

5th NATURAL SILICATE GLASSES
CONFERENCE
BOOK OF ABSTRACTS

August 22 – 24, 2013

Museo di Storia Naturale
Aula Strozzi
Florence, Italy

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5th Natural Silicate Glasses Conference						
Florence, 22-24 August 2013						
		Thursday, 22nd	Friday, 23rd	Saturday, 24th		
9.00	9.10				9.00	9.10
9.10	9.15				9.10	9.15
9.15	9.30				9.15	9.30
9.30	9.40			Milke R.	9.30	9.40
9.40	9.50				9.40	9.50
9.50	10.00		Natural Glasses keynote talk: KOEBERL C.	Jahn S.	9.50	10.00
10.00	10.10	Registration opens			10.00	10.10
10.10	10.20			Conte S.	10.10	10.20
10.20	10.30		Gimeno D.		10.20	10.30
10.30	10.40				10.30	10.40
10.40	10.50				10.40	10.50
10.50	11.00		coffee break	coffee break & POSTER session	10.50	11.00
11.00	11.10				11.00	11.10
11.10	11.20		Amalberti J.	Fornacelli C.	11.10	11.20
11.20	11.30				11.20	11.30
11.30	11.40				11.30	11.40
11.40	11.50				11.40	11.50
11.50	12.00				11.50	12.00
12.00	12.10				12.00	12.10
12.10	12.20		Giuli G.		12.10	12.20
12.20	12.30			Pierce E.	12.20	12.30
12.30	12.40				12.30	12.40
12.40	12.50		Takada A.	Closing Ceremony	12.40	12.50
12.50	13.00				12.50	13.00
13.00	13.10				13.00	13.10
			LUNCH time!	LUNCH time!		
14.50	15.00				14.50	15.00
15.00	15.10	Opening Ceremony			15.00	15.10
15.10	15.20		Industrial Glasses keynote talk: FALCONE R.	Guided Tour of the Museum of Mineralogy (University of Florence)	15.10	15.20
15.20	15.30	Silicate Melts keynote talk: RUSSELL K.			15.20	15.30
15.30	15.40				15.30	15.40
15.40	15.50		Baldi G.		15.40	15.50
15.50	16.00				15.50	16.00
16.00	16.10	Neuville D.R.			16.00	16.10
16.10	16.20				16.10	16.20
16.20	16.30				16.20	16.30
16.30	16.40				16.30	16.40
16.40	16.50	coffee break	coffee break & POSTER session		16.40	16.50
16.50	17.00				16.50	17.00
17.00	17.10				17.00	17.10
17.10	17.20	Cicconi M.R.			17.10	17.20
17.20	17.30				17.20	17.30
17.30	17.40				17.30	17.40
17.40	17.50	Moretti R.			17.40	17.50
17.50	18.00				17.50	18.00
18.00	18.10		Guided Tour of the Museum of Zoology and Natural History (best known as "La Specola")		18.00	18.10
18.10	18.20				18.10	18.20
18.20	18.30				18.20	18.30
18.30	18.40	Wine tasting			18.30	18.40
18.40	18.50				18.40	18.50
18.50	19.00				18.50	19.00

Program and abstracts available at:
<http://www.unicam.it/geologia/natglass2013/index.html>

5th NATURAL SILICATE GLASSES CONFERENCE

Book of Abstracts

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*This workshop is supported by the Commission on Physics of Minerals of the
International Mineralogical Association*

August 2013

Foreword

The 5th Natural Silicate Glasses meeting is a satellite workshop of the Goldschmidt Conference 2013. The previous four conferences have taken place in Alfred (1983), Prague (1987), Jena (1996) and Lyon (2002).

The conference is organized around four main topics: Natural Glasses, Silicate Melts and Glasses, Glasses in Archaeology, and Glasses for Industrial Applications.

The Natural Silicate Glasses meeting will provide a forum for discussion of both experimental and computational results related to glass structure and physical-chemical properties.

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Modelling natural silicate melt viscosity

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Abstract

The viscosity of silicate melts controls magma transport dynamics, eruption style and rates of physicochemical processes in natural magmas. A predictive model for viscosity of natural silicate melts at geological conditions has been a long-term goal in earth science for over half a century. During that time, the number of viscosity models has increased and the rate of increase is accelerating. This growth in the *viscosity modelling industry* is driven by innovations in the experimental laboratory over the last 30 years allowing for viscosity measurements over larger ranges of temperature and composition. Here we review the models and modelling strategies for melt viscosity from the original work of Shaw [1] and Bottinga and Weill [2] to now [3-7]. We suggest that the best models are those that conform to the operational definition of a model [8]; in addition to a strong predictive capability, models must comprise: “*well-constrained logical propositions (i.e. construct) with necessary, testable consequences*”. For example, the GRD [7] model predicts the non-Arrhenian viscosity of natural silicate melts as a function of T and melt composition, but, can also predict and be tested against other transport properties including T_g , melt fragility, and activation energy. Such testing, by hundreds of users, has delineated the strengths and weaknesses of the GRD model. As we begin to develop the next-generation model, we are currently assessing whether the key is: i) more data, ii) better data, or iii) a better physical chemical guiding model?

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Al speciation in silicate glasses and melts: new idea and old story?

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Abstract

The first human glasses were made 3500 BC. It was essentially soda-lime silicate glass. To improve the chemical resistance, the thermal properties and increase the viscosity it is interesting to add aluminum in these silicates. And now aluminosilicate melts and glasses are materials widely used in several industrial applications (glass, glass-ceramic and ceramic materials), and implicated in large-scale geological processes. Their properties and structure, imposed by their chemical composition, drive for instance the eruptive dynamics of volcanoes as well as industrial processes of the glass-making industry.

