region of sufficient elevation and slope, especially at the rims of craters, along water outflow channels, and especially in correspondence of Valles Marineris, a huge gorge cutting the Martian crust for 4,000 km along the equator. There, landslide span over a large interval of volume and aerial distribution, ranging from 0.15 km<sup>2</sup> to a maximum of 12,000 km<sup>2</sup> (Crosta et al, 2013). Landslide slope stability methods equivalent to the ones used for the Earth may be adapted to shed light on the nature of deep Martian rock and of the mechanisms of failure.

One of the important point that should be solved concerns the factors controlling the spatial distribution of such failures. Mechanical properties of the heavily cratered Martian upper crust could have been controlled by different factors: lithology, “tectonic” stresses, weathering, water circulation and impact cratering. In this work, we concentrate especially on the role of meteoroid impacts as a predisposing factor for failures in Valles Marineris. Impacts resulted in a fractured crust covered by breccia layers (1 to 3 km thick) and impact ejecta overlain by Aeolian, aqueous and unconsolidated regolith. Numerical models, laboratory impact experiments and seismic data all support the idea that fractured zones exist around craters and extend both radially and at depth below the crater to a distance equal to half the crater diameter. This damage zone presents poor mechanical properties, affecting the hydrology and the slope instabilities along the valley flank on Mars. Considering that the craters are very frequent and evenly distributed on Mars’ surface, we make the hypothesis that the control of shock damage zone on landslide size can regulate the size frequency distribution of Martian landslides (Frattini et al, 2014). Preliminary numerical simulations performed with a 3D Janbu simplified method corroborate this view, but other predisposing factors may have been at work during the history of Mars.

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## Geological map of Victoria quadrangle (H-2) of Mercury from MESSENGER images

Galluzzi V.<sup>\*1-2</sup>, Di Achille G.<sup>3</sup>, Ferranti F.<sup>1</sup>, Rothery D.A.<sup>4</sup> & Palumbo P.<sup>2</sup>

1. Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse - Università degli Studi di Napoli "Federico II". 2. Dipartimento di Scienze e Tecnologie - Università degli Studi di Napoli "Parthenope". 3. INAF - Osservatorio Astronomico di Collurania, Teramo. 4. Department of Physical Sciences - The Open University, Milton Keynes, UK.

Corresponding email: [valentina.galluzzi@unina.it](mailto:valentina.galluzzi@unina.it)

Keywords: Mercury (planet), Planetary Geologic Mapping, Geographic Information System.

Identifying geological units and their superposition relationships is fundamental for understanding the evolution of Mercury. Hermean geological units are strictly related to impact processes, whose deposits are often recognised through geomorphological interpretation of remote sensing datasets. The first stratigraphical and geological study of Mercury was released by Spudis & Guest (1980), whose work was based on the images taken by Mariner 10 covering 42% of the total surface of Mercury. The planet has been officially divided into fifteen quadrangles: 2 polar, 5 equatorial and 8 at mid-latitudes. Quadrangle H-2 (= Hermes sheet n. 2), named "Victoria" (20°N – 65°N Lon.; 270°E – 0° Lat.), has been partially mapped by McGill & King (1983), though a wide area (~64%) remained unmapped due to the lack of imagery. Following the terrain units recognised and described by the above authors, we produced a geological map of the entire quadrangle using MESSENGER (MErcury Surface, Space ENvironment, GEOchemistry and Ranging) data. The images taken by the Mercury Dual Imaging System (MDIS) Wide Angle Camera (WAC) and Narrow Angle Camera (NAC) allowed us to map geologic and tectonic features in much greater detail than the previously published map. We used the MDIS map projected BDR (Basemap reduced Data Record) at 256 px/deg (~166 m/px) as a reference layer together with the released global mosaics at 500 m/px (Becker et al., 2009) and 250 m/px. Also, we added WAC and NAC images from the released datasets at different resolutions and illumination directions when needed. In addition to that, MLA (Mercury Laser Altimeter) topography and stereo topography from MESSENGER flyby "M2" (Preusker et al., 2011) were used to better constrain unit boundaries. Victoria quadrangle is characterised by a N-S thrust array constituted by Victoria Rupes, Endeavour Rupes and Antoniadi Dorsum. A previous study made on craters cross-cut by these thrusts reveals fault dips of 15-20° and a near dip slip motion (Galluzzi et al., 2014). Completion of the geological map along with the structural analysis of this array enable a complete geological overview of the area, which will lead to a better understanding of the tectonic evolution of Mercury.

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## Dating a thrust system on Mercury: implications for the planet's thermal evolution

Giacomini L.\*<sup>1</sup>, Massironi M.<sup>1-2</sup>, Marchi S.<sup>3</sup>, Fassett C.I.<sup>4</sup>, Di Achille G.<sup>5</sup> & Cremonese G.<sup>6</sup>

1. Centro Interdipartimentale di Studi e Attività Spaziali, Università di Padova. 2. Dipartimento di Geoscienze, Università di Padova. 3. Southwest Research Institute, Boulder, USA. 4. Department of Astronomy, Mount Holyoke College, South Hadley, USA. 5. Istituto Nazionale di Astrofisica-Osservatorio Astronomico di Collurania, Teramo. 6. Istituto Nazionale di Astrofisica, Osservatorio Astronomico di Padova.

Corresponding email: [lorenza.giacomini@unipd.it](mailto:lorenza.giacomini@unipd.it)

Keywords: Mercury, thrust system, dating.

The tectonic evolution of Mercury is dominated at a global scale by contractional features such as lobate scarps that are widely distributed across the planet. These structures are thought to be the consequence of the secular cooling of Mercury. Therefore, dating these features is essential to place constraints upon the timing of planetary cooling, which is important for understanding the thermal evolution of Mercury. The Messenger cameras (MDIS WAC and NAC), acquired images of new regions of the Mercury surface that allowed us to detect several new lobate scarps especially where the illumination geometry is more favorable for structural analysis. Among them a 2000-km long thrust system, located between 80°-100°E and 30°N-15°S, has been detected which consists of several individual lobate scarps exhibiting a north-south orientation and a westwards vergence. We dated this system using several different methods. Traditional stratigraphic analysis was accompanied by buffered crater counting of units that overlap the thrust system, allowing us to determine an absolute model age for the tectonic feature. These complementary methods give consistent results, implying that activity on the thrust ended between 3.5–3.7 Ga, depending on the adopted absolute-age model. These data provide important constraints on thermal evolution models of Mercury.

## **Ancient Martian lakestands and fluvial processes in Iani Chaos: geology of Light-Toned Layered Deposits and their relationship to Ares Vallis outflow channels**

Guallini L.\*<sup>1</sup>, Gilmore M. S.<sup>2</sup> & Marinangeli L.<sup>1</sup>

1. Laboratorio di Telerilevamento e Planetologia, Dipartimento di Scienze Umanistiche Psicologiche e del Territorio, Università d'Annunzio. 2. Department of Earth and Environmental Sciences, Wesleyan University, Middletown, CT, USA.

Corresponding email: [guallini@irsps.unich.it](mailto:guallini@irsps.unich.it)

Keywords: Mars, Iani Chaos, Ares Vallis, Outflow Channels, Light-toned Layered Deposits, Water, Evaporites.

Iani Chaos is a ~30,000 km<sup>2</sup> region that lies at the head of the Ares Vallis outflow channel system (Pacifci et al., 2007; Warner et al., 2009). Mapping of Ares Vallis reveals multiple episodes of erosion, likely linked to several discharge events from the Iani Chaos aquifer. We present the first detailed map of the Iani region. Five chaos units have been distinguished with varying severity of modification (primarily by erosion and fracturing), starting from a common terrain (Noachian highlands). We observe a general progressive decrease of their mean elevation from the Mesas, Mesas & Knobs and Hummocky terrains to the Knobs and Knobby morphologies. This trend is consistent with a greater initial collapse of the original surface with an increase of the fracturing and/or of the erosional degree of terrains. Light-toned Layered Deposits (LLD) have been mapped and described in Iani Chaos. These terrains are clearly distinguished by a marked light-toned albedo, high thermal inertia and their pervasively fractured morphology. The LLD deposits both fill the basins made by the collapsed chaotic terrains and are found to be partially modified by the chaos formation. LLD also overlap chaos mounds or are themselves eroded into mounds after deposition. These stratigraphic relationships demonstrate that LLD deposition occurred episodically in the Iani region and throughout the history of the development of the chaos. The composition and morphologies of the LLD are consistent with deposition in an evaporitic lacustrine environment, likely to be the surface manifestation of a subsurface aquifer. For the first time, we have mapped and analyzed potential fluvial features (i.e., channels, streamlined islands, terraces, grooved surfaces) on the surface of the LLD. These landforms mark a fluvial system that can be traced from central Iani, some to all of which is linked northward to Ares Vallis. Using HRSC Digital Elevation Models, we have compared the elevation of the LLD and channel units and find that the altitudes of the chaos units are strictly comparable with the altitude of the floors of the major Ares Vallis channels. This is a decisive evidence of a possible fluvial system within Iani linked to the Ares Vallis outflow system. Also, on the contrary of previous works (Warner et al., 2011) it suggests that LLD are coeval with the Iani Chaos and Ares Vallis formation.

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## Possible mud volcanism and astrobiological potential on Mars

Komatsu G.\*

International Research School of Planetary Sciences - Università d'Annunzio

Corresponding email: [goro@irsps.unich.it](mailto:goro@irsps.unich.it)

Keywords: Mars, mud volcano, geology, astrobiology, exploration.

Mud intrusion and extrusion on Earth are well-known phenomena whereby fluid-rich, fine-grained sediments ascend within a lithologic succession mainly because of their buoyancy (Kopf, 2002). The buoyancy maybe given because the involved sediments are in overpressured or undercompacted conditions with abnormally high porosities for their depths due to processes such as rapid sedimentation, tectonic loading, gas hydrate dissociation, or diagenesis and mineral dehydration reactions, among others. Mud volcanoes (MVs) on Earth typically exhibit cone- or pie-shaped edifices and flows, which are made of a clay mineral-rich matrix and a range of clasts. Mound features interpreted to be MVs occur at various locations on Mars, including Isidis Planitia, Utopia Planitia, the Utopia/Isidis overlap, Acidalia Planitia, Arabia Terra, and Chryse Planitia (e.g. Ori et al., 2000; Oehler & Allen, 2010; Pondrelli et al., 2011; Komatsu et al., 2011). Confirmation of the MV hypothesis on Mars has not been obtained yet but improved spacecraft data provide further support for the purported MVs. Mud volcanism on Mars would be very important in understanding the processes of sedimentation, water saturation, and fluid and gas movement in the crust.

The surface environment of Mars is considered to be hostile for life or organic materials due to radiation and oxidation. Thus Martian subsurface environment may have been more suitable for biological activity, and astrobiological exploration of subsurface is an approach worth consideration. On Earth, MVs are an important “window” into the underlying strata, because both a low-competence parent bed (clay-rich layer) and some rock fragments are transported to the surface. Similarly, mud volcanism on Mars would provide a window into subsurface crustal materials that were deposited earlier in geologic records. Fluids such as water and methane are relevant to the topic of biology/astrobiology, and fine-grained sedimentary materials have the potential to preserve biosignatures or even result from biological processes (Komatsu & Ori, 2000), making accumulations of subsurface materials transported upward to the surface by mud volcanism potential astrobiological investigation sites.

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## **Relationship between surface geology and impact cratering: global and local studies from Mars and Mercury**

Mancinelli P.\*<sup>1</sup>, Mondini A.<sup>2</sup>, Pauselli C.<sup>1</sup> & Federico C.<sup>1</sup>

1. Dipartimento di Fisica e Geologia, Università degli Studi di Perugia. 2. CNR - IRPI, Perugia.

Corresponding email: [pamancinelli@gmail.com](mailto:pamancinelli@gmail.com)

Keywords: Craters, geology, planets.

Understanding which are the relations between impact crater and geology on a planetary surface is a fundamental step in the comprehension of the geological evolution of the planet. Here we present some examples about impact craters on Mars and Mercury, in particular we will show the modelling of a large impact on Mars and the geological mapping of the Raditladi crater on Mercury using Mars Global Surveyor (MGS) and MESSENGER data respectively. The aim of our work is to highlight relations at different scales, between the impact phenomena and the geological and geophysical consequences that the impact produces on the target body, both on the surface and in the crust.

## Geological constraints for carbonate occurrence within Elorza Crater central pit

Marinangeli L.\*<sup>1</sup>, Liberi F.<sup>1</sup>, Piluso E.<sup>2</sup>, Pompilio L.<sup>1</sup>, Cardinale M.<sup>1</sup>, Rosatelli G.<sup>1</sup>, Tranquilli A.<sup>1</sup> & Pepe M.<sup>3</sup>

1. Dipartimento di Studi Psicologici, Umanistici e del Territorio DISPUTer, Università degli Studi "G. d'Annunzio", Chieti-Pescara. 2. Dipartimento di Scienze della Terra, Università della Calabria, Arcavacata di Rende (CS). 3. CNR-IREA, Milano.

Corresponding email: [lucia.marinangeli@unich.it](mailto:lucia.marinangeli@unich.it)

Keywords: carbonates, Elorza Crater, central pit, carbonatites.

Elorza Crater is located just North of the Ophir Cavus and is characterized by a prominent and well-preserved central pit. The latter appears to be affected by several fault and fracture systems, although the most noticeable structural lineament cut through its NW sector with a NE-SW trending.

The structural and geological evolutions of Elorza Crater appear to be quite complex. The HiRISE images of the central uplift area allow to identify aeolian deposits and detrital materials, that partially fill the central and nearly flat depression of the pit. Two different types of terrains exposed along the internal and external slopes of the central pit can be observed: highly fractured massive rocks showing light to very-light tones and layered rocks showing darker tones.

CRISM data clearly show the carbonate signature near 2.3  $\mu\text{m}$ . Carbonates occur on top of the pit rim, where dust is less abundant. On the base of this preliminary study, we advance different hypotheses to explain the occurrence of carbonates at Elorza Crater.

Models for central pit formation imply the collapse of the central peak, whose formation is related to the impact, as the result of the presence of subsurface volatile phases such as water or ice (Barlow, 2010). As a consequence, the subsurface rocks are uplifted and exposed to surface and the thickness of the stratigraphic uplift is related to the diameter of the impact crater. In this context, the carbonate rocks can be interpreted as part of an older and deeper Martian crust, exhumed during the impact crater formation and relate processes, although the origin remain unknown.

Similarly, Michalski & Niles (2010) explain the formation of carbonate rocks at Leighton Crater as the result of metamorphic processes, which acted on interlayered carbonate-siliciclastic sediments buried under basalts or, alternatively, as metasomatization of the basaltic crust by CO<sub>2</sub>-rich fluids of unknown origin.

The complex structural and geological setting of Elorza Crater, associated to the analogies of the central bulge with a volcanic morphology, as well as the occurrence of carbonate signature, can also be explained by volcano-tectonic processes. On Earth, carbonate rock of igneous origin are named carbonatite; they occur as dikes or sills within zoned alkaline igneous complexes, otherwise they occur as lava flows or, more often, pyroclastic deposits. The presence of diagnostic minerals, such as melilite, monticellite, phlogopite is useful to distinguish them from sedimentary carbonates. We compared the CRISM spectra and those acquired on samples of terrestrial carbonatites and the similarities are marked.

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## First geological observations of 67P/CHURYUMOV-GERASIMENKO comet nucleus from Rosetta mission

Massironi M.\*<sup>1-2-3</sup>, Cremonese G.<sup>3</sup>, Giacomini L.<sup>2</sup>, Pajola M.<sup>2</sup>, Marchi S.<sup>4</sup>, Besse S.<sup>5</sup>, Thomas N.<sup>6</sup>, Oklay N.<sup>7</sup>, Vincent J.B.<sup>7</sup>, Barucci M.A.<sup>8</sup>, Bertini I.<sup>2</sup>, Ferri F.<sup>2</sup>, Fornasier S.<sup>8</sup>, Lazzarin M.<sup>9</sup>, Magrin S.<sup>2</sup>, A'Hearn M.F.<sup>10</sup>, Marzari F.<sup>9</sup>, La Forgia F.<sup>9</sup>, Snodgrass C.<sup>7</sup>, Naletto G.<sup>11-2</sup>, Jorda L.<sup>12</sup>, Barbieri C.<sup>9</sup>, Sierks H.<sup>7</sup> & the OSIRIS team

1. Department of Geosciences, University of Padova, Italy. 2. Centro di Ateneo di Studi e Attività Spaziali "Giuseppe Colombo" (CISAS), University of Padova. 3. Istituto Nazionale di Astrofisica (INAF-OAPD), Padova. 4. Southwest Research Institute, Boulder, USA. 5. ESA/ESTEC, Noordwijk, The Netherlands. 6. University of Bern, Switzerland. 7. Max-Planck Institute for Solar System Research, Göttingen, Germany. 8. LESIA-Paris Observatory, Paris, France. 9. Department of Physics and Astronomy, University of Padova. 10. Department of Astronomy, University of Maryland, College Park, USA. 11. Department of Information Engineering - University of Padova. 12. Laboratoire d'Astrophysique de Marseille, France.

Corresponding email: [matteo.massironi@unipd.it](mailto:matteo.massironi@unipd.it)

Keywords: Cometary nuclei, Rosetta-OSIRIS, 67P/CHURYUMOV-GERASIMENKO.

Up to date several cometary nuclei have been acquired at different resolutions (9P/Tempel 1 up to 10 m/pixel, 19P/Borrelly up to 47 m/pixel, 103P/Hartley 2 up to 7m/pixel, 81/Wild2 up to 14 m/pixel) revealing that the geomorphology of cometary nuclei is extremely variable but with several recurrent features such as spike/pitted and mottled terrains, flat floored craters, smooth and flat surfaces, mesas, ridges and troughs (e.g. Basilevsky et al. 2006). The great inhomogeneity of cometary surfaces is thought to be mostly due to different degree of repeated sublimation which leads to planation, slope retreats, development of lag deposits of variable thickness, focused ablation on pits, smoothing, widening and degradation of impact craters. Jet activity has been instead seen associated to rough areas and mounds on 103P/Hartley 2 comet (Syal et al. 2013). Finally layered terrains (recognized on 9P/Tempel 1, Thomas et al. 2007), fractures, pits and faults can give important hints on the geological evolution of the body since they might reflect primordial aggregation as well as later thermal and impacting evolution. All these geomorphological features are prone to modifications due to cometary activity, while the comet is approaching the Sun. The Rosetta mission, following the comet along its path towards the Sun will give the unique opportunity of realizing detailed geological maps with the aim of defining primary stratigraphic and structural relationships among geological bodies as well as monitoring surface changes. In particular on August 2nd, 2014, the Rosetta far approach trajectory towards 67P/C-G, will end up reaching a distance from the comet surface of about 720 km. At this time, the 67P/C-G nucleus will be imaged through 288 OSIRIS-Narrow Angle Camera (NAC) pixels covering its diameter with a spatial resolution of 13 m. From August 3rd, up to August 31st, i.e. during the Comet Approach Trajectory (CAT), the fore seen spacecraft distance will be rapidly reduced down to 52 km, giving the unique opportunity to get full frame images (2048 X 2048 px) and a complete coverage of the nucleus with a scale of 90 cm/px. It is worth pointing out that such images will provide the best ever cometary surface characterization to date. We will present the preliminary geological observations from these images.

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## Synthesis of Fe<sup>2+</sup>- bearing plagioclases: a valuable tool for interpreting reflectance spectra from Solar System bodies

Orlando A.<sup>1</sup>, Serventi G.\*<sup>2</sup>, Carli C.<sup>3</sup>, Borrini D.<sup>4</sup>, Pratesi G.<sup>4</sup>, Sgavetti M.<sup>2</sup> & Capaccioni F.<sup>3</sup>

1. C.N.R. - Istituto di Geoscienze e Georisorse, U.O.S. di Firenze. 2. Dipartimento di Fisica e di Scienze della Terra "Macedonio Melloni", Università di Parma. 3. Inaf-IAPS Tor Vergata, Roma, 4 Dipartimento di Scienze della Terra, Università di Firenze.

Corresponding email: [giovanna.serventi@unipr.it](mailto:giovanna.serventi@unipr.it)

Keywords: plagioclase, VNIR spectra, synthesis.

The acquisition of Visible and Near-infrared reflectance (VNIR) spectra is a tested methodology in order to infer compositional information about the surface of Solar System bodies. Nonetheless, because this methodology is sensitive to Crystal Field absorptions and Vibrational Overtone, different types of uncertainties on the interpretation of the mineralogy can occur using VNIR spectra. In this regard it would be desirable to be able to count on spectroscopic database of minerals (and rocks) to be compared with the acquired spectra of Solar System bodies. The database can be assembled taking into consideration both natural (terrestrial or extra-terrestrial) and synthetic materials. Aim of this study is to synthesize Fe<sup>2+</sup>- bearing plagioclases and characterize them through the acquisition of VNIR spectra. In fact, this mineral represents a main phase on the surface of many Solar System bodies, like Vesta, as it was found in Howardite - Eucrite - Diogenite (HED) meteorites, and Moon, as it was found in lunar samples and meteorites, as Anorthitic (An) rich phase containing Fe<sup>2+</sup> as a minor element. Plagioclase is a common phase on the Earth too, but Fe can be present as 3+ and 2+ oxidation state. Thus, a treatment process in a controlled atmosphere was necessary in order to synthesize An<sub>90</sub> plagioclases with variable amounts of FeO (up to 1 wt%). Synthesis were performed at 0.1 MPa using a Deltech DT-31 vertical gas mixing quench furnace in which oxygen fugacity is controlled by means of a mixture of CO and CO<sub>2</sub> flowing through the furnace and measured by a SIRO<sub>2</sub> oxygen sensor. Starting materials were usually contained on a Pt wire loops and suspended in the hot spot by means of a thin Pt wires. Different synthesis procedures were followed in order to get the best homogeneous composition of products. Indeed the varied parameters were the following: bulk of starting material (Fe<sup>2+</sup> or Fe<sup>3+</sup> in oxides and carbonates mixtures), vitrification cycles (0-2), T and duration of vitrification (1550-1580 °C, 15-90 minutes), duration of sintering at 1400 °C and logfO<sub>2</sub>= -9 (18-28 hours). Products were analyzed by XRD and EPMA before VNIR characterization. In general, synthesized plagioclases have a good homogeneity as regards An contents but not for their FeO contents when nominal FeO is > 0.5 wt%. VNIR spectra on both glasses and plagioclases, besides showing the typical Fe absorption bands, proved to be a sensitive approach to test the compositional homogeneity of synthetic products.

## Geological-geomorphological map of ExoMars 2016 landing site

Pacifici A.\*<sup>1</sup>, Cannarsa F.<sup>1</sup>, Murana A.<sup>1</sup>, Aboudan A.<sup>1</sup>, Ori G.G.<sup>1</sup>, Marcer A.<sup>2</sup>, Portigliotti S.<sup>2</sup> & Lorenzoni L.<sup>3</sup>

1. Int'l Research School Planetary Sciences, Università d'Annunzio. 2. Thales Alenia Space Italy.  
3. European Space Research and Technology Centre.

Corresponding email: [pacifici@irsps.unich.it](mailto:pacifici@irsps.unich.it)

Keywords: ExoMars, landing site, Mars.

Geological mapping is of paramount importance for landing site selection and analysis, and is an essential part of the planning process for a space exploration mission. As part of the ETSA (Environmental Terrain Support Analysis) framework, we realized a geomorphological map of the ExoMars 2016 Entry Descent Landing module (EDL) landing site. ExoMars 2016 represents the first mission of the European Space Agency (ESA) Aurora Exploration Programme, realized in collaboration with Thales Alenia Space Italia (TAS-I) as prime contractor. The target landing of EDL is an ellipse (110x24 km) in the Meridiani Planum area of Mars. The geomorphological map (scale about 1:100K) has two main purposes: i) to characterize the landing area from the geological and geomorphological point of view and ii) to provide useful information for to support the engineering design of the EDL. Data utilized consist of low, high and very high resolution data. In order to mitigate the misalignments of data acquired from different spacecraft, the entire dataset have been manually coregistered, proceeding from lower to higher resolution data. Low and high resolution data consist of MOLA, THEMIS, HRSC and CTX data. Very high resolution data consists of MOC NA and HiRISE images. The landing ellipse of ExoMars 2016 partially overly, but not coincide, to the landing ellipse of NASA mission Mars Exploration Rover Opportunity. As a consequence, part of the ExoMars 2016 landing site is densely and completely covered by very high resolution images (MOC NA and HiRISE), while in the other part high resolution images are discontinuous and sparse. Furthermore, Opportunity data of the Martian surface have been utilized in order to better distinguish and characterize geomorphological units of investigated area. The ExoMars 2016 landing site area is one of the flattest and featureless region of Mars. In the entire landing ellipse the altitude vary only about 300 m, and larger part of the landing site is covered by aeolian features characterized by wavelengths ranging from few meters to few decameters. Larger part of impact craters appears widely reworked or buried. In such condition (sparse high-resolution images and almost featureless surface) the main difficulty of this work consisted in the possibility of distinguish and map different aeolian bedforms and rocky outcrops. The main units have been locally distinguished trough very high resolution images, and then their boundary extended on the base o high and low resolution data. To this purpose, a novel algorithm called Multi Scale Tonal Roughness (MSTR) has been developed in order to enhance and quickly map metric and decametric-scale features in high and very high resolution images. Recognized geomorphological units consist mainly of bedrock units, probably belonging to the so called Bourn Formation, some different aeolian units, and impact crater related units.

## The exploration of Galileian satellites by the JANUS camera onboard the ESA JUICE mission

Palumbo P.\*<sup>1</sup>, Di Achille G.<sup>2</sup>, Adriani A.<sup>3</sup>, Cremonese G.<sup>4</sup>, Debei S.<sup>5</sup>, Della Corte V.<sup>3</sup>, Ferranti L.<sup>6</sup>, Galluzzi V.<sup>1-6</sup>,  
Magrin D.<sup>4</sup>, Marinangeli L.<sup>7</sup>, Massironi M.<sup>8</sup>, Mazzotta Epifani E.<sup>9</sup>, Popa C.<sup>9</sup>, Ragazzoni R.<sup>4</sup>, Schipani P.<sup>9</sup>, Tosi F.<sup>3</sup>,  
Zusi M.<sup>9</sup>, Jaumann R.<sup>10</sup>, Hoffmann H.<sup>10</sup>, Lara M.L.<sup>11</sup>, Holland A.<sup>12</sup> & the International JANUS team

1. Dipartimento di Scienze Applicate, Università degli Studi di Napoli "Parthenope". 2. INAF, Osservatorio Astronomico di Teramo. 3. INAF, Istituto di Astrofisica e Planetologia Spaziale. 4. INAF, Osservatorio Astronomico di Padova. 5. CISAS, Università degli Studi di Padova. 6. Dipartimento di Geoscienze, Università di Napoli Federico II. 7. DISPUTer, Università di Chieti-Pescara. 8. Dipartimento di Geoscienze, Università degli Studi di Padova. 9. INAF, Osservatorio Astronomico di Capodimonte. 10. DLR – Institute of Planetary Research, Berlin, Germany. 11. CSIC – Instituto de Astrofisica de Andalucia, Granada, Spain. 12. Open University, Milton Keynes, UK.

Corresponding email: [palumbo@uniparthenope.it](mailto:palumbo@uniparthenope.it)

Keywords: Jupiter satellites, Icy surfaces, remote sensing.

JANUS (Jovis, Amorum ac Natorum Undique Scrutator) is a camera selected for the ESA JUICE (JUper ICy moons Explorer) mission, which is the first ESA large-class mission planned for launch in 2022 and arrival at Jupiter in 2030 (Grasset et al., 2013). The mission will be operative for at least three years making detailed observations of the giant gaseous planet Jupiter and three of its largest moons, Ganymede, Callisto and Europa.

The Galileian satellites Io, Europa, Ganymede and Callisto show an increase in geologic activity with decreasing distance to Jupiter (Stephan et al., 2013). Io, nearest to Jupiter, is volcanically active. Europa could still be tectonically and volcanically active today, while Callisto, the outermost Galileian satellite, is geologically inactive but bears witness to past processes in the system through its surface features. Ganymede holds a key position in terms of geologic evolution because it features old, densely-cratered terrain, like most of Callisto, but also widespread resurfaced regions, similar to most of the surface of Europa. Ganymede observations from an orbiter are essential to investigate: (1) its wide range of surface ages which reveals a geologic record of several billions of years; (2) its great variety in geologic units and geomorphical features; (3) its active magnetic dynamo; (4) the possible presence of a subsurface ocean. The three icy Galileian satellites show tremendous diversity of surface features, witnesses of significantly different evolutionary paths. Each of these moons exhibits its own fascinating geologic history – formed by competition and also combination of external and internal processes. Their origins and evolutions are controlled by factors such as density, temperature, composition (volatile compounds), stage of differentiation, volcanism, tectonism, rheological behavior of ice and salts to stress, tidal effects and interactions with the Jovian magnetosphere and the space. These interactions are still recorded in the present surface geology which displays also possible cryovolcanism, widespread tectonism, surface degradation and impact cratering.

JANUS design is tuned to: (i) achieve Ganymede global coverage at pixel scale ranging from about 400 to 3 m/px in 4 colour filters (the mission available data volume being the limiting factor for JANUS coverage vs. resolution capabilities), (ii) observe 1.1% of Europa's surface at ground resolution  $\leq 200$  m/px and 3.2% at  $\leq 400$  m/px with maximum resolution of 6.5 m/px for selected targets, (iii) cover 14% of Callisto's surface at ground resolution of  $\leq 400$  m/px with maximum resolution down to 5-10 m/px for selected targets.

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## Magnetic behaviour of the high Ni NWA6259 iron meteorite

Pernechele C., Solzi M., Mantovani L. & Tribaudino M.\*

Dipartimento di Fisica e Scienze della Terra, Università di Parma.

Corresponding email: [mario.tribaudino@unipr.it](mailto:mario.tribaudino@unipr.it)

Keywords: iron meteorite, permanent magnet, tetrataenite.

Magnetic properties of metallic meteorites are of interest as a model for the effect of textures and cooling history on the planetary magnetism. Among metallic minerals present in meteorites tetrataenite, an ordered FeNi alloy has a special interest as a strong permanent magnet, with an appeal also beyond the Earth Science community: recently tetrataenite structures were proposed as potential for time-resolved records of planetesimal dynamo fields (Bryson et al. 2014), but also as permanent rare-earth free magnets (Lewis et al 2014).

Here we present the results of the characterization of magnetic properties in a tetrataenite from the NWA6259 high Ni metallic meteorite. NWA6259 is the second highest Ni content meteorite (42.6 wt%) and was described as a strong permanent magnet iron meteorite (Mubarok et 2013).

X-ray diffraction and microprobe analysis performed on a 11.3 g slice showed that the microstructure of the NWA6259 meteorite consists almost completely of tetragonal L10 FeNi tetrataenite. The phosphide inclusions found by Mubarok et al. 2013 were instead not found.

Room temperature magnetic characterization was performed by means of Superconducting Quantum Interference Device Magnetometry (SQUID). Hysteresis loops with maximum applied field of 30 kOe were performed along two different directions, as well as Isothermal Remanence Magnetization (IRC) and DC Demagnetization (DCD) curves. The magnetic analysis of the meteorite fragment was completed by measuring room temperature recoil curves.

M(H) curves measured at room temperature give magnetization value of  $1.2 \cdot 10^3 \text{ emu/cm}^3$ , in agreement with literature data (Mubarok et al 2013). The presence of the secondary soft phase (bcc FeNi) was investigated measuring recoil curves. In fact, if a soft phase was present, a reversible portion of the recoil curve would be observed, according to what happens in exchange-spring magnets. No clear effect of “exchange-spring” behavior was measured confirming XRD data.

The measured coercive field is  $H_c \approx 400 \text{ Oe}$ , which is slightly smaller than what generally observed, from 500 Oe up to 4000 Oe, as a function of the sample texture (Lewis et al 2014, Mubarok et al 2013). The lower measured coercive field may indicate the presence of regions of the sample with different sample texture, as suggested by the lower coercive field, may indicate the presence of a sample structure/orientation of the easy magnetic axes, to be investigated by EBSD methods.

The presence of a different sample texture respect to previous investigations, as suggested by the lower coercive field, indicates further textural heterogeneity in magnetic structure, likely related to magnetic domains within a chemically homogeneous structure. A potential as a cooling rate indicator of magnetic behavior is discussed.

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## Evolution of the fluvio-lacustrine system of the Eberswalde crater (Mars)

Pondrelli M.\*<sup>1</sup>, Rossi A.P.<sup>2</sup> & Marinangeli L.<sup>3</sup>

1. International Research School of Planetary Sciences (IRSPS), Università d'Annunzio, Pescara. 2. Jacobs University Bremen (JUB), Bremen, Germany. 3. Dipartimento di Scienze Psicologiche, Umanistiche e del Territorio (DISPUTer), Università d'Annunzio, Chieti.

Corresponding email: [monica@irsps.unich.it](mailto:monica@irsps.unich.it)

Keywords: Eberswalde crater, Mars, fluvio-lacustrine environments.

