

AperTO - Archivio Istituzionale Open Access dell'Università di Torino

Micro-PIXE Determination Of Zr In Rutile: An Application To Geothermometry Of High-P Rocks From The Western Alps (Italy)

This is the author's manuscript

Original Citation:

Availability:

This version is available <http://hdl.handle.net/2318/27849> since 2017-06-02T22:20:10Z

Published version:

DOI:10.1002/xrs.1048

Terms of use:

Open Access

Anyone can freely access the full text of works made available as "Open Access". Works made available under a Creative Commons license can be used according to the terms and conditions of said license. Use of all other works requires consent of the right holder (author or publisher) if not exempted from copyright protection by the applicable law.

(Article begins on next page)



UNIVERSITÀ DEGLI STUDI DI TORINO

This is an author version of the contribution published on:

Questa è la versione dell'autore dell'opera:

*VAGGELLI G., BORGHINI A., CALUSI S., COSSIO R., GIUNTINI L. & MASSI M. (2008):
Micro-PIXE Determination of Zr in Rutile: An application to geothermometry of high-
P rocks from the Western Alps (Italy).*

X- Ray Spectrometry, 37, 146-150

The definitive version is available at:

La versione definitiva è disponibile alla URL:

<http://onlinelibrary.wiley.com/doi/10.1002/xrs.1048/pdf>

Micro-PIXE Determination Of Zr In Rutile: An Application To Geothermometry Of High-P Rocks From The Western Alps (Italy)

Gloria Vaggelli¹, Alessandro Borghi², Silvia Calusi³, Roberto Cossio², Lorenzo Giuntini³ and Mirko Massi³

1)CNR- Istituto di Geoscienze e Georisorse, Via V. Caluso, 35, Torino, Italy. vaggelli@igg.cnr.it

2)Dipartimento di Scienze Mineralogiche e Petrologiche, Via V. Caluso, 35, Torino, Italy.

3)Dipartimento di Fisica – INFN Via Sansone 1, Sesto Fiorentino, Firenze, Italy

Abstract

The Western Alps of Northern Italy mostly consist of lithotectonic units which re-crystallised and were metamorphosed at high depth in a subduction zone. During their exhumation to shallow crustal levels, however, the high pressure mineral assemblages were pervasively re-equilibrated under low pressure conditions, making difficult to estimate the metamorphic thermal peak.

Rutile [TiO₂] is a typical high-pressure mineral, occurring as relict phase in low-P re-equilibrated metamorphic rocks. Recent studies of minor element abundances in metamorphic minerals suggest that, in thermodynamic systems buffered by the occurrence of quartz and zircon in the rock, Zr content in rutile is a temperature-dependent function that can be modelled quantitatively.

An application of rutile Zr-geothermometer to continental and oceanic rocks of the Western Alps, pervasively re-equilibrated under low-P conditions, is presented.

The selected rutile crystals were analysed at the external scanning proton microprobe facility, placed on a beam line of the new 3MV Tandetron accelerator at the LABEC laboratory of INFN in Florence. A 3 MeV proton microbeam with ~10 micrometer spatial resolution and beam current of 1-2 nA was used. The PIXE spectra and maps were processed by Geopixe software package. Micro-PIXE analyses allowed determining the concentration and the distribution of Zr and other trace elements as Nb and Fe.

The performed Zr-rutile thermometric estimates allowed to better constraining the metamorphic T conditions suffered by Alpine metamorphic rocks with respect to phase relations and conventional geothermometry, indicating that determination of Zr concentration in rutile by micro-PIXE technique is an useful tool to reconstruct metamorphic events suffered by orogenic chains.

The continental units, outcropping in separate zones of Western Alps, show two slightly different thermal peaks ($T_{\text{mean}}=530 \pm 10$ and $T_{\text{mean}}=555 \pm 10$ °C) for the same metamorphic event. The oceanic units provide T_{mean} estimates of 575 ± 10 °C slightly higher than the continental units.

Keywords: Micro-PIXE, Rutile, Zr-geothermometer, Western Alps.

INTRODUCTION

The determination of major and trace elements in mineral phases has long been regarded as a useful tool in understanding petrologic processes as they can be used to reconstruct equilibrium and pressure – temperature conditions of crystallization and growth [1]. However, at high temperature major element growth zoning may be significantly modified by intra-crystalline diffusion [2]. Consequently, the study of distribution of trace element (i.e., from a geological perspective, those occurring in abundance < 1000 ppm) is fundamental because they are less susceptible to diffusion processes induced by temperature variations [3].

Analytical techniques as Secondary Ion mass Spectrometry (SIMS) [4], Laser Ablation - Inductively Coupled Plasma - Mass Spectrometer (LA-ICP-MS) [5, 6], Proton Induced X-Ray Emission microanalysis (micro-PIXE) [7,8] and synchrotron X-ray fluorescence microanalysis (micro-SRXRF) [9], with a detection limit in the ppm range, allow the determination of trace element concentrations in single crystals by in – situ analysis.

In very recent years two geothermometers, based on Zr concentration in rutile have been developed [10,11], permitting far more precise temperature estimates of metamorphic rock crystallisation under high-pressure condition. Indeed, rutile [TiO_2] is a typical high-pressure accessory mineral in most metamorphic rocks belonging to metapelite and metabasite chemical systems [12]. In buffered systems by quartz [SiO_2] and zircon [ZrSiO_4] occurrence, Zr content in rutile results temperature dependent but not pressure dependent [10, 11]. In this paper, the Zr-geothermometers are applied to rutile crystals coming from various geological units of Western Alps (Italy; Fig. 1) which