But what is the speciation of the aluminum and how it varies according to the chemical composition and to the temperature? The aluminum appears essentially in four or five fold coordination in glasses and melts. In alkali aluminosilicate compositions, Al is essentially in four fold coordination whereas the proportion of ^[5]Al increases with earth-alkaline substitution, or with alumina content and with temperature. In the case of alkali aluminosilicate glass and melts, Al is compensated by alkali element and as a function of alkali element (Li, Na, K) a new glass order can be observed. In a second part, we can observe the presence of ^[5]Al in earth-alkaline aluminosilicate compositions. And its proportion varies as a function of Al and T. In particular, as a function of temperature, ^[5]Al play different roles, close than glass transition temperature ^[5]Al can be a new network former and at more high temperature ^[5]Al can be insure the network dynamics.

In all case, ^[4]Al and ^[5]Al play important role on the structure and properties of silicate glasses and melts and they are the key of network dynamics and nucleation processes.

The effect of alkali [Na/(Na+K)] ratio on Fe speciation in phonolitic glasses

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Abstract

Silicate glasses of phonolitic compositions have been synthesised to infer the effect of the [Na/(Na+K)] ratio on the Fe structural role and, as final goal, on the physical properties.

Fe can exist in silicate melts in a variety of oxidation states and coordination geometries [1-2] and variation of the relative proportions of these species imply variations in <Fe-O> distances and bond strengths, thus affecting glass/melt polymerisation, Fe molar volumes, melt density and viscosity [3]. The phonolitic compositions have been chosen to fill lack in literature data and to explore the bulk compositions for which theoretical models for Fe oxidation state and melt viscosity give less accurate results. This study will possibly contribute to improve the empirical equations and the theoretical models developed until now [4-5]. The Phonolitic Glasses synthesised at room pressure and in a range of oxygen fugacity ($\log(fO_2)$ from -0.68 to -11) will be useful to infer if the alkali ratio in these conditions will influence the local environment around divalent and trivalent Fe.

In this study, by using Fe K-edge XAS spectra (both XANES and EXAFS), we can determine the Fe structural role (oxidation state, coordination number, bond distances) of phonolitic glasses to infer the influence of Temperature, [Na/(Na+K)] ratio (0.0, 0.25, 0.5, 0.75, 1.0, respectively) and redox environment. Further studies are in progress in order to assess if the [Na/(Na+K)] ratio also influences the physical properties of the melts (i.e. viscosity and calorimetric measurements).

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The redox state of silicate melts and glasses: why should we pursue with empirical approaches?

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Abstract

Melt evolution and properties in Earth Sciences and glass-making industry is heavily affected by redox equilibria, especially because of their impact on the melt/glass structure. Redox equilibria in melts are not only sensitive to changes in intensive parameters, especially T and oxygen fugacity (fO_2), because extensive parameters (composition) have major effects. This chemical control, which includes amphoteric behaviour of some component, hinders a direct application of experimentally calibrated redox equilibria to melt systems and demands understanding of the link between redox, acid-base properties and structure, which is very often overlooked, particularly in Earth Sciences. The need of techniques for determining the oxidation state of magmas from iron and/or sulfur redox ratios has pushed scientists to yield composition-based semi-empirical equations, without much interest for the understanding of how electron transfer takes place, thus disregarding true, or at least most plausible, redox exchanges occurring in melts. Not secondary, it has generated notations (*i.e.*, chemical equilibria) in which standard states, species and components are mixed. Nowadays, the great advancement in the performances of spectroscopic techniques allows a full characterization of oxidation, coordination and speciation state of heterovalent elements, whereas, on the theoretical side, progresses in polymeric modeling for melt mixing properties and *ab-initio* simulations of molecular silicate and aluminate clusters provide a basic framework to build more comprehensive models about the reactivity of multiple valence state elements in magmas, as well as in industrial systems. It is the effective three-way link between these approaches that will allow bringing together structure and thermodynamics into a single interpretative framework able to exploit the relationship between acid-base and redox properties, thus contributing to fill our current gap of knowledge on the formal P-T- fO_2 -composition relationship.

Natural glasses formed by meteorite impact

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Abstract

Impact cratering is an important geological process in the solar system that affects all bodies with solid surfaces. The Earth has been subjected to a large number of impacts of large meteorites (asteroids) and comets over its history; some impact events have influenced the geological and biological evolution of the planet. Currently 184 impact craters have been identified on the Earth's surface. Identification of impact craters requires confirmatory evidence, such as the presence of meteorite fragments (or traces of meteoritic material), and/or the presence of shock metamorphic effects in the affected rocks. Shocked minerals and high pressure polymorphs are common shock metamorphic effects, but rocks melted by the shock pressure and/or high temperatures involved can also be present. Distinctive shock effects are not limited to the deformation or transformation of target rock minerals at pressures < 40 GPa. Higher shock pressures, especially > 50 GPa, produce increasingly high residual temperatures in the target rocks through which they pass. In any impact, large or small, a significant volume of the target rock close to the impact point will be raised to post-shock temperatures > 1500 °C, sufficient to melt and decompose minerals that are unaffected by the lower temperatures produced in non-impact geological environments. Such melting and decomposition reactions, observed in the rocks and glasses of impact structures, can serve as independent evidence of meteorite impact events. The high temperatures involved also serve to homogenize the chemical composition of the resulting melts and to reset isotopic systems used in radiometric age measurement, so that such impact melts are extremely valuable in determining the age of the impact event and the resulting crater.

The most common indicator of such impact-produced high temperatures is the occurrence of lechatelierite, or silica glass, which indicates temperatures ≥ 1750 °C, far above the range of normal near-surface geological processes. The formation of large and small bodies of melted target rocks (from mm-size to thousands of km³ in volume) is a common characteristic of meteorite impact events. During the initial stages of impact, the more intense shock waves (≥ 40 GPa) generated near the impact point produce near-instantaneous heating to extreme temperatures (≥ 2000 °C) throughout a large volume of the surrounding target rock. The resulting impact melts may form small glassy bodies that are ejected from the developing crater or may produce larger dike-like and sill-like bodies of igneous rock that remain within the resulting structure.