The Eberswalde crater (33° W–24° S) hosts a delta-like landform (Malin & Edgett, 2003), that has been interpreted as fan delta thus entailing that a standing body of water filled the crater (Bhattacharya et al., 2005; Wood et al., 2008; Pondrelli et al., 2008). According to some authors (e.g., Mangold et al., 2012), it lasted over several years to hundreds of years, while others (e.g., Bhattacharya et al., 2005) suggest a duration of a 100.000 years.

The sedimentary deposits of the Eberswalde crater rest nonconformably on top of an older Substratum which include the Holden crater ejecta blanket. They consists of layered to faintly layered and non-layered light-toned deposits (Pondrelli et al., 2011).

According to Malin and Edgett (2003), Moore et al. (2003), Bhattacharya et al. (2005), Wood (2006) and Pondrelli et al. (2008), delta plain, delta front and prodelta can be recognized. Several minor fan deltas debouches in the crater from all the directions.

The Eberswalde fan delta consist of five lobes (four deltaic) which relative stratigraphy can be unraveled through cross-cutting relations. We inferred the approximate water level correspondent to each lobe from where the transition between delta plain and delta front occurs. This water level is different for each deltaic lobe.

Lobes are divided by unconformable surfaces, erosional truncations and flooding surfaces. We tentatively inferred a water level curve in which we distinguish three water level fluctuations to which a higher order regressive trend is superimposed (Pondrelli et al., 2008).

The three lower order cycles appear to reflect water level fluctuations. Most probably, hinterland-related processes controlled part of the deposition, but the cyclic water level fluctuation inferred suggest some form of climatic forcing. The higher order trend records the progressive drying out of the basin.

The progressive drop of the water level inferred from the main deltaic system is consistent with the observation in the contributing basin, where a younger channel incised older lacustrine deposits and in the basin, where fluvial channels prograde on the offshore.

Such an evolution appears not to be consistent with a 10s to 100s years long geological history nor with a localized controls. We favor instead a longer duration with mixed local and external, possibly climatic, controls.

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## Fractal clustering analysis and numerical modeling results from Firsoff Crater (Mars)

Pozzobon R.\*<sup>1</sup>, Mazzarini F.<sup>2</sup>, Lucchetti A.<sup>3</sup>, Massironi M.<sup>4</sup>, Rossi A.P.<sup>5</sup>, Marinangeli L.<sup>1</sup> & Cremonese G.<sup>6</sup>

1. IRSPS-DISPUTer, Università G. D'Annunzio, Pescara. 2. Istituto Nazionale di Geofisica e Vulcanologia, Pisa. 3. CISAS- Università Degli Studi di Padova. 4. Dipartimento di Geoscienze- Università degli Studi di Padova. 5. Jacobs University Bremen, Bremen. 6. INAF-Oapd, Padova.

Corresponding email: [r.pozzobon@unich.it](mailto:r.pozzobon@unich.it)

Keywords: Mars, Firsoff Crater, Impact simulations, fractal modelling, fluid source depth.

Arabia Terra is dominated by heavily cratered terrains, and some peculiar landforms can be found mostly in craters interior. With high-resolution images from HiRISE (25 cm/px) and CTX (6 m/px) cameras pitted cones, mounds and knobs can be easily recognized. Those are interpreted as the surface expression of pathways for subsurface fluid. It is commonly hypothesized that Arabia Terra is an area of past fluid activity, being crater central bulges a place of sulfate precipitation (Andrews-Hanna, 2011, Pondrelli et al, 2011, Franchi et al., 2013).

We investigated the presence, origin and timing of mounds formation as well as the depth of the fluid source according to their fractal clustering. In fact, the spatial distribution of eruptive structures within volcanic areas on Earth has been linked to fracture systems with hydraulic connection between surface and magma reservoirs. Self-similarity in vents distribution is described by a power law distribution with fractal exponent  $D$  and defined over a range of lengths comprised between a lower limit (lower cutoff,  $L_{co}$ ) and an upper limit (upper cutoff,  $U_{co}$ ). On Earth, volcanic vents as well as mud volcanoes have shown that the  $U_{co}$  of their fractal distribution scales with the depth of pressurized fluid reservoirs (Mazzarini et al., 2011). The same approach has been applied to mounds mapped at Firsoff and Crommelin craters assuming a similar relation between the surface distribution of mounds and the depth of the connected deep pressurized water table.

431 mounds (most with a central orifice) were mapped on Firsoff Crater's floor and 160 on Crommelin Crater's floor. Preliminary result on the  $U_{co}$  depth estimation shows that a shallow and common reservoir for Firsoff e Crommelin is likely.

We also investigated the origin and pristine shape of Firsoff crater depending on the Martian target composition.

The aim of simulating an impact process on a complex environment such as the Martian surface (due to erosion and strong degradation) is to reproduce a pristine realistic crater shape in order to better understand the geologic processes that led to its latter modification. We simulated two endmembers depending on the rheological structure and composition of the Martian upper crust in order to understand which type of target layering (basalt layering vs basalt/anorthosite layering) is more likely. Interestingly the best fit has been obtained with a jointed basalt/anorthosite transition at the same depth of the pressurized water table predicted by the surface mound distribution.

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## Correlation between chaotic terrains and impact craters on Mars

Roda M.\*, Kleinhans M.G., Govers R. & Zegers T.

Faculty of Geosciences - Universiteit Utrecht, The Netherlands.

Corresponding email: [m.roda@uu.nl](mailto:m.roda@uu.nl)

Keywords: chaotic terrains, impact craters, sub-ice lake.

In this contribution we present the results of a statistical analysis performed on 50 chaotic objects around Xanthe Terra. For each object we measure the diameter and the maximum and minimum depth respect to the surrounding non-collapsed area. We also measure the maximum collapse as the difference between the maximum and minimum depth.

The most part of the measured objects has a maximum depth greater than 1.2 km. The latter represents the maximum collapse achievable by complete pore-space closure of 20 km depth cryosphere after groundwater release. This indicates that the groundwater outflow process is not responsible for the high collapse observed in the most part of the chaotic terrains. Only 5 have a maximum depth greater than the pristine depth of impact crater, calculated from 4 different diameter vs depth relations. Furthermore, the relation between diameter and maximum depth is statistically similar to the relation between diameter and pristine depth of impact craters. This similarity is much more significant when the minimum collapse achieved by chaotic terrains is taken into account vs diameter. In fact, the difference in slope between chaos and crater relations is less than the statistical interpolation error.

The high collapse shown by the most part of the chaotic terrains and strong correlation between diameter vs collapse relation and the same relation for pristine crater suggest that they can be formed on older impact craters, after the collapse of sediment partially filling the craters. Of the four major processes proposed to explain the evolution of the chaotic terrains, only the buried sub-ice lake scenario seems to match the results of this statistical analysis. The scenario starts with the partial filling of the crater by water ice and the subsequent burial under a thick overburden sequence. The buried ice unit starts melting as a result of the thermal insulation by the overburden in combination with the planetary heat loss, creating a subsurface lake. When the melt layer reaches a remarkable thickness the overburden collapses, resulting in massive expulsion of liquid water to the surface (Roda et al., 2014). This scenario can explain the high collapse of chaotic terrains, the similarity with impact craters and the shifting between the chaos collapses and the pristine crater depths relative to the same diameter. The latter can be explained by the partial filling of crater by sediments. Magma cryosphere scenario can only explain the high collapse but not the strong correlation between chaos and impact craters, while gas-hydrated and aquifer scenarios disagree with both observations (Roda et al., 2014).

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## Analysis of reflectance spectra from Proclus and Copernicus craters

Serventi G.\*<sup>1</sup>, Carli C.<sup>2</sup> & Sgavetti M.<sup>1</sup>

1. Dipartimento di Fisica e Scienze della Terra, Università degli studi di Parma. 2. IAPS-Inaf, Tor Vergata Roma.

Corresponding email: [giovanna.serventi@unipr.it](mailto:giovanna.serventi@unipr.it)

Keywords: Moon, plagioclase, spectroscopy.

The Moon is one of the most studied planetary body in the Solar System. A large portion of lunar rocks has been classified as ferroan anorthosite (Warren, 1985) and contain up to 90% plagioclase (PL). So, PL is widespread on the surface.

Several missions spectroscopically analyzed the lunar surface, e.g. SELENE and Chandrayaan, and detected the presence of an absorption band at ca. 1250 nm, due to Fe<sup>2+</sup> transition in PL, in central peaks of impact craters (Matsunaga et al., 2008; Cheek et al., 2012; Cheek & Pieters, 2012). Ohtake et al. (2009) recognized areas with PL amount higher than 98%.

Here we analyzed reflectance spectra from Proclus and Copernicus craters, relating the spectral parameters to the mineralogical composition, particularly focussing on PL.

Proclus is a 28 km crater situated in the west of Mare Crisium. We recognized regions with different spectral behavior: 1) PL regions located mainly in the crater walls; 2) pyroxene (PX) regions in both the walls and the floor of the crater; 3) olivine (OL) region in the south-east portion of the crater walls; and 4) PL+PX regions in the crater wall. Reflectance spectra from 1) are comparable with PL with iron content of 0.1 and 0.5 wt.% (Serventi et al., 2013b), and spectra from 4) are comparable with mixtures composed with more than 90% PL and low PX (Serventi et al., 2013a).

Copernicus is a 93 km crater located in the eastern portion of the Oceanus Procellarum. We recognized: 1) OL-bearing regions in the central peak and in the north-west wall; 2) PX-rich areas outside the crater; and 3) featureless spectra and spectra with a broad absorption at ca. 2000 nm in the crater floor. A detailed analysis of spectra from the central peak suggests the presence of PL in 1), where spectra indicate more than 90% iron-poor PL (Serventi et al., 2013a).

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## Pedogenetic processes on Mars

Tangari A.C.\*<sup>1</sup>, Marinangeli L.<sup>1</sup>, Piluso E.<sup>2</sup>, Pompilio L.<sup>1</sup> & Scarciglia F.<sup>2</sup>

1. DISPUTer-Università G.D'Annunzio di Chieti-Pescara. 2. Dipartimento di Ecologia, Biologia e Scienze della Terra, Università della Calabria.

Corresponding email: [a.tangari@unich.it](mailto:a.tangari@unich.it)

Keywords: Mars, soils, clay minerals.

Clay minerals may provide important information on the rock/fluid interaction and, thus, on the climatic conditions under which they formed. We have compared the mineralogy detected on Mars from CRISM data and terrestrial analogues samples. These data reveal clay minerals in the eastern part of Valles Marineris and Margaritifer Terra regions and we compared the mineral assemblages with soils sampled on the Etna volcano (Sicily) and Cerviero Mount (Calabria, Southern Italy). Our integrated approach of combining remote sensing observations with real pedological, petrographical and mineralogical analyses can help to identify the main alteration processes (weathering vs. hydrothermal) in the Martian study area. We found good analogies between the Andosols developed on the 600-700 years old basaltic substrates of Etna (Branca et al., 2011) and on the Upper Jurassic- middle Cretaceous pillow basalts of Cerviero Mount (Iannace et al., 2007), and the Martian soils, based on their spectral response and propose similar formation processes. CRISM data show limited evidence of illite and smectite in the eastern part of Valles Marineris, but these phases are widely exposed in Margaritifer Terra, where we also detected allophane (poorly crystalline clay) as well as vermiculite, chlorite and smectite. This suggests an intense and widespread water-bedrock interaction. The analysis of terrestrial soil profiles using X-ray diffraction shows similar characteristics to Martian terrains in terms of bedrock composition and clay mineralogy inferred from remote observations. We relate the different clay minerals to different formation processes such as: a) chemical weathering of the main primary minerals present in the bedrock (i.e. plagioclase and pyroxenes); b) neoformation processes of different clays; c) hydrothermal alteration of volcanic glass. Although we cannot totally exclude hydrothermal events at places due to the presence of chlorite and smectite, the geological setting of the studied region of Mars seems to support the presence of standing bodies of water and thus the formation of clay minerals after weathering processes, which implies a humid climate in the past. According to our analysis of the Etnean soils, the formation of clay minerals from weathering started on lavas of about 600 years under warm temperate, humid climatic conditions. This time range can be scaled to Martian-like conditions to find a minimum time for the permanence of water in the Martian study area.

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## The meteoritical collection of the Parma mineralogical museum

Tribaudino M.\* & Mantovani L.

Dipartimento di Fisica e Scienze della Terra.

Corresponding email: [mario.tribaudino@unipr.it](mailto:mario.tribaudino@unipr.it)

Keywords: meteorites, Parma Museum, historical samples.

In the internet site of the Mineralogical museum of Parma, the existence of an interesting meteoritical collection is reported, coming from former late 18th-beginning 19th century private collections (Linati, Piroli), later gathered in the mineralogical museum. However the samples were almost disappeared since recently, when they were found in the drawer of a retired professor. A preliminary observation showed that most samples were mislabeled, or even not labeled. For instance an olivine-metal meteorite, which turned out to be the Krasnojarsk historical pallasite, was labeled as Ensisheim, which is the locality of the fall in 1492 of a chondrite.

A hint for the correct attribution was given by the "Cocconi catalogue" (1867-70) of the mineralogical museum of Parma, where 16 samples are cited: 2 as ferri nativi (native iron), 4 ferri meteorici (metallica meteorites) and 10 aeroliti (silicatic meteorites). Of the 10 aerolites two (Pieve di Cisignano-Borgo san Donnino) are a pairing. Also in the Cocconi catalogue we find several misreported names, which could be hardly referenced to an existing sample. However, combining the historical locality, internet imaging of the candidate meteorites, the date of the fall (only when reported), and finally petrographic evidence we could assign each sample the historical name.

Two samples are absent from the Cocconi catalogue: one is a native iron labeled as "Incerta" by Cocconi, the other loss is of the Siena meteorite, already absent in 1870, according to the note of the museum curator Prof. Strobel. For the other the actual weight is much lower than reported in the sample description. The only addition is a small piece of the Alfianello meteorite fall in 1883. Second younger is the Juvinas eucrite, which fell in 1824.

Metallic meteorites were examined by SEM-EDS; of them two were discarded as non-meteorites (Brianza and Florac), one is likely the smelting product of a larger mass (Bitburg), and only Zacatecas IIIAB iron and Krasnojarsk pallasite are confirmed.

Among the silicatic meteorites we have two achondrites (Juvinas and Stannern eucrites) and seven chondrites (Borgo san Donnino, Alfianello, Renazzo, Benares, Salles, L'Aigle, Ensisheim). Most interesting is the large mass of the Borgo san Donnino (now Fidenza) LL6 chondrite, which is one of the very few falls in the Provincia of Parma. The analysis of the silicatic samples is underway.

## Morphometric analysis comparison of differently degraded simple craters on the Moon

Vivaldi V.\*<sup>1-2</sup>, Ninfo A.<sup>1</sup>, Massironi M.<sup>1</sup>, Martellato E.<sup>2-3</sup> & Cremonese G.<sup>2</sup>

1. Dept. of Geosciences, University of Padova. 2. INAF-Astronomical Observatory of Padova. 3. Dept. Physics and Astronomy, University of Padova.

Corresponding email: [vivaldivalerio@gmail.com](mailto:vivaldivalerio@gmail.com)

Keywords: morphometry, craters, degradation.

In this research we analyzed DTMs from LROC (Lunar Reconnaissance Orbiter Camera) NAC (Narrow Angle Camera), which have a mean resolution range from 0.5 to 1.5 m/pixel and WAC (Wide Angle Camera), that is providing a global lunar surface coverage with a resolution of about 100 meters/pixel. (<http://lroc.sese.asu.edu/about>).

The morphometric analysis was carried out using a multiscalar approach, by testing different ranges of window kernel size (e.g. 15-35-50), in order to retrieve morphometric variables such as slope and curvatures, calculate along different planes, which can be potentially used to characterize the different sectors of a crater (rim crest, floor, slopes and related boundaries) and to evaluate its degradation. For example, a rheological boundary at a depth of 200 m within the small fresh Linné crater (diameter: 2.22 km), firstly hypothesized throughout numerical investigation (Martellato et Al.), has been well identified as a bland morphological step on the inner crater scarp, by using slope and curvature maps derived from a NAC DTM, also this discontinuity, located on the inner crater scarp, is expressed by a very low topographic relevance (8-10 meters).

A change in morphometry values is also expected in relation to craters' ages and diameters. Indeed degradation is influenced by gravitative processes, as well as space weathering, that induce a smoothing effect on the morphological features with the main results of lowering and enlarging the rim crest. We have quantified this variations using morphometric variables derived by NAC and WAC DTMs of several craters with different diameters, that can be considered representative of the 4 relative age classes of degradation, firstly defined in literature (Arthur et al., 1963).

## **SESSIONE S34**

### **Structural geology studies in extensional and compressional plate tectonic settings: petroleum geology implications**

#### *CONVENORS*

*M.R. Barchi (Univ. Perugia)*

*S. Corrado (Univ. RomaTre)*

*C. Magistroni (Eni E&P)*

## Thermal and tectonic evolution of the SW Zagros (Fars province) from internal to external zones

Aldega L.\*<sup>1</sup>, Carminati E.<sup>1</sup>, Bigi S.<sup>1</sup>, Trippetta F.<sup>1</sup>, Corrado S.<sup>2</sup> & Shaban A.<sup>3</sup>

1. Dipartimento di Scienze della Terra, Sapienza Università di Roma. 2. Sezione di Scienze Geologiche, Università degli Studi Roma Tre.  
3. National Iranian Oil Company, Tehran, Iran.

Corresponding email: [luca.aldega@uniroma1.it](mailto:luca.aldega@uniroma1.it)

Keywords: Lithospheric scale geological cross-section, Thermal modeling, hydrocarbon generation.

The Fars province is characterized by complex deformation and multiple petroleum systems. Timing of deformation and development of petroleum systems are clearly linked and far from being fully understood. In particular, differences of levels of thermal maturity between the internal and external sectors of the belt (separated by the High Zagros thrust fault) have been so far poorly investigated. In this work we aim at bridging this gap presenting a coupled structural and thermal evolutionary model for the Fars area along a transect crossing internal and external sectors of the chain. The proposed evolutionary model is based on a lithospheric scale geological cross-section from the High Zagros to the Persian Gulf, constrained by surface and subsurface data.

The Zagros accretionary wedge is structurally organized as a stack of thrust sheets, composed of uppermost Neoproterozoic and Phanerozoic sedimentary strata. The stratigraphic column is approximately 7 to 12 kilometers thick, in the external part of the southwest-migrating orogenic wedge. Late Neoproterozoic–Cambrian evaporites, where present, acted as an important detachment horizon during the structural evolution of the fold-and-thrust belt, and formed numerous complex salt diapirs. In addition, other detachment layers occur in the stratigraphy, further complicating the structures.

The front of the fold-and-thrust belt is characterized by salients where evaporites occur at the base of the deformed succession and recesses where no such evaporites occur. In addition the spacing among thrust-faults is larger and the topographic envelope shallower in areas characterized by the occurrence of Cambrian salt. In this case, anticlines are believed to be detached along the salt layer.

In addition to structural data, crucial constraints are from X-ray diffraction of clay-size fraction of sediments and, subordinately, from organic matter optical analysis that allowed us to reconstruct the thermal evolution of sediments in both internal and external areas.

Temperature dependent clay minerals show a slight decrease of levels of thermal maturity from the internal to the external part of the Zagros fold-and-thrust belt. In the inner zone, mixed layers illite-smectite are short-range ordered structures with an illite content of 60-70% in the Gurpi and Pabdeh Formations and decrease down to random ordered structures with an illite content of 35-40% in frontal areas. One dimensional thermal models point out that sedimentary burial is the main factor responsible for measured levels of thermal maturity. In the end, we discuss that the complex deformation of the region results from Paleozoic to Mesozoic rifting phases and Tertiary subduction and collision related tectonics. In particular, we show that changes in facies and thickness linked to the pre-Tertiary extensional-transensional tectonics control the geometry of contractional structures along the transect.

## **Periodical post-rift shear reversal along the Pernambuco Fracture Zone, NE Brazil: implications for hydrocarbon exploration in passive continental margins**

Balsamo F.\*<sup>1</sup>, Nestola Y.<sup>1</sup>, Storti F.<sup>1</sup>, Nogueira F.C.C.<sup>2</sup> & Bezerra F.H.R.<sup>3</sup>

1. NEXT – Natural and Experimental Tectonics Research Group, Department of Physics and Earth Sciences, Parma University. 2. Universidade Federal de Campina Grande, Brazil. 3. Universidade Federal do Rio Grande do Norte, Brazil.

Corresponding email: [fabrizio.balsamo@unipr.it](mailto:fabrizio.balsamo@unipr.it)

Keywords: Oceanic fracture zone, NE Brazil, passive margin.

Oceanic fracture zones are among the most evident bathymetric features of seafloors which include transform faults that connect adjacent mid-ocean ridge segments and accommodate opposite spreading directions. According to the plate tectonics theory, oceanic fracture zones are considered inactive and only transform faults are tectonically active. Nevertheless, intraplate earthquakes occur in stable continental areas such as the NE-Brazilian craton, where seismicity is clustered along fault systems reactivating major Neoproterozoic shear zones like the Pernambuco Lineament. In this contribution we illustrate a detailed analysis of the offshore pattern of seafloor age domains on both sides of the Pernambuco Fracture Zone (PFZ), which indicates non-uniform spreading rates on the two lithospheric lanes separated by the PFZ. The differential spreading rate, calculated in 8 age provinces from Upper Cretaceous to Present, varies between 1.3 and 8.8 mm/yr and periodically switched from right-lateral to left-lateral excess transform shear along the PFZ. Five major inversions were found, including a Tortonian inversion from right-lateral to left-lateral excess shear, consistently with structural data acquired in Miocene to Quaternary sediments along the PFZ. In the proximity of the Pernambuco shear zone, we found evidence for fault-related paleofluidization structures in Quaternary deposits, where mobilized materials include cm-dm-sized, heterogeneous angular clasts in a sandy-dominated matrix. Our results further improve the knowledge of recent tectonic activity along the Pernambuco shear zone and, in particular, provide additional information on the role of oceanic fracture zones in determining the brittle deformational pattern in continental passive margins. We also discuss the implications for hydrocarbon exploration and reservoir-scale fracture pattern.

## Tectonic setting of the SE sector of the Taurus Mountains (Kurdistan, Iraq)

Bolis G.<sup>1</sup>, Bresciani I.<sup>2</sup>, Calabrò R.\*<sup>1</sup>, Feltre L.<sup>1</sup>, Perotti C.R.<sup>2</sup> & Zucca F.<sup>1</sup>

1. Edison Spa, Milano. 2. Dipartimento Scienze della Terra e dell'Ambiente, Università di Pavia.

Corresponding email: [roberto.calabro@edison.it](mailto:roberto.calabro@edison.it)

Keywords: Satellite images, seismic interpretation, structural analysis.

The tectonic setting of the SE sector of the Taurus Mountains (Kurdistan) was studied through remote sensing interpretation of multispectral (Landsat and ASTER) and panchromatic stereo (ASTER and Corona) satellite images, integrated and controlled by few seismic lines and geological maps. The stereo 3D analysis of the stereoscopic ASTER and Corona images revealed with great details the morphometric features of the terrain. In the area, the outcropping tectonic structures are clear and well exposed and several wide structural slopes coinciding with bed surfaces are present. This allowed a quantitative interpretation of the stereo images, carried out by determining the co-ordinates and the elevation of selected points, lines and areas directly by stereo computer-dedicated programs in a digital environment.

The Paleozoic, Mesozoic and Cenozoic units, largely outcropping in the northern sector of the area, are affected by a series of E-W trending synclines and anticlines, generally faintly south-vergent, associated with thrusts and reverse faults that indicate a crustal shortening with a general N to S transport direction.

Minor second-order asymmetric folds affect the limbs of the major anticlines and synclines that deform the Mesozoic and Cenozoic Formations. These minor folds, which are always vergent towards the fold hinges of the major folds, may develop if a flexural-slip or shear mechanism of folding has acted on a multilayered succession characterised by alternating competent and incompetent layers. In fact, they are particularly developed in the less competent tertiary units such as Kolosh and Gercus Formations, provoking a partial mechanical decoupling and disharmony between the upper Cenozoic and the lower carbonatic succession. This phenomena is also evident in the seismic sections.

The best examples of such minor folds are visible along the northern limb of the Bayguwah syncline and E of the Shiranish village, at the northern limb of the great syncline of the Zakho valley.

The thrusts and reverse faults visible show a strict connection with folds, but they are occasionally masked in the outcropping areas (generally at the core of the synclines) by recent unconformable deposits. Strike-slip faults cross-cutting the folds are not uncommon. Locally these faults seem to have a dip-slip component of extension (transtension).

The structural analysis and seismic interpretation lead to consider the folds of the study area as forced folds connected to subsurface thrusts or as faulted detached folds, that initiated as detachment folds and subsequently were faulted in a progressive deformation regime.

## **A new multi-method approach to assess thermal maturity of Lower Paleozoic sedimentary successions: the case history of Polish Baltic Basin**

Caricchi C.\*<sup>1</sup>, Corrado S.<sup>1</sup>, Di Paolo L.<sup>2</sup>, Romano C.<sup>1</sup>, Aldega L.<sup>3</sup>, Grigo D.<sup>2</sup> & Vona A.<sup>1</sup>

1. Dipartimento di Scienze, Sezione di Scienze Geologiche, Università "Roma Tre". 2. ENI spa – Exploration & Production Division, San Donato Milanese (MI). 3. Dipartimento di Scienze della Terra, Sapienza Università di Roma.

Corresponding email: [chiara.caricchi@uniroma3.it](mailto:chiara.caricchi@uniroma3.it)

Keywords: Thermal maturity, Polish Baltic Basin, Lower Paleozoic.

The problem of the reliable assessment of thermal maturity of sedimentary successions is crucial for the evaluation of hydrocarbons generation/expulsion. Sometimes, the use of traditional indicators of thermal maximum exposure might be misleading or insufficient to define thermal maturity levels, in particular in sedimentary successions that are devoid of vitrinite-huminite group macerals (e.g., Lower Paleozoic in age). To solve this problem we propose a successfully adopted multi-method approach to assess thermal maturity. This strategy consists of: (i) measurement of organoclasts reflectance; (ii) FT-IR and (iii) Raman spectroscopic analysis (iv) pyrolysis on dispersed organic matter and (v) X-Ray diffraction on fine grained sedimentary rocks. This approach guaranteed a robust cross check among thermal indicators as an input to burial and thermal modeling. Studied Lower Paleozoic sections derive from three deep wells, recently drilled in the Polish Baltic Basin by ENI, with analysed depth intervals ranging between about 2 and 3 km. Firstly, from spectroscopic analyses (both Raman and FT-IR), we have devised selected indexes, sensitive to temperature increase, and correlated them to commonly adopted parameters (eg., vitrinite reflectance, Tmax etc). In the three analysed sections the integration among organoclasts reflectance, FT-IR and Raman indexes and XRD analyses provide a robust and well constrained assessment of thermal maturity that ranges from mid-late mature to over-mature. Furthermore, the late diagenetic zone has been identified by means of XR-Diffraction in agreement with results obtained from organic matter analyses. In conclusion this multi-method approach provided very encouraging results that make it a powerful tool for the assessment of thermal maturity of problematic organic facies. This could drastically reduce uncertainties concerning thermal modeling and positively influence decisions on the development of prospects, especially when aimed at exploring shale gas targets.

## **Structure and tectonic evolution of the Western Carpathians: new insights from sequentially restored balanced cross-sections integrated with low-temperature thermochronometry**

Castelluccio A.<sup>1</sup>, Andreucci B.<sup>1</sup>, Grigo D.<sup>2</sup>, Jankowski L.<sup>3</sup>, Ketcham R.A.<sup>4</sup>, Mazzoli S.\*<sup>5</sup>, Szaniawski R.<sup>6</sup> & Zattin M.<sup>1</sup>

1. Dipartimento di Geoscienze, Università di Padova. 2. ENI, Exploration and Production, Milan. 3. Polish Geological Institute-Carpathian Branch, Cracow. 4. Jackson School of Geosciences, The University of Texas, Austin TX, USA. 5. Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse (DiSTAR), University of Naples "Federico II". 6. Institute of Geophysics, Polish Academy of Science, Warsaw, Poland.

Corresponding email: [stefano.mazzoli@unina.it](mailto:stefano.mazzoli@unina.it)

Keywords: Fold and thrust belts, burial history, rock exhumation.

Traditionally, the Western Carpathians have been divided into two distinct parts, namely the Inner and the Outer Carpathians, separated by the so-called 'Pieniny Klippen Belt', a narrow zone of intensely deformed and sheared Mesozoic to Palaeogene rocks. Our reappraisal of the 'Pieniny Klippen Belt' suggests it includes sediments originally deposited in a foreland basin that developed during the Late Cretaceous in front of the Inner Carpathian orogen. Such a Pieniny foreland basin succession was later deformed and partly thrust over the Outer Carpathian orogenic wedge. Our balanced cross-sections, showing a mix of thin-skinned thrusting and thick-skinned tectonic inversion involving the reactivation of pre-existing basement normal faults, have been sequentially restored in order to unravel the tectonic evolution of the thrust belt–foreland basin system. The cross-sections, integrated with a large thermochronometric dataset, including apatite fission tracks and apatite and zircon (U-Th-(Sm))/He ages, allow us to unravel the various stages of the tectonic development of the thrust belt–foreland basin system of Slovakia, Poland and Ukraine and to provide new constraints on the burial and exhumation history of both source and reservoir rocks.

Our structural and thermal modeling highlight different timings, exhumation processes and amounts of shortening for the Polish and Ukrainian Carpathians. Thermal modelling suggests that the exhumation history is characterized by a first rapid erosion phase (0.5-1.1 mm/yr) followed by a stage with lower cooling rates (0.2-0.05 mm/yr). In the western Polish Carpathians, exhumation is mainly syn-thrusting, starting from the Late Oligocene. In this area, erosion is the leading process in exhumation, although high-angle normal faults also occur. According to the sequentially restored cross sections, shortening values are around 55% in the Polish Carpathians, increasing westward toward the Ukrainian region. In the border area between Poland and Ukraine, the low relief, 'collapsed' topography combined with the balanced cross-sections suggest a significant control by extensional tectonics in the exhumation history. This is further supported by the occurrence of cooling ages younger than the latest thrusting and the rapid exhumation rates recorded in this area. On the other hand, the Ukrainian Carpathians are characterized by more homogeneous, post-thrusting cooling ages, consistent with exhumation mainly controlled by erosion during post-collisional regional uplift.

## **Seismic transects through the Somali Basin gravity-driven Deepwater Fold and Thrust Belt (East Africa)**

Cruciani F.\* & Barchi M.R.

Dipartimento di Fisica e Geologia, Università di Perugia.

Corresponding email: [fra.c85@hotmail.it](mailto:fra.c85@hotmail.it)

Keywords: deepwater fold and thrust belt, East Africa, seismic reflection profiles.

Over the last 25 years, following advances in deep-water drilling technology, passive margins have become site of high prospectivity for the oil industry. The availability of new data, such as seismic profiles and wells, has allowed a better understanding of the tectono-sedimentary evolution of the post-rift sequences, which are often affected by extensive slope-failure phenomena, related to gravity-driven deformation processes. In particular, the area offshore Kenya and southern Somalia hosts a giant-scale deepwater fold and thrust belt (DW-FTB), detached over a regional shale décollement. In this study we have investigated the structural style of the DW-FTB on a 2D seismic dataset, that includes the offshore Lamu Basin and the Somali Basin. This region records the oldest sedimentary section of the Indian Ocean, since the breakup of Gondwana began in the Middle-Lower Jurassic separating Madagascar and Africa. From the Late Cretaceous to the Early Miocene, the margin has been characterized by gravitational collapse leading to the formation of a DW-FTB extending more than 400 km along-strike, and covering an area exceeding 50000 km<sup>2</sup>. The overall structure is sharply split into a northern portion, over 150 km wide, and a southern portion, only few tens of km wide. In this work we have interpreted four representative NW-SE seismic transects through the Somali Basin DW-FTB, which allowed us to identify remarkable variations of the structural style both along-dip and along-strike. Each transect shows different structural sectors, characterized by various degree of deformation and shortening. The outer sectors generally show asymmetric imbricate thrusts with mainly basinward vergence, forming a low-angle critical taper, with a thin, landward-dipping basal detachment. Toward the continent, where the sedimentary section is thicker, the thrust belt is characterized by a more complex geometry, including stacked imbricate horses and double-verging out-of-syncline thrusts, transporting bowl-shaped syn-kinematic basins. The inner sectors show pseudo-symmetric detachment folds with break thrusts, over a thick undercompacted mobile unit. The southernmost transect displays a more recent, small-scale thrust-belt, detached on the top of the oldest structure. The main phases of activity appear to be related to high paleo-rainfall conditions and large sandy input to the basin in the Late Cretaceous-Early Paleogene, due to tectonic rejuvenation of African craton, and in the Early Miocene, corresponding to the Kenya Rift Valley uplift. This seems to confirm the close connection between the amount of sediment supply and the onset of these gravity induced tectonic processes. The several and rather abrupt differences in the structural styles are likely related to a combination of factors, such as the thickness and the dip of the décollement levels, the slope gradient, and lateral variations in the stratigraphy of the sedimentary successions involved in the deformation.