Smaller impact melt bodies, mm to cm in size and generally glassy, may be ejected from the impact crater, often to regional or global distances, as individual “splash-form” objects, *e.g.*, spherules and microspherules, dumbbells, droplets, and other aerodynamically shaped forms. On deposition, these objects often accumulate in distinct layers or as widely-distributed strewnfields. Tektites and microtektites are the best-known and most-studied of these ejecta deposits, but a variety of other glass-rich ejecta deposits, of both Precambrian and Phanerozoic ages, have also been identified. Intermediate-sized (cm to dm) bodies of impact-produced glass in some cases

occur as individual objects composed either of dense glass or of scoriaceous and vesicular melt. Many of these glassy bodies are clearly associated with a definite or possible impact structure, *e.g.*, Meteor Crater (Arizona), Lonar (India), Aouelloul (Mauritania); Henbury (Australia); Rio Cuarto (Argentina); Darwin (Australia), and various others. There are also some occurrences of scattered glass fragments for which no impact crater has yet been identified, such as Libyan Desert Glass. In some cases, it was the detection of an extraterrestrial component in glasses that allowed confirmation of the impact origin of a geological structure; such identification is done with a variety of geochemical tools, especially trace element contents and the isotopic composition of elements such as Os or Cr.

Basanite-alkali rhyolite mingled glass bombs of the initial cycle (October 2010) submarine eruption at La Restinga, El Hierro island, Canary Islands (Spain)

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Abstract

The A submarine eruption close to the La Restinga village (south of El Hierro island, Canary Archipelago, Spain) started around October the 11th 2011 and was considered concluded at March 2012. During some weeks the eruption was manifested by a discolored plume (green) of dissolved gas (and probably suspended fine-sized particles) marking the site of submarine vents on the sea surface, and by the punctual emission of a rare type of decimeter to meter-sized buoyant pyroclasts, ovoid in shape, formed by two types of mingled magma (a black thin sideromelane crust with a white pumitic core). The first unequivocal emission of this kind of pyroclast was at October the 13th 2011, the last 22 October. Rhyolite-basanite composite mingled pyroclasts “Restingolite” pyroclasts are formed by two parts intimately mingled: a white microvesiculated pumice, alkali rhyolitic in composition and a deep green-black glassy basanite with porphyritic (phenocrysts < 3 %) and locally macrovesicular textures. The basanite constitutes the skin of the pyroclasts. while the inner part is formed by planar pumitic discontinuous plastic fragments roll-wrapped with black partings of basanite. Locally, the basanite clearly looks vitreous with concoidal fracture (sideromelane). Taking into account geochemical data, isotopic data, termogravimetric data, porosity, size and morphology of vesicles and bombs (among other data) this note will illustrate the plausible eruptive mechanism, the at least balanced participation of basanita and rhyolite volumes (till now explains 1:10 ratio of rhyolite respect basanite), involved in the initial weeks of the eruption, inferred depth of basanite-rhyolite interaction and the significance in terms of potential explosivity of the eruption and managing of volcanic risk.

He and Ar diffusivity in basaltic glasses and melts

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Abstract

The noble gases are well known tools for tracking the degassing of magma, and processes important for understanding volcanic eruptions. The diffusion of noble gases can also be used as a probe for understanding the behaviour of volatiles in silicate liquids and glasses. Due to experimental difficulties, He and Ar (and other noble gases) diffusivities are poorly constrained in natural silicates at magmatic conditions [1-2]. In order to address this lack of noble gas diffusion data, we have measured He and Ar diffusivities in silicate glasses using classical in vacuo stepped heating approaches [3].

Our results show that He and Ar diffusivities converge at high temperature, as do the diffusivities of the individual Ar isotopes (^{40,38,36}Ar), such that their diffusivities are equal at $T > 750$ °C. This observation is consistent with the theory of “diffusion compensation” which predicts an isokinetic temperature due to correlated activation energies (E_a 's) and pre-exponential factors (D_0) [4].

The compensation temperature plays an important role for understanding volatile fractionation during magma degassing. Little or no noble gas fractionation should occur at temperatures close to or above the compensation point; similarly, noble gas isotopic fractionation can only occur during low temperature processes and not during the degassing itself [5]. This behaviour can most probably be extended to other volatile species in the magma.

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Fe oxidation state and water content of moldavite tektites

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Abstract

Moldavites are tektites which are thought to be related to the impact event that formed the Ries crater in Germany. They are distributed in a strewn field across Check Republic, Germany and Austria at distances ranging from 200 to 450 km from the source crater [1]. A set of moldavites from the Bohemian, Moravian and Cheb sub-strewnfields have been analysed by X-ray Absorption Spectroscopy (XAS) and FTIR spectroscopy in order to get quantitative information on the Fe oxidation state and water content. Most moldavites show $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$ ratios $\leq 0.1 \pm 0.05$, similar to tektites from the other strewn fields studied by XAS [2-4], Mössbauer [5-7] or wet chemistry [8]. Also the average Fe coordination number (which is intermediate between 4 and 5) is in agreement with previous studies [2-4]. However, few moldavites studied here display $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$ ratios of 0.15 ± 0.05 and up to 0.22.

Transmission FTIR data on the same samples allowed to determine water contents ranging from 60 to 200 ppm. No correlation has been found between water content and Fe oxidation state. This means that the high temperature of the impact melt forming the moldavites cannot be the only responsible for both the low water content and the relatively low Fe oxidation state.

Preliminary data are also presented here on few samples of layered moldavites whose water content display a strong zonation mimicking the layer orientation.

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Structural simulation on silica glasses and crystals

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Abstract

Molecular dynamics simulation has been used to investigate the similarity and dissimilarity in dynamical structural changes between silica crystals and glasses. Many simulation studies have been performed for quartz, cristobalite and silica glasses [1-3], however, there is scarcely any simulation studies on tridymite. The structural building block is the same between in tridymite and cristobalite, nevertheless, structural changes due to the thermal effects is more complex in tridymite than in cristobalite. Such complexity hinders the theoretical study. First, the structural changes of tridymite phase due to thermal effects are investigated by using molecular dynamics simulation. Next, the calculated complex structural changes are compared with those of the other structures such as cristobalite and glasses. Finally, we discuss the similarities and dissimilarities in dynamical structural changes in terms of microscopic structure.

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Production and optical properties of soda-lime-silica industrial glasses

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Abstract

Soda-lime-silica (SLS) glass is the most widely used of all commercial types of glass. This type of glass composition is mainly used for manufacturing glass containers (*e.g.* bottles, jars) for foodstuffs and beverages, household glassware and windowpanes. These products are produced by melting a “batch” of appropriately weighed quantities of raw materials; the manufacturing process includes five main steps: batch preparation, melting, fining, forming, and post forming. Optical properties are one of the most important features of SLS glass product. For glass containers the choice of the color mainly depends on two requirements, food preservation and marketing. Colorless glass containers promote the visibility of the contained product but provide poor protection to photosensitive foodstuff, whereas colored yellow-green and amber glass containers provide the highest level of protection to photosensitive foods and beverages. Flat glasses are also produced with different optical features basing on the requirements of the final end product application (building, automotive, and furniture). In industrial glasses, color is produced by the selective absorption of radiation in the visible range by transition metal ions (*e.g.*, iron, chromium, cobalt, copper, manganese) added to the batch as oxides or other compounds in small quantities in order to produce the desired glass color. Moreover, since polyvalent coloring ions produce different glass colors at different oxidation states, the monitoring and the stability of the redox state of the melt is very important for the quality and color stability of the final glass product.

Evolution of iridescent glass weathering layers and some consequences

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Abstract

Iridescent weathered glass is well known from archaeological objects. The optical effect has long been explained by the evolution of laminated weathering layers. The mechanism responsible for this lamination seems to remain in the dark, however, and might be of general importance to glass weathering research.

Together with several colleagues I have analysed the surfaces of beer bottles thrown away on Australian Opal fields a few decades ago, that all show iridescence. The multi-method approach includes optical microscopy, electron microprobe analysis, X-ray diffractometry, infrared spectroscopy, Raman spectroscopy, focussed ion beam extraction, scanning transmission electron microscopy, high-resolution TEM, electron energy loss spectroscopy, and thermal induced mass spectrometry of the Rb-Sr and Sm-Nd isotope systems.

The surface weathering layers consist of an amorphous opaline substance. Its uptake in chemical elements and isotopes indicates that the surface weathering layers have formed by an exchange process between a salinar soil fluid and the original bottle glass. There is an absolutely sharp interface between the original glass and the weathering layers. The opal weathering layer is structured into dense layers of constant thickness in the 150 nm range separated by porous layers. This self-structuring is explained by a dissolution-precipitation mechanism with subsequent loss of water from increasingly polymerising opal.

Glass surfaces provide links between geosphere and biosphere. The weathering layers provide substrates for single cell organisms, while the iridescence effect seems to interfere with the mating behaviour of local beetle species.

Structure and transport properties of calcium and magnesium aluminate melts and glasses: A molecular dynamics study

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Abstract

Calcium and magnesium aluminates are refractory materials of technological importance. From a glass physics perspective, calcium aluminates are of special interest as they are very fragile glass formers. The rapid change in physical properties, for instance of the viscosity, of such systems close to the glass transition is thought to be related to changes in the atomic structure between the melt and the glass. Recently, x-ray and neutron diffraction experiments as well as molecular dynamics simulations were performed to investigate the structure of the such melts and glasses [1-4]. Here, new results from extensive molecular dynamics simulations are presented that link the structural evolution of calcium and magnesium aluminate melts during cooling to their transport properties, which includes the shear viscosity, self-diffusion coefficients and the thermal conductivity. From a structural point of view, we will especially discuss the abundance of structural motifs such as four- and five-fold coordinated Al, OAl₃ triclusters or the connectivity of Ca- and Mg-centered polyhedra as a function of temperature and quench rate.

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Archaeometrical analyses of late and post Roman glass from Butrint (Albania)

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Abstract

In Late Roman period, Butrint city (SW Albania), was one of the most important seaport of the eastern Mediterranean, due to its very favorable position and its long human presence (from the 5th century BC to the modern age). The city seems to have particularly flourished after being declared a Roman colony under Augustus in 31 BC, but even after the Roman period, Butrint was still at the center of the trade routes to the Eastern regions. During the archaeological campaign of 2011 directed by David Hernandez (University of Notre Dame - US), aimed at identifying the eastern border of the Butrint Roman Forum, several glass artifacts, dated to the late Roman period, were recovered. In this study we analysed 43 fragments of glass (38 transparent, 5 opaque) of different objects (drinking glass, bowls, mosaic tesserae) dated from the 4th to the 6th centuries AD. The aims of this work are: i) understand the raw materials, the manufacturing techniques employed for glass production and understand their evolution through the time; ii) produce a correct classification of pieces of uncertain date; iii) interpret the economic development and the trade models of this area. The chemical analyses were performed by electron microprobe (EMPA) for major and minor elements and by ICP mass spectroscopy (LA-ICP-MS) for trace elements. The chemical results indicate that, after the exclusion of some outliers, the samples can be classified into two groups: i) produced with natron as fluxing agent (38 sample) and ii) produced with plant ash as source of flux (5 samples)-with these latter probably representing a later intrusion and not belonging to the original group of materials. The natron glass can be further divided, on the basis of the concentration of Fe, Ti and Mn, in the two main compositional groups widespread in the Mediterranean from the 4th century onward: HIMT (24 samples) and Levantine I (14 samples) [1]. Among the HIMT samples, we found both “weak” HIMT (14 samples) and “strong” HIMT (7 samples) [2]. The 3 remaining samples seem to form a new HIMT group showing higher iron and a different Fe/Ti ratio never found up to now in Late Roman glass.

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New developments in early industrial stained glasses

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Abstract

In the present work, 50 samples of stained glass have been studied in order to disclose the improvements in glass production introduced after the growth of industry in the late 18th and early 19th centuries; the large scale production of glass and the development of new techniques led to a revival of stained glass manufacture, culminated during the late 19th century with the addition to the batch of many new colouring agents, or synthetic versions of the old ones, and synthesized raw materials (such as Solvay processed soda).