## **Inversion structure in the Po Plain and Adriatic foreland (Northern Italy)**

Fantoni R.\*<sup>1</sup>, Dal Zotto O.<sup>1</sup>, Fattorini A.<sup>1</sup> Martinis S.<sup>1</sup> & Stanculete A.<sup>2</sup>

1. Eni e&p. 2. Former Imperial College, current Landmark Halliburton.

Corresponding email: [roberto.fantoni@eni.com](mailto:roberto.fantoni@eni.com)

Keywords: Po Plain, Adriatic foreland, Apennines, Dinarides, Southern Alps, Cenozoic compression, Mesozoic.

The Po Plain and Adriatic foreland is shared by three partially coeval orogenic belt: the Southern Alps in the north, the Apennines in the west and the Dinarides in the east (Fantoni & Franciosi, 2010). Inversion structures of Mesozoic extensional basin are preserved in the more external sectors of the foreland (Fantoni et al., 2004). In the central Po Plain, the inversion structure of a Jurassic extensional basin N trending is preserved (Lacchiarella structure). Reactivation of the former normal faults and complete recovery of vertical offset occurred during eoalpine (or pre-Adamello) and neoalpine (or post-Adamello) tectonic stages (Fantoni et al., 2004). Another inversion structure, of a Middle Triassic basin, is preserved in the western Po Plain (Trecate structure). The low relief eoalpine structure has been involved in a new fault propagation fold of neoalpine age (Fantoni et al., 2004). In both cases offset due to pre-Adamello inversion is anyway lower than that produced by the subsequent post-Adamello deformation, accommodated by new faults (Trecate) and by reactivation of the pre-existing ones (Lacchiarella). In the North Adriatic area a wide inversion structure is present (Stanculete et al., 2014). The structure is delineated by NE trending SE dipping faults reactivated on an older Mesozoic extensional faults. The inversion structure is defined by two culminations, Agata culmination located to the south and Amira culmination to the north. The structure showed pervasive dolomitization on its higher Agata culmination, affecting the whole Mesozoic carbonate successions from the shallow water Calcari Grigi (Lower Jurassic) to the pelagic Scaglia (Middle Eocene), while on the lower Amira culmination, the dolomitization reached the pelagic Maiolica (Lower Cretaceous). The growth of the structure, mostly pronounced on Agata culmination, is of eo-mesoalpine age; the activity started between late Cretaceous and middle Eocene and ended in early Oligocene. Long wavelength and high structural relief features are typically related to inversion of the wide and deep Jurassic basins; short wavelength and low structural relief structures, instead, are typically related to the smaller Middle Triassic basins. Some inversion structures are active just during a single tectonic stage (Agata, in the Adriatic foreland). Other structures are characterized by polyphase activity (spanning eo and neoalpine tectonic stages), but always connected to reactivation of a previous extensional fault (Lacchiarella, in the central Po Plain foreland). Finally, structures, located in the more internal sectors of the foreland are characterized by basin inversion during the eoalpine phases, and by fault propagation folding during the southward shift in deformation of the neoalpine phase.

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Fantoni R. & Franciosi R. 2010. Mesozoic extension and Cenozoic compression in Po Plain and Adriatic foreland. *Rend. Fis. Acc. Lincei*, 21, 197-209.

Stanculete A., Corrao A., Cosgrove J., Ronchi P., Vandeginste V. & Fantoni R. 2014. Inversion structure of dinaric age in the Adriatic foreland (Northern Italy). *Mesozoic Carbonates of the Neo-Tethys: old and new concepts for petroleum exploration*, 25-26 march 2014, Naples, Italy, AAPG Europe Region.

## Continuous Fracture Modeling: from well data to dynamic flow. Methodology and application

Felici F.\*<sup>1</sup>, Alemanni A.<sup>1</sup> & de Montleau P.<sup>1-2</sup>

1. Enel Trade S.p.A., Upstream Gas Division, Roma. 2. Groupement Isarene, 01, Chemin Doudou Mokhtar, Algiers (Algeria).

Corresponding email: [fabrizio.felici@enel.com](mailto:fabrizio.felici@enel.com)

Keywords: Fracturation, modeling, methodology.

Fault arrays and natural fractures distribution within reservoirs levels, exert an important control on subsurface fluids migration, trapping and production. Present-day E&P exploration and development are increasingly focused on tight or low (primary) porosity rocks for which the knowledge of fractures distribution, at full field levels, represents a critical aspect of the production.

Natural fractures array is usually the result of superimposed tectonic events that control intensity, orientation, spatial distribution, length, connectivity, and aperture of different fracture sets.

The most common approach to model subsurface fractures is the Discrete Fracture Network (DFN) where each fracture is modeled as a planar feature with specific geometrical, spatial, and mechanical properties. Basis for discrete fracture modeling is the creation of a robust conceptual model by integration of well data (wireline logs, image logs, core data), inter-well data (geomechanical analysis, seismic attribute analysis, outcrops analogs), and dynamic analysis.

The main aim of DFN is to upscale fractures properties to reservoir static model cells (together with dynamic calibration) taking into account the expected fracture geometry and, finally, to extend them at full field level for dynamic simulation purposes. However, high computing resources are needed for large and highly fractured fields. In this work we propose a simplified and faster methodology in order to reach similar goals in fractured reservoir characterization.

Our complete workflow has been set as follows:

- 1) fracture data collection from FMI interpretation and cores analyses aimed at selection of possible open and/or semi-open fractures (instrumentally conductive and partially conductive fractures);
- 2) data elaboration aimed at average fracture density synthetic logs calculation within available static model facies;
- 3) conceptual model elaboration where main fracturation drivers (fault lengths and hypothetical damage zones width) have been studied, implemented and finally modeled in the software;
- 4) software modeling, performed on Petrel in order to distribute a continuous fracture intensity as a petrophysical property into the reservoir volume according to the main fracture drivers;
- 5) dynamic modeling aimed at conversion of the fracture intensity distribution into petrophysical properties ( $k$ ,  $\Phi$ ,  $\sigma$ ) and dynamic data match according to the fracture aperture.

Our case study is an appraisal field located in southern Algeria (Illizi basin) where nine appraisal wells have been actually drilled.

The main aim of this work is to address a simple approach on fractured reservoir characterization that could be applied in several type of reservoirs (carbonates, sandstones, etc) when wells data (FMI, cores, logs, well test) are available together with a previously established static model of the field. This approach is useful for light study when full DFN approach is hardly applicable.

## **The thermal history of the Baltic Basin evaluated by means of a multidisciplinary approach, the IMPR – Integrated Maturity Profile**

Grigo D.\*<sup>1</sup>, Aldega L.<sup>2</sup>, Andreucci B.<sup>3</sup>, Caricchi C.<sup>4</sup>, Corrado S.<sup>4</sup>, Di Paolo L.<sup>1</sup>, Romano C.<sup>4</sup> & Zattin M.<sup>3</sup>

1. Eni e&p – Exploration & Production Division, San Donato Milanese (MI). 2. Dipartimento di Scienze della Terra, Università “Sapienza”, Roma. 3. Dipartimento di Geoscienze, Università di Padova. 4. Dipartimento di Scienze, Sezione di Scienze Geologiche, Università “Roma Tre”.

Corresponding email: [domenico.grigo@eni.com](mailto:domenico.grigo@eni.com)

Keywords: Petroleum System Modeling, thermal history, Baltic basin.

The definition of the thermal history of a sedimentary basin in the oil industry is classically made collecting vitrinite reflectance data and calibrating them with a PSM tool on the basis of some geologically reliable postulations. Sometimes the experimental data are not able to describe a homogeneous maturity profile for lack of data reliability or for absence of vitrinite macerals. So the maturity profile results quite discontinuous for the lack of shaly sequences or cloudy for the lack of good vitrinite fragments. This will increase the uncertainties on the maturity evaluation.

The usage of additional parameters based on FT-IR and Raman spectroscopic analysis, both on dispersed organic in addition to X-ray diffraction on fine grained sedimentary rocks will help in reducing the uncertainties of the maturity profiles.

In any case vitrinite reflectance does not help in defining the timing of heating processes and sometimes the geological postulations risk to link to an infinite number of combinations affecting again the uncertainty of the model.

The usage of thermochronological techniques (fission-tracks and U-Th/He analysis, both on apatite) can help in reducing those uncertainties for two main reasons. First of all they permit to fill the gap in the maturity profile because they cover the terrigenous part of the sequence usually scarce of not reworked vitrinite fragments. Moreover they can also reduce the uncertainties in the definition of the timing of heating processes because they permit to fix some important time points in the thermal history of the basin.

The application of all these techniques to the Polish Baltic basin permitted to develop some important issues in the thermal history evolution of the eastern margin of the Russian craton. In particular a Meso-Cenozoic heating event can be postulated and will help in explaining the differences that exist between the present thermal regime and the maturity trend.

## **Tectonic evolution of the Sarvestan area (Fars region, Zagros): constraints from seismic lines, field data and thermal maturity of sediments**

Minelli G.\*<sup>1</sup>, Bigi S.<sup>2</sup>, Aldega L.<sup>2</sup>, Carminati E.<sup>2</sup>, Lupattelli A.<sup>1</sup> & Shaban A.<sup>3</sup>

1. Dipartimento di Fisica e Geologia, Università degli Studi di Perugia. 2. Dipartimento di Scienze della Terra, Sapienza Università di Roma.  
3. National Iranian Oil Company, Tehran, Iran.

Corresponding email: [giorgio.minelli@unipg.it](mailto:giorgio.minelli@unipg.it)

Keywords: seismic reflection, thermal history, structural geology, Iran.

The Zagros accretionary wedge is a southwest-migrating orogenic wedge developed from the superimposition of thin-skinned and thick-skinned tectonics. The stratigraphic column is approximately 7 to 12 kilometers thick. The Fars area is characterized by complex deformation and multiple petroleum systems. Timing of deformation and development of petroleum systems are clearly linked and far from being fully understood. In the Fars region, Late Neoproterozoic–Cambrian evaporites, acted as an important detachment horizon during the structural evolution of the fold-and-thrust belt, and formed numerous complex salt diapirs. Other detachment horizons further complicate the structures. Changes in facies and thickness related to the pre-Tertiary extensional-transensional tectonics control the geometry of contractional structures. N-S trending extensional faults associated with the Paleozoic-Triassic thick-skinned rifting and Mesozoic thin-skinned extensional tectonics were reactivated as lateral-oblique ramps during the development of the Zagros belt. One of these structures borders the eastern side of the Sarvestan area, a triangular-shape flat area surrounded by anticlines. We reconstruct the 3D geometry of this area using surface (available geological maps, measured stratigraphic sections, and original fieldwork data) and subsurface (wells and seismics) data. We show that the geometry of buried and outcropping structures was strongly controlled by the reactivation of inherited normal faults and by associated facies changes. Further constraints for the evolutionary model come from X-ray diffraction of clay-size fraction of sediments that allowed us to reconstruct and model the thermal evolution of sediments in the area. One dimensional thermal models point out that sedimentary burial is the main factor responsible for measured levels of thermal maturity of the sedimentary succession except for those sediments sampled at the footwall of main thrust faults. In this case, tectonic burial controlled the thermal maturity of sediments.

## Structural evolution of the syn- and post -rift domain of West Africa sheared margin and Implications for Petroleum Potential: Ghana Margin Case

Obiri G.\*, Cella G.M., Italiano D., Aiolfi C., Ronchi P. & Benalia L.

Eni e&p, San Donato Milanese (MI)

Corresponding email: [gideon.obiri@eni.com](mailto:gideon.obiri@eni.com)

Keywords: West Africa, sheared margin, Petroleum Potential.

The structural complexity of syn- and post-rift sequences of atypical African Atlantic sheared margin was investigated using 3D seismic data and 2D restoration technique. The study area is located at the termination of a transform fault zone with low angle respect to the continental margin, and the analyzed time interval was from the Early Cretaceous to Holocene.

The deformation has both extensional and contractional components from the transtension and transpression phases respectively.

The evolution of the area is controlled by the faults termination splay of Romanche transform fault, the related strike-slip faults trend ENE-WSW and displace the blocks along in a dextral strike-slip motion to tens of kilometers. The main depocenter, located South-East of the transform splay is bounded by a minor strike-slip fault parallel to it. The main structural high instead is controlled by two main rift-extensional faults trending NW-SE nearly orthogonal to strike-slip fault.

Two different structural style stile are recorded in the area: the Early Cretaceous rift characterized by normal faults trending NW-SE and some minor normal faults trending NE-SW, and the Upper Albian to Late Cretaceous compression (transpression) related with the contractional faults trending E-W and NE-SW and their intervening folds, and oblique reactivation of the older extensional faults.

Five main deformation events were identified:

- (1) Barremian to Aptian time recorded the block faulting and syn-sedimentation related to the oblique rifting (transtension);
- (2) Lower to Intra Albian recorded syn-rifting deposition and the Intra Albian unconformity marks the top;
- (3) Upper Albian to Cenomanian (early post -rift) time recorded compressive activity which created the inversion, folding along the strike-slip faults, reverse and thrust faulting and gentle folding. The reactivation of main strike slip in Albian time created shallow normal faults;
- (4) Turonian/Conianian to Santonian Upper Cretaceous recorded the inversion, gravitational slide and slump (MTCs);
- (5) Neogene time (late post-rift) recorded relatively undisturbed sequence with recent normal faults that dip basinward and related to the reactivation of the deep buried master strike-slip fault.

Potential petroleum systems exist as the early Cretaceous rift phase has a preservation of sediments (containing both source and reservoirs) with important structural and stratigraphic controls. Structural traps are created by the widespread rotated fault blocks associated by half graben and the compressional structures, including folds and inversion. Other potential traps are the stratigraphic ones associated with the MTCs related to the later inversion phase. Understanding the timing of the deformation events is crucial to the petroleum system due the tectonic complexity related to the strike-slip activities.

## Multi-scale fracture networks of faulted and fractured Apulian carbonates, Italy

Panza E.<sup>\*1-3</sup>, Zambrano M.<sup>2-3</sup>, Agosta F.<sup>1-3</sup> & Tondi E.<sup>2-3</sup>

1. Dipartimento di Scienze, Università della Basilicata. 2. Scuola di Scienze e Tecnologie, Università di Camerino. 3. Reservoir Characterization Project [www.rechproject.com](http://www.rechproject.com).

Corresponding email: [elisa.panza@unibas.it](mailto:elisa.panza@unibas.it)

Keywords: Tight carbonates, fracture network, Discrete Fracture Network modelling.

The work is aimed at deciphering the contribution of both background and fault related deformation on the fluid flow properties of tight platform carbonates. Taking advantage of 3D exposures present in the Murge area of southern Italy, we are able to analyze, at different scales, the fracture networks that crosscut the layered Cretaceous limestone of the Altamura Fm (Korneva et al., 2014). The background deformation consists of (i) stratabound fractures, consisting of bed-perpendicular joints and sheared joints and (ii) non-stratabound fractures, represented by incipient strike-slip faults with cm offsets, which crosscut several beds and confined within individual bed-packages. Persistent fracture zones, which are made up of small strike-slip faults that offset several bed-packages and display tens of cm-offset, are also present along the study outcrops. The latter features include thin damage zones and very discontinuous, if not absent, cataclastic fault cores. At larger scales, well-developed faults, characterized by m to tens of m-offset, form a conjugate system of sub-vertical strike-slip faults. These larger faults include 10's of m-thick fractured and faulted damage zones, which surround up to 1 m-thick cataclastic fault cores. For each fracture/fault set documented along the study outcrops, we assess the dimensional, spatial and scaling properties. Data were gathered in the field by mean of scan line and scan area measurements. By computing the mean orientation, size distribution, aspect ratio, aperture, N (number of fractures per sample volume) and fractal dimension of each fracture/fault set, we build up multi-scale DFN (Discrete Fracture Network) models of representative rock volumes. In particular, concerning the background deformation, different DFN models are constructed based upon the investigated bed thicknesses (stratabound fractures) and bed-packages thicknesses (non-stratabound fractures). One larger model is generated for the persistent fracture zones crosscutting several bed-packages, in which both stratabound and non-stratabound fractures are included. Finally, DFN models representing the structural architecture of larger strike-slip faults are also constructed. Outputs of individual models are used to compute, at different scales, the overall P32, porosity and 3D permeability (K<sub>x</sub>, K<sub>y</sub>, K<sub>z</sub>) values of the limestone rocks: from single beds to multiple bed-packages and, finally, to large fault zones. The results enable us to assess the multi-scale properties of the fracture network at different scales and, hence, to discuss the role exerted by brittle deformation on subsurface fluid flow within tight layered carbonates.

Korneva I., Tondi E., Agosta F., Rustichelli A., Spina V., Bitonte R. & Di Cuia R. 2014. Structural properties of fractured and faulted Cretaceous platform carbonates, Murge plateau (southern Italy). *Journal of marine and Petroleum Geology*, in press.

## **The Vietri di Potenza relay ramp, Southern Apennines, Italy**

Prosser G.\*, Agosta F. & Giano S.I.

Dipartimento di Scienze - Università della Basilicata (Potenza).

Corresponding email: [giacomo.prosser@unibas.it](mailto:giacomo.prosser@unibas.it)

Keywords: Relay ramp, fault rocks, Southern Apennines.

The Southern Apennines are dominated by a set of nearly NW-trending normal faults, which are mainly located in the axial zone of the chain. Evidences from studies on neotectonics and seismology indicate the presence of two main right-stepping seismogenic faults in the Campania–Basilicata region, which border the large relay ramp area of Vietri di Potenza. This work is aimed at describing the geometry, kinematics, and relative chronology of the high-angle fault system present in the relay ramp area. In addition, detailed micro-structural analysis of the cataclastic fault rocks of the cores associated to the larger high-angle faults permit to further decipher the progressive development of individual fault sets during exhumation. The work is therefore focused on the structural analysis of the fault system, on the stratigraphic characterization of the Quaternary deposits possibly involved in deformation, and on the 3D geological modeling of the study relay ramp area by means of Move (Tm) software.

In the area, the two main high-angle fault sets trend about N120-140E and N60-N70E. Minor high-angle fault sets trend N90-100E and N160-170E. All aforementioned fault sets crosscut the whole pile of allochthonous units that overrode the inner Apulian platform carbonates. In the study area, the allochthonous units consist of 1-1.5 km thick, Campania-Lucania platform carbonates of late Triassic-Jurassic age, with Dolomites at the base and limestones at the top, which are tectonically juxtaposed against deep-sea Lagonegro deposits of late Triassic to Eocene age, including pelagic limestones, radiolarites, marls and turbiditic calcarenites, by means of low-angle thrust faults. The most developed high-angle faults show a maximum throw of about 400 m. Crosscutting relationships, geomorphologic evidences, and sheared Quaternary slope deposits generally show that the NW-trending (N120-140E) faults are the most recent of the whole structural assemblage. Textural analysis of dolomitic fault rocks points to thin veneers of ultracataclasites, which localize in the innermost portions of the fault cores, as the most evolved product of brittle deformation. By taking into account only the cumulative thickness of these ultracataclasites, and applying a simplistic rheological model, it looks like that the two main high-angle fault sets developed at dissimilar confining pressures. Summing up, several lines of evidence indicate that the NE-trending fault set developed earlier with respect to the NW-trending set. This may suggest that the lateral propagation of NW-trending segments during the development of the relay ramp took place in an area dominated by older structures.

## Visualization and modeling techniques in complex tectonic settings for petroleum potential assessment, a geometrical example from a collisional mountain belt

Sala P.\*<sup>1-2</sup>, Pfiffner A.<sup>2</sup> & Frehner M.<sup>3</sup>

1. Eni E&P, Milano. 2. Institute of Geological Sciences, Bern, Switzerland. 3. Geological Institute, ETH Zurich, Switzerland.

Corresponding email: [paola.sala@eni.com](mailto:paola.sala@eni.com)

Keywords: Pseudo 3-D modeling, Fold and thrust belt, Helvetics.

In the last decade, a number of innovative geophysical and geological techniques were developed to investigate and model complex geologic settings (e.g., Caumon et al., 2009). This, in combination with an almost unlimited computational power that allows handling large datasets, is the key to generate elaborate 3D geological models (e.g., Zanchi et al., 2009). One of the main goals of a 3D model, for example in the oil industry, is to reproduce the exact features of a structure to reduce the explorative risk. Robust and accurate structural models are therefore of utmost importance in the exploration workflow. Understanding the processes that generated potential traps (e.g., Cristallini and Allmendinger, 2001; Galera et al., 2003; Moretti, 2008) allows discriminating between a discovery and a dry well.

This approach is extremely useful in areas with low or no seismic coverage such as onshore collisional belts. Here we present an example of such a situation aimed at investigating the geometrical relationships between folding and thrusting in a collisional mountain belt even although not relevant for oil exploration. A small area of the Helvetic nappes from the Swiss Alps is reconstructed from several existing cross-sections, partly redrawn and line-length balanced. The cross-sections were interpolated in 3D to obtain eight main surfaces corresponding to formational tops and a number of fault surfaces.

This 3D model represents a very intuitive tool for examining a portion of a complex nappe structure. The model highlights the shape of the main anticline-syncline pairs and how these fold trains vary in amplitude and wavelength, and variations in fold style along strike and in map view. The changes correlate with regional shortening as determined from line-length balancing. The model also puts in evidence the lateral extension, the strike, and the variation in displacement of the principal faults. The 3D model allows understanding how the internal nappe structures, namely folds and thrust faults, change along strike.

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## **SESSIONE S35**

### **Poster - Open Session**

#### *CONVENORS*

*B. Cesare (Univ. Padova)*

*E. Erba (Univ. Milano)*

## The “Geoitaliani” project: history of geology as a key for the spreading of scientific knowledge in Italy

Argentieri A.<sup>1-4</sup>, Console F.<sup>5</sup>, Doglioni C.<sup>3-4</sup>, Fabbi S.<sup>3-4</sup>, Pantaloni M.<sup>2-4</sup>, Petti F.M.\*<sup>4</sup>, Romano M.<sup>3-4</sup> & Zuccari A.<sup>4</sup>

1. Provincia di Roma - Dipartimento IV- Servizio Difesa del Suolo. 2. ISPRA- Servizio Geologico d'Italia. 3. Sapienza- Università di Roma, Dipartimento di Scienze della Terra. 4. Società Geologica Italiana. 5. ISPRA- Servizio Biblioteca e Documentazione.

Corresponding email: [alessandro.zuccari@socgeol.it](mailto:alessandro.zuccari@socgeol.it)

Keywords: History of geology, communication strategies, science outreach, Geoitaliani.

“*Geology has been an Italian science*” (“Principles of Geology”, proem to 1st edition, 1830). Sir Charles Lyell’s tribute to forerunners in earth sciences field seems today neglected by Italian society, whose relationships with geoscientific community in the last decades have been compromised by several tragic events. In such a context, promoting public awareness and understanding of earth sciences importance is thus a crucial issue for a ‘geologically young’ country, constantly facing the consequences of natural hazards.

The history of geological thought and its evolution through time can play a key epistemological role for the spreading of a more holistic and multidisciplinary science knowledge in Italy. In our country other scientific disciplines (e.g. medicine, biology, physics and mathematics among others) rely on a consolidated awareness of the importance of their own tradition, whereas contribution by Italian earth scientists to this cultural operation is still subordinate.

The Italian Geological Society has recently established a History of Geosciences Section and then a website ([www.geoitaliani.it](http://www.geoitaliani.it)) activated in March 2013. The site has been conceived as a common space for the “storytelling” of people, places and events representative of the Italian geological culture, by means of texts, images, photos, historical maps and multimedia. About one hundred contributions by nineteen different authors (researchers, teachers, geologists, historians) have hitherto been published.

Precious information come from the historical archives of both the Italian Geological Society and the library of the Italian Institute for Environmental Protection and Research (ISPRA), which represent the principal collections of original bibliographic and cartographic material (about 50.000 maps) belonged to the Geological Survey of Italy. The digitalization process of about 1.000 historical maps, catalogued according to the International Standard Bibliographic Description for Cartographic Materials, has almost been completed.

Participation to meetings and publication of thematic papers is part of the cultural process. History of Geosciences section members also cooperate with the Institute of the Italian Encyclopedia as authors of geoscientists biographies published in the Italians Biographic Dictionary ([www.treccani.it](http://www.treccani.it)).

Since its activation, GEOITALIANI has been consulted by more than 28000 visitors from Italy and all over the world. Social networks (Facebook: [www.facebook.com/geoitaliani](http://www.facebook.com/geoitaliani); Twitter: [@geoitaliani](https://twitter.com/geoitaliani)) represent strategic communication tools, reaching younger audience and trespassing boundaries of the geological community: the majority of the almost 800 Facebook followers are indeed “non geologists”, actively involved in general discussion.

In our vision, a new meaning of the Actualism principle should thus be considered for the future of the Italian Geosciences: “*the present is the key to the past, and the past is the key to the future*”.

## The utilization of the electron microprobe analyses to non-silicatic systems: examples of applications

Braschi E.\*, Orlando A. & Ruggieri G.

C.N.R., Istituto di Geoscienze e Georisorse, Firenze.

Corresponding email: [eleonora.braschi@igg.cnr.it](mailto:eleonora.braschi@igg.cnr.it)

Keywords: electron microprobe, non-silicate systems.

In the last five years the JEOL-8600 electron microprobe hosted in the new labs at the Department of Earth Sciences of the University of Florence has been updated in both software and hardware components. The instruments is controlled by the XMAS, IDFix, HiMax, MaxView software packages (developed by SAMx) which allow to perform quantitative analyses utilizing the equipped four spectrometers, each constituted by two analyzing crystals. In addition to be involved in routine analysis, such as those performed to characterize the mineral chemistry of silicates, in the recent past the instrument has been used to “non-conventional” researches who have interested different fields of Earth Sciences *sensu lato*, such as Paleontology and Archeometry. In this context, the importance of analyses on materials such as bones, teeth, bryozoa, and phases such as apatites and oxides are invaluable in the interpretation of the processes responsible of their formation and evolution. The optimization of the analytical conditions was therefore properly approached adjusting several different instrumental parameters such as accelerating voltage, beam current and counting times. Besides adjusting these parameters, the calibration included the choice of the appropriate emission lines to be analyzed and the consequent selection of the analyzing crystal (and spectrometer) to be used in WDS analyses. For this purpose the calibration was mainly concerned in the minimization of the detection limits of the elements to be analyzed.

The aim of this communication is to provide some examples of analytical set-up utilized during analyses of “non conventional” material. Thus, the acquired analyses of teeth (either enamel and dentin) and bones fossil remains of *Ursus spelaeus* from Grotta all’Onda cave (Camaiole, Italy) were invaluable to reconstruct the paleo-environment in which the animal lived. Similar information was obtained after analyzing *Chiastosella* bryozoa from different depth in Southern Ocean (Antarctica). Appropriate analytical setting allowed to estimate MgCO<sub>3</sub> mol% contents to be related to water temperature variations and climate changes. Further researches involved analyses on apatites from a pseudotachylite sample and its host rock collected south of Terranova Bay (Antarctica). These analyses have the aim to verify the depletion in minor and trace elements due to the pseudotachylite formation, as suggested by the variation of U contents in the pseudotachylite and its host rock, derived from apatite fission-track analysis. As a final example, an appropriate calibration procedure was necessary to measure out trace elements (e.g. W) in oxides and metallurgical slag, thought to be valid tracers in ancient metallurgical processes finalized to the production of Fe in Tuscany.

## A "group of Oil&Gas Geology" within the Geological Society of Italy. Why? What? How?

R. Calabrò<sup>1</sup>, P. Martini<sup>2</sup>, A. Pica<sup>3</sup>, G. Rigo<sup>4</sup>, P. Shiner<sup>5</sup>, P. Vecchia\*<sup>3</sup>

1. Abu Qir Petroleum, Sidi Gaber, Alexandria-Egypt; 2. Geomarpa Consulting Ltd, London-UK; 3. Irminio srl, Rome-Italy.  
4. Cygam Energy Italia spa, Rome-Italy; 5. Petroceltic Italia spa, Rome-Italy.

Corresponding email: [geo.idrocarburi@socgeol.it](mailto:geo.idrocarburi@socgeol.it)

Keywords: Oil, Gas, Geological Society of Italy, Social Responsibility.

Italy has always been a strong consumer of Oil and Gas. It was also, and potentially it is still now, a major producer of hydrocarbons; we could be the 5th largest European producer of oil, following the countries bordering the North Sea, ie Norway, Netherlands, UK and Denmark. Oil&Gas are a strategic resource of the State, an indispensable good of the community, or all of us.

The "Italian oil history" began in 1802 with chemical studies from Giuseppe Mojon: the streets of Genoa were illuminated with the "nafta" naturally outcropping along the Taro River near Parma. The early production of Oil in Italy was finalized to this kind of use, as reported by Abbot Antonio Stoppani (1824-1891), author of "Geology of Italy" and of the most famous "Il Bel Paese".

Gas has a similar story, which began in the late eighteenth century with the studies of the Abbot Lazzaro Spallanzani and Alessandro Volta on the properties of hydrocarbons. The agreement between the City of Turin and "Society of Gas Lighting for the City of Turin", funded in 1837 to brighten the first capital of Italy with gas distilled from solid fuels, is dated 1846.

Since the beginning, these activities were based on scientific and technical knowledge, on the professional skills of the men and women who devoted themselves. The presence and the excellence of Italian science was important, giving global footprint in all the innovative processes that guided the development of energy sources.

### *WHY A GROUP OF OIL&GAS GEOLOGY?*

Underground resources and Earth Sciences. An indissoluble union, an enviable school of geosciences, a huge hunger for energy, an incredible dependence on imported energy resources and a very important domestic potential. The need to operate in full respect of the surrounding territory, the material contribute a hydrocarbon geologist can give to a proper dissemination of knowledge and to increase awareness of our surrounding land, the need of a Corporate but also Personal Social Responsibility.

All this is at the base for creating the Group for Oil&Gas Geology within the Geological Society of Italy. A section that wants to have the aim to contribute to the knowledge of the territory and the development of our country.

### *WHAT TO DO?*

Promoting knowledge on the scientific and technological aspects of the exploration and production of hydrocarbons, on their importance in the context of a proper energy mix, and on their contribution to a sustainable development of the country. Dissemination and sharing of knowledge, awareness of the importance of Geosciences, accurate information.

### *HOW?*

Through the combination of the following possible actions:

- Organisation of, and participation in, seminars and conferences
- Publications
- Visits to facilities and production sites
- Lecturers to schools and universities
- "Twinning" with similar sections and / or foreign companies and associations

## **Rus in Urbe: GIS for archaeobotanical data collection of green spaces of ancient Pompeii**

Cirillo C.<sup>1</sup>, Scarpa L.<sup>2</sup>, Acampora G.\*<sup>1</sup>, Bertoli B.<sup>1</sup>, Russo M.<sup>1</sup> & Esposito R.<sup>1</sup>

1. CNR Institute of Agro-Environmental and Forest Biology, Napoli. 2. University of Naples Federico II – Master Urban Planning.

Corresponding email: [giovanna.acampora@ibaf.cnr.it](mailto:giovanna.acampora@ibaf.cnr.it)

Keywords: Archaeobotany search, ancient Pompeii, GIS systems, soil anthropization.

The creation of a GIS information system for the green spaces of Ancient Pompeii is intended to support the development of a coordinated and consistent system of useful data to realize enhancement projects based on contents of recognized scientific validity. The setting up of analytical methods, inspired to the principles of geography, is aimed at producing information layers to be used in geo-referenced modeling of physical spaces. The analysis and processing of data extracted from the observation of the real world, is performed using advanced technologies, designed to dynamically produce information, data and procedures useful for the knowledge of natural and cultural resources. The current debate on the use of GIS tools in the field of archaeological studies, since a few years finds a significant acceleration, thanks to the increasing awareness of the analysis potential of this technology. To support this development means to intensify the debate and discussion between all the different specialists involved in the issues, placing in the foreground the premises and conditions necessary for a scientifically correct development for the diffusion of geographical knowledge of the historical territory (Scarpa, 2012). Based on the census of plant elements, found in ancient Pompeii (Ciarallo, 2004), a GIS platform was developed aiming at making archaeobotanical data accessible and usable. The list of the collected plant specimens, amounting to 13,680 referred to 1,710 entities (Ciarallo, 2012) was compiled on the basis of all available data: archive, bibliographic and analytical data. The achieved ecodata come mainly from the study of vegetation (paleobotanical analysis and pollen analysis) and provide the reconstruction not only of the vegetative cover of the archaeological site but also the analysis of the human impact on the vegetation and soils that support it. The inclusion of archaeobotanical data in a digital environment will make the realization of a software possible able to collect and organize data in a consistent, rational and organic manner (Farinetti, 2012). The ability of GIS systems to integrate information layers concerned with the environmental context allows to check and assess the relationship between archaeobotanical data and environmental data, bringing the archaeobotanical research back to an environmental determinism.

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Ciarallo A. 2004. Flora Pompeiana Antica. Electa Napoli, 48 pp.

Farinetti E. 2012. I Paesaggi in Archeologia analisi e interpretazione. Carocci Ediotre, 128 pp.

Scarpa L. 2012. Metodologie e strumenti multimediali per l'analisi e la modellizzazione dello spazio storico del territorio, in Ambiente Multimediali per i Beni Culturali a cura di F.Cantone.

## Hunting for a putative trackmaker: “élite prints” 3D morphology as an objective tool to recognize osteological patterns and to infer locomotor functionality

Citton P.\* & Romano M.

Dipartimento di Scienze della Terra, “Sapienza” Università di Roma.

Corresponding email: [paolo.citton@uniroma1.it](mailto:paolo.citton@uniroma1.it)

Keywords: *Dimetropus*, “pelycosaur”, photogrammetry.

Tetrapod footprints referred to the ichnogenus *Dimetropus* have been traditionally attributed to carnivorous eupelycosaurian synapsids (*i.e.*, Sphenacodontidae; see Gand & Haubold, 1984; Haubold, 1971; Tilton, 1931; Voigt, 2005). Despite the broad agreement on this attribution, the characters connecting the ichnogenus to specific osteological features of “pelycosaurian” (non-therapsid synapsids in the new cladistics conception) autopods have never been clearly identified.

The discovery of superbly preserved footprints referable to *Dimetropus* from the Lower Permian Midco Member of the Wellington Formation (Perry, Noble County, Oklahoma, USA), has allowed to define these features, emphasizing their intimate correlation with autopod structure and inferred functionality in non-therapsid synapsids. In a first analysis, digit length in considered footprints has been morphometrically compared with digit length in known “pelycosaurian” autopods. The analysis has been conducted separately for the manus and pedes impressions and the respective fore and hind autopods. Subsequently, the impression differential depth has been studied in detail. For each considered footprint portion, the osteological pattern mirrored in the impressions has been recognized, and the possible path of weight loading during a complete cycle of locomotion has been highlighted. To obtain a more quantitative and objective appraisal of differential depth of impression, the method of photogrammetry has been applied and a high-resolution three-dimensional model of the footprints, through the VisualSFM and MeshLab softwares, has been obtained.

The ichnological characters, in connection with the comparative analysis of known skeletal remains and tracks, highly suggest the attribution of the studied material to a new *Dimetropus* ichnospecies and allow inferring a putative trackmaker within the Family Caseidae (Synapsida, Caseasauria), even if an edaphosaurid affinity cannot be completely excluded. In addition, as a more general conclusion, the study has shown that footprints ascribed to *Dimetropus* are characterized by a substantial variability, which is most likely a direct reflection of a wide range of different zoological taxa among non-therapsid synapsids.

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Voigt S. 2005. *Die Tetrapodenichnofauna des kontinentalen Oberkarbon und Perm im Thüringer Wald – Ichnotaxonomie, Paläoökologie und Biostratigraphie*, Cuvillier, Göttingen.

## Petrographic features of foliated leucocratic body in the Migmatite Complex from northeastern Sardinia

Columbu S.<sup>1</sup>, Costamagna L.G.<sup>1</sup>, Cruciani G.<sup>1</sup>, Elter F.M.<sup>2</sup>, Fancello D.\*<sup>1</sup>, Franceschelli M.<sup>1</sup> & Scodina M.<sup>1</sup>

1. Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari. 2. Dipartimento di Scienze della Terra dell'Ambiente e della Vita, Università di Genova.

Corresponding email: [darfan@hotmail.it](mailto:darfan@hotmail.it)

Keywords: Foliated leucogranite, migmatite, Variscan Sardinia.

At Punta Bados, a few kilometers north of Olbia city, an elongated foliated leucocratic body striking N160°-170°, characterized by coarse-grained garnets up to 4-5 cm in diameter is hosted in a sequence of igneous and sedimentary derived migmatite and fibrolite-rich metapelites with minor metabasite and metaultramafics (Cruciani *et al.*, 2002, 2008). The leucocratic body shows an alternation between poorly and moderately foliated domains, as well as a great variability in garnet size and abundance. Rock grain size is strongly variable reaching up, locally, a pegmatitic texture. The contact between the leucocratic body and the metapelites is marked by a 30 cm-thick cataclastic band with S-C structures and kinematic indicators suggesting a dextral shear component. It mainly consists of quartz, plagioclase, microcline, muscovite, biotite and garnet, with zircon, apatite and tourmaline as accessory minerals. Plagioclase is mainly unzoned albite (An<sub>5</sub>). Garnet is unzoned to poorly zoned with composition Alm<sub>75</sub>, Pyr<sub>10</sub>, SpS<sub>15</sub>, Grs<sub><1mol.%</sub>. It is free from inclusions and/or from other microstructural relics. Muscovite occurs as centimetre-sized crystals with Si content near to 6.15 a.p.f.u. and X<sub>Na</sub> = 0.10. The whole-rock composition of a few representative samples shows following major element content ranges: SiO<sub>2</sub>: 72.8-74.7; Al<sub>2</sub>O<sub>3</sub>: 15.0- 15.4; Fe<sub>2</sub>O<sub>3</sub>tot: 0.5-0.7; MnO: 0.05-0.08; MgO: 0.1-0.7; CaO: 0.4-2.0; Na<sub>2</sub>O: 4-5; K<sub>2</sub>O: 3.2-4.8 wt.%. The rocks are peraluminous with normative composition matching those of granite/trondhjemite. Preliminary data suggest that barium ranges from 71 to 634 ppm, whereas Rb and Sr vary between 36-252 and 54-327 ppm, respectively. Rare earth element (REE) content of the leucocratic body is ~50 ppm with moderately fractionated pattern for light and medium REE, and flat for heavy REE (Ce<sub>N</sub>/Yb<sub>N</sub> ~1.5, La<sub>N</sub>/Sm<sub>N</sub> ~1.5, Gd<sub>N</sub>/Yb<sub>N</sub> ~1.0) with no Eu anomaly. Field geological data and petrographic features indicate that the leucocratic felsic body of Punta Bados resembles the foliated leucogranites described in Golfo Aranci and Arzachena areas (northern Sardinia) interpreted as anatectic bodies emplaced during the late deformative event related to the exhumation of the metamorphic basement.

Cruciani G., Franceschelli M., Jung S., Puxeddu M., Utzeri D. 2008. Amphibole-bearing migmatites from the Variscan Belt of NE Sardinia, Italy: partial melting of mid-Ordovician igneous sources. *Lithos*, 105, 208-224.

Franceschelli M., Carcangiu G., Caredda A.M., Cruciani G., Memmi I., Zucca M. 2002. Transformation of cumulate mafic rocks to granulite and re-equilibration in amphibolite and greenschist facies in NE Sardinia, Italy. *Lithos*, 63, 1-18.

## The Variscan (?) Settiballas "Micaschists" (SW Sardinia): geological and petrographical investigations

Costamagna L.G.\*<sup>1</sup>, Cruciani G.<sup>1</sup>, Elter F.M.<sup>2</sup> & Franceschelli M.<sup>2</sup>

1. Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari. 2. Dipterus, Università di Genova.

Corresponding email: [lucakost@unica.it](mailto:lucakost@unica.it)

Keywords: Variscan chain, Metamorphic rocks, Sardinia.

In SW Sardinia crops out the Monte Filau Complex, a Variscan medium-grade metamorphic complex built by the Monte Filau Orthogneiss and the Settiballas "Micaschists" (Minzoni, 1981): this complex intrudes the clastics of the Variscan Bithia Complex (Junker & Schneider, 1983). While the Monte Filau Complex is referred to the amphibolitic facies, the enclosing Bithia Fm pertains to the greenschist metamorphic facies (Franceschelli et al., 2005). The Monte Filau Orthogneiss is a Middle Ordovician granitoid metamorphosed by the Variscan events. The Settiballas "Micaschists", whose age is still uncertain (Precambrian?), are mainly surrounded by the Monte Filau Orthogneiss (Monte Settiballas area) except for a few outcrops (Monte Cogoni coastal area) that are surrounded by the Variscan intrusive complex. Thermometamorphic evidences due to the intrusion of the orthogneiss protolith and/or of the Variscan granitoids are evident in the Monte Settiballas area where the "micaschists" are turned into hornfels. Conversely, in the southern Monte Cogoni area the "micaschists" show a stronger regional metamorphic imprint. Besides, in this area intercalations of metavolcanics and carbonate and mixed carbonate-siliciclastic beds (now turned into marbles and calcsilicate rocks) have been found. The geological survey evidenced in the "micaschists" a variable schistosity trend; in the western outcrop it strikes about NS dipping West. Conversely, in the eastern area it is mainly N°150 dipping East. An antiformal structure is thus evidenced. Petrographic investigations in the studied areas indicate that the micaschists are well-foliated rocks characterized by an alternation of granoblastic and lepidoblastic millimetric layers. The most common minerals are quartz, muscovite, biotite, and Al-silicates. Andalusite is partially replaced and pseudomorphosed by muscovite. Chloritized biotite still retains significant titanium content. Accessory minerals are ilmenite, monazite and, sometimes, tourmaline. Calcsilicate intercalations show a layered microstructure consisting of dark-coloured phyllosilicate-rich layers alternated with light-colored epidote rich layers. The geological features suggest that the "micaschists" may be a thin cover over Ordovician and Variscan intrusives. The original nature and age of the protolith is still matter of debate.

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## The high-grade metamorphics from Pittulongu to Golfo Aranci (NE Sardinia): an attempt of lithological reconstruction

Costamagna L.G.<sup>1</sup>, Cruciani G.\*<sup>1</sup>, Elter F.M.<sup>2</sup>, Fancello D.<sup>1</sup>, Franceschelli M.<sup>1</sup>, Massa F.<sup>2</sup> & Spano M.E.<sup>1</sup>

1. Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari. 2. Dipartimento di Scienze della Terra dell'Ambiente e della Vita, Università di Genova.

Corresponding email: [gcrucian@unica.it](mailto:gcrucian@unica.it)

Keywords: igneous-sedimentary sequence, northeastern Sardinia, Variscan orogeny.

In NE Sardinia, along the coastline from Olbia to the Capo Figari southern side, crops out a high-grade metamorphic complex pertaining to the Axial Zone of the Southern Variscan chain. The main outcrops are formed by migmatitic paragneisses, orthogneisses, eclogites, and mafic to ultramafic amphibolites (Franceschelli et al., 2002, Cruciani et al., 2008). Orthogneisses dated  $469 \pm 3.7$  Ma prevail in the northern part (Capo Figari), while migmatitic paragneisses, minor amphibolites with relic eclogite parageneses (this latter with an age of  $460 \pm 5$  Ma) and rare lenses of orthogneisses are present in the southern part. In the paragneisses, swarms of calc-silicatic nodules probably representing former carbonate beds (?) now completely shattered are locally concentrated. By a detailed geological mapping along the coast, an attempt has been made to unravel the pre-metamorphic sequence: we tried to refer every metamorphic rock to its former protolith. The mapping evidenced the presence of alternations of metamorphic rocks passing frequently from each other through gradual or alternated boundaries: this could be related to the original boundaries of the former sedimentary or igneous protoliths, thus probably suggesting the original composition of the succession. This may be composed by acidic and basic volcanics and immature siliciclastics. The geometrical upper part of the succession may be located in the Capo Figari area (Cala Moresca), where the thick augen-orthogneiss outcrop may be related to the Middle Ordovician volcanic complex widely outcropping along all the Variscan Sardinian transect. These rocks show also the oldest radiometric age ever found in the area and are characterized by primary/interdigitated contacts with paraderivates (paragneiss with calcsilicate nodules). In the lower part of the succession, in the M. Nieddu-Pittulongu beach area, alternations of migmatitic paragneiss with calcsilicate nodules and amphibolites could be related to former immature siliciclastics intercalated by carbonate beds (?) and basic volcanics. Thus, this work could allow to relate the low- to middle-grade metamorphics of the Variscan Nappe Zone with the ones of the Variscan Axial Zone and to confirm the local persistence in the Olbia area of the same sedimentary environments existing during lower Paleozoic times in the south and central part of the island.

Cruciani G., Franceschelli M., Jung S., Puxeddu M., Utzeri D. 2008. Amphibole-bearing migmatites from the Variscan Belt of NE Sardinia, Italy: partial melting of mid-Ordovician igneous sources. *Lithos*, 105, 208–224.  
Franceschelli M., Carcangiu G., Caredda A.M., Cruciani G., Memmi I., Zucca M. 2002. Transformation of cumulate mafic rocks to granulite and re-equilibration in amphibolite and greenschist facies in NE Sardinia, Italy. *Lithos*, 63, 1–18.

## The Lower Pleistocene Arda river invertebrate fauna: palaeoecology, palaeoclimatology and biochronology

Crippa G.\*<sup>1</sup>, Felletti F.<sup>1</sup> & Raineri G.<sup>2</sup>

1. Dipartimento di Scienze della Terra 'Ardito Desio', Università degli Studi di Milano. 2. Riserva Naturale Geologica del Piacenziano, Castell'Arquato, Italy.

Corresponding email: [gaia.crippa@unimi.it](mailto:gaia.crippa@unimi.it)

Keywords: Palaeoecology, Arda River, Boreal guests.

The Arda River succession, cropping out in Western Emilia, Northern Italy, is a marine succession of Early Pleistocene age; it is composed mainly of sandstones, siltstones and claystones and it is bounded at its top by continental conglomerates, representing a major sea level drop and the establishment of a continental environment with vertebrate faunas and fresh water molluscs.

Numerous fossiliferous levels very rich in macroinvertebrates are present along the marine succession; the very diverse fauna comprises bivalves, brachiopods, gastropods, corals, serpulids, bryozoan, echinoderms, scaphopods and barnacles. Fossils are generally well preserved with several articulated specimens in life position and often preserving the color and the spiny fragile ornamentation.

The results of the analysis of the faunal association are the following:

Palaeoecologic implication. The Arda fauna is characterized by both infaunal and epifaunal species, mainly of infra- and circalittoral environment. The higher biodiversity has been recorded in fine sandstones, which contain the typical shallow water association with *Chamelea gallina*, *Acanthocardia tuberculata* and *Glycymeris insubrica*; a lower biodiversity has been instead recorded in siltstones barren of sedimentary structures and characterized by a deeper water fauna, mainly typified by the bivalve *Venus multilamella* and the gastropod *Turritella tricarinata*. The palaeoecological analysis of the fauna confirms the general regressive trend of the marine succession; several alternation of lower order transgressive and regressive sedimentary cycles are present, but no event of emersion or shift to very deep water setting has been recorded.

Palaeoclimatic implication. The occurrence of boreal guests, such as *Arctica islandica*, *Pseudamussium septemradiatum*, *Mytilus edulis* and *Acanthocardia echinata*, suggests that a climatic change occurred in the section causing a shift from warm to cold seawater temperatures. The evolution of this climatic deterioration is complex, but it prepares the ground for the onset of the continental glaciation of the Middle and Late Pleistocene.

Biochronologic implication. Based on the analysis of its fauna, the Arda river succession entirely belongs to the Early Pleistocene age (Gelasian and Calabrian). The extinction of the bivalves *Aequipecten scabrella* and *Flabellipecten flabelliformis* and the first occurrence of *Arctica islandica* allow to better constrain the age in some part of the section.

## The late Variscan Monte Linas Pluton (SW Sardinia): a source of granophile element ore

Cuccuru S.\*<sup>1</sup>, Casini L.<sup>1</sup>, Naitza S.<sup>2</sup>, Puccini A.<sup>1</sup>, Secchi F.<sup>1</sup> & Oggiano G.<sup>1</sup>

1. Dipartimento di Scienze della Natura e del Territorio - Università di Sassari. Via Piandanna 4, 07100 Sassari 2. Dipartimento di Geoingegneria e Tecnologie Ambientali - Università di Cagliari. Piazza d'Armi, Cagliari.

Corresponding email: [scuccuru@uniss.it](mailto:scuccuru@uniss.it)

Keywords: Fayalite, hydrothermal ore deposits, Corsica-Sardinia Batholith.

The Monte Linas Pluton (MLP) and its host rocks offer a good chance in unveiling the relationships between late-Variscan geodynamics, magmatism and ore formation. Late-Variscan ore deposits are known since pre-historic ages; however, some petrological features of MLP such as the occurrence of uncommon fayalite bearing terms and their association with hydrothermal ore deposits remain unclear. The MLP emplaced at  $289 \pm 1$  Ma in the Sardinian Variscan Foreland, between the allocthonous Arburese Unit and the underlying para-autochthonous Iglesias Unit. The pluton consists of coarse-grained monzogranite permeated by medium- to fine-grained co-magmatic monzogranites. These fine-grained facies form an almost continuous sub-horizontal sheet, up to 50 m thick. The magmatic fabric is poorly defined by the shape preferred orientation of biotite, feldspar and plagioclase; however, a flat or gently dipping overall geometry is defined by the geometry of concordant porphyritic sheets, metamorphic xenoliths and pegmatites at the top of the pluton, and by the shape of rare micro-granular mafic enclaves. The MLP emplaced within already exhumed very low grade basement. A shallow level of emplacement is also inferable from the occurrence of andalusite in the metamorphic aureole. The composition of MLP is characterized by the occurrence of large, idiomorphic, zoned plagioclase and Fe-rich Ti-biotites, ipidiomorphic orthoclase and quartz. Common accessory phases include ilmenite, zircon, monazite fluorite and apatite. Fayalite has been rarely observed and is generally replaced by pseudomorphic patches of Fe oxides/hydroxides. Medium to fine grained rocks, instead, are characterized by plagioclase with inverse zoning often containing drop-like inclusions of Y- and Ta-oxides. Fayalite generally appears as a fundamental phase in pegmatites associated to these fine-grained rocks.

A wide range of ore deposits are associated to MLP, including Mo-W/Mo-Cu greisens, Fe  $\pm$  Sn skarns, and W-Sn, Sn-Pb-Zn-Cu and F-Pb-Zn hypothermal to mesothermal veins. A striking metallogenic feature is the occurrence Mo and Sn in the same vein swarm, pointing to probable variations in the oxidation state of magma (from ilmenite-dominated to magnetite-bearing), which involved also the metal bearing fluids during a late intrusive phase. Field relationships and petrographical observations suggest that: i) MLP emplaced along a first order tectonic discontinuity (i.e., a major thrust plane developed in the more internal part of the Variscan Foreland), ii) the more evolved melts, relatively enriched in W-Sn-Pb-Zn-Cu, emplaced in the apical part of MLP in response to filter pressing processes enhanced by thermal contraction and fracturing of the already solidified monzogranitic terms. Hence, the MLP shares the same metallogenesis of equivalent late-Variscan plutons exposed in Cornwall, Herzgebirge and the Central Iberian Zone.

## Foraminiferal assemblages in active volcanic areas: two study cases from Azores Archipelago (Atlantic Ocean) and Pantelleria Island (Mediterranean Sea)

Di Bella L.<sup>1</sup>, Frezza V.\*<sup>1</sup>, Conte M.A.<sup>2</sup>, Falese F.<sup>1</sup>, Martorelli E.<sup>3</sup>, Sposato A.<sup>3</sup> & Chiocci F.L.<sup>1</sup>

1. Dipartimento di Scienze della Terra-“Sapienza” Università di Roma. 2. CNR-IGG-U.O.S. di Roma c/o Dipartimento di Scienze della Terra-“Sapienza” Università di Roma 3. C.N.R.-IGAG Istituto di Geologia Ambientale e Geoingegneria, Roma.

Corresponding email: [virgilio.frezza@uniroma1.it](mailto:virgilio.frezza@uniroma1.it)

Keywords: benthic foraminifers, recolonisation, marine volcanic areas.

Recent studies demonstrated the capability of foraminifers to adapt to a wide range of environmental conditions and to give a response to environmental stress due to natural or human origin as environmental indicators (Alve, 1991; Hess et al., 2005; Carboni et al., 2009; Schönfeld et al., 2012). This work aims to document the benthic foraminiferal response to natural stressed environments in two areas, Azores Archipelago and Pantelleria Island, interested by similar active volcanism. The Azores area has been affected by a recent volcanic activity occurred in 2001, while the last submarine eruption of Pantelleria Island dates at 1891. The different periods of eruption of the two areas allow to investigate on the way and time of the re-colonisation process by foraminiferal assemblages. Petrographic, sedimentological and microfaunistic analyses were conducted on selected samples in order to obtain an environmental characterisation of the two active volcanic areas.

The inorganic fraction of samples collected in both areas is constituted of blackish, sand-sized glass shards, whereas the organic component is mainly constituted by foraminifers. Faunal composition, diversity and density highlight two different structure of the assemblages relatively to the two areas. In fact the foraminiferal assemblages of the Azores area are dominated by opportunistic species (*Angulogerina angulosa*) and represent the first stage of re-colonisation after the eruption occurred in 2001, while the associations of Pantelleria Island (*Globocassidulina subglobosa*, *Lenticulina rotulata*, *Lobatula lobatula* and miliolids) have to be considered as an advanced stage of resettlement with stable rich and well diversified assemblages. Moreover, in the Azores area many morphological abnormalities were recognised confirming a more stressed environment than Pantelleria bottom. In both areas a lot of specimens showed test alterations probably due to hydrothermal fluids that lead to the dissolution of calcium carbonate.

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Schönfeld J., Alve E., Geslin E., Jorissen F., Korsun S., Spezzaferri S. & Members of the Fobimo Group 2012. The FOBIMO (FORaminiferal BIo-MONitoring) initiative towards a standardised protocol for soft-bottom benthic foraminiferal monitoring studies. *Mar. Micropal.*, 94-95, 1-13.

## Living foraminiferal assemblages in two submarine canyons (Polcevera and Bisagno) of the Ligurian Basin (Italy)

Ferretti A.<sup>1</sup>, Ferri A.<sup>1</sup>, Moraga D.J.<sup>1</sup>, Pica D.\*<sup>2</sup> & Di Bella L.<sup>1</sup>

1. Dipartimento di Scienze della Terra, "Sapienza" Università di Roma. 2. Dipartimento di Scienze della Vita e dell'Ambiente, Università Politecnica delle Marche, Ancona.

Corresponding email: [letizia.dibella@uniroma1.it](mailto:letizia.dibella@uniroma1.it).

Keywords: Foraminiferal assemblages, submarine canyons, Ligurian basin (Italy).

Recently the scientific interest is focused on the deep marine ecosystem because they can play an important role to recycle of the global carbon cycle. Particularly the submarine canyons act as sediment and organic matter traps into which material originating from the continental shelf is conveyed (Van Weering et al., 2002). Therefore, canyons, compared to the adjacent continental slope, represent areas characterized by more eutrophic conditions.

This study is part of the RITMARE Project: BioLig - Biodiversity, ecosystem functioning and pelagic-benthic coupling in Ligurian submarine canyons. In this work two types of environmental settings (from 200 to 2000 m depth) were investigated: the Polcevera and Bisagno canyons and the adjacent open slopes (Ligurian Sea). Living (Rose Bengal stained) and total benthic foraminiferal assemblages, collected by mean box corer, were analyzed and processed by statistical analyses (Cluster Analyses). The data results highlight different foraminiferal assemblages in slope and canyon areas due to the quantity and quality of organic matter fluxes.

The main difference consists of high frequencies of *Bolivina* spp., typical low oxygen taxa, in canyon sites. Moreover a comparison between the benthic foraminiferal assemblages of the studied sites and other canyons in the Atlantic (Nardelli et al., 2010) and Mediterranean basins (Schmiedl et al., 2000), showed similarities in compositional and structural features.

Nardelli M.P., Jorissen F.J., Pusceddu A., Morigi C., Dell'Anno A., Danovaro R., De Stigter H.C. & Negri A. 2010. Living benthic foraminiferal assemblages along a latitudinal transect at 1000m depth off the Portuguese margin. *Mar. Micropaleont.*, 56, 323-344.

Schmiedl G., De Bovée F., Buscail R., Charriore B., Hemleben C., Medernach L. & Picon P. 2000. Trophic control of benthic foraminiferal abundance and microhabitat in the bathyal Gulf of Lions, western Mediterranean Sea. *Mar. Micropaleont.*, 40, 167-188.

Van Weering T.C.E., De Stigter H.C., Boer W., De Haas H. 2002. Recent sediment transport and accumulation on the NW Iberian Margin. *Prog. Oceanogr.*, 52, 349-371.

## Geochemical constraints on late Variscan granitoid magmatism in central Calabria (Southern Italy)

Fiannacca P.\*, Bonanno F., Carciotto M., Militello. G. & Cirrincione R.

Dipartimento di Scienze Biologiche, Geologiche ed Ambientali - Università di Catania.

Corresponding email: [pfianca@unict.it](mailto:pfianca@unict.it)

Keywords: Petrogenesis, Serre Batholith, Calabria.

The Serre Batholith, in central Calabria, is a Late Variscan granitoid complex that makes up the middle portion, c. 13 km thick, of an almost complete and continuous section of continental crust. Petrogenetic studies on these granitoid rocks, although providing important advancements, highlighted the difficulty of elaborating reliable and univocal models and stopped ultimately the mid nineties. In this study, major and trace element analyses of 300 literature samples and 60 new samples have been investigated by means of classical petrological tools, but also in the light of recently proposed, or recently modified, classification schemes. Geochemical data indicate that the batholith rocks range with continuity in composition from quartz diorite and quartz monzodiorite to tonalite, granodiorite and monzogranite, with minor syenogranite samples; a well distinct group of leucotonalites also occurs.

The granitoids are on the whole magnesian and calcic to calc-alkalic, with only some of the more evolved rocks (two-mica granites) showing a ferroan calc-alkalic to alkali-calcic composition. Quartz diorites, quartz monzodiorites and tonalites are metaluminous to weakly peraluminous, while granodiorites and granites are weakly to strongly peraluminous, with two-mica porphyritic types being the only population with a genuine strongly peraluminous character. Fe\*-number, MALI and ASI features highlight a strong affinity of the Serre Batholith rocks with Cordilleran granitoids, inherited from the compositions of the source rocks rather than reflecting the real tectonic environment of the magmas. Silica-rich peraluminous granites show also affinity with leucogranites formed by pure decompression melting of crustal rocks.

Major and trace element clusters and trends in Harker diagrams are consistent with an origin of the Serre Batholith from the assembling of several batches of magmas with different original compositions. Multielement diagrams and literature Sr-Nd isotope data also provide evidences for large heterogeneities within the magma sources. This does not exclude that the resulting magmas did interact between them, as indeed suggested by the diffuse presence of mafic microgranular enclaves in the weakly peraluminous granitoid rocks and by geochemical trends consistent with mixing processes.

A role for fractionation is also not ruled out and it appears indeed as the main process involved in the production of leucotonalites and in the geochemical variations within a population of weakly peraluminous granodiorites. Comparison with mixing curves and with compositions of experimental melts produced by partial melting of metasedimentary and intermediate-mafic metamagmatic sources suggests a general derivation of studied rocks from mixing, in varying proportions, of mantle- and metasediment-derived melts. It also confirms a pure crustal origin of the strongly peraluminous porphyritic granites, by partial melting of dominantly metagreywacke sources.

## **$^{40}\text{Ar}$ - $^{39}\text{Ar}$ results on amphibole and biotite of an anatectic amphibole-bearing migmatite from the Variscan basement of NE Sardinia, Italy**

Franceschelli M.\* & Cruciani G.

Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari.

Corresponding email: [francmar@unica.it](mailto:francmar@unica.it)

Keywords:  $^{40}\text{Ar}$ - $^{39}\text{Ar}$  age, amphibole-bearing migmatite, Variscan Sardinia.

The amphibole-bearing migmatite forms a decametric lens-shaped body at Punta Sirenella, a few km north of Olbia in NE Sardinia. The leucosomes are coarse-grained granoblastic rocks occurring as elongated, tightly folded leucosomes, ranging in thickness from 2 to 4 cm, or as pods or patches up to 30-50 cm long. Both leucosome and mesosome mainly consist of variable proportions of quartz, plagioclase, biotite,  $\pm$  amphibole,  $\pm$  garnet. Accessory minerals are apatite, zircon, titanite, Fe-oxides, Fe-sulphides, and epidote. The mesosomes show an oriented fabric defined by the alignment of biotite and amphibole parallel to the  $D_2$  foliation. Amphibole abundance is strongly variable from one leucosome to the other, or even along the same leucosome. In amphibole-rich leucosomes, amphibole occurs as large, green porphyroblasts (up to 4 cm in size) with several inclusions mainly of plagioclase, quartz, garnet, and biotite (Cruciani et al., 2008). According to Massonne et al. (2013), the migmatite protolith was an intermediate igneous rock metamorphosed at high pressure. At the final prograde metamorphic stage, the migmatite was heated to reach P-T conditions of about 1.3 GPa and 700°C. Close to these P-T conditions, melt separated from the rock to form leucosomes. Subsequently, pressure release and slight cooling resulted in the crystallization of the leucosome melt to form, among other phases, relatively large amphibole crystals that were partially resorbed later. Probably, the resorption process occurred at about 0.9 GPa and 680°C, just prior to the final crystallization of the leucosome melt. This implies that melt must have resided in the rock from about 45 km to 30 km depth. Pb-Pb zircon dating yielded a mean value of 452 $\pm$ 3 Ma and an isochron age of 461 $\pm$ 12 Ma which is interpreted as the emplacement age of the migmatite protolith (Cruciani et al., 2008). In order to improve our knowledge on the age of the amphibole-bearing migmatite, we analysed by the  $^{40}\text{Ar}$ - $^{39}\text{Ar}$  laser step-heating method amphibole and biotite separates. Amphibole yielded a slightly discordant age profile, characterized by a concordant segment representing  $\sim$ 75 % of the  $^{39}\text{Ar}_K$  released, yielding an error-weighted mean age of 317.4 $\pm$ 2.0 Ma. We interpreted the measured age of amphibole as the age at which the migmatite passed, during exhumation, through the temperature 450-520 °C. In contrast, biotite gave a hump-shaped age spectrum, most probably due to the presence of minor interlayered chlorite. The total gas age is  $\sim$ 283 Ma and is taken as a minimum argon age for the biotite.

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## The role of flavonoids on the weathering of iron and manganese minerals in the rhizosphere

Gattullo C.E.<sup>1</sup>, Cuccovillo G.<sup>1</sup>, Pizzigallo M.<sup>1</sup>, Medici L.\*<sup>2</sup>, Tomasi N.<sup>3</sup>, Mimmo T.<sup>4</sup>, Cesco S.<sup>4</sup> & Terzano R.<sup>1</sup>

1. Dipartimento di Scienze del Suolo, della Pianta e degli Alimenti, Università degli Studi di Bari. 2. Istituto di Metodologie per l'Analisi Ambientale, CNR, Tito Scalo (PZ). 3. Dipartimento di Scienze Agrarie e Ambientali, Università degli Studi di Udine. 4. Facoltà di Scienze e Tecnologie, Libera Università di Bolzano.

Corresponding email: [luca.medici@imaa.cnr.it](mailto:luca.medici@imaa.cnr.it)

Keywords: flavonoids, Fe (hydr)oxides, Mn oxides, X-ray diffraction.

Iron (Fe) and manganese (Mn) are essential micronutrients for plants but, in most agricultural soils, they are present in scarcely bioavailable forms. Iron occurs mainly as Fe(III) in poorly soluble oxides (hematite, maghemite), oxyhydroxides (goethite, lepidocrocite), amorphous hydroxides and poorly crystalline minerals like ferrihydrite, or is included as Fe(II) or Fe(III) in the lattice of primary and secondary minerals. Manganese is present mainly as Mn(IV) and Mn(III) in amorphous secondary phases as well as in crystalline oxides (birnessite) and hydroxides (manganite), but it is taken up by plants only in the reduced form Mn(II).

To increase the bioavailability of these nutrients, plants have developed different mechanisms, among which the active release of flavonoids into the rhizosphere. Flavonoids are polyphenolic compounds with multifunctional properties, such as the protection of plants against pests and diseases, the regulation of root growth and function, and the induction of allelopathy. Very few studies have focused on the mechanisms of Fe and Mn mobilization operated by flavonoids in the soil and, particularly, in the rhizosphere.

It can be hypothesized that flavonoids dissolve Fe and Mn minerals by means of reducing or complexing processes, or by a combination of these two mechanisms. In a recent experiment, we observed that rutin mobilized a high amount of Fe from an alkaline soil by reducing it to Fe(II), and quercetin was very efficient in Mn solubilisation from an acidic soil by reducing it to soluble ions Mn(II). When quercetin was used in combination with citrate, Mn solubilisation further increased due to reduction and complexation processes.