The sample repertory includes both transparent and opalescent glasses produced by some Italian, German and American glassworks between the late 19th and the first half of the 20th centuries. All samples have been preliminarily analyzed by SEM-EDS and XRF in order to characterize the batch composition and the colouring agents. XRD has been utilized as well to identify crystalline phases employed as opacifying agents.

Based on major element contents, the majority of samples can be considered as soda-lime-silica glasses, with few examples of mixed alkali-lime and lead-potash glasses. Concerning coloured transparent glasses, the addition of new colouring agents synthesized during the 19th century such as pure cobalt (mainly used for blue tints), cadmium (yellow and orange), selenium (pink and amber) and zinc (associated with sulphur to produce a deep red tint) has been confirmed. Moreover, high contents of calcium and fluorine have been detected in all opalescent samples by SEM-EDS and XRF (XRD analysis confirmed the presence of fluorite, CaF₂), while zirconium (introduced as zircon, ZrSiO₄ or zirconium dioxide, ZrO₂), has been detected as well in some samples.

Glass corrosion: integration of experimentation and modeling to develop a mechanistic understanding of glass-water interfacial reactions

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Abstract

Glass-water interfacial reactions play a critical role in the evolution of natural and engineered systems (*e.g.*, geologic repositories). Furthermore, the desire to design durable glasses for various industrial applications has also resulted in significant interest in glass-water interfacial reactions. For aluminosilicate and borosilicate glasses, one of the existing scientific challenges is to decipher the complex coupled reactions controlling the formation, evolution, and transformation of silica-rich surface layers. Silica-rich surface layers, similar to inorganic coatings on natural minerals, can affect the microscopic processes (*e.g.*, ion diffusion, adsorption, *etc.*) that impact elemental release rates. Accurately describing the impact of these layers on the glass chemical durability and long-term corrosion behavior requires a molecular level understanding of the rates and mechanisms occurring at the glass-water interface. This presentation will highlight recent advances in experimental approaches and computational models that are currently being implemented to improve our understanding of these processes for aluminosilicate and borosilicate glasses.

Glass-ceramic materials for building and ballistic protection

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Abstract

In the field of material science there's an emerging interest for glass ceramic materials and their applications in buildings and ballistic protection. The behaviour of this class of materials, bridging across ceramic and glass, can lead to a series of innovative products very promising in the view of competitiveness of Italian industry in front of aggressive competitors, especially in Asia.

In the Colorobbia Italia research centre CERICOL we started more than 10 years ago with an activity based on the development and industrialization of new glass ceramic materials. Due to the use of nucleation and crystallization techniques we have obtained composite materials with sub micrometric or even nanometric crystalline textures, this led to opaque materials with advanced mechanical and aesthetical features that can be used in building as architectural items or interiors elements [1]. The high mechanical modulus and hardness drove the development activity towards the production of materials for ballistic protection while the control of crystalline size at a nanometric scale led to the production of a series of transparent materials with improved ballistic and architectural features. The industrial scale-up allows the production of sheet and other items with different size and shape while advanced decoration techniques based on nanotechnology, allows the development of surfaces aesthetically innovative and technologically advanced. The use of nano-oxide and nano-metals led to the development of "smart" surfaces [2] as antibacterial, self-cleaning and anti-smog, giving an added value to these products in terms of safeness and healthiness for the consumers. It has been investigated the nucleation and crystallization behaviour of a glass-ceramic material in the $\text{Li}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ system, with interest in its opaque-transparent behaviour for building and ballistic protection, associated to good mechanical strength, surface hardness and low thermal expansion. The application of nano TIO_2 and AgO nanostructures on the surface gives to the products advanced characteristics as self-cleaning, antibacterial and anti-smog.

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Kinetics of iron reduction in anhydrous pantelleritic glasses

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Abstract

The kinetics of Fe reduction in pantelleritic melts have been investigated by means of colorimetric wet chemistry and Fe K-edge X-ray Absorption Near Edge Spectroscopy (XANES). Samples with ca. 5 wt% Fe₂O₃ have been synthesized in air and re-melted in Re-boats in a gas mixing furnace (Ar/H₂/H₂O) under reducing conditions (log *f*O₂/bar: -13.90). Kinetic experiments have been performed at different melting times, ranging from 1h to 72 hours.

The iron speciation ratio in these glasses was checked by a colorimetric wet chemistry method, which confirms the increase of Fe²⁺/Fe_{tot} in the samples with time. As shown by Magnien et al. [1], the evolution of Fe²⁺/Fe_{tot} with time at a given temperature can be reproduced by expressions of the form

$$(F_t - F_{eq}) = (F_0 - F_{eq}) \exp(-t/\tau).$$

The equilibrium Fe²⁺/Fe_{tot} value in our sets of samples ranges from 89 to 94% with a relative uncertainty of 4%. At temperatures near 1250 °C, equilibration times of 20 hours were found to be sufficient to achieve the equilibrium in all the glasses.

XANES Pre-edge peak data clearly indicate that Fe³⁺ is in fourfold coordination and its role as a network former is consistent with previous works [2-5]. Divalent iron displays an average coordination number intermediate between 4 and 5. Only small differences have been detected in the integrated area of the pre-edge peaks for glasses having different K/(K+Na) ratio, indicating that the increasing of the K/(K+Na) ratio produced only small variations in the average coordination number of Fe for these compositions.

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Properties and structural role of iron in silicate melts and glasses

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Abstract

Iron is an important element to probe the properties and the structure of silicate melts. In earth science most of lava contains more than 10% of iron whereas the proportion is much smaller in industrial materials. Iron usually occurs in two different valence states (Fe^{2+} or Fe^{3+}), and three coordinations: 4, 5 and 6. Thus, the influence of iron oxide on the melt properties is complicated. Consequently, the redox ratio of silicate glasses and melts is an important parameter which role must be properly studied to understand the physical and chemical properties of these materials.

The coordination of iron may evolve as a function of the redox state. These changes are due to the fact that iron is essentially present in the form of Fe^{3+} in tetrahedral position at lower temperatures whereas it mainly occurs as Fe^{2+} in 6-fold coordination at higher temperatures. These changes in the iron coordination may influence the short range order around network modifier, such as Na or Ca.