On the basis of these experimental evidences, the present study aims at investigating the effects of some flavonoids (rutin, quercetin and genistein), both alone and in combination, on the alteration of some of the most representative Fe and Mn (hydr)oxides of the soil (goethite, hematite and birnessite). For each flavonoid, saturated aqueous solutions are prepared, containing Na<sub>3</sub>N (10 mM) as bacteriostatic agent. Synthetic Fe and Mn minerals are mixed at 20% (w/w) with an inert glass powder and let to interact for 24 h with 30 mL flavonoid solutions under continuous stirring. After centrifugation, the liquid fraction is filtered and analysed to determine: (i) the amount of Fe and Mn by ICP-AES and voltammetry; (ii) the concentration of flavonoids and other secondary products by HPLC analyses. The solid fraction is dried and analysed by (iii) XRD and (iv) SEM-EDX in order to study any structural modification of the minerals. Results are compared to a control without flavonoids and a control prepared using citrate, a well-known complexing molecule in plants.

## Complex electrical resistivity measurements on alluvial sediment samples toward sedimentological and petrographic properties estimation

Inzoli S.\*<sup>1</sup>, Giudici M.<sup>1-2-3</sup>, Mele M.<sup>4-2</sup> & Bersezio R.<sup>1-2</sup>

1. Dipartimento di Scienze della Terra "A. Desio", Università degli Studi di Milano. 2. IDPA-CNR (Consiglio Nazionale delle Ricerche, Istituto per la Dinamica dei Processi Ambientali), Milano. 3. CINFAI (Consorzio Interuniversitario per la Fisica delle Atmosfere e delle Idrosfere), c/o Università degli Studi di Milano. 4. i.Geo Snc, Cassano d'Adda (MI).

Corresponding email: [silvia.inzoli@unimi.it](mailto:silvia.inzoli@unimi.it)

Keywords: hydrogeophysics, complex electrical resistivity, alluvial sediments.

In the last decades, geophysical methods have been increasingly used for groundwater exploration to gain information on geometry and properties of the subsurface. However, the knowledge on petrophysical relationships achieved with the longstanding experience in hydrocarbon exploration and available for reservoirs characterization cannot be applied in a straightforward way for near-surface environments, due to typical lower temperature, pressure and consolidation degree. Moreover hydrogeological studies have less financial support and higher interactions with human activities than hydrocarbon exploration, so that different techniques are used, e.g. surface instead of well-log acquisitions.

Essentially, hydrogeophysics is based on the relationships of electrical resistivity and hydraulic conductivity with the porous medium texture. In this work the resistivity-texture relationship is investigated through laboratory measurements of complex electrical resistivity on reworked alluvial sediment samples, texturally ranging from slightly sandy mud to gravelly sand, and saturated with NaCl and CaCl<sub>2</sub> solution with electrical conductivity varying between 20 and 1400 S/cm. Data are collected in the frequency range between 10 mHz and 100 kHz with a spectrometer connected to a sample holder, which allow to investigate a volume of about 2500 cm<sup>3</sup>. Amplitude and phase spectra are modelled through the Cole-Cole analogue electrical circuit, in order to obtain the best-fitting parameters (direct current resistivity, chargeability, relaxation time and frequency exponent) describing conduction and polarization processes within the samples.

The fit of the experimental data is performed not only with a standard least-squares approach, but also with a multi-objective approach, which considers separately the amplitude and the phase spectrum. The latter approach allows to emphasise polarization phenomena primarily linked to the amount and the dispersion degree of the silty-clayey fraction, even if phase values for sediments free from metallic particles are usually smaller than a few mrad. Moreover, the multi-objective approach permits the identification of upper and lower limits for model parameters. However, preliminary results show that the superposition of comparable effects originated from different variables (e.g. both the decrease in the water electrical conductivity and the increase in silt and clay content yield an increase of polarization) prevents one-to-one correlations among the model parameters and the sediments' litho-textural properties; a multivariate statistical analysis could be a valid support in the interpretation of experimental data.

## Quantitative phase analysis of clay soils via the Rietveld-RIR method and thermal analyses coupled with evolved gasses mass spectrometry

Laurora A.<sup>1</sup>, Brigatti M.F.<sup>1</sup>, Malferrari D.<sup>1</sup> & Medici L.\*<sup>2</sup>

1. Dipartimento Scienze Chimiche e Geologiche, Università di Modena e Reggio E.. 2. CNR - Istituto di Metodologie per l'Analisi Ambientale, Tito Scalo (PZ).

Corresponding email: [luca.medici@imaa.cnr.it](mailto:luca.medici@imaa.cnr.it)

Keywords: Rietveld-RIR, soil, thermogravimetry.

The present study deals with Quantitative Phase Analysis (QPA) of clay soils obtained via the Rietveld-RIR method, the General Structure Analysis System (GSAS; Larson & Von Dreele, 2000), and thermal analyses coupled with evolved gasses mass spectrometry.

As far as we know, there are very few applications of the Rietveld method to the estimation of quantitative mineralogical composition of soils (Brinatti et al., 2010; Prandel et al., 2014). The application of the Rietveld method represents a major step forward in QPA with respect to conventional methods, especially as far as accuracy and detection limits are concerned. The GSAS is a comprehensive and detailed system for refinement of both structural models and quantitative mineralogical composition of powder mixtures, starting from X-ray or neutron diffraction data.

Thermogravimetry (TGA) allows the determination of the mass as a function of temperature or time; this thermal technique provides information concerning thermal stability and composition of the sample and of any intermediate compound which may be formed. When these measures are combined with chemical analysis of evolved gases, it is possible to determine the reactions that are at the base of each thermal effect.

During the GSAS refinements, a Chebyshev polynomial of the first kind was used for background modeling. For peak shape modeling a multi-term Simpson's rule integration of pseudo-Voigt was adopted. The amount of amorphous phase present in the analyzed powder mixtures was estimated via the combined Rietveld and Reference Intensity Ratio (RIR) methods. Corundum NIST SRM 674a was used as internal standard.

Identified phases in analyzed soil samples include tectosilicates, layer silicates, carbonates, and in minor amount sulphates. Irregular interstratified phyllosilicates were also detected. Since treatments with ethylene glycol did not enhanced any appreciable changes in the low angle peaks of the pattern, it is conceivable that no expandable interstratified phyllosilicates are present in the analyzed soils. One or more amorphous phases were detected.

In selected samples the amount of carbonates and hydrated phases measured via X-ray diffraction was then compared with the values estimated via TGA by measuring the quantity and type of the reaction products (i.e., H<sub>2</sub>O and CO<sub>2</sub>) released.

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## Prospecting and assessing structurally controlled bentonite deposits by employing Electrical Resistivity Tomography

Longo V.\*<sup>1</sup>, Testone V.<sup>1</sup>, Oggiano G.<sup>1</sup> & Testa A.<sup>2</sup>

1. Dipartimento di Scienze della Natura e del Territorio, Università degli Studi di Sassari. 2. Minersarda S.p.a.

Corresponding email: [vlongo@uniss.it](mailto:vlongo@uniss.it)

Keywords: Mineral exploration, Electrical Resistivity Tomography, bentonitic deposits.

Sardinian bentonite deposits are commonly linked to hydrothermal alteration of thick sequences of pyroclastic flows and epiclastites, associated with the Oligo-Miocene calcalkaline volcanic cycle. Faults represent an efficient hydrothermal plumbing system, which combined with textural features (mainly open porosity) of the pyroclastic pile, controls the geometry of the deposits. Making out this interplay between faults, rock texture and the resulting clay deposits is not easy. Conventional methods, such as structural and stratigraphic studies followed by drilling investigations and trenches, despite high costs, can fail predicting the actual three-dimensional structure of a deposit. The geoelectrical methods, instead, provide an important contribution, not only in prospecting but also in defining the volume of mineralized bodies. The effectiveness of these techniques depends on the high-resistivity contrast between hydrothermally altered pyroclastites and the host rocks. In this paper we propose the application of Electrical Resistivity Tomography (ERT) to localize and evaluate a smectite clay deposit in northern Sardinia. 2D ERT surveys were performed close to a faulted area, to define the location, thickness and lateral continuity of the clayey body and to define its relations with faulting and stratigraphy. A quasi-3D ERT data acquisition was carried out in a selected area to estimate the available clay reserves. The reliability of the resistivity models was assessed by means of cross-checking with boreholes data. Finally, the interpretation of field survey has been optimized through synthetic modeling of the electrical resistivity imaging technique. The ERT surveys were carried out using a multielectrode system, consisting of an Abem Terrameter SAS1000 device combined with an ES 10-64 electrode selector. The results allow defining, with good accuracy, the extent and geometry of the deposit and evidenced its genetical relationships with both faults and definite pyroclastic horizons. Overall, the suitable conditions under which the ERT method might provide optimal results for prospecting clay deposits were defined.

## Depositional environment of calcite-alabaster: two compared case studies

Marengo A.\*, Costa E. & Borghi A.

Dipartimento di Scienze della Terra, Università di Torino.

Corresponding email: [alessandra.marengo@unito.it](mailto:alessandra.marengo@unito.it)

Keywords: calcite, alabaster, karst.

Calcite-alabaster is a sedimentary orthochemical rock which forms in karst environments as a consequence of the precipitation of consecutive layers of calcium carbonate crystals (mostly calcite, rarely aragonite). In some cases, calcite-alabasters are characterized by the presence of bands irregularly disposed between the layers. These consist of detrital material deriving from the surrounding rocks and deposited on the surface of calcite layers. Their presence is probably due to transport events e.g. episodic flooding of cave passages (Lascu & Feinberg, 2011). The aspect and the properties of every layer, as well as calcite fabric, are strongly influenced by the fluctuations of environmental parameters through time. Changes in factors, such as temperature, water composition (trace elements, presence of dissolved organic matter), detrital material, drip and precipitation rates, affect the features of calcite-alabaster at both microscopic and macroscopic levels. This preliminary study aims to compare two calcite-alabaster *varieties* along with their formation sites, observing similarities and differences of the rocks and of their depositional environments. We compare two Italian sites: Busca (Piedmont) and Belmonte Mezzagno (Sicily); both exploited in past times as quarries. Effectively, calcite-alabaster has been used since ancient times in churches and historical buildings as a construction and ornamental stone. From a geological point of view Busca area belongs to the southern sector of Dora-Maira Massif (Penninic domain of Western Alps), the deposits are hosted in a Liassic-Triassic cover of dolomitic marble (Sandrone et al., 1993). Belmonte Mezzagno district belongs to the Famusi Formation (Noric age); in this case, the host rock is a microcrystalline porous dolostone. The macroscopic appearance of both calcite-alabaster samples is extremely heterogeneous: white translucent bands of pure calcite of variable thickness (few mm to 2 cm) are alternated with brown bands full of dissolved organic material, likely humic and fulvic acids deriving from decomposed vegetal matter. In both cases one can recognize merged speleothem structures, such as stalactites and stalagmites. A multi-technique approach has been chosen to start this project. Calcite-alabaster samples of both localities have been petrographically examined and described. The mineralogical characterization has been done by micro-Raman spectroscopy; while geochemical analyses have been carried out by trace elements identification using micro-XRF. Furthermore, stable isotope analysis has been done in order to acquire data on  $^{18}\text{O}$  and  $^{13}\text{C}$  isotopic fractionation, to reconstruct the ambient temperature in the time of deposition.

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## **Petrography, major-trace elements and isotopic compositions of the lavas from El Tigre volcano (Fonseca Gulf, Honduras): increasing data on the Central America Volcanic Front**

Mattioli M.<sup>1</sup>, Renzulli A.\*<sup>1</sup> & Agostini S.<sup>2</sup>

1. Dipartimento di Scienze della Terra, della Vita e dell'Ambiente, Università di Urbino "Carlo Bo", PU.

2. Istituto di Geoscienze e Georisorse, CNR, Pisa.

Corresponding email: [alberto.renzulli@uniurb.it](mailto:alberto.renzulli@uniurb.it)

Keywords: El Tigre, Honduras, Central America Volcanic Arc, calc-alkaline magmatism.

El Tigre volcano is located within the Fonseca Gulf, Honduras, where there is a break in the strike of the Central America Volcanic Front (Walker et al., 2000; Carr et al., 2003; Bolge et al., 2009). The origin of this gulf arise from the intersection of three first-order tectonic structures, and such a complex tectonic setting is the result of the oblique subduction on the Central American trench (Carr et al., 2003; Burkart & Self, 1985). For these reasons, the knowledge of El Tigre is of paramount importance for unravelling the magmatological and volcanological evolution of this area.

Lavas from El Tigre consist of basalts and basaltic andesites with calc-alkaline affinity. The fundamental mineralogical assemblage is typical of relatively primitive subalkaline rocks, and is made of plagioclase, olivine, clinopyroxene, orthopyroxene and opaques. Lavas show a significant LILE enrichment and Nb depletion, a strong slab signature and incompatible element contents similar to those in the main front of the adjacent volcanoes from El Salvador and Nicaragua (e.g. Ba/La up to 80). However, a small group of basalts from El Tigre, with higher MgO content (> 5 wt%) and lower Ba/La, Ba/Nb and Zr/Nb ratios (34-39, 35-49 and 5-7, respectively), emphasizes that mantle-derived magmas were not produced by the same source or process throughout the span-time activity of the volcano.

El Tigre lavas are characterized by higher  $^{87}\text{Sr}/^{86}\text{Sr}$  (0.7038) and lower  $^{143}\text{Nd}/^{144}\text{Nd}$  (0.51301) with respect to arc volcanoes of El Salvador and Nicaragua, whereas  $^{208}\text{Pb}/^{204}\text{Pb}$  and  $^{206}\text{Pb}/^{204}\text{Pb}$  isotope ratios are very similar (38.2 and 18.5, respectively).

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## Geochronology of travertines and calcite veins in the Tafone Graben area (Manciano, southern Tuscany)

Messina R.\*, Berardi G., Rossetti F., Soligo M. & Vignaroli G.

Dipartimento di Scienze, Sezione di Geologia, Università degli Studi di Roma Tre.

Corresponding email: [rossmess@live.it](mailto:rossmess@live.it)

Keywords: hydrothermalism, travertine, southern Tuscany.

The Tafone Graben is a key area to study the interaction between active tectonics, hydrothermalism and travertine deposition in southern Tuscany. Moreover, the graben is known for the occurrence of stibnite ore deposits, whose origins are related to the rise of hydrothermal fluids (Dessau et al., 1972). The Tafone Graben formed as consequence of the Miocene-Quaternary crustal thinning that operated in the inner domain of the Northern Apennines and led to diffuse volcanism (e.g. the Vulsini Volcanic District) as geothermal anomalies (Larderello, Amiata, Latera) along the Tyrrhenian side of the belt.

A preliminary geological-structural survey in the area revealed that a complex fault array controls the tectonic relationships between the main exposed lithotypes that, locally, show evidence of intense hydrothermal alteration. A main travertine body, characterized by a tabular geometry and sub-horizontal layering, is positioned on top of a fault-related damaged zone and a few hundred meters away from an active degassing spot. N-S-striking, sub-vertical calcite-sulphide vein arrays cut through the Quaternary deposits surrounding the travertine body. By the means of the Uranium-series disequilibrium method ( $^{230}\text{Th}/^{234}\text{U}$ ) we obtained an age older than 350 ka for the travertine body, whereas the calcite-sulphide veins reported an age of  $148\pm 21$  ka. Stable isotopes analysis shows a positive  $\delta^{13}\text{C}$  range (5-7‰, PDB) confirming the hydrothermal origin of both the dated carbonates. The field and geochronological data presented in this work provide further constraints to the age and the structural control on the hydrothermal mineralization in southern Tuscany (cf. Minissale et al., 2004; Brogi et al., 2010). Specifically, the  $148\pm 21$  ka can be referred to the fluid-rock interaction processes responsible for the ore deposition in the Tafone Graben area.

Dessau G., Duchi G. & Stea B. 1972. Geologia e depositi minerari della zona Monti Romani - Monteti. Mem. Soc. Geol. It., 11, 217-260.

Minissale A. 2004. Origin, transport and discharge of CO<sub>2</sub> in central Italy. Earth Sci. Rev., 66, 89-141.

Brogi A., Capezzuoli E., Aqué R., Branca M. & Voltaggio M. 2010. Studying travertines for neotectonics investigations: Middle-Late Pleistocene syn-tectonic travertine deposition at Serre di Rapolano (Northern Apennines, Italy). Int. J. Earth Sci., 99, 1383-1398.

## **Burial contexts in the protohistorical necropolis of Torano Castello: SEM and XRF spectroscopy analyses**

Prezio T.\* & D'Alessio A.

Museo Archeologico Nazionale della Sibaritide, Cassano allo Ionio (CS).

Corresponding email: [tizianaprezio@libero.it](mailto:tizianaprezio@libero.it)

Keywords: Calabrian Iron Age, XRF spectroscopy analysis, X-ray, archaeometric studies.

The archaeological and protohistoric site of Torano Castello is a hill site located at Cozzo la Torre. The excavations that took place in 1965 discovered an indigenous necropolis dating to the 8th century BC and lying on the plateau just below the hill: a mound and twelve burials were exposed. The modalities of deposition and the typology of grave goods exhibited features typical of the necropolises of the Calabrian Iron Age. The most important artefacts recovered were SEM-EDX analysed at the Dipartimento DiBEST of the Università della Calabria; whereas XRF spectroscopy was carried out at the Dipartimento di Fisica e Scienza della Terra of the Università della Calabria. The materials that were analysed were: iron and bronze rings; brooches; an iron and bronze knife; decorated bronze pendants; weapons of various kinds. The XRF spectroscopy analysis aimed to distinguish the composition of a pendant, some brooches and a dagger, while the superficial analysis conducted through the use of an X-ray beam over the surface of the objects provided information on the most representative elements in the composition of the sample.

Overall, this research highlighted a series of innovative aspects that had never been shown before and that distinctly differentiated from analogous contexts belonging to the same period that had previously been investigated. The archaeometric studies put in evidence the fine decorations and high level of standardisation reached in the creation of the analysed objects. For instance, it was possible to note that all the iron rings exhibited a specific decoration that was eventually revealed to be characteristic of the place, known as to small botton.

## A global crustal model from the inversion of GOCE gravity observations

Reguzzoni M.<sup>1</sup> & Sampietro D.\*<sup>2</sup>

1. DICA, Politecnico di Milano. 2. GReD s.r.l.

Corresponding email: [daniele.sampietro@g-red.eu](mailto:daniele.sampietro@g-red.eu)

Keywords: Global crustal model, GOCE satellite, inverse gravimetric problem.

The boundary between Earth crust and mantle, the so called Moho, is commonly estimated by means of seismic or gravimetric methods. The former methods can be locally very accurate since seismic profiles give an almost direct observation of the actual crustal structure, but can be quite far from reality in large regions where no data are available. The latter methods, although often based on simplified hypotheses to guarantee the uniqueness of the solution, are nowadays becoming more and more important thanks to the improved knowledge of the gravitational field. In particular satellite gravity missions, like the European Space Agency mission GOCE (Drinkwater et al., 2003), provide a very accurate and spatially homogeneous dataset that can be used to validate the existing global crustal models or to estimate a new one by constraining the relation between Moho depth and crustal density (Reguzzoni et al. 2013).

In this work the GEMMA1.0 crustal model (Reguzzoni & Sampietro, In Press) with a spatial resolution of  $0.5^{\circ} \times 0.5^{\circ}$  and constrained with GOCE observations is presented. For this purpose several additional external information has been used, such as topography, bathymetry and ice sheet models from ETOPO1, a recent  $1^{\circ} \times 1^{\circ}$  sediment global model and some prior hypotheses on crustal density. In particular the main geological provinces, each of them characterized by its own relation between density and depth, have been considered. A model describing lateral density variations of the upper mantle is also taken into account. Starting from this prior information, an inversion algorithm is applied to the GOCE space-wise grid of second radial derivatives of the gravitational potential (Reguzzoni & Tselfes, 2009) to estimate the bottom of the crust. The computed Moho global model is well consistent not only with other global/regional models, but also with the actual gravity field, thus overcoming the main limitation of seismic Moho models, like the CRUST1.0.

Drinkwater M., Floberghagen R., Haagmans R., Muzi D. & Popescu A. 2003. GOCE:ESA's first Earth Explorer Core mission. Earth Gravity Field from Space – From Sensors to Earth Sciences, vol. 18. Kluwer Academic Publishers, Dordrecht, Netherlands, 419–432.

Reguzzoni M. & Sampietro D. In Press. GEMMA: An Earth crustal model based on GOCE satellite data. Int J Appl Earth Obs, Available online 10 May 2014, ISSN 0303-2434, <http://dx.doi.org/10.1016/j.jag.2014.04.002>.

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Reguzzoni M. & Tselfes N. 2009. Optimal multi-step collocation: application to the space-wise approach for GOCE data analysis. J. Geod., 83 (1), 13–29.

## Using PCA and standard deviation analysis to evaluate the reliability of digit length impression as sound ichnotaxonomical character

Romano M.\* & Citton P.

Dipartimento di Scienze della Terra, "Sapienza" Università di Roma.

Corresponding email: [marco.romano@uniroma1.it](mailto:marco.romano@uniroma1.it)

Keywords: Principal Component Analysis, Standard Deviation analysis, tetrapod ichnology.

In tetrapod ichnology, relative length of digit impression is often adopted as a binding character, both for ichnotaxa discrimination and in the search for a putative trackmaker (e.g., Voigt et al., 2007; Voigt & Ganzelewski, 2010).

To evaluate the reliability of this character in ichnotaxonomy, a Principal Component Analysis and a standard deviation analysis have been performed on well-preserved footprints referred to as *Ichniotherium sphaerodactylum* from the Early Permian Tambach Formation (Thuringia, Germany). The studied footprints can be referred with a good chance to a unitary kind of trackmaker within Diadectidae (Diadectomorpha), as suggested by a functionality analysis recently performed on the same material. Therefore, the peculiarities observed in different slabs can be traced to differences in posture and locomotion of the same typology of tetrapod, rather than to a real taxonomic diversity.

Despite the soundness traditionally ascribed to this character, digit impression relative length has proved to vary consistently even within the same trackway, due to mode of locomotion and substrate conditions. Overall, the digit relative length in manus impressions results much more variable with respect to the condition observed in pedes impressions, indicating a less biomechanically constrained front autopods, probably linked to their greater exploratory attitude during the progression of stroke. The analysis has also highlighted a substantial variability in digit impression length even as regards digit IV, often adopted as reference in ichnotaxonomic studies.

The obtained results clearly indicate the need to conduct a preliminary explorative analysis on the whole available ichnological material, in order to detect which digit is the most consistent by an ichnotaxonomical standpoint (i.e., the less variable digit impression, and maximally connected to the actual functional prevalence of autopods) and, therefore, to avoid an arbitrary selection. In this regard, a standard deviation analysis and a multivariate one are strongly recommended as an empirical basis for sound and communicable studies and diagnoses. Such a preliminary analysis, obviously case-specific, should provide a greater control on ichnotaxonomy, particularly in the case of allied footprints, and can also be considered an enlightening tool, if associated to biomechanical analysis, in improving and refining trackmaker identification.

Voigt S., Berman D.S. & Henrici A.C. 2007. First well-established track-trackmaker association of Paleozoic tetrapods based on *Ichniotherium* trackways and diadectid skeletons from the Lower Permian of Germany. *Journal of Vertebrate Paleontology*, 27(3), 553-570.

Voigt S. & Ganzelewski M. 2010. Toward the origin of amniotes: Diadectomorph and synapsid footprints from the early Late Carboniferous of Germany. *Acta Palaeontologica Polonica*, 55, 57-72.

## Forensic Geosciences

Sacchi E.<sup>1-2</sup>, Roncacè S.<sup>1-2</sup>, Nicosia U.<sup>1</sup>, Romano M.\*<sup>1-2</sup>

1. Sapienza - Università di Roma, Dipartimento di Scienze della Terra. 2. Società Geologica Italiana.

Corresponding email: [eva.sacchi@uniroma1.it](mailto:eva.sacchi@uniroma1.it)

Keywords: Forensics, Criminalistic, Criminology.

Forensic Geosciences are the set of all disciplines that focuses on Earth system and that can play a resolutive role in law enforcement and in intelligence activities. The word “Forensic Geosciences” replaces the obsolete “Forensic Geology” because the latter gave a reductionistic and misleading image of all the possible applications and outcomes of Earth Sciences in Criminalistic and Criminology. Geosciences more often used in Forensics are Geology “*sensu stricto*”, Paleontology, Mineralogy, Petrography, Geological engineering, Geophysics and Geochemistry. Leading countries in Forensics, such as United States, Canada and Germany among the other, have a long tradition of Forensic Geosciences used as a standard procedural tool in investigations and in court, while such discipline are only scarcely applied in Italy.

Only recently, a new section of the Italian Geological Society dedicated to this topic has been opened, taking into account that Forensic Geosciences are still scarcely known in Italy. The new section aims to be a lively forum for communication between geologists working in different fields of the Earth Science, who want to approach and provide their valuable contribution to this new horizon of Geosciences.

## **New findings of contourite deposits in an active continental margin (Southern Tyrrhenian Sea)**

Spatola D.\*, Pennino V. & Sulli A.

Dipartimento di Scienze della Terra e del Mare - Università degli Studi di Palermo.

Corresponding email: [daniele.spatola@unipa.it](mailto:daniele.spatola@unipa.it)

Keywords: Contourites, Bottom Currents, Loop Current.

Contourites are marine sediments deposited or reworked by bottom currents which are able to erode, transport and deposit the sediments on the seabed (Rebesco and Stow, 2001).

They have been recognized in different variety of context, ranging from the abyssal plain to the outer-shelf or upper slope. Elongated-mounded drifts represent one of the most common recognized typologies especially in the Mediterranean Sea (Faugeres et al., 1999; Martorelli et al. 2010).

This study is based on high and very high resolution seismic reflection profiles and Multibeam data collected along the northern Sicily continental margin, in the sector between Palermo and Castellammare Gulfs, during 2009 MaGIC Project oceanographic cruise, by using CHIRP, Sparker and MultiBeam acoustic systems.

The data show the occurrence of different types of structures with highly contrasting seismic and morphologic signatures, but we have been focused attention on those who have lenticular, convex-upward shapes, and internally are characterized by sub-parallel, moderate to low-amplitude reflections, interpreted as deriving from contourites. In particular, we recognized these structures, which comprise drifts and associated erosional elements (moats), in the eastern Castellammare Gulf. Contourites were found in depth range of 350-600 m, are about 3 km wide, up to 20 m thick from basal erosional surface, have asymmetric profile and divergent reflectors resulting in a non-uniform thickness between drift and moat. On the basis of several examples documented in other basins we classified them as elongated-mounded drifts.

Their deposition and distribution is mainly controlled by effect of continental climate on bottom currents, sediment availability and morphostructural context. Offshore northern Sicily the dominant wind-driven current flows eastward but in proximity of the gulfs can form loop current. In particular, in the western Castellammare Gulf it curves to south where it hits warmer water so the denser water sinks to the bottom running parallel to the coast and finally exits towards northeastern. This anticlockwise deep path acts as a bottom current, therefore contourites depositional systems can be formed.

These data allow us to document for the first time the presence of contourites along the northern Sicily continental margin, revealing that the morphology of the margins is one of the main controlling factor for their deposition.

Faugères J.C., Stow D.A.V., Imbert P., Viana A.R. 1999. Seismic feature diagnostic of contourite drifts. *Marine Geology*, 162, 1–38.

Martonelli E., Falcini F., Salusti E., Chiocci F.L. 2010. Analysis and modeling of contourite Drifts and contour currents off promontories in the Italian Seas (Mediterranean Sea). *Marine Geology*, 278, 19-30.

Rebesco M. & Stow D., 2001. Seismic expression of contourites and related deposits: a preface. *Marine Geophysical Researches*, 22, 303-308.

## **Structural analysis of the Laguna Blanca basin in the Central Andean Plateau (Catamarca, Argentina)**

Traforti A.\*, Zampieri D. & Massironi M.

Dipartimento di Geoscienze- Università degli Studi di Padova.

Corresponding email: [anna.traforti@yahoo.it](mailto:anna.traforti@yahoo.it)

Keywords: strike-slip tectonics, pull-apart basin, Southern Central Andes.

The Southern Central Andes are characterized by an oblique subduction between the Nazca and South-America plates, with a ENE-WSW convergence, determining a transpressive stress regime. The aim of this study is to define the nature of the rhomb-shaped Laguna Blanca basin (26°35'S-66°49'W), which is located along the SE margin of the Puna plateau. Indeed, the Neogene tectonic evolution of this area is a debated topic. According to a first model a polyphase compressive tectonics, probably reflecting a change in plates convergence, involved the entire region where a former NW-SE shortening was followed, at 4-2 Ma, by a ENE-WSW contraction continuing in the Present (Marrett & Strecker 2000). Alternatively, a second model excludes large-scale stress field variations, but suggests a simultaneous activation of differently oriented faults within a heterogeneous deformation of the upper crust. In this view, the deformation of the Puna plateau appears dominated by a southward-increasing crustal strength, related to the absence of Quaternary magmatism south of 27°S, accordingly to the abrupt change in the subduction angle. This strength gradient is responsible for the southward mid crustal flow and the related formation of sinuous transpressive zones and rhomb-shaped domains, bordered by N-S and NE-SW fault systems (Riller et al. 2012). In this context the N-S faults should have left-lateral transpressive kinematics, contrary to what is expected from the general ENE- WSW convergence between plates.

In order to evaluate the two models a series of meso-structural data were collected during the fieldwork, analyzing the major fault zones that bound the Laguna Blanca basin. These data were used to retrieve local paleostress fields through stress-inversions methods. The results have shown a general NW-SE horizontal shortening, compatible with the left-lateral strike-slip kinematics of the N-S faults bounding the Laguna Blanca basin. On the other hand, a pure extensional regime has been recorded within the basin, although the maximum horizontal axis holds steadily along a NW-SE trend. All these results, together with macro- and meso-scale morphological and structural evidences, support the interpretation of the Laguna Blanca basin as a pull-apart basin generated at a releasing stepover along N-S sinistral strike-slip master faults. Hence, our results agree with Riller et al. (2012) since the formation of a pull-apart basin at the scale of tens kilometers is compatible with a stable sinistral strike-slip regime along N-S faults.

Marrett R. & Strecker M. R. 2000. Response of intracontinental deformation in the central Andes to the late Cenozoic reorganization of South American Plate motions. *Tectonics*, 19, 452-467.

Riller U., Cruden A. R., Boutelier D. & Schran C. E. 2012. The causes of sinuous crustal-scale deformation patterns in hot orogens: Evidence from scaled analogue experiments and the southern Central Andes. *J. of Structural Geology*, 37, 65-74.

## Gentle sample preparation methods for specimen contained in complex matrix

Vigliaturo R.<sup>1-2</sup>, Harries D.<sup>2</sup>, Pollok K.<sup>2</sup>, Langenhorst F.<sup>2</sup>, Capella S.<sup>1</sup> & Belluso E.<sup>1-3</sup>

1. Earth sciences department, University of Torino. 2. Analytical Mineralogy of Micro- and Nanostructures department, Friedrich-Schiller University of Jena, Germany. 3. CNR, Institute of Geosciences and earth resources, Torino.

Corresponding email: [vigliaturo\\_ruggero@libero.it](mailto:vigliaturo_ruggero@libero.it)

Keywords: TEM sample preparation, asbestos, complex matrix.

The target of this work is to present different sample preparation methods that permits to characterize, by different TEM techniques, the inorganic fibers or particulate matters contained in an organic or artificial complex matrix.

We will present two type of methods: the first kind includes the complete removal of the matrix component, in order to concentrate the analyses only on the target fibers or particles; the second kind, is planned in order to conserve and allows to characterize also the matrix component.

The used method has to avoid any damage to the inorganic material extracted from the matrix. Moreover, it should not generate artefacts through chemicals or mechanical stress.

In this study, different techniques of preparation have been evaluated and tested, giving priority to the most rapid and simple ones.

For organic matrix, we preferred chemical digestion for the first kind methods and embedding techniques combined with microtomy for the second kind. The digestion of the biological component of the sample was performed by sodium hypochlorite (NaClO 14%) in an oven at 60 C for 6-24 hours. The embedding was made in paraffin and epoxy resin.

For the artificial matrix (in this case cement), we choose to use different amount of mechanical stress to partially or totally separate the matrix from the fibers/particles. The mechanical stress in this case is represented by grinding and sonication.

The cement pieces was suspended in acetone to avoid dispersion and the possible chemical interaction between the sample and the suspension medium.

Substantially, a simple preparation allows an appreciable flexibility of applications. With the possibility to modify and adapt the steps at the different biological (e.g. urine, intestine tissues etc) or artificial samples (concrete, wallpaper, ropes etc).

This technique allows to make TEM detailed investigation to fully characterize exogenous inorganic materials that enter the organism or lies in manufacts and the transformations that occur during mineral-matrix interactions. The extrapolated data can be used in an interdisciplinary study (by mineralogists, chemists, biologists, pathologists) to better understand the pathological effects caused by the inorganic materials penetrated into human body.

## **Regional unconformities in the Plio-Pleistocene sedimentary successions of the Calabrian Block (central Mediterranean)**

Zecchin M.\*<sup>1</sup>, Ceramicola S.<sup>1</sup>, Praeg D.<sup>1</sup> & Muto F.<sup>2</sup>

1. OGS (Istituto Nazionale di Oceanografia e di Geofisica Sperimentale) – Trieste. 2. Dipartimento di Scienze della Terra, Università della Calabria.

Corresponding email: [mzecchin@ogs.trieste.it](mailto:mzecchin@ogs.trieste.it)

Keywords: Unconformity, Pliocene, Pleistocene, Calabria, Tectonics, Forearc basin.

Three main unconformities typify the Plio-Pleistocene fill of the basins that lie in both onshore and offshore areas of the Calabrian Block, an arcuate terrane migrating to the SE above the Ionian lithosphere, between the southern Apennines and Sicily (Malinverno & Ryan, 1986; Sartori, 2003). These surfaces consist of the mid-Pliocene unconformity (developed between late Zanclean and early Piacenzian), the early Pleistocene unconformity (Gelasian) and the mid-Pleistocene unconformity (late Calabrian) (Zecchin et al., 2012). Their occurrence varies significantly depending on the considered location, so that one to three unconformities may be recognizable at a given basin. Several lines of evidence suggest that the three unconformities are the result of main tectonic events related to interferences between the Calabrian Block and adjacent microplates, which led to deformation and uplift, and interrupted phases characterized by tectonic subsidence in the Calabrian basins and forward migration of the entire Block (Zecchin et al., 2012). The discontinuous occurrence of the unconformities is inferred to be related to the position of the basins with respect to the areas that underwent tectonic disturbance, which varied during the Plio-Pleistocene interval. Important implications arise from the recognition of a synchronicity in the development of the unconformities in the Calabrian basins, as this allows to define key references for the study of the geodynamic evolution of the central Mediterranean.

Malinverno A. & Ryan W.B.F. 1986. Extension in the Tyrrhenian Sea and shortening in the Apennines as a result of arc migration driven by sinking of the lithosphere. *Tectonics*, 5, 227-245.

Sartori R. 2003. The Tyrrhenian back-arc basin and subduction of the Ionian lithosphere. *Episodes*, 26, 217-221.

Zecchin M., Caffau M., Civile D., Critelli S., Di Stefano A., Maniscalco R., Muto F., Sturiale G. & Roda C. 2012. The Plio-Pleistocene evolution of the Crotona Basin (southern Italy): Interplay between sedimentation, tectonics and eustasy in the frame of Calabrian Arc migration. *Earth-Sci. Rev.*, 115, 273-303.

## **SESSIONE S36**

### **Poster - Geoscience outreach: a challenge to be faced**

*CONVENORS*

*Gemma Musacchio (INGV)*

*Giovanna L. Piangiamore (INGV)*

## The secret to *lustrò* between art, science and mineralogy

Ambrosi D.\*

Liceo scientifico Galileo Galilei di Perugia, Università degli studi di Perugia.

Corresponding email: [scienza.0@gmail.com](mailto:scienza.0@gmail.com)

Keywords: problem based learning, clay, cluster, ITC.

The European Reference Framework of Key Competences for Lifelong Learning (OJEU, 2006) defines key competences as knowledge, skills and attitudes applied appropriately to a given context (Pepper, 2011). The Framework identifies eight key competences as necessary for personal fulfilment, active citizenship, social inclusion and employment; languages; mathematical competence and basic competences in science and technology; digital competence; learning to learn; social and civic competences; sense of initiative and entrepreneurship; and cultural awareness and expression. Each has a concise definition of its scope and all emphasise critical thinking, creativity, initiative, problem solving, risk assessment, decision taking, communication and constructive management of feelings. The latter are also known as 'transversal skills'.

Earth sciences are an example of the teaching-learning based on problem-based learning. The question to which students must answer is what secret lies behind the preparation of Luster, from where the clay rich in silver and copper. As through the chemical and mineralogical analyzes can solve a riddle of the Renaissance. The first step is setting, students are divided into groups of three or four boys; each of them is assigned a specific role as a geologist, archaeologist, historian, chemist, physicist. It operates in a context of asking a question apparently extraneous: What is the luster when this technique was born in Umbria who was Piccolpasso. After an initial investigation students will visit a master potter in Deruta. Here you will learn the practical technique to achieve the luster. By means of a physical-chemical analysis, it turns out the nature of microcrystalline clusters of silver or copper immersed in an amorphous matrix a colloidal system that undergoes a redox environment in a non-oxidizing. The secret that allowed the production of luster was the clay with which to make the Bolo, that is, a colloidal clay and vinegar. From which location came the clay. The secret has been handed down from father to son and is lost. Today, thanks to a geological and petrographic study has identified the region in Siena from which to draw useful material.

## **Seismological literacy, a contribution to the mitigation of seismic risk. The educational project for the schools of Arezzo (Italy) and its province**

Azzara R.M.\*<sup>1</sup>, Bartolomei L.<sup>2</sup>, Romizi A.<sup>3</sup> & Senserini L.<sup>4</sup>

1. Istituto Nazionale di Geofisica e Vulcanologia, Osservatorio Sismologico di Arezzo. 2. Associazione di Promozione Sociale “La Voce dei Piccoli”, Anghiari. 3. Comune di Arezzo, Ufficio Ambiente. 4. Comune di Arezzo, Ufficio Protezione Civile.

Corresponding email: [riccardo.azzara@ingv.it](mailto:riccardo.azzara@ingv.it)

Keywords: educational project, seismology, Arezzo.

In the last six years an educational project has been developed involving seismologists of the local Seismological Observatory of the Istituto Nazionale di Geofisica e Vulcanologia (INGV), geologists and experts of civil defense from the Municipality of Arezzo and of a local cultural association, the “Associazione di Promozione Sociale La Voce dei Piccoli” from Anghiari (Arezzo, Italy). The aim of the project is to address the pupils from the earliest years of school (from preschool to the junior high school) to the knowledge of the dynamics of the Earth. In this context, the main subjects of geophysics and seismology are illustrated during courses of four weekly lessons.

The contribution of local geologists allows to drop the scientific information directly to the places where pupils live, in order to increase their knowledge about the local geological and seismological peculiarities and to make them aware of the environmental hazards, especially of the local seismic hazard. In this perspective, the project is an important cultural contribution to the mitigation of seismic risk. From the beginning of the project more than 1500 pupils have attended the courses. The strict cooperation between researchers, local experts and teachers has allowed to target the school activity in producing tangible results. Small books of short stories about earthquakes, brochures to illustrate the correct behavior to undertake before, during and after an earthquake, essential handbooks of seismology are examples of the final products of the courses. Pupils have diffused what they have learned to their peers and to adults organizing scientific popular conferences and participating with their posters at the scientific exhibitions promoted by the Seismological Observatory. The project and its products have been supported by the local administrative authorities, the Province and the City of Arezzo, conscious of the importance of the diffusion of the knowledge as first stage in a successful plan toward risk mitigation.

## Dissemination through InFEA Project: the water, an inalienable right

Calligaris C.\*<sup>1</sup>, Zini L.<sup>1</sup>, Turpaud P.<sup>1</sup>, Iervolino D.<sup>2</sup>, Lippi F.<sup>2</sup>, Cucchi F.<sup>1</sup>

1. Dipartimento di Matematica e Geoscienze - Università degli Studi di Trieste 2. Regione Friuli Venezia Giulia –  
Direzione Centrale Ambiente ed Energia.

Corresponding email: [calligar@units.it](mailto:calligar@units.it)

Keywords: hydrogeology, dissemination, Friuli Venezia Giulia Region, groundwaters.

While drawing up the Water Protection Plan, the Water Resources Department of the Friuli Venezia Giulia Region jointly with the Mathematics and Geosciences Department of the Trieste University has carried out a three-year study aimed at assessing the sustainability of the groundwater use in the Friuli Venezia Giulia Region. In this territory is still very common to get water from artesian wells for domestic purposes and to leave them flowing free. These so called “fountains”, widespread located in the Low Plain, can be considered an integral part of the popular culture, a sort of cultural heritage to be preserved. Their density varies considerably according to the geographic settlements distribution and to the boundary conditions. The withdrawals interest the artesian aquifer systems and being free flowing, withdrawals are real and much more than the needs. The unsustainability lies in the fact that, high quality waters, withdrawn from medium to high depths, end up in the sea through irrigation and drainage canals or go to feed the shallow phreatic aquifer system of the Low Plain without producing any recharge for the groundwaters. The study highlighted that more than 50% of the total used groundwaters come from the domestic wells that get the waters from the deep aquifer systems. These withdrawals are approximately 70 times more than the estimated demand (250l/day per person, for a European citizen). In the Friuli Venezia Giulia Region, even if do not exist a problem of water quantity, going on with the same way of living, there will be, for sure, a quality problem. In the system in fact, through the effective infiltration, worse quality waters go into the water cycle. Furthermore, this great discharge that reaches the drainage system causes malfunctions in sewage plants and an increase of the pumping costs. Then comes the need to raise awareness on this specific subject. Thanks to the national InFEA Project, Friuli Venezia Giulia Region, jointly with researchers of the Trieste University, started a dissemination program in the hydrogeology field. The foreseen activities, within the time, will involve all the Low Plain municipalities. The methodological approach involve all the primary schools (class 4 and 5), teachers, local administrators and citizens. To the scholars, after a starting front lecture (two hours for each class), a field daily activity is offered. At the end of the cycle, all the students are involved in an active cooperation allowing to realize posters, models, poems and short stories that are later presented during an evening dedicated to a discussion among researchers, politicians/administrators and citizens. The involvement of the young students (9-11 years old) with the constant and active participation also of the teachers, authorities, parents and citizens, can be considered an educational experience for everybody. At the same time, this creates a conscious awareness of the critical issues of our fragile territory.

## Because the ERN belongs to public: lesson learned at INGV

D'Addezio G.\*, Rubbia G., Musacchio G., Lanza T., Marsili A. & Piangiamore G.L.

INGV, Roma.

Corresponding email: [giuliana.daddezio@ingv.it](mailto:giuliana.daddezio@ingv.it)

Keywords: European Researchers Night, interactive outreach, scientific theatre, educational games.

“The European Researchers' Night (ERN) aims to bring researchers closer to the general public and to increase awareness of research and innovation activities, with a view to supporting the public recognition of researchers, creating an understanding of the impact of researchers' work on citizen's daily life, and encouraging young people to embark on scientific careers.” This is the objective of European Commission, as shown in the Participant Portal for funding opportunities ([ec.europa.eu/research/participants/portal/](http://ec.europa.eu/research/participants/portal/)).

Since 2009, the Istituto Nazionale di Geofisica e Vulcanologia (INGV) participates to ERN in the framework of Associazione Frascati Scienza ([www.frascatiscienza.it](http://www.frascatiscienza.it)) with activities on Earth Sciences outreach aimed at intriguing and stimulating audiences of all ages.

For the September 27th 2013 Night, INGV contributed with programs in the INGV headquarters in Rome, including guided tours to laboratories, seminars held by researchers, exhibitions, educational games. Other activities took place in Frascati, the main venue of the Night at the Museo Geofisico in Rocca di Papa, and in L'Aquila, the city stricken by the 2009 earthquake. For the latter location, INGV is participating to the renaissance of the city with on site researchers and special research projects.

Activities combined education with entertainment.

In Frascati, children and adults attended a science theatre performance “When the sky flashed red”. The plot invites general public to consider science as a big story of pioneering ideas. The theatrical experience survey was aimed investigating emotions and learning. Other activities concerned a novel hands-on educational activity for kids curious about science. They learned about Earth inner structure, fragile lithosphere, waves propagations, impact of waves on building etc, handling eggs, cookies, honey, sugar and pudding. People of all ages and professions came, giving us the opportunity to evaluate different types of audience. Evaluation of impact on different type of audiences was performed. Appreciation surveys, compiled by visitors at INGV headquarter and by the scientific theatre's audiences, supplied our team with feedback, revealing some precious hints about users themselves, appreciation, emotions, learning and margins of improvement. The most frequent comment was the invitation to repeat more frequently such events.

The science venue was the result of common efforts among scientists that found themselves enjoying the challenging public. About forty people participated, and beyond the authors, they were: C. Acerra, G. Alessio, L. Alfonsi, A. Bannoni, S. Bucci, P. Burrato, F. Caprara, A. Caramelli, S. Conte, D. Di Luigi, G. Ferrari, R. Forsinetti, G. Galli, V. Gallotti, G. Gaudiosi, I. Hunstad, V. Lazzarini, N. Lo Bue, M. Miconi, R. Nappi, R. Nave, M.C. Piazza, C. Piccione, D. Pietrangeli, S. Pinzi, V. Pirro, M. Puppio, L. Raimondi E. Rocchetti, E. Spagnuolo, L. Spogli, R. Tozzi, M. Vallocchia, A. Winkler.

## A National Civil Service project at INGV: for contributing to Earth Sciences outreach

D'Addezio G.<sup>1</sup>, Rubbia G.<sup>1</sup>, Abbruzzese D.<sup>2</sup>, Caddeo G.<sup>2</sup>, Di Stefano M.<sup>2</sup>, Giordani A.<sup>2</sup>, Le Pera T.\*<sup>2</sup>,  
Ramieri C.<sup>2</sup>, Scipilliti F.<sup>2</sup>, Todaro R.<sup>2</sup>, Tosto E.<sup>2</sup> & Valle V.<sup>2</sup>

1. Istituto Nazionale di Geofisica e Vulcanologia – Roma. 2. Servizio Civile Nazionale.

Corresponding email: [leperateresa87@gmail.com](mailto:leperateresa87@gmail.com)

Keywords: science outreach, civil service, learning by doing.

INGV – Istituto Nazionale di Geofisica e Vulcanologia is one of the major Italian public funded Research Institute and the largest European body dealing with research in Geophysics and Volcanology. Its main mission is the monitoring of geophysical phenomena in both the solid and fluid components of the Earth. INGV accredited with the National Civil Service since 2011 and has subscribed its ethical commitment describing values, goals, rights and responsibilities of the volunteers.

The aim is to involve young generations in “homeland defense” that is in social services which enforce the relationships between people, territory and living. Volunteers will spend one year fully involved in the activities of the organization, taking the opportunity to grow up, perform a real work experience and learn by doing. Among the projects funded in 2014 there is the project “*Science and Outreach: a comprehensive approach to the divulgation of knowledge of Earth Sciences*”, designed by the Laboratorio Divulgazione Scientifica e Attività Museali of INGV, Roma.

The project, dedicated to initiatives of earth sciences outreach, started in May 2014 and will last one year. Among its aims: 1) to contribute to the increase and the diffusion of a correct and informed scientific culture especially with regard to seismic and volcanic phenomena; 2) to extend to cultural associations, universities and citizens, scientific information on events for wider dissemination of basic information and for a correct approach to geophysical issues; 3) to extend the dissemination of scientific information on the Web and social media.

To achieve these objectives, the project involves an initial part of general and specific training, a phase of planning and sharing of the activities, the formation of working groups, and a part of the activities in which the volunteers are included.

From the point of view of volunteers there is a wide series of motivation including: increase knowledge in the field of science communication to share with the public; acquire specific skills to improve communication between the research organization and the citizen.

The outreach activities carried out by the Laboratory in the initial period included participation in dissemination events in and around Rome like: Scienza Aperta 2014 Open Day, 5 April, Albano Insieme, 18 May; Roma Drone, 24 – 25 May, to which volunteers participated.

During the “Albano Insieme” event, volunteers proposed the game: What shall I do in case of an earthquake? involving children in the activity and giving insight on appropriate behavior in case of earthquake meanwhile playing a game. Volunteers also participated to educational courses and workshops with schools, performed in Rome INGV headquarter.

Volunteers were pleasantly surprised by the interest and participation shown by the public to the issues raised. Participation to events of different nature has given them the opportunity to work alongside experts from various fields and interact with a diverse audience.

## **“I luoghi di Mercalli”: a travelling exhibition as a tool for scientists to dialogue with the public on volcanoes and earthquakes**

De Lucia M.\*<sup>1</sup>, Alessio G.<sup>1</sup>, Altavilla R.<sup>1</sup>, Avvisati G.<sup>1</sup>, Casapullo R.<sup>2</sup>, Cubellis E.<sup>1</sup>, Del Gaudio C.<sup>1</sup>, De Natale G.<sup>1</sup>, de Vita S.<sup>1</sup>, Di Laura F.<sup>3</sup>, Di Vito M.A.<sup>1</sup>, Gaudiosi G.<sup>1</sup>, Loddo M.<sup>1</sup>, Marotta E.<sup>1</sup>, Mattoni S.<sup>3</sup>, Milano G.<sup>1</sup>, Molisso G.<sup>4</sup>, Nappi R.<sup>1</sup>, Nave R.<sup>1</sup>, Pino N.A.<sup>1</sup>, Ricciardi G.P.<sup>1</sup>, Riposati D.<sup>3</sup>, Russo M.<sup>1</sup>, Salerno G.<sup>4</sup>, Serio C.<sup>1</sup>, Siniscalchi V.<sup>1</sup>, Torello V.<sup>1</sup>, Trimarchi E.<sup>1</sup> & Uzzo T.<sup>1</sup>

1. Istituto Nazionale di Geofisica e Vulcanologia, sezione di Napoli, Osservatorio Vesuviano. 2. Università degli Studi Suor Orsola Benincasa. 3. Istituto Nazionale di Geofisica e Vulcanologia, Amministrazione Centrale. 4. Liceo Ginnasio Statale Vittorio Emanuele II Napoli.

Corresponding email: [maddalena.delucia@ov.ingv.it](mailto:maddalena.delucia@ov.ingv.it)

Keywords: exhibition, Giuseppe Mercalli, seismic hazard, volcanic hazard, history of volcanology.

On March 19, 1914 Giuseppe Mercalli, a seismologist and volcanologist, well-known around the world for the Intensity scale of earthquakes bearing his name, died tragically. A hundred years after, the Istituto Nazionale di Geofisica e Vulcanologia (INGV) has promoted a variety of activities and cultural events that will take place under the Patronage of the President of the Italian Republic within a year, the so called “Anno Mercalliano” (the Year of Mercalli).

The opening ceremony took place in Naples, Italy, on March 19, 2014, in the Convitto Nazionale Vittorio Emanuele II. A scientific conference was held with the participation of experts from INGV and the university of Milano – Bicocca, and presentations of students. On that day the exhibition entitled “I luoghi di Mercalli” (Mercalli's places) was also inaugurated, at the presence of local authorities.

The exhibition, organized by INGV, was realized in collaboration with the high school Vittorio Emanuele II, where Mercalli has been teaching for 19 years, and the Università degli Studi Suor Orsola Benincasa, where he was professor of natural sciences.

A biographical and geographical description of the places where Mercalli operated introduces the exhibition, which is organized in sections:

- Mercalli educator (he taught at high schools in Reggio Calabria and Naples);
- Mercalli volcanologist (Mercalli studied Vesuvius volcanic activity for more than twenty years, he was a scientific witness of the Vesuvius 1906 eruption, and of the eruptions occurred at Vulcano (1888-90) and Stromboli (1891) islands.
- Mercalli seismologist (Mercalli Intensity scale definition, based on his experience as witness of catastrophic earthquakes, such as Casamicciola in 1883 and Messina in 1908).

Another section deals with the Vesuvius Observatory, directed by Mercalli between 1911 and 1914, and the description of the three active volcanoes of the Campania region (Vesuvius, Campi Flegrei and Ischia island), which have been the subject of studies by the well-known scientist. The exhibition is enriched by documents, manuscripts, photos and field notebooks of Mercalli.

It is not intended to be only a celebratory exhibition; rather it is designed as a tool for dissemination of scientific culture and to raise awareness about seismic and volcanic hazards.

In the exhibition path a continuous thread between the figure of Mercalli as a researcher and the role of an Earth Science researcher today is highlighted, pointing to the development of scientific knowledge in the past century. The goal is to improve the capability of learning from the disasters occurred in the past to implement preventive actions to safely deal with future events.

The exhibition is travelling and will be provided on request to institutions and schools.

## The island of Ustica, an open-air geoscience museum: the role of geoparks in the dissemination of the Earth Sciences

de Vita S.<sup>1</sup> & Foresta Martin F.\*<sup>2</sup>

1. Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Napoli, Osservatorio Vesuviano. 2. Centro Studi e Documentazione Isola di Ustica.

Corresponding email: [sidereus@rocketmail.com](mailto:sidereus@rocketmail.com)

Keywords: Ustica, Volcano, Geopark.

In the Earth sciences, as well as in many other scientific disciplines, the availability of experimental laboratories is of paramount importance for the transfer of knowledge through the performance of practical experiences, which must be conveniently conducted and founded on a firm footing. In geology, in particular, the contact with rocks and landforms exposed in the field, is an irreplaceable tool to understand the processes that lie at their origin.

In this sense Geoparks may play a leading role, as, from the definition of the UNESCO European Geoparks Network, “a Geopark must comprise a certain number of geological sites of particular importance in terms of their scientific quality, rarity, aesthetic appeal or educational value”. Therefore, as Geoparks contain these sites in quite restricted areas, they have a great educational potential, if conveniently organized in a series of easy enjoyable and well equipped paths, thought to be interlinked to each other.

In recent years, following extensive geo-volcanological studies, the island of Ustica was gratified by two flattering definitions: “emerging singularity” and “open-air museum of volcanology”.

The first definition derives from the consideration that the island is the only anorogenic volcano emerged in the Southern Tyrrhenian Sea, in a context dominated by the presence of the orogenic Aeolian Islands volcanic arc. For more, Ustica preserves the signs of the geodynamic processes that led to the oceanization of the Tyrrhenian Sea and to the opening of fractures that fed its volcanism. Ustica is, at the same time, the fruit and the precious witness to these events.

The second definition, refers to the wealth and variety of volcanic landforms and products that sightseers can observe in conditions of absolute safety, as the Ustica volcanism has been extinct for over one hundred thousand years. Moreover the marine transgressions that have alternated during Pleistocene generated marine terraces, and leaved typical fossiliferous deposits.

With an area of 8.6 km<sup>2</sup>, a circuit of about 12 km and a maximum height of 248 m a.s.l., Ustica lies 60 km north of the Palermo coast and represents the emerging small part of a vast submerged volcanic complex, rising more than 2,000 m from the Southern Tyrrhenian Sea bottom.

At Ustica, submarine and subaerial lava flows, pillow lavas, monogenetic volcanoes and stovolcanoes, relics of ancient craters, deposits of ash and other pyroclastic rocks, lava tubes, bombs of various sizes, dykes, extinct fumaroles, faults, and spectacular morphologies, unfold the researcher and the student as the pages of a manual that can be browsed through the roads and trails of the Island, or diving in its waters.

With this paper we want to float the proposal to institute a new Geopark, aimed at enhancing the value of Ustica geo- volcanological aspects, by presenting a collection of illustrated routes, which lead the visitor through the geological and volcanological history of the island.

## **Volcanoes, a window into the Earth's interior: the dissemination of scientific knowledge in the new exhibit of the Royal Observatory of Vesuvius (ROV)**

Di Vito M. A., de Vita S.\*, Ricciardi G.P., Marotta E., Avvisati G., Uzzo T., De Natale G., Ghilardi M.  
Istituto Nazionale di Geofisica e Vulcanologia.

Corresponding email: [sandro.devita@ingv.it](mailto:sandro.devita@ingv.it)

Keywords: Earth Sciences, Outreach, Volcanoes.

Southern Italy has the largest concentration of high-hazard active volcanoes in Europe, with nine volcanoes in the densely inhabited areas of Campania and Sicily. These volcanoes have long been objects of study, destinations for cultured travelers and provided inspiration for works of art that may be found in numerous collections the world over. The Royal Observatory of Vesuvius (ROV) currently houses a remarkable scientific, historical and cultural heritage that at present is partially displayed in its historical building.

The INGV (National Institute of Geophysics and Volcanology) has a long tradition in the study of volcanoes and has produced an enormous quantity of scientific works from 1841 onwards, the foundation date of the Vesuvius Observatory, the first institution of this kind in the world and now the Naples section of the Institute.

This huge cultural production led to the inauguration of many educational activities, aimed at promoting a more modern view of the science dissemination.

Presently, one of the main INGV goals is to improve and expand the extent to which this important legacy may be put to use, in order to reach the widest possible audience.

This task can be accomplished only by the previous performance of a sociological study, inspecting the expectations of sightseers divided by age, education and origin.

However, the use of museum collections is still linked to a concept of exhibits accompanied by brief explanations ending in itself, and directed towards making the material accessible only to specialists and enthusiasts, without any broad-based educational aims.

The innovative idea that animates the reorganization plan of ROV is to convey correct information concerning the earth sciences, the dangers of volcanoes and the strategies for risk mitigation, drawing on collections, documents and historic scientific instruments, together with the appeal exerted by volcanic activity itself, by means of the combined use of traditional methods, modern multimedia and interactive techniques. The ROVE exhibit provides the implementation of the wonderful collections of rocks and minerals, old books, instruments and paintings, with computer graphics reconstructions, HD and 3D documentaries, scenographic decors reproducing in virtual and increased reality volcanic eruptions, and their effects on the environment, interactive dioramas showing the evolution of Italian volcanoes, multimedia systems of communication to guide the visitors throughout the exhibition, digitalizing of old books and documents for the creation of a virtual library, aimed at sharing the huge cultural heritage of the Vesuvius Observatory.

The use of volcanoes and related phenomena to provoke interest in the earth sciences is undoubtedly a successful tool, which has significant implications especially in active volcanic areas, where volcanism strongly affected the landscape and influenced the development and life of human communities.

## The trust of Italian students in geoscientists: a quantitative pilot study

Eva E.<sup>1</sup>, Musacchio G.\*<sup>2</sup>, Piangiamore G.L.<sup>3</sup> & Solarino S.<sup>1</sup>

1. Istituto Nazionale di Geofisica e Vulcanologia (INGV), sede di Genova. 2. Istituto Nazionale di Geofisica e Vulcanologia (INGV), sede di Roma.  
3. Istituto Nazionale di Geofisica e Vulcanologia (INGV), sede di Portovenere (SP).

Corresponding email: [gemma.musacchio@ingv.it](mailto:gemma.musacchio@ingv.it)

Keywords: science outreach, education.

If the Layman is to fulfil his responsibility as a citizen in this globalized modern society he will have to know about science in an understandable form. Geosciences may deeply impact on everyday lives as it relates to natural hazards. However there is a stringent paradox that drives to underestimate the potential of Geosciences to help people live with natural hazards, take decision towards land use and vulnerability of infrastructures. We might argue that one of the reasons for geoscience not playing a major role in modern society is due to incomplete or inefficient communication and the consequent lack of trust of citizens toward geoscientists. High school students represent a specific kind of Layman as they are close to become “adult” citizen entitled to take decisions or contribute to them.

In this study we present the results of a poll conducted on high school students (age 14-19) aiming at estimating the trust of the young Italian citizens in the geoscientists and their studies. The sample refers to Northwestern Italy, in areas prone to natural hazards from low to moderate intensity. Although limited to about 180 students and then not representative of the whole nation, the information, collected directly in schools before conferences or laboratories, can be used for a rough picture of level of trust of a part of the society towards the Geosciences.

The poll contained very few questions, the form in fact was organized in three sections only. The first to collect age and region of the compilers, the second to know about the sources students usually use to get info about catastrophes and natural phenomena and the last aiming at estimating the trust towards the scientists and their studies.

First results show that, students get their information mainly from the internet (about 60%) in its various forms (social media, Wikipedia) and TV (31%). However newspapers (17%) and schools (10%) still represent a significant fraction of sources of information.

In regard to the trust in science, some 87% believe that scientists are reliable but only 73% consider their research also useful. Only less than 5% declare that both scientists and their studies are not reliable and not useful.

Finally, about 75 % of the sample believe in the potential of future studies in Geoscience to help the society face natural catastrophes.

It must be remarked that the regions where the poll took place were not hit by main earthquakes in the last years. However the pool is part of an ongoing research that will include regions prone to higher level of natural hazards and recently hit by earthquakes, which will allow to compare the relationship between preparedness, hazard and the role of scientists in different contexts. Additionally, it would be necessary to estimate the bias introduced by the fact that the poll, although anonymous, is conducted before a scientific talk given by scientists. This may in fact introduce a sort of “respect” that could in turn influence the answers. For this reason we plan to propose the questionnaire to schools that had no relationships with geoscientists in the last five years.

## **The Serra d'Ivrea (NW Italy) as a didactic example of lateral moraine devoted to the scientific dissemination**

Gianotti F.\*, Forno M.G., Ajassa R., Ferrando S., Ghidone G. & Oreglia E.

Dipartimento di Scienze della Terra - Università degli Studi di Torino.

Corresponding email: [franco.gianotti@unito.it](mailto:franco.gianotti@unito.it)

Keywords: Ivrea Morainic Amphitheatre, geoheritage, Piedmont.

The Ivrea Morainic Amphitheatre (IMA) is well-known worldwide among the European south-alpine end moraine systems for its remarkable geomorphology. The *Serra d'Ivrea*, its most typical evidence, constitutes an unusually straight, continuous and long (16 km) set of lateral moraines, which crests gradually decline from 937 m to 250 m asl. The *Serra d'Ivrea*, regarded as the biggest moraine of the Alps, represents a very didactic example of a marginal glacial landform result of the glacial sedimentation. However, until now it has not been the subject of many specific researches (Forno & Gianotti, 2005) and its age, ranging from the Middle Pleistocene to the Late Pleistocene, still remain a controversial issue.

The PROGEO-Piemonte Project, promoted by the Turin Earth Sciences Department, points to increase the scientific knowledge of the IMA geological features. A 55 m long core was drilled in 2013 into the sedimentary sequence. The radiocarbon dating and the palinological analysis of two superimposed lacustrine bodies, in addition to the study of soils developed on the outcropping glacial sediments, are going to strongly revise the *Serra d'Ivrea* stratigraphy. Moreover, researches on the petrographic composition of clasts forming the different glacial deposits are carrying out to define the clast source and the relation between clast features and transport/deposition processes.

A significant aim of this project is the dissemination of the results by geological brochures, posters and itineraries books, as well as lectures, workshops and short courses for teachers and naturalistic guides. A travelling exhibition on the IMA geology (supported by the IMA Ecomuseum since 2012) is going round the local municipalities and schools, with a series of lectures and the publication of a popular book (Gianotti & Marra, 2012). The scientific dissemination is essentially based on sketches of geologic elements and processes. A permanent exhibition on the IMA geology was also placed (May 2014) in a strategic site offered by the Caravino Municipality. This location is closed to the frequently visited Masino castle, on a panoramic moraine crest rising above the IMA internal depression. The exhibition consists of display panels regarding the IMA geology, a big plastic model and some old and modern geological maps. It will be soon supplemented with other materials also concerning the Serra d'Ivrea. This institution has to become, according to our intention, an active centre of vulgarization of the IMA geological knowledge, managed by the Ecomuseum.

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## **The Eco-Museum an innovative educational methodology to discover the earth sciences**

La Longa F.\*, Crescimbene M. & Lanza T.

Istituto Nazionale di Geofisica e Vulcanologia, Roma.

Corresponding email: [federica.lalonga@ingv.it](mailto:federica.lalonga@ingv.it)

Keywords: eco-museum, proactive educational methods, geoscience outreach.

The eco-museum is a revolutionary concept compared to traditional museum because it considers the social dimension. The environment is described through history, culture, landscapes and human activities linked to the places that generated them.

The work describes the realization of the pilot project "Towards an Eco-Museum of the Castelli Romani". The project conceived by a group of researchers of the Laboratory of Education and Science Communication of Istituto Nazionale di Geofisica e Vulcanologia (INGV) in collaboration with the Regional Park of the Castelli Romani, involved students of the Classic and Socio-Psycho-Pedagogical High School of the Mancinelli Falcone Institute of Velletri (RM).

The project aimed at promoting the knowledge and the awareness of the territory by using innovative and proactive educational methods.

The educational activities carried out in the school year 2009-2010 have been structured in multidisciplinary training programs designed to create eco-museum routes.

These training programs have been organized in several areas: historical, archaeological, literary, geological, city planning, ecological and naturalistic representative of the geological and anthropological complexity of the Nemi Lake's territory.

It is a highly innovative educational project. Promote participatory planning. Led by experts and teachers, students participate in all the stages of the design, by choosing the itinerary, identifying the training needs, playing scenic actions and evaluating the effectiveness of the project.

The proactive techniques used in the project (dramatization, creative writing, music, etc.) facilitated the acquisition of knowledge and skills enhancing the territorial resources improvement and the sharing with the community.

Last but not least, the innovative project methodology places the school world not as the final recipient of knowledge but as a viewer and at the same time a partner who takes an active role in the dissemination of knowledge.

## Teachingearthsciences: a website for teachers without a geological background

Lancellotti L.\*, Invernizzi C. & Paris E.

School of Science and Technology, Geology Division, University of Camerino.

Corresponding email: [lorenzo.lancellotti@unicam.it](mailto:lorenzo.lancellotti@unicam.it)

Keywords: Web, geosciences, high school.

In the last decades the development of virtual and useful tools for teaching science at school has increased really fast and “even without going totally virtual, the Internet can provide a rich and valuable learning environment for anyone interested in the sciences” (Doherty, 1996). Anyway the largest part of the web production is in English and it seems not to be really well known by Italian teachers. The purpose of this research is: 1) to evaluate the need of an updated web tool for Earth science teachers in Italian, 2) to select the main themes it should contain, 3) to build it, 4) to test its usefulness.