X-ray Absorption Spectroscopy experiments are very valuable to determine short-range order. It should allow us to study the iron valence and coordination, as well as the sodium and calcium environment. However this technique is not always accessible. Therefore, other experimental methods must be used to study the network modifications such as Raman spectroscopy and electron microprobe.

We focused our work on the changes which happen in the glass during the transition between different redox states. Especially with regard to the network structure and the local environment of network-modifier elements.

Sulfur in alkaline melts: An experimental study

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Abstract

We present preliminary results from experiments to establish the solubility and fluid/melt partitioning 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 $\text{FeO}_{\text{total}}$ and SiO_2 [1]. 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 sulfate and sulfide solubility and fluid/melt partitioning. Sulfur saturated and undersaturated experiments have been carried out over a range of oxygen fugacities ($\log fO_2 = -12$ to -6 , ranging from ca. the iron-wustite buffer to $\text{NNO}+3.45$), pressures of 1 bar and 1 kb and temperatures above the silicate liquids (1030 and 1200 °C for phonolite and basanite, respectively). This range of experimental conditions and analyses of the sulfur contents via electron microprobe and sulfur and iron speciation and coordination geometry via XANES will allow sulfur solubility and partitioning to be evaluated with respect to the above listed experimental parameters.

Preliminary results indicate a marked increase in total S solubility in evolved phonolite melt relative to primitive basanite at similar T- fO_2 conditions. In addition, we have established the effect of fO_2 on the solubility of total S at 1 kbar in basanite KI-04 based on experimental run products containing sulfur-bearing crystal phases (i.e. sulfate, sulfide). Experiments indicate a steep increase in S solubility at highly oxidizing conditions ($fO_2 = \text{NNO}+1.53$; ≈ 1000 ppm dissolved S) and minimum solubility at moderately oxidizing conditions ($fO_2 = \text{QFM}+0.23$; ≈ 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 (1 GPa) and analyses of all experimental products via XANES will elucidate the roles of oxygen fugacity, pressure, Fe and S oxidation state, and Fe and S coordination geometries in controlling S solubility in basanites and phonolites. Comparisons of our results to similar data from more polymerized (low-alkali) melts and incorporation of data from an unpublished experimental study of S in phonolite at conditions below the silicate liquidus [2] 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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Implementation of the Panum Crater dome (California). Rheological study and diffusion of water in the pumice and obsidian

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Abstract

Despite the findings of previous studies, the influence of physicochemical properties of magmas on the construction and dynamic of volcanic domes is not fully understood. Particularly, the viscosity of magmas strongly influences the structure and stability of volcanic domes. This parameter strongly depends on the temperature, the chemical composition, the volatile dissolve and the bubbles content of magmas. With these considerations, it is important to understand volatile behaviour which is a parameter of the first order that will control the eruptive dynamics. Water is the most important volatile, which causes a drastic influence on the viscosity. Panum Crater is the most recent dome eruption at the chain of Mono Craters in the north of Long Valley caldera (California). It is a dome composed of obsidian and pumice, which was established in 1350 AD [1]. Least lava emissions contain a great contrast of different pumices. Its structure and morphology represent a particular interest and a simple object of study to understand the relationship between the gas phase and its implementation through the dynamic eruption. Goals are to measure diffusion in the border around bubbles to understand the formation of the gas phase. The profiles of water diffusion to the walls of each type of bubble shows an opposite process: the rich pumice water diffuses water in obsidian while around micrometric bubbles water content decreases, approaching the bubble implying that water diffuses into the bubble obsidian. Therefore the dynamics behind these two profiles are different. In the case of highly deformed pumice, it is possible that a generation of bubbles formed in more depth in a water-rich magmas rise. These processes will therefore have implications for the understanding of the dynamics of development of the dome. Modelling of diffusion profiles by Fick's second law on the experimental data used to constrain several parameters on the conditions of formation of bubbles. These results allow better constraining the parameters of the dynamic establishment of Panum Crater and potentially extending these results to other domes.

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Determining the provenance of Mediterranean obsidian artifacts

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Abstract

Providing a generally valid model to classify and determine the provenance of obsidian archaeological artifacts of the Mediterranean area, was the aim of this research. This has been carried out to overcome the actual problem of the wide uncertainty arising when trying to distinguish samples from similar, although separate sources or to compare them to literature data. Reported chemical analyses of obsidian are characterized by being obtained with a variety of analytical methods, laboratories or sets of analyzed elements, introducing a major difficulty when trying to use these data for provenance studies of ancient artifacts.

The development of a comprehensive statistical method applied to take into consideration all the chemical parameters characteristic of each obsidian source has been carried out using different statistical methods, organized in a sequence that allows the discrimination, step by step, of all the sources. The method is based on the building of a large chemical database reporting both geological and archaeometrical literature obsidian data from the volcanic districts of the Mediterranean - Aeolian, Pontine, Sardinian, Pantelleria, Carpathian and Aegean.

As a first step, comparison of Normal Probability Plots between different sources and interrelations between elemental abundances allowed us to individuate discriminating elements and tracers, like Sc, Rb, Cs, Sr, Ba, Ta, Hf, Zr, Nb, Y, Th, U and REE. Then multivariate data analysis allowed us to develop effective discriminating models, using Principal Component Analysis (PCA), Linear Discriminant Analysis (LDA), Soft Independent Modeling of Class Analogy (SIMCA) and Partial Least Squares Discriminant Analysis (PLS-DA). The established procedure allows to select the discriminating elements to be compared with the geological fingerprint of different sources. The procedure, tested on both literature and new data, has the advantage of making the provenance study of obsidian artifacts independent from the analytical method used as well as from the need of large number of reference samples.

The amphoteric behavior of water in silicate melts from the point of view of their ionic-polymeric constitution

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Abstract

Dissociation of water into hydronium and hydroxyl ions is a fundamental feature of aqueous solutions. Although it exerts a profound influence on properties of magmas, this autoprotolysis reaction has been hitherto neglected for water dissolved in silicate melts. As made here with an acid-base model, one has in fact to deal with molecular water ($\text{H}_2\text{O}_{\text{mol}}$) and two kinds of hydroxyl groups, bonded or not to network-forming cations (OH and OH^- , respectively) in hydrous silicate melts. By mixing cations and anions on distinct sublattices and quantifying the disproportionation of water dissolved in silicate melts into its ionic products, H^+ and OH^- , we reconcile spectroscopic determinations of water speciation, and explain the contrasting rheology of hydrous basaltic and rhyolitic melts. In fact basalts show much less depression of viscosity by water addition because of a relative predominance of OH^- , such that water increase tends immediately to limit depolymerization rather than enhance it. This opens new perspectives to the understanding of the chemical control leading to either effusive or explosive eruptions. In addition, our model may be applied to precipitation of hydrous minerals such as amphiboles or micas from depolymerized melts.

Rheological constraints in welded pyroclastic alkaline rhyolites: a case study from Nuraxi Formation, SW Sardinia, Italy

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Abstract

Viscosity of pyroclastic flow deposits has a strong interest for risk assessment in volcanic hazards, as an input variable for eruption modelling; and also in the interpretation of the emplacement of ancient volcanic units. However, it is hampered by lack of an extense rheological database. Data presented here characterize the evolution of viscosity in a vertical profile of the Nuraxi tuff, which can be of interest when studying the emplacement of the rest of nearly peralkaline and peralkaline ignimbritic units in the Sulcis region. Petrographical observations revealed complete devitrification of the rock, but the composition of former glass, and by extension, former magmatic liquid, have been obtained by measuring chemical composition of the matrix by EMPA.

Determination of viscosity depending on temperature was attempted on cylindrical rock cores, powdered rock, quenched molten rock and synthetic glass by means of dilatometry and hot-stage microscopy. The effect of volatile contents on viscosity was calculated through numerical modelling [1], mainly based in chemical composition. In addition to measured viscosity, petrographic analysis was performed in order to establish a relationship between real viscosity, deformation and devitrification. Analyses on dry materials determined that deformation started well over 1100 °C (higher than natural temperatures of rhyolitic flows). However, viscosity decreased sharply when volatiles were taken into account. An amount around 1-2 wt % of water would reduce viscosity under 108 Pa·s inside the 700 - 850 °C range, thus enabling the rhyolitic glass to flow.

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Spherulites in trachytic melts

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Abstract

Spherulites are cluster of radiating crystals that occur commonly in rhyolitic melts under highly non-equilibrium conditions [1-2]. Textural data on spherulites of alkali-feldspar and pyroxene are shown in this study. Spherulites grew in trachytic melts during cooling and decompression experiments with water-saturated conditions. The aim of this work is to better understand the growth of spherulites as a function of undercooling (ΔT), P_{H_2O} , time and superheating. Experiments were carried out using Cold Seal Pressure Vessel apparatus at pressure range of 30 ÷ 200 MPa, temperature range of 750 ÷ 850 °C and duration of 2 ÷ 16 hours. This study presents preliminary quantitative data on spherulitic morphologies obtained both by electron microscopy (SEM) and phase-contrast synchrotron X-ray microtomography. Because experiments were performed at different experimental durations, the evolution of spherulites can be studied and furthermore the crystallographic misorientation, the changes in size and the aspect ratio can be measured.

Three kinds of spherulites occurred during our experiments: (i) spherulites characterized by widely spaced crystals arranged radially around the nucleus, in agreement with previous observations [3-4]; (ii) spherulites characterized by acicular and tiny fibers radially aggregated; (iii) spherulites characterized by the transition from a single crystal into a polycrystalline spherulite (densely branched spherulitic morphology). The preliminary results about alkali feldspar spherulites show that their growth rate is about 10^{-7} cm/s. Spherulites were grown between 100 and 200 MPa, thus at high water contents. Moreover, low ΔT along with large superheating can enhance the nucleation and growth of spherulites. Therefore, low ΔT , large superheating and high P_f conditions can trigger the crystallization of spherulitic morphologies.

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V local environment in phosphate glasses

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Abstract

Glasses containing vanadium find applications in a variety of scientific and technological fields like sensors, catalysis, electronic devices and glass ceramics. The valence state of V depends on the oxygen fugacity, thus vanadium in glasses is redox sensitive and can be used as an oxygen barometer [1]. Synthetic glasses containing V oxides have been widely studied because of their peculiar polaronic semiconductive behavior [2]. However, the structural role of vanadium in glasses is not completely understood, yet.

X-ray absorption spectroscopy (XAS) in the near edge (XANES) part of the spectrum is proposed to study the V local environment (oxidation state, coordination geometry and bond distances) in two glasses: VPNa10 (starting composition 10 % V₂O₅ - 45 % P₂O₅ - 45 % Na₂O) and VPNa80 (starting composition 80 % V₂O₅ - 10 % P₂O₅ - 10 % Na₂O). The pre-edge feature of a XANES spectrum is a fingerprint of the coordination geometry and valence state [3,4,5]. The comparison between the pre-edge peak of a set of standards with known structure and the two unknown glasses allow us to obtain qualitative informations on the V local geometry and valence of the glasses: VPNa10 is mainly 4+ in 5-fold coordination and VPNa80 is mainly 5+ in 5-fold coordination.

Since the pre-edge feature alone is not able to give a full quantitative information about bond distance and coordination distortion, *ab-initio* modeling for the continuum part of the XANES spectrum is shown using the MXAN procedure [6]. Calculations performed for the model compounds are in good agreement with the experimental spectra. This step allow us to build a framework to study in a quantitative way the V local structure of the glasses. Preliminary calculations are shown for the two glasses.