The project is to make virtual lessons that are a sort of “repository” for the most interesting and useful Earth science existing tools, adapt them to Italian school system, organize them in different sections with animations, movies, hands-on activities, but also tests and evaluation papers for Italian teachers. The final aim is to provide an effective support to the Italian Earth science teachers without a geological background.

The first step of the project consisted on the development of a questionnaire for investigating the effective use of educational multimedia activities in the Earth science teaching in Italian high schools. Moreover the purpose of the questionnaire was also to select the Earth science topics of greater interests. The sample chosen was the group of teachers who inscribed their school at the 2012 edition of Natural Science Olympiad (more than 350 teachers).

On the basis of the preliminary results we designed a website trying to respond to all the needs showed by the teachers. Within the selected Earth science topics we collected the existing web teaching material (hands-on activities, simulation, models, animations, etc.) that best fit the real teachers needs. In this regard, the selection criteria are defined as the relevance to the selected topics, the scientific validity, the ease of use, the economic and logistical needs, the link with everyday life and the relation with the territory.

At the moment the website hosts different kind of files that undergo the Creative Common Licence, and that are free to be used and even modified by the registered teachers. The idea is that teachers can find in the website most of the material they said were interested about.

Right now the first 4 unit are complete and they are structured in different lessons, each one formed by different learning objects:

- a power point file, consisting on a key point text with a list of web links to the most useful external materials and the most interesting images available in the web
- a pdf file, consisting on the transcript of the whole lesson
- a set of exercises, consisting on a group of multiple choice and a group of open answers questions
- a video of the lesson, consisting on a MP4 file lasting about 10 minutes and describing the entire content of the lesson
- a set of specific short movies concerning key concepts.

Actually the website is in a experimentation phase and it is tested by in-service teachers, in order to evaluate its usefulness and efficiency. After that a new data will follow to report the results.

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## **Using narrative to disseminate Earth sciences culture**

Lanza T.\*

Laboratorio di Didattica e Divulgazione Scientifica INGV-Roma.

Corresponding email: [tiziana.lanza@ingv.it](mailto:tiziana.lanza@ingv.it)

Keywords: narrative, earth sciences, science communication, sustainability.

Since ancient times, narrative have been used not only as a way of experiencing the world but also as a vehicle of culture and values. Ancient myths and legends, poetry, and today literature, theatre and movies very often deals with the relation of human kind with nature.

Today industrialization have brought men to be day by day ever more detached from nature at the point to be not able to survive outside civilization and with consequences for the environment. Narrative can be a valid tool to convey messages and values for re-awakening in the inhabitants of the Earth the sense of beauty and responsibility for a better planet sustainability.

The present work gives examples of how narrative is used to this aim. Examples include the work done within the Laboratorio di Didattica e Divulgazione Scientifica in Rome in the past four years using narrative in different formats. Some preliminary consideration will concern the evaluation of narrative as a vehicle of science communication.

## ScienzAperta: Earth Science for everyone... finally in Milan!

Musacchio G.<sup>1</sup>, Piangiamore G. L.\*<sup>2</sup>, Solarino S.<sup>3</sup>, Pino N.A.<sup>4</sup>, Eva E.<sup>3</sup>, Sansivero F.<sup>4</sup>, D'Addezio G.<sup>1</sup>, Augliera P.<sup>5</sup>,  
Piccarreda D.<sup>5</sup>, D'Amico M.<sup>5</sup>, Gomez A.C.A.<sup>5</sup>, Lovati S.<sup>5</sup>, Luzi L.<sup>5</sup> & Massa M.<sup>5</sup>

1. Istituto Nazionale di Geofisica e Vulcanologia (INGV), Roma. 2. Istituto Nazionale di Geofisica e Vulcanologia (INGV), Portovenere (SP). 3. Istituto Nazionale di Geofisica e Vulcanologia (INGV), Genova. 4. Istituto Nazionale di Geofisica e Vulcanologia (INGV), Napoli. 5. Istituto Nazionale di Geofisica e Vulcanologia (INGV), Milano.

Corresponding email: [giovanna.piangiamore@ingv.it](mailto:giovanna.piangiamore@ingv.it)

Keywords: Science outreach, special venue, open days.

ScienzAperta is an outreach science venue that the Istituto Nazionale di Geofisica e Vulcanologia started in 2011 as the spring of science: the doors of the headquarters of science were finally opened to public.

A number of events, conferences, seminars, guided tours through the Institute and its laboratories are every year offered to general public. The venue is held in most of the cities where the Institute is located, giving a special priority to high seismic and/or volcanic risk regions.

On May 2014 we held ScienzAperta for the first time in Milano and open up the doors to schools specifically dealing mostly with seismic hazard in a region where general public not necessarily think it might be of any need. We offered students conferences, seminars and educational activities to highlight the fun of science and jet raise awareness on proper behaviours in case of earthquake shaking. We asked students and teachers, ranging from elementary to high schools, to fill in a questionnaire that we use to evaluate the appreciation the venue had. One hundred years after Giuseppe Mercalli's death we could not forget to celebrate his science in Milano, the city where he was born.

## **The Geophysical Museum of Rocca di Papa: between knowledge and scientific research**

Pagliuca N.M.\*<sup>1</sup> & Calcagni E.<sup>2</sup>

1. Istituto Nazionale di Geofisica e Vulcanologia. 2. Orizzonte Natura.

Corresponding email: [nicola.pagliuca@ingv.it](mailto:nicola.pagliuca@ingv.it)

Keywords: Geophysics, Seismology, Museum.

The Geophysical Museum of Rocca di Papa is located in an historical, three floor building, of the small town Rocca di Papa, twentyfive kilometres from Rome. The edifice was, until 1931, the place of the Geodynamic Observatory, created in 1889 by the famous seismologist Michele Stefano De Rossi. The museum is due to an agreement between the Town Council of Rocca di Papa and the Istituto Nazionale di Geofisica (INGV, one of the most important European Research Institutions operating in geophysics) signed in 2000. After bureaucratic passages and two years of important restoration the Museum was open to the public at 26th February 2005. During last two years, in 2013 have been completed other major restructuring that have expanded the Museum display capacity.

The main aim of the Geophysical Museum is to illustrate how experimental data and information, accumulated by science in the course of time, led to new hypotheses on the internal structure of the Earth.

The target of the educational and of the scientific disciplines of the Museum is mainly school students of all ages, but also local residents, and tourists: since its opening, the Museum has been visited by thousands people by year. Posters, movie presentations, plastics, games and interactive experiments explain to visitors the main topics of geophysics and the stages of scientific research which led to the modern concept of the Earth internal model. Seismic instruments and games are easily accessible so that the visitor can interact with them: experimental data are recorded in real time and displayed through different monitors placed throughout the rooms. The museum has also a small cinema for three dimensional projections which allow visitors to experience a virtual tour on the Alban Hills, the seismic zone where the museum is located, and also on some other Italian tectonic belts where earthquakes occurred in past.

In addition, the Museum maintains the typical skills related to activities observatory due to the presence of modern seismic station of the national seismic network, as well as a GPS station, managed by INGV.

In addition to this, The Museum is located on the top of southernmost Quaternary volcano, the Alban Hills (Italian Colli Albani) which is considere a quiescent volcanic complex in Italy, located 20 km (12 mi) southeast of Rome. So guided visit tours, are organized at the Museum for showing at the visitors walking around the dominant peak (but not the highest) *Monte Cavo* at 950 m, two small calderas which contain lakes, Lago Albano and Lake Nemi. The rock of the hills sourced by explosion of these calderas is called Peperino (lapis albanus) a particular Tuff, a combination of ash and small rocks that is useful for construction, and provides a mineral-rich substrate for grape vines.

## The Tree of Natural Hazard Education

Piangiamore G.L.<sup>1</sup> & Musacchio G.\*<sup>2</sup>

1. Istituto Nazionale di Geofisica e Vulcanologia (INGV), sede di Portovenere (SP). 2. Istituto Nazionale di Geofisica e Vulcanologia (INGV), sede di Roma.

Corresponding email: [gemma.musacchio@ingv.it](mailto:gemma.musacchio@ingv.it)

Keywords: natural hazard, science outreach, education.

Natural hazards are often thought as being, beside a difficult issue, a major problem forcing the community to deal with the economic and social development. For this reason they require specific actions tailored on the local environment. It is fundamental to build a ground to rely on when dealing with the governance of a territory and when the economic factors intersect scientific knowledge and available technical solutions. Science outreach could usefully focus on simple, clear and yet accurate information. The social projection of natural disasters is not just the faith of careless attitude towards hazard as it might get strongly influenced by emotions triggered by an event close in time. On the other end people might misperceive risks ineffectively choose recovery over prevention, when the latter is proved to be far less costly.

There is a general mindset of people towards a culture of prevention and the relationship established between the concepts of *hazard* and *disaster*, as if one would automatically always turn into the other just as like a nature curse towards which humans have no power.

There is much of emotions involving hazards response so that to be effective education should not only convey information in *strictu sense* (to explain natural phenomena and their causes), but drives the understanding through interpersonal skills and explicitly use the language of emotions (and in particular the positive ones, eg. reassurance, confidence, serenity, optimism, etc... ).

The Istituto Nazionale di Geofisica e Vulcanologia is a scientific institution monitoring of geophysical phenomena through networks of technologically advanced equipment which approach outreach and education to the dissemination of scientific culture through publications for schools and web pages, exhibitions, special venues and open-days.

We envisage a virtual tree of natural hazard education where science actively interacts with general public to implant awareness on the urge of science knowledge in modern society when it comes to help citizens to have independent opinions or participate to crucial decisions. Here we display on a tree several ways of doing outreach and education towards natural hazards.

Activities encompass volcanic, seismic, hydrogeological hazard and risk education to explore and understand natural processes lying behind the hazard. The general concept of risk is also exploited, where children and teachers will have to think on what could be the actions to be taken to avoid risks, whether there are risks we are willing to take, what we think we cannot avoid and, above all, how do we behave facing a risky situation. We definitely remark the link between inhabitants and their land emphasizing on the sense of responsibility towards land preservation.

## **SESSIONE S37**

### **Poster - Le geoscienze a scuola**

#### *CONVENORS*

*S. Occhipinti (Associazione Nazionale Insegnanti di Scienze Naturali)*

*F. Pagani (Associazione Nazionale Insegnanti di Scienze Naturali)*

*E. Paris (Università di Camerino)*

*M. Pelfini (Università di Milano)*

## **Geosciences in virtual worlds: a path in the volcanic area of the Phlegraean Fields**

Boniello A.\*, Paris E.

I. School of Sciences and Technology, University of Camerino, Geology division.

Corresponding email: [annalisa.boniello@unicam.it](mailto:annalisa.boniello@unicam.it)

Keywords: teaching, geosciences, virtual worlds.

Today, virtual worlds represent an innovative strategy and an educational opportunity to learn in a socially-interactive learning community and in a immersive environment. To experience this approach, this research aims at introducing digital contents in geosciences and, in particular, to address the theme of volcanic hazard, taking as an example the area of the Phlegraean fields (Napoli, Italy).

The project makes use of a MUVE (multi user virtual environment), addressed to students of various ages (13-15 and 15-18 years old). A virtual island, called UNICAMearth, was created in 3d on the University of Camerino server, using the software open SIM and the singularity viewer. Through an online access, using a role play, learners go through activities built using inquiry based science education (IBSE) with a adaptive path. Students, in a serious game, must pass ability and expertise steps/tests, solving paths and pre- and post-tests. By following the path and answering to tasks and questions, they acquire scientific skills.

The simulations in virtual environments recreates contexts similar to reality, which can be used to study an area and its transformations with time. For example, it is possible to recreate in 3d environments a volcanic environment, where the student as an avatar, can learn with an immersive training the different types of volcanoes, simulate volcanic eruptions and earthquakes, to understand which events may occur in an area at risk of eruption. The first of these paths is currently being tested in the secondary schools of grade I and grade II of the Napoli area. The path is divided into 6 areas of investigation: the distribution of volcanoes, interior structure of the earth and the formation of magma, the classification of volcanoes and eruptions, igneous rocks, volcanic phenomena in the Solfatara and the volcanic history of the Phlegraean fields. In each area there are animations and interactive chats. In this way the student plays the role of a scientist - a geologist studying a volcano. Experimentation has shown that students learn in a more engaging way by using these environments, especially if they can be changed by the user.

## **Dal laboratorio al palcoscenico: il teatro-scienza per apprendere e divulgare le discipline scientifiche**

Ciceri P.\*<sup>1</sup>, Cicconi A.<sup>2</sup>, Pierro L.<sup>1</sup>, Tizzoni P.<sup>1</sup>

1. I.C "Alighieri", Scuola secondaria di primo grado "Ottolini", Rescaldina (Mi).  
2. School of Science and Technology, Geology Division, University of Camerino.

Corresponding email: [pieraciceri@alice.it](mailto:pieraciceri@alice.it)

Keywords: Scienze polari, Teatro scienza, Laboratori didattici.

Spesso i percorsi di scienze vengono proposti agli studenti seguendo l'organizzazione per nuclei tematici suggerita dal libro di testo. A questa si agganciano esempi di collegamenti con la realtà, disciplinari e solo a volte interdisciplinari.

In questo progetto l'ottica è stata ribaltata.

Partendo dalle testimonianze di esploratori e ricercatori polari gli allievi sono stati coinvolti in attività *hands-on* e in *role plays* e sono diventati essi stessi gli sceneggiatori di un copione teatrale. E così la mirabolante avventura di E. Shackleton e della sua nave *Endurance* (1914/16) intrappolata dai ghiacci antartici è diventata il pretesto per imparare come si forma il pack, in cosa si differenzia dal ghiaccio continentale, quali dati può fornire quest'ultimo sul clima del passato, come si originano le correnti oceaniche, quale relazione esiste tra l'inclinazione dei raggi solari e i climi polari, come spiegare la durata notte-di a diverse latitudini o per comprendere alcuni fenomeni termici legati agli adattamenti degli organismi polari.

Il teatro è stato il luogo per "mettere in scena" alcuni degli esperimenti effettuati nelle lezioni di scienze ma anche per spiegare le attuali ricerche compiute nelle zone polari e la loro importanza per la ricostruzione del passato della Terra.

In questo lavoro viene messo in evidenza "un percorso" proprio perché spesso a scuola è soprattutto quello che è importante più del prodotto finale. Un percorso che è partito, con la collaborazione delle insegnanti di lettere e geografia, dalla lettura di diari di esploratori del Polo a cui sono state agganciate attività di laboratorio riguardanti le Scienze Polari e una riflessione sull'utilità della ricerca in Antartide e che si è concluso con l'allestimento di uno spettacolo teatrale realizzato dagli alunni di due prime classi di una scuola secondaria di primo grado.

Lo spettacolo, realizzato con la collaborazione del Piccolo Teatro di Milano e dell'associazione Scienza Under 18, è stato rappresentato per altre scolaresche in occasione dell'evento "La Statale incontra la scuola" presso l'Università Statale di Milano e all'Auditorium del Comune della scuola per la cittadinanza.

Questo percorso mette in evidenza come approcci alternativi come quelli del teatro scienza possano veicolare, in maniera efficace, contenuti scientifici non solo all'interno del gruppo classe ma anche nella comunità locale.

La storia avvincente facilita il coinvolgimento e il teatro l'immedesimazione. La messa in scena richiede un uso attento della parola: agli studenti è richiesto di saper suscitare curiosità e interesse attorno ai temi scientifici proposti e di saperli presentare utilizzando un linguaggio che si mantiene in equilibrio tra rigore e semplicità.

Infine a teatro è permesso mettere in scena il valore universale della ricerca e della scienza promuovendo l'educazione scientifica nel senso più ampio.

## Star bene per far star bene la terra

Colli A.\*<sup>1</sup>, Spadaro G.<sup>2</sup>

1. collaboratrice C.R.E.A. 2 funzionario responsabile C.R.E.A.

Corresponding email: [luriboni@libero.it](mailto:luriboni@libero.it)

Keywords: ecological footprint, carbon footprint.

Atmosfera, idrosfera, geosfera, biosfera: basta poco per turbare il difficile equilibrio che mantiene in salute il nostro pianeta. I nostri consumi quotidiani possono provocare cambiamenti climatici e mettere a rischio le riserve di acqua utilizzabile. Per far sì che sulla terra la vita continui bisogna partire dalla consapevolezza che “siamo tutti sulla stessa barca”: dobbiamo individuare i problemi e cercare di risolverli con una progettualità diffusa e una condivisione di significati. Il C.R.E.A. (Centro Regionale Educazione Ambientale) del Comune di Pavia, è un organismo di riferimento per l'educazione ambientale. Innumerevoli progetti e attività sono offerti alle scuole e ai cittadini, con lo scopo di favorire buone pratiche per uno stile di vita più sostenibile. Da anni collabora con l'Università di Pavia e con l'ANISN (Associazione Nazionale Insegnanti Scienze Naturali). Il progetto “Star bene” invita gli studenti di scuole di diverso ordine e grado a riflettere criticamente sulle conseguenze del proprio stile di vita attraverso laboratori interattivi, con l'utilizzo di giochi, per i più piccoli, di semplici fogli di calcolo e/o di siti Web. Sono state calcolate: **l'impronta ecologica** (ecological footprint), la superficie di terra e acqua necessaria per rigenerare le risorse consumate da una popolazione umana e per assorbire i rifiuti prodotti, **l'impronta di carbonio** (carbon footprint), la misura in unità di anidride carbonica dell'impatto che le attività umane hanno sull'ambiente in termini di ammontare di gas serra prodotti, e **l'impronta idrica** (water footprint), la quantità di acqua consumata da un processo, un ente o una nazione. Nell'anno scolastico 2013-2014 sette classi quinte elementari e tre seconde medie hanno partecipato ai laboratori. Con gli alunni della scuola elementare è stato realizzato un gioco a squadre: “**La mia piramide per la salute della terra**”. Ogni squadra deve rispondere a domande sui gruppi di alimenti, sull'alimentazione mediterranea, sull'impronta ecologica, sulle conseguenze legate a una impronta eccessiva. Ogni risposta esatta dà diritto a una scheda raffigurante la porzione di un alimento o a un jolly con cui si possono “comprare” porzioni dei diversi gruppi. Sul retro di ogni scheda sono scritte le diverse impronte: ecologica, della CO<sub>2</sub>, dell'acqua. Le squadre devono costruire una piramide con le porzioni dei diversi gruppi che un bambino/a di 10 anni mangia in un giorno. Una volta completata la piramide bisogna girare le carte e calcolare le impronte relative alla dieta giornaliera. Vince chi ha la piramide più equilibrata, ricca di frutta e verdura colorate, e con l'impronta minore.

<http://www.comune.pv.it/site/home/canali-tematici/ambiente-e-territorio/c.r.e.a./>

## **Familiarizzare gli studenti del Liceo Scientifico con le geoscienze attraverso attività seminariali e di terreno**

Giudici M.\*<sup>1</sup>, D'Orsi P.<sup>2</sup>, Caironi V.<sup>1</sup>, Baratelli F.<sup>1</sup>, Cattaneo L.<sup>1</sup>, Comunian A.<sup>1</sup>, De Filippis G.<sup>1</sup>,  
Dell'Arciprete D.<sup>1</sup>, Durante C.<sup>1</sup>, Inzoli S.<sup>1</sup>, Mele M.<sup>1</sup>, Vassena C.<sup>1</sup>

1. Dipartimento di Scienze della Terra "A. Desio", Università degli Studi di Milano. 2. Liceo Scientifico "Giordano Bruno", Melzo (MI).

Corresponding email: [mauro.giudici@unimi.it](mailto:mauro.giudici@unimi.it)

Keywords: geoscienze, didattica, metodologie.

La ricchezza delle Geoscienze, che utilizzano una vasta gamma di metodologie di indagine per lo studio del pianeta Terra e che hanno un ampio spettro di applicazioni, non è facilmente valorizzabile nell'ambito delle attività previste dai programmi ministeriali. Per questo, numerose attività di carattere seminariale o dimostrativo vengono organizzate in collaborazione tra le scuole medie secondarie superiori e gli Atenei.

A partire dal 2007, e poi regolarmente dall'A.S. 2009/10, in collaborazione tra l'Università degli Studi di Milano e il Liceo Scientifico "G. Bruno" di Melzo (MI) è stata svolta un'attività per familiarizzare gli studenti con la conoscenza della geofisica, e in particolare dei suoi aspetti applicativi. Il progetto, che nell'A.S. 2011/12 è stato inserito anche nel POF dell'istituto scolastico, prevede: (1) una lezione introduttiva di carattere seminariale sulla geofisica e in particolare sui suoi aspetti applicativi per indagini a piccola profondità; (2) l'esecuzione di misure geoelettriche, sismiche e magnetiche dimostrative nel prato della scuola; (3) una lezione in cui vengono presentati e discussi i risultati delle misure eseguite dagli studenti. La realizzazione del progetto ha previsto la partecipazione e la collaborazione: (a) di dottorandi, assegnisti di ricerca e ricercatori dell'Università degli Studi di Milano a supporto della giornata dedicata alla esecuzione delle misure sul terreno; (b) di docenti di diverse materie, prevalentemente scientifiche, del Liceo "G. Bruno", per permettere ai ragazzi di diverse classi di partecipare alle attività.

Con alcune classi è stata svolta anche un'ulteriore attività di approfondimento delle metodologie di studio proprie delle Geoscienze, consistente in una visita guidata dei laboratori analitici del Dipartimento di Scienze della Terra, affiancata da una esercitazione di osservazione di minerali e rocce in campioni macroscopici ed al microscopio.

Il riscontro è in generale positivo, in quanto i ragazzi da un lato possono familiarizzare con alcuni argomenti meno conosciuti e meno approfonditi delle Geoscienze e dall'altro entrare in contatto con aspetti meno "astratti" e più "concreti" di discipline scientifiche, che spesso vengono viste dai ragazzi come "aride" e poco attraenti. Si ritiene quindi che questo tipo di attività possa effettivamente fornire un contributo alla diffusione della cultura scientifica e più in particolare delle Geoscienze tra le giovani generazioni.

## Teachingearthsciences: un sito web per insegnanti

Lancellotti L. \*, Invernizzi C., Paris E.

Scuola di Scienze e Tecnologie, sezione di Geologia, Università di Camerino.

Corresponding email: [lorenzo.lancellotti@unicam.it](mailto:lorenzo.lancellotti@unicam.it)

Keywords: web, docenti, geoscienze.

In prevalenza gli insegnanti di scienze naturali della scuola secondaria sono biologi e solamente una piccola parte sono geologi (Costa & Zauli, 1982). Questa formazione disciplinare e le poche ore di lezioni a disposizione, hanno portato a sacrificare l'insegnamento delle scienze della Terra a favore di biologia e chimica (Massa & Pedemonte, 1983). Il presente progetto ha lo scopo di fornire un supporto agli insegnanti di scienze delle scuole secondarie che non sono geologi, al fine di rafforzare la loro sicurezza verso questa disciplina.

Nel web sono presenti numerosi strumenti virtuali per l'insegnamento delle scienze della Terra, ma sono per lo più in inglese e non sembrano essere ben conosciuti e sfruttati dai docenti italiani. Quindi gli scopi di questa ricerca sono: 1) valutare la necessità di uno strumento web in italiano per insegnanti di scienze della Terra, 2) selezionare i temi principali che dovrebbe contenere, 3) sviluppare lo strumento nel complesso, 4) valutare la sua utilità.

Il progetto è creare lezioni virtuali che siano una sorta di meta contenitore per gli strumenti didattici di scienze della Terra più interessanti e utili, adattati al sistema scolastico italiano.

Nella prima fase del progetto è stato formulato un questionario per indagare l'utilizzo delle attività multimediali nel campo delle scienze della Terra nella scuola secondaria e per selezionare i relativi argomenti di maggior interesse per gli insegnanti. Il campione è stato il gruppo di docenti che ha iscritto la propria scuola all'edizione 2012 delle Olimpiadi di Scienze Naturali (più di 350).

Sulla base dei primi risultati è stato progettato un sito web, il più possibile rispondente alle esigenze mostrate dagli insegnanti. A tale proposito è stato creato materiale ad hoc ed è stato raccolto quello già esistente nel web, che meglio si adatta alle necessità degli insegnanti. I criteri di selezione sono stati: la validità scientifica, la facilità di utilizzo, le esigenze economiche e logistiche, il legame con la vita quotidiana e con il territorio.

L'unità didattica sulla tettonica delle placche è stata la prima ad essere caricata sul sito; quindi un questionario di gradimento è stato inviato agli insegnanti registrati. Il campione ha fornito una valutazione nel complesso positiva, dichiarando di trovare il sito utile per aumentare il proprio background geologico e di volerlo estendere ad altri argomenti.

Dopo la fase di sperimentazione altre tre unità didattiche sono state caricate e attualmente sono in valutazione da parte di insegnanti in servizio, per estrapolare l'utilità e l'efficienza dell'intero sito. Al termine del presente anno scolastico seguiranno i risultati di questa ultima parte dell'indagine.

Costa M. & Emiliani Zauli F. 1982. Indagine sui titoli di studio degli insegnanti di "Scienze matematiche, chimiche, Fisiche e Naturali" in servizio presso la scuola media – COASSI, quaderno n.1, 1-20.

Massa B. & Pedemonte G.M. 1983. L'insegnamento delle Scienze della Terra nella scuola secondaria superiore: Una indagine su scala regionale. Ed. Tilgher, Genova, 1-97.

## Darwin, il geo-investigatore - Ripercorrere in chiave inquiry based alcuni esperimenti storici del teorico dell'evoluzione

Lancellotti L.<sup>1</sup>, Macario M.\*<sup>1</sup>

1. School of Science and Technology, Geology Division, University of Camerino, Camerino (MC), Italy.

Corresponding email: [lorenzo.lancellotti@unicam.it](mailto:lorenzo.lancellotti@unicam.it), [maddalena.macario@unicam.it](mailto:maddalena.macario@unicam.it)

Keywords: Darwin, geo-esplorazioni, IBSE

Forse i più non sanno che Charles Darwin fu prima di tutto un geologo, come egli stesso si definì nei suoi taccuini “Io, un geologo...” (Darwin, 1838).

Fu proprio la passione per le scienze della Terra che gli permise di osservare l’ambiente con lo sguardo attento alle trasformazioni, consentendogli di elaborare la teoria dell’evoluzione.

In questo poster si presentano due elaborazioni sperimentali che Darwin condusse per risolvere questioni geologiche. Da un lato egli misurò la profondità alla quale si trovavano i coralli negli atolli (Darwin, 1842), per poterne definire il meccanismo di formazione, mentre dall’altro misurò la velocità dell’erosione di depositi gessosi, per datare l’età delle scogliere del Sud Est britannico “recuperando” tempo profondo, necessario ai tempi dell’evoluzione (Darwin, 1859; Burchfield, 1974).

I due esperimenti sono proposti in modo semplificato, con materiale di semplice reperibilità. L’approccio utilizzato è quello IBSE (Bybee et al., 2006), nel quale lo studente si comporta da *geoinvestigatore*, mentre l’impiego di documenti originali e risorse multimediali (Google Earth; DVD “Nel giardino di Darwin”, 2010) rende l’attività fruibile anche nel contesto CLIL (Coyle et al., 2010)

Di seguito sono sintetizzati i due laboratori didattici.

### Darwin e il problema dell’origine degli atolli corallini

L’esperimento simula quanto realizzarono Darwin e Fitzroy, per provare che i coralli non crescono oltre ad una certa profondità. Le misure compiute servirono per dimostrare che i coralli si formano a basse profondità e lentamente sprofondano e non, come si credeva allora, sul fondo del mare per poi risalire spinti dai vulcani sottomarini.

Gli alunni realizzano uno scandaglio con una vasca piena d’acqua, dello spago e un peso. Con questo modello, sono invitati a eseguire rilevamenti sulle profondità dei diversi tipi di fondale e a compiere deduzioni su quali ospitano i “coralli” vivi.

### Darwin e il dilemma del tempo geologico

Attraverso alcune osservazioni sulle formazioni geologiche dei terreni circostanti la sua abitazione di Down House, e alcuni assunti sulla loro velocità di erosione, Darwin calcolò che il tempo necessario alla formazione delle scogliere gessose dei South Downs doveva essere estremamente lungo, circa 300 milioni di anni. Pertanto l’età della Terra doveva essere di sicuro maggiore. Solo un tempo così lungo poteva dare ragione del lento svolgersi dei processi evolutivi attraverso la selezione naturale.

Gli alunni ripercorrono, attraverso un semplice esperimento di corrosione di una roccia calcarea con soluzione acida, il concetto che sta alla base del calcolo utilizzato da Darwin, mettendo in evidenza quali sono i punti critici del ragionamento e venendo condotti alla scoperta della necessità di una datazione relativa e assoluta delle rocce.

## **Scuola terra e fantasia: un progetto sperimentale per la diffusione delle geoscienze nelle scuole dell'infanzia**

Merlini A.\*<sup>1</sup>, Grieco G.<sup>2</sup>, Oneta C.<sup>3</sup>

1. Associazione IL GECO, 2. Dipartimento di Scienze della Terra, Università di Milano. 3. Scuola dell'infanzia Alessandrini di Zibido San Giacomo.

Corresponding email: [aemerlini@gmail.com](mailto:aemerlini@gmail.com)

Keywords: bambini, geoscienze, didattica, laboratori, sperimentazione, apprendimento.

Il progetto didattico “Scuola Terra e Fantasia” nasce dalla collaborazione tra il mondo universitario, quello della professione del geologo e le scuole statali; da questa unione è nata l’associazione IL GECO, una collaborazione tra geologi e insegnanti che propone alle scuole di ogni ordine e grado tematiche di carattere scientifico. L’associazione IL GECO si sviluppa dalla passione per la geologia e dalla consapevolezza della necessità di un coinvolgimento più dinamico degli studenti verso le materie scientifiche e in particolare verso le scienze della Terra; una disciplina estremamente complessa e di fondamentale importanza nella vita dell'uomo. Da esse, e in particolare dalla geologia, dipende anche una parte importante della qualità della vita di un'intera comunità, grande o piccola che sia. Purtroppo questo concetto spesso non è percepito né dalla popolazione né dalle pubbliche istituzioni; ne sono un triste esempio le immani catastrofi naturali a cui si assiste sempre più spesso e in cui l'uomo, con il suo sfruttamento sconsiderato del suolo, è l'unico vero responsabile. La geologia deve essere spiegata e raccontata alla popolazione per riuscire a fare quel grosso cambio di mentalità che permetterà ai singoli individui e alla comunità intera di sintonizzarsi sui tempi e i modi in cui la Terra evolve. Per ottenere questi importanti obiettivi è necessario educare, fin dalla più tenera età, il cittadino a comportamenti “ambientalmente corretti”.

In particolare il progetto “Scuola Terra e Fantasia” è stato sperimentato per un periodo di tre mesi alla scuola materna Alessandrini di Zibido San Giacomo di Milano. Con questo progetto si è voluto sfidare l’abitudine di rimandare tematiche di carattere scientifico in età esclusivamente scolare. I bambini fino ai 5 anni di età sono generalmente più liberi da stereotipi e preconcetti e maggiormente predisposti al contatto con la natura e l’ambiente circostante facilitando il processo di comprensione e assimilazione di esperienze anche molto complesse. La base quindi del progetto “Scuola Terra e Fantasia” è stata la sperimentazione sfruttando gli ambienti circostanti come laboratorio nel quale verificare tutti quei concetti alla base di un corretto approccio scientifico.

Le scienze della terra nelle scuole dell'infanzia sono state introdotte in modo semplice con l’ausilio di un personaggio, Mariolino, creato appositamente per far rispecchiare ogni bambino nelle sue esperienze. Mariolino è stato introdotto tramite il racconto del suo viaggio molto particolare, che parte dal pianeta Terra verso l’intero Sistema Solare per andare a scoprire quale sarà il pianeta in cui vorrà fermarsi. In ogni sua tappa Mariolino propone sempre attività differenti da realizzare con i materiali che ci circondano e chiede sempre ai bambini di verificare anche le cose più ovvie tramite la percezione sensoriale che costituisce la base del programma didattico e favorisce la manipolazione dei materiali a disposizione.

## Earth-net: una rete per la didattica delle scienze della terra

Paris E. \*<sup>1</sup>, Occhipinti S. <sup>1-2</sup>

1. Scuola di Scienze e Tecnologie, sezione di Geologia, Università di Camerino. 2. ANISN –Valle d’Aosta.

Corresponding email: [eleonora.paris@unicam.it](mailto:eleonora.paris@unicam.it)

Keywords: didattica, scuole-università, rete.

La comprensione del sistema Terra contribuisce alla formazione della coscienza ambientale tra i giovani che, come futuri cittadini, con le loro azioni determineranno la qualità dell’ambiente e della vita sul Pianeta. La conoscenza dei fenomeni naturali permette una migliore prevenzione dei rischi e una riduzione dei danni alle persone e alle cose, mentre la consapevolezza della fragilità del Pianeta suggerisce un uso più sostenibile delle risorse e un’attenzione all’inquinamento ambientale. È quindi necessario migliorare la sensibilità dei giovani verso questi temi, aumentando l’interesse verso le Scienze della Terra lungo tutto il curriculum scolastico tramite uno studio attivo, evidenziando i riscontri e le implicazioni per l’ambiente naturale e la vita dell’uomo.