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Natural silicate glasses from the deep crust

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Abstract

Small ($\leq 20 \mu\text{m}$) droplets of granitic melt produced by partial melting (anatexis) of the deep metasedimentary crust can be enclosed by minerals (peritectic phases) growing during melting reactions [1-3]. These data repositories may survive, shielded by the host, during the subsequent P-T-t history of the rock, and may provide compositional information (major and trace elements, and volatile contents) on natural crustal melts otherwise impossible to retrieve [4, 5]. In some exceptional geological contexts (*e.g.*, the Neogene Volcanic Province of SE Spain; La Galite, Tunisia), fragments of the partially melted crust may be rapidly brought to the Earth's surface by magma uprise, and quenched from temperatures of c. 800-900 °C. This allows the preservation of the melt as glass [2, 4]. However, the coexistence of totally crystallized inclusions (nanogranites) along with preserved glassy inclusions in more conventional, slowly cooled, anatectic rocks such as migmatites and granulites, is a geological oddity. Despite the comparable compositions, glassy and nanogranite inclusions appear to have different size distributions in khondalites (S India), suggesting that the nucleation was inhibited in the smaller inclusions [1]. The pore size effect seems to find less evidence in Ronda migmatites (S Spain), where the size of glassy inclusions is often equal to, and sometimes even larger than, that of the nanogranites, suggesting that additional factors (*e.g.*, impurities within the inclusions or surface irregularities) may significantly affect nucleation kinetics.

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Archaeometric study of samples glass from the Ciutadella de Roses site (Empordà, Girona), NE Spain

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Abstract

The archaeological excavations conducted in renaissance fort area of the Ciutadella of Roses (15 km north of the greek-roman city of Emporium) have shown the rests of the Greek city of Rhode, founded at 776 B.C. by Rhodian people; the Hellenistic quartier (especially important at IV-III centuries B.C.); a roman villa (occupied between centuries II B.C. and VI D.C.); a romain-lombard monastery (XI century), and a series of rests till XIX century. A number of 25 samples were chosen and cleaned in order to characterize its main chemistry by EMPA. The major constituents Si, Al, Na, K, Fe, Mn, Ca, Mg, Ti and P were analyzed, as well as a number of trace elements (metals) that give indication on the colour of glass: Co, Cu, Cr, Sb and Pb. The archaeological data allow dating the concerned strata in several periods: end of VI century-beginning of VII (3 samples) and from middle XVI century to XVIII century. All the studied glass fragments show a sodic-lime composition, being the ones corresponding to VI-VII of low magnesia and potassium content (and therefore of roman tradition and produced with natron) near in composition (but not exactly identical) to the "Levantine I" group of roman glass (*i.e.* when plotted in a CaO vs Al₂O₃ diagram). The rest of the glass can be interpreted as the product of fusion of silica sands with a flux of vegetal origin (ash of halophytic plants, widespread in the marsh sector of Roses bay. Although most of the glass fragments are uncolored, two glass fragments of blue and greenish-blue color take this pigmentation due to the presence of little amounts of cobalt. Another greenish-blue colour glass fragment is due to the coexistence of high contents of iron and copper (a well-known colour recipe since - at least - XIII century).

Glasses containing copper slag for ceramic glazes

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Abstract

Large quantities of waste materials such as copper slag are produced as a by-product of industrial operations. The extraction of copper from sulphide ores is usually carried out within a pyrometallurgical process route, which involves the mining activities and concentration of the ore often via flotation followed by smelting and refining operations to produce pure copper metal [1]. During smelting, an oxide-rich phase known as slag forms and is segregated from the copper-matte (sulphide) phase. Disposal of such large quantities of copper slag often presents waste management problems since copper slag is classified as hazardous materials because it contains heavy metals. The aim of the present work is the reuse and valorization of copper slag as glazed coatings for ceramic substrates. The copper slag was previously characterized in terms of X-ray diffraction (XRD), X-Ray fluorescence analysis (XRF), particle size distribution and hot stage microscopy (HSM). The XRF results show that the slag is characterized by significant levels of iron zinc and silicon, while the XRD patterns suggest that the powder is vitreous with some crystalline peaks. Finally the HSM of the powder reveals too high T_{sphere} and $T_{\text{hemisphere}}$; which make it not useful for the selected ceramic application. For this reason, the slag powder was mixed with two different waste glasses and sodium carbonate in order to promote the decrease of the temperature of interest and to facilitate the melting conditions. The batches were mixed, melted and quenched in water to obtain frits. The frits, which exhibited lower T_{sphere} , $T_{\text{hemisphere}}$ and T_{flow} , were used to prepare glazes for ceramic tile coatings. The final glazes were characterized by means X-ray diffraction (XRD), Color Hunter parameter (L, a, b) and chemical properties.

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Alumina/alumina La-glass composites for dental prosthetic applications

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Abstract

The present work is focused on the development of glass frits optimized for the infiltration of porous Al₂O₃ composite preforms. Chopped fiber in alumina glass composites were previously developed as innovative material for all ceramic dental prosthetic solutions such as crowns, bridges, and fixed partial dentures. The process was effective for obtaining dense, strong, net shape ceramics. Glass compositions belonging to lanthanum silicate borate systems (named La-glasses) have been considered and synthesized to reinforce and confer an aesthetic appearance. Through a Design of Experiments (DoE) approach, fifteen formulations of different raw materials (input factors) were produced using a “mixture design”. The formulations were melted and quenched in water at room temperature to obtain the frits. The frits that showed lower T_{flow} were used for the glass infiltration of Al₂O₃ to obtain Al₂O₃/La-glass samples. The frits were dispersed in water and applied as a slip on the surface of Al₂O₃ porous surface. The slip coated specimens were heated from room temperature to 1200 °C. During this thermal process the La glass frits melts and diffuses from the surface deep inside the alumina composite. The frits and the glass infiltrated samples were characterized through X-Ray diffraction (XRD), differential thermal analysis (DTA), hot stage microscope (HSM), Color Hunter parameters (L, a, b), and scanning electron microscopy (SEM). The flow temperatures (T_{flow}), obtained from the HSM, and the L parameter values were analyzed by statistical methods to obtain two models, which describe the relationships between the formulation factors and these two properties of interest. The frit composition along with the sintering parameters plays an important role to achieve zero porosity, and consequently good mechanical properties. The generation of compressive residual stress on the surface, improves the mechanical properties of the ceramics. Eventually it will seal and oppose to fine surface cracks produced during the sintering and machining process of the alumina preform.

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