Cosa può fare l’insegnante per affrontare questi temi? Può: a) utilizzare metodi e materiali ben testati e sperimentati, ma disponibili spesso solo in inglese sul web e difficilmente esportabili, b) creare e sperimentare percorsi e materiali propri. In ambedue i casi, gli insegnanti sono lasciati da soli a investigare, testare, sviluppare ed applicare, con spreco di energie e tempo, che spesso porta a rinunciare alla sperimentazione. Alcune Università, Musei e enti di ricerca hanno attivato progetti didattici e attività per le scuole. Questo sforzo individuale è lodevole, ma non più sufficiente: i fondi sono pochi, ma soprattutto le iniziative, seppur utili e coinvolgenti sono spesso locali, si concludono e purtroppo si perdono. Bisogna ottimizzare il lavoro svolto da singoli gruppi pubblicizzandolo, come in una cassa di risonanza, in modo che il lavoro di pochi sia un beneficio per tutti. È necessario costruire delle relazioni concrete tra i vari attori, per facilitare lo scambio di risorse, conoscenze e competenze, da condividere con scuole, insegnanti, educatori.

L’Università di Camerino, ha creato il gruppo UNICAMearth, che svolge ricerca e divulgazione nell’ambito delle scienze della Terra e collabora con le scuole, con attività specificamente dedicate agli insegnanti e un dottorato di ricerca in “Teaching Earth Sciences”, ha un sito web e una mailing list per divulgare le iniziative. UNICAMearth ha lanciato una proposta che è stata raccolta da alcuni gruppi di ricerca (UNIMI, UNIPI, UNITO, UNIUD, INGV,...). A luglio 2013, al workshop di Camerino, è stata lanciata la creazione di **EARTH-NET**, una rete nazionale per la didattica delle Scienze della Terra, che nasce per “avviare sinergie di risorse umane e scientifiche con lo scopo di promuovere la cultura delle Scienze della Terra, con particolare attenzione al tema dei rischi naturali, tra gli studenti di Istituzioni scolastiche del territorio”. Il successo del meeting di LE GEOSCIENZE A SCUOLA di Pisa 2013 e la nuova edizione di Milano 2014 sono la dimostrazione che c’è interesse a “**FARE RETE**”.

## **Le scienze della terra sul campo: applicazioni didattiche per la comprensione dell'evoluzione del paesaggio**

Pelfini M.\*, Bollati I., Zucali M.

Dipartimento di Scienze della Terra, Università di Milano.

Corresponding email: [manuela.pelfini@unimi.it](mailto:manuela.pelfini@unimi.it)

Keywords: Geoscienze, itinerari didattici, attività in campo.

Lo scopo di questo lavoro è di raccogliere alcune applicazioni didattiche predisposte e sperimentate, aventi come obiettivo l'osservazione e la comprensione dell'evoluzione del rilievo e del paesaggio geografico fisico a diverse scale spaziali e temporali, mediante contatto diretto con la realtà geologico-geomorfologica. Molte delle attività realizzate sono state testate su vari campioni di studenti della scuola secondaria: i) attraverso l'osservazione di pareti rocciose, attrezzate per l'arrampicata sportiva, la cui struttura condiziona le tecniche di progressione, sono stati proposti approcci per la comprensione sia dei litotipi sia delle forme erosionali di origine glaciale su cui le stesse sono impostate (Bollati et al., 2014); ii) l'analisi della morfologia e dei depositi fluviali in siti didatticamente strategici ha rappresentato lo strumento per un approccio alla paleogeografia, al controllo strutturale e al modellamento fluviale (Bollati et al., 2011); iii) itinerari in ambiente alpino e appenninico si sono rivelati uno strumento chiave in termini di attività didattico-laboratoriali sul terreno. L'applicazione di tecniche dendrocronologiche semplificate su scansione di campioni lignei prelevati da alberi ubicati su depositi di diversa origine hanno favorito una miglior comprensione dei processi di modellamento del territorio e dei tempi di evoluzione del paesaggio (es. Garavaglia & Pelfini, 2011; Bollati et al., 2011). Il collegamento con i concetti di pericolosità geomorfologica ha rappresentato inoltre un'occasione per l'educazione al rischio geologico (Bollati et al., 2013).

Bollati I., Pelfini M., Pellegrini L., Bazzi A. & Duci G. 2011. Active geomorphosite and educational application: a didactical itinerary along Trebbia river (Northern Apennines Italy). In: Reynard E. & al. Eds., *Les géosciences au service de la société*. Géovision, 37, 219-234.

Bollati I., Pelfini M. & Smiraglia C. 2013. Assessment and selection of geomorphosites and itineraries in the Miage glacier area (Western Italian Alps) according to scientific value for tourism and educational purposes. *Environmental Management*, 51(4), 951-967.

Bollati I., Zucali M., Giovenco C. & Pelfini M. 2014. Sport climbing sites as a new approach for education in Earth Sciences: scientific representativeness of Montestrutto area (Austroalpine Domain, Piemonte, Italy). *Italian Journal of Geosciences*. doi: 10.3301/IJG.2013.24.

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## Canale Geotube

Porta M.<sup>1-3</sup>, Grieco G.<sup>2</sup>, Merlini A.\*<sup>3</sup>

1. Liceo "A. Banfi" Vimercate, MB. 2. Dipartimento di Scienze della Terra, Università di Milano. 3. Associazione "Il Geco", Milano.

Corresponding email: [aemerlini@gmail.com](mailto:aemerlini@gmail.com)

Keywords: Geoscienze, misconcezioni, video, media.

Le Geologia è una Scienza poco conosciuta al grande pubblico e che genera l'accumulo di una serie di misconcezioni errate. Una delle criticità che abbiamo evidenziato, sulla base di pluriennali studi dei risultati di apprendimento degli studenti in uscita dalle scuole secondarie in termine di competenze nella lettura e nella gestione del territorio, è da attribuirsi ad una didattica della disciplina di tipo "statico", decontestualizzata e che promuove un tipo di apprendimento nozionistico e riduzionistico. Partire dalla tassonomia è senz'altro un elemento necessario per la comprensione dei fenomeni naturali ma non è sufficiente per promuovere la visione "olistica" di spessore evolucionistico. Lo scopo di questo lavoro di ricerca, avviato in un Liceo Scientifico della provincia di Monza e Brianza in collaborazione con il Dipartimento di Scienze della Terra dell'Università degli Studi di Milano, è stato quello di indagare nuove forme di comunicazione delle geoscienze con la creazione di un canale digitale attraverso il quale poter trasmettere i classici contenuti del programma ministeriale. La comunicazione mediata dal video ha permesso di partire dal protagonismo degli studenti rendendoli attori/maestri; di ritornare a spirale sul contenuto, sia nella fase di "scrittura" del copione che nella fase di "registrazione" delle diverse repliche; di trasmettere il dinamismo spazio-temporale dei fenomeni naturali attraverso l'uso di immagini e spezzoni cinematografici utilizzati nella fase di montaggio; di promuovere competenze progettuali nella realizzazione della scenografia; di sviluppare forme di apprendimento collaborativo ("cooperative learning"); di sviluppare capacità critiche nella fase di revisione del prodotto finito; di render consapevoli dell'esistenza di luoghi comuni radicati (le "misconcezioni"); educare ad un uso consapevole dei media grazie alla condivisione di protocolli e di regole da assumere nell'approccio all'uso dei diversi ambienti disponibili in rete. I risultati ottenuti, soprattutto in termini di interesse e di motivazione, ci convincono dell'efficacia della strategia oltrechè della possibilità che tale canale possa avere una diffusione maggiore e diventare uno strumento di divulgazione della scienza al grande pubblico.

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## **Preparazione indagine sull'insegnamento delle Scienze della Terra nei licei italiani post-riforma**

Realdon G.\*<sup>1</sup>, Paris E.<sup>1</sup>, Invernizzi C.<sup>1</sup>

1. Scuola di Scienze e Tecnologie, sezione di Geologia, Università di Camerino.

Corresponding email: [giulia.realdon@unicam.it](mailto:giulia.realdon@unicam.it)

Keywords: Geoscienze, licei, didattica.

Dopo la recente riforma della scuola secondaria di II grado (2010), in quasi tutti i licei è presente un curriculum di Scienze Naturali di 5 anni, per il quale il Ministero ha fornito indicazioni di massima scandite in 1°, 2° biennio e 5° anno, senza separazione cronologica predefinita tra le discipline di Scienze della Terra, Biologia e Chimica. Data la novità del contesto, si è voluto indagare come i docenti stiano effettivamente costruendo il nuovo curriculum di Scienze della Terra, che attualmente dovrebbe essere insegnato nell'intero quinquennio. La ricerca è stata condotta su un campione stratificato casuale di docenti di Scienze Naturali di licei pubblici italiani, suddivisi per regioni in proporzione al numero di scuole. Si è utilizzato un questionario anonimo somministrato on-line nei primi mesi del 2014. Sono stati raccolti 120 questionari da 76 licei (pari al 4,5% dei licei pubblici italiani).

Da essi risulta che le indicazioni ministeriali dei temi da trattare sono state seguite fedelmente nel 1°biennio e un po' meno nel 2° biennio, mentre le scelte tematiche per 5° anno di corso risultano più diversificate. Nell'intero quinquennio vengono considerati come più importanti i temi già presenti nel curriculum pre-riforma. L'organizzazione didattica sembra risentire del limitato monte-ore settimanale, e le attività pratiche (di laboratorio e sul campo) dichiarate dai docenti sono estremamente ridotte. Per quanto riguarda le scelte dei libri di testo, pochi autori sono presenti in alte percentuali, mentre i rimanenti figurano molto distanziati dai primi. Interpellati sulla propria preparazione nelle Scienze della Terra, i docenti esprimono un'auto-percezione complessivamente soddisfacente, accompagnata da apertura alle proposte di formazione in servizio, preferibilmente in forma mista (in presenza + on-line).

Il quadro fornito dal campione mostra un lavoro di costruzione dei nuovi curriculum di Scienze della Terra realizzato in modo autonomo e sostanzialmente basato sull'esperienza di quelli del vecchio ordinamento. Le scelte tematiche eterogenee per l'ultimo anno di corso potrebbero essere condizionate dalle incertezze sull'esame di stato per il nuovo ordinamento. Lo studio suggerisce la necessità di intraprendere e potenziare le attività di formazione in servizio dei docenti per sfruttare a pieno le potenzialità insite nei nuovi curriculum di Scienze Naturali: interesse e motivazione appaiono presenti. Occorre fare perno su questi punti di forza per promuovere il superamento di prassi didattiche che a tutt'oggi sembrano fondate quasi esclusivamente sull'approccio teorico alle Scienze della Terra.

## Le argille, protagoniste del paesaggio attorno a Baiso (RE)

Scacchetti M. \*, Fantini R.

Società Reggiana di Scienze Naturali.

Corresponding email: [mauscacchetti@alice.it](mailto:mauscacchetti@alice.it)

Keywords: argilla, calanchi, melange, impermeabilità

Dovunque si giunga a Baiso, si notano pendii interrotti da vistose erosioni: i calanchi, dissesti che interessano i terreni argillosi e che si sviluppano in tempi lunghi, dell'ordine di migliaia di anni. I calanchi sono per il geologo una preziosa occasione per osservare in affioramento la composizione del sottosuolo. I terreni argillosi che compaiono sembrano molto simili, ma in realtà si differenziano fra loro per struttura ed età. Ad esempio, le cosiddette "Argille varicolori" hanno sfumature rossastre, rosate o violacee che lasciano intravedere la stratificazione: si sono depositate su una piana abissale oceanica da 95 a 75 milioni di anni fa. Altra formazione è il "Melange di Baiso": si tratta di depositi di mare profondo di circa 40 milioni di anni, a prevalente composizione argillosa, dovuti a frane sottomarine, per colata o lento scivolamento, che hanno inglobato lembi di altre formazioni, calcaree o arenacee. Il colore è generalmente grigio scuro, con frequenti chiazze e focature di colore rossastro, violaceo o verdino. Abbiamo infine le "Marne di Monte Piano", argille marnose in strati molto sottili ma poco evidenti, di colore passante dal rossastro, al verdino ed infine al grigio, depositatesi da 40 a 35 milioni di anni fa su una scarpata oceanica profonda e sul bacino abissale contiguo.

L'argilla è una roccia sedimentaria, di solito pseudocoerente: si comporta cioè in condizioni asciutte come una roccia compatta, mentre quando è impregnata d'acqua assume le caratteristiche di un fluido. È costituita da granuli di dimensioni piccolissime, inferiori a 2 millesimi di millimetro, aventi composizione chimica differente; tuttavia i più frequenti sono illite, caolinite, clorite e montmorillonite, tutti appartenenti al gruppo dei silicati idrati di alluminio, con quantità variabili di altri elementi metallici, quali magnesio, sodio, potassio, calcio e ferro. La loro struttura microscopica è formata da strati di atomi o molecole combinati a formare solidi geometrici riuniti in "pacchetti", che costituiscono l'unità fondamentale del minerale. Tra gli interstrati dei pacchetti, oltre ad elementi come sodio e potassio, risiedono alcune molecole d'acqua tipiche dei minerali argillosi. All'interno di queste strutture geometriche sono presenti gruppi ossidrilici OH. Il basso valore delle dimensioni medie dei granuli, unitamente alla loro struttura fogliare, implica una caratteristica importante, ossia l'elevata superficie per unità di peso. Questi minerali argillosi hanno proprietà uniche:

a- immersi in soluzioni acquose fissano sulle loro superfici molecole di acqua e di alcune sostanze disciolte nella soluzione, aumentando in peso e volume;

b- danno facilmente masse plastiche quando sono mescolati con poca acqua; tuttavia in condizioni particolari questi minerali favoriscono la formazione di masse quasi liquide, incoerenti;

c- trattengono molti elementi, fra cui il potassio, che dapprima si legano alla loro superficie in modo debole, ma poi si fissano in modo più forte all'interno della struttura chimica.

## **Il learning cycle delle 5e per introdurre l'IBSE nella didattica delle Scienze Della Terra**

Scapellato B.\*

Liceo scientifico dell' IISS Paciolo-D'Annunzio, Fidenza (PR).

Corresponding email: [barbarascapellato@gmail.com](mailto:barbarascapellato@gmail.com)

Keywords: didattica, IBSE, geoscienze

Negli ultimi tempi anche in Italia si è cominciato a parlare di educazione scientifica basata sull'investigazione (IBSE, inquiry-Based Science education). Con il termine inquiry si intende una serie di processi messi in atto dagli studenti in modo intenzionale come: saper diagnosticare problemi, commentare in modo critico gli esperimenti, individuare soluzioni alternative, saper pianificare un'indagine, formulare congetture, ricercare informazioni, costruire modelli, saper discutere e confrontarsi tra pari, formulare argomentazioni coerenti. Una tale rivoluzione nell'insegnamento/apprendimento non può essere compiuta in breve tempo per cui le ricerche suggeriscono di avvicinarsi all'inquiry attraverso un percorso progressivo in quattro livelli – confermativo, strutturato, guidato e aperto – che si differenziano per il grado di responsabilità dato agli studenti, ossia per quante informazioni (domande da investigare, procedure, risultati attesi) vengono fornite dall'insegnante. Uno degli approcci più efficaci per progettare lezioni inquiry-based è il cosiddetto learning cycle. Ne esistono molte varianti, tra cui il modello delle 5E, dove ciascuna e descrive una fase di apprendimento: engage, explore, explain, elaborate ed evaluate. Nel poster vengono descritte le fasi di un percorso di inquiry (strutturato) sviluppato con il modello delle 5E.

## Un'esperienza didattica di studio del paesaggio geologico con il supporto dello smartphone

Sperone P.\*<sup>1</sup>, Magagna A.<sup>2</sup>, Giardino M.<sup>2-3</sup>, Ferrero E.<sup>4</sup>, studenti classi 1H-1P<sup>1</sup>

1. Liceo Scientifico Carlo Cattaneo, Torino. 2. Dipartimento di Scienze della Terra, Università degli Studi di Torino  
3. NatRisk, Centro Interdipartimentale, Università degli Studi di Torino. 4. CISAO, Centro Interdipartimentale, Università degli Studi di Torino.

Corresponding email: [sperone.paola@libero.it](mailto:sperone.paola@libero.it)

Keywords: patrimonio geologico, didattica, nuove tecnologie, paesaggio

Nell'a.s. 2013/2014 due classi prime hanno sperimentato un'attività preparata e guidata dalla Dott.ssa Alessandra Magagna, nell'ambito della sua ricerca di dottorato e del progetto GeoMedia-web: multimedialità e reti per la diffusione della conoscenza sul patrimonio geologico e sui rischi naturali (L6/2000).

Durante un incontro preliminare sono state valutate preconoscenze e misconoscenze degli studenti ed è stato presentato il progetto ed il funzionamento della Applicazione Trimble Outdoors Navigator free per la successiva escursione in Val Sangone (TO). Sul terreno, i ragazzi hanno svolto, in gruppi di 4/5, attività pratiche di osservazione, fotografia, raccolta campioni, cartografia, rilevamento di punti nelle 6 tappe del percorso e registrazione dell'intera traccia con lo smartphone. Al termine i gruppi hanno svolto una riflessione guidata con l'aiuto di una scheda. L'attività sul campo è stata approfondita con un incontro in laboratorio di informatica, quando è stata scaricata la traccia registrata, quindi analizzata e visualizzata su Google Earth e confrontata con quella segnata sulla carta topografica.

Il focus delle attività è stato condurre i ragazzi alla scoperta del paesaggio con la raccolta di indizi utili per ricostruirne l'evoluzione geologica (caratteristiche e le dimensioni spaziali e temporali) e per acquisire consapevolezza sul rapporto tra agenti, processi e forme del paesaggio. Il percorso è stato concluso con un questionario di gradimento sottoposto agli studenti, una verifica di conoscenze e competenze acquisite e un questionario di valutazione sottoposto all'insegnante.

Dall'esperienza vissuta sono emersi alcuni risultati significativi, che suffragano l'ipotesi di partenza: gli studenti hanno partecipato con interesse alle diverse attività proposte e la loro attenzione è stata catalizzata dalla possibilità di usare in modo nuovo smartphone o tablet; l'uscita sul campo ha consentito l'apprendimento ex-novo e/o il consolidamento di alcune conoscenze/competenze; la partecipazione ad un progetto di ricerca a livello universitario è stata stimolante per docente e studenti e si è rivelata perfettamente integrata nella programmazione curricolare del docente stesso.

L'esperienza didattica ha evidenziato l'importanza e il valore aggiunto dell'interazione e della collaborazione tra l'Università e il mondo della ricerca e la scuola, secondaria di II grado, in particolare.

## **Ammoniti: gli abitanti più famosi dell'appennino accompagnano gli studenti alla scoperta dei fossili**

Stroppa P.\*

Scuola di Scienze e Tecnologie, sezione di Geologia, Università di Camerino.

Corresponding email: [pierluigi.stroppa@unicam.it](mailto:pierluigi.stroppa@unicam.it)

Keywords: ammoniti, didattica, paleoambienti

Le ammoniti erano molluschi molto diffusi nelle acque del mare della Tetide durante l'era Mesozoica. Sono comparse sulla Terra nel periodo del Devoniano (era Primaria o Paleozoica), circa 415 milioni di anni fa e si sono estinte alla fine dell'era Secondaria o Mesozoica, al termine del periodo Cretacico, circa 65 milioni di anni fa, insieme ai dinosauri terrestri e marini. Esse vengono rinvenute in tutte le formazioni rocciose della successione umbro-marchigiana del periodo Giurassico.

Lo scopo di questo laboratorio è di far conoscere alcuni elementi di paleontologia e di stratigrafia ad alunni e docenti delle scuole delle Marche, tramite attività di tipo "hands on" che prevedono l'osservazione e la manipolazione delle ammoniti.

Man mano che il laboratorio si svilupperà, sarà possibile conoscere le abitudini di vita degli ammoniti e la loro evoluzione nel tempo. Diversi kit di ammoniti, quasi tutti provenienti dalle rocce giurassiche dell'Appennino umbro-marchigiano, sono stati allestiti per simulare delle attività da poter svolgere in campagna durante una escursione scolastica o in classe. Il laboratorio può essere svolto per studenti di diverse età. Il prerequisito di questa attività è un'introduzione alla vita e alla storia della Terra, alla fossilizzazione e alle rocce sedimentarie.

Per familiarizzare con le ammoniti sono mostrati alcuni caratteri che i paleontologi esaminano per riconoscerli e classificarli. L'attività inizia con l'analisi della conchiglia dell'ammonite, divisa in camere separate tra loro da setti sinuosi (linea di sutura) e continua con l'esame del profilo e della presenza o meno delle ornamentazioni, protuberanze o inflessioni del guscio. Si introducono gli studenti al concetto di classificazione. Successivamente si pongono i fossili all'interno di una ricostruzione dei paleoambienti del periodo Giurassico, sottolineando il fatto che si tratta di ipotesi basate su diversi parametri ed evidenziando le caratteristiche di ciascun ambiente di vita, con confronti con gli ambienti attuali.

Infine si studia il tipo di avvolgimento degli ammoniti (da evoluto a involuto) e il loro significato, quindi, grazie a un modello in polistirolo, si esamina una delle proprietà di questi fossili più utili ai paleontologi, ossia quella di fossile guida dell'era Mesozoica, in particolare del periodo Giurassico. Un cenno ai principi della stratigrafia e della cronologia relativa completano l'argomento.

Al termine dell'attività gli alunni dovrebbero aver acquisito i concetti di fossilizzazione e di evoluzione di queste specie, avere familiarità con i metodi di osservazione e studio dei fossili e sul loro significato, e avranno potuto riflettere sulle caratteristiche degli ambienti e dei paleoambienti.

## **Viaggio spazio-temporale nel geosito del Monte Conero (Marche): uno strumento per la didattica delle geoscienze nelle scuole**

Stroppa P.\*, Pierantoni P., Invernizzi C., Paris E.,

School of Science and Technology, Geology Division, University of Camerino.

Corresponding email: [pierluigi.stroppa@unicam.it](mailto:pierluigi.stroppa@unicam.it)

Keywords: geositi, didattica delle geoscienze, scuole.

Lo scopo di questo progetto di ricerca è quello di promuovere lo studio delle Scienze della Terra nelle scuole delle Marche utilizzando i geositi più rappresentativi dell'evoluzione geologica della regione. Dopo la preparazione di materiali didattici sul sito di Frasassi, già disponibile on-line in <http://d7.unicam.it/teachingearthsciences/>, che racconta la storia geologica del periodo Giurassico (da 210 a 140 milioni di anni fa) e degli ultimi 2 milioni di anni, il secondo geosito scelto per questo progetto è quello del Monte Conero in cui è rappresentata la storia geologica da 140 milioni di anni fa ad oggi.

Nel geosito del Monte Conero sono stati scelti diversi luoghi e percorsi che permettono agli insegnanti di affrontare lo studio delle Scienze della Terra, sia approfondendo i temi del curriculum scolastico con un'attenzione alla geologia della regione, sia con la possibilità di trattazioni degli argomenti in maniera interdisciplinare, secondo lo spirito dei nuovi programmi. Analogamente a quanto predisposto e già testato sul geosito Frasassi, è stato preparato materiale didattico di supporto e di approfondimento per gli insegnanti e gli studenti su una serie di temi di ampio respiro, che prendono spunto dalla geologia del Monte Conero.

I seguenti percorsi-argomenti, sono stati già proposti agli insegnanti per mezzo di seminari di presentazione dell'attività e visite guidate, in preparazione della sperimentazione con le classi:

1) Passo del Lupo, dove in un'anticlinale asimmetrica si può osservare l'Evento Anossico Oceanico 1 "Livello Selli", riferibile a circa 124 milioni di anni fa (periodo Cretacico);

2) Passeggiata al limite K-T (nella formazione della Scaglia rossa), con il Livello Marchesini e il limite K-T di 65 milioni di anni fa, quello dell'estinzione non solo dei dinosauri marini e terrestri, ma anche degli ammoniti, delle belemniti e delle rudiste;

3) Cava di Massignano, nella Scaglia cinerea, nota per il GSSP (Global Stratotype Section Point) di 33,7 milioni di anni fa, che indica il passaggio tra l'epoca dell'Eocene con quella dell'Oligocene;

4) Punto panoramico su Monte dei Corvi, per lo stratotipo di 11 milioni di anni fa nella F.ne dello Schlier;

5) Spiaggia di Mezzavalle dove un affioramento della Formazione della Gessoso-solfifera illustra la crisi di salinità del Mediterraneo di 6 milioni di anni fa;

6) Baia di Portonovo, per osservare e comprendere i meccanismi dei fenomeni franosi dell'area avvenuti nelle ultime centinaia di anni.

I percorsi scelti sono facilmente utilizzabili per escursioni scolastiche e permettono di poter effettuare raccolte di dati da rielaborare in classe, oltre che esperienze hands-on. Nell'ambito di questo progetto gli insegnanti potranno usufruire di un sito web con il materiale didattico prodotto, esempi di esperienze e progetti per gli studenti, approfondimenti, una guida virtuale alle escursioni, un tutorato on line.

## Le scienze della terra nei libri di testo della scuola secondaria di secondo grado italiana: cambiamenti ed evoluzione

Sturani M.\*<sup>1-3</sup>, Porta M.<sup>1,-2</sup>, Esposto S.<sup>1</sup>, Pelfini M.<sup>1</sup>

1. Dipartimento di Scienze della Terra "A. Desio", Università di Milano. 2. Liceo Scientifico "A. Banfi", Vimercate.  
3. Liceo Scientifico "P. Gobetti", Torino.

Corresponding email: [matteo.sturani@unimi.it](mailto:matteo.sturani@unimi.it)

Keywords: Scienze della Terra, libri di testo, attività sperimentale.

L'approccio alle tematiche delle scienze della Terra nell'insegnamento nella scuola secondaria di secondo grado ha subito un'evoluzione consistente in relazione sia alle direttive ministeriali sia agli sviluppi della ricerca scientifica. I libri di testo rappresentano uno strumento fondamentale a supporto dell'attività didattica (Keine, 2014) e seguono anch'essi l'evoluzione complessa del settore scolastico. Nell'ambito del dottorato in Scienze Ambientali, dell'Università degli Studi di Milano, è in corso un progetto di ricerca che, sulla base di una ricostruzione storica degli approcci ai singoli argomenti oggetto di insegnamento, dei testi disponibili e dell'ampliamento del settore multimediale, si pone come obiettivi di analizzare l'impatto e l'efficacia delle diverse impostazioni su un vasto campione di studenti, verificare la percezione dell'immagine della disciplina negli studenti, elaborare proposte didattiche basate sui più innovativi strumenti di comunicazione e sull'attività sperimentale in campo.

I primi risultati mostrano come nell'ultimo ventennio si è assistito a un incremento significativo dell'offerta editoriale, particolarmente differenziata a partire dal 2010-2011, anno in cui le tematiche relative alle Scienze della Terra compaiono nei programmi già dal primo biennio. Sensibili cambiamenti si osservano anche nei titoli dei testi dove termini come *Sistema*, *Gaia* prendono il posto dei tradizionali *geografia*, *geografia generale*, e compaiono verbi come *osservare*, *capire*, *scoprire*, a supporto di un approccio più sperimentale. I cambiamenti osservati e in fase di analisi aprono a una necessaria discussione sui fattori che possono averli determinati e sulla necessità di ampliare l'approccio sperimentale sul terreno come indicato sia dalle ultime indicazioni ministeriali sia dalla ricerca in didattica delle Scienze della Terra (es. Bollati et al., 2011; 2013).

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## Microcosmo suolo

Villa M.\*<sup>1</sup>, Spadaro G.<sup>2</sup>

1. Biologo – consulente del C.R.E.A di Pavia. 2. C.R.E.A (Centro Regionale di Educazione Ambientale) di Pavia.

Corresponding email: [michela.villa.studio@gmail.com](mailto:michela.villa.studio@gmail.com)

Keywords: Suolo, ecosistema, didattica

Il suolo è un comparto ambientale complesso, poco conosciuto e poco tenuto in considerazione dai non addetti ai lavori. Non si tratta di un semplice substrato ma di una componente viva, essenziale al compimento dei principali cicli biogeochimici e inaspettato serbatoio di biodiversità. Il suolo svolge un ruolo determinante negli equilibri ambientali e riveste innumerevoli funzioni; i servizi garantiti dall'ecosistema suolo sono indispensabili per l'uomo: basti pensare che l'umanità dipende dal suolo per la propria alimentazione e che il suolo è un importante serbatoio di carbonio con rilevanti conseguenze sui cambiamenti climatici. Capirne l'importanza è cruciale per sviluppare l'attenzione necessaria nei confronti di questa preziosa risorsa e per contribuire allo sviluppo di una cultura della sostenibilità che dipende anche da come consideriamo ciò che si trova sotto i nostri piedi.

Il C.R.E.A, centro regionale di educazione ambientale del comune di Pavia, da alcuni anni propone agli insegnanti ed alle classi delle scuole secondarie di primo grado un progetto che si propone di far scoprire il mondo nascosto che sta nel suolo attraverso un approccio sperimentale ed il ricorso a modalità di coinvolgimento diretto dei ragazzi. La presenza di aria ed acqua e l'evidenziazione delle diverse componenti (attraverso una prova di sedimentazione) sono condotte su campioni di suolo raccolti dai ragazzi. L'osservazione è mediata da schede di lavoro che non anticipano il risultato ma che, attraverso una serie di domande, guidano i ragazzi nella formulazione di ipotesi. Molto spazio viene lasciato all'osservazione della pedofauna intesa come spaccato della biodiversità che il suolo può ospitare. Le attività prevedono in questo caso l'estrazione della pedofauna dai campioni di suolo raccolti e l'utilizzo di chiavi dicotomiche semplificate per l'identificazione degli organismi. Presentazioni e video didattici accompagnano e preparano l'attività sperimentale. Analizzando i risultati dei campioni di suolo raccolti si introduce il concetto dell'utilizzo della pedofauna come bioindicatore della qualità del suolo stesso e di come questa qualità non debba assolutamente darsi per scontata.

## **Addendum**

## Crustal modelling of the Ivrea-Verbano Zone in Italy re-examined: new observations preclude lower-crustal extension and 90° rotation

Garde\*<sup>1</sup> A.A. & Boriani<sup>2</sup> A.

1. Geological Survey of Denmark and Greenland. 2. Dipartimento di Scienze della Terra, Università degli Studi di Milano.

Corresponding email: [attilio.boriani@unimi.it](mailto:attilio.boriani@unimi.it)

Keywords: Teleseismic brittle deformation; pseudotachylites; Ivrea-Verbano; megashear zones.

Several independent lines of evidence prevent crustal tilting of the previously proposed Ivrea-Verbano – Serie dei Laghi crustal section in northern Italy. The Ivrea-Verbano zone (IVZ) is separated from the Serie dei Laghi (SdL) by the Cossato-Mergozzo-Brissago (CMB) and Pogallo lines and from the Alpine belt in the north-west by the Insubric Line (IL).

New observations of the supposed rotated, lower crustal extensional shear zone system in the IVZ reveal that this consists of localized, mostly brittle teleseismic deformation on the SE side of the Insubric line. Widespread crushing, intense planar microjoint fabrics, tectonic deformation lamellae in quartz, dm-scale block rotation, fluidised, dyke-like microbreccias and associated pseudotachylites are observed, but we have not found evidence of a major shear zone. We ascribe all these features to early Alpine, earthquake-induced, in-situ seismic reverberation in a broad belt south-east of the IL, without significant lateral displacements outside the IL itself.

Recent geological mapping also shows that the CMB Line is not just a fault but a major dextral shear zone, clearly visible from the Sottoceneri (Canton Ticino, CH) to Lago d'Orta; its best exposure is in Valle Cannobina. Its thickness is about 6 km; its activity postdates Variscan regional metamorphism and predates the Permian intrusion of mafic stocks and dykes. After the Permian the CMB shear zone and the entire crustal section cannot have been tilted by more than 20°, as indicated by the low dip of the upper, miarolitic layer of the Baveno-Mottarone granitic pluton and by the vertical attitude of Permian mafic dykes with chilled margins. The CMB shear zone juxtaposes two units (the IVZ and SdL) that had nothing in common until the Lower Permian. It is a major Lower Permian discontinuity that could be part of the dextral megashear between Gondwana and Laurasia (Muttoni et al., 1996). The Pogallo line is a steep sinistral Permian fault that cuts across the CMB shear zone with an offset of 12 km. Our field observations show that it is coeval with the intrusion of the mafic dykes along it. We conclude that the IVZ and SdL are not parts of a coherent crustal section. Furthermore, the previously proposed Variscan lower crustal extensional shear zone system is re-interpreted as Alpine teleseismic deformation features without major displacement. A thorough re-evaluation and simplification of the crustal structure in the IVZ seems to be appropriate.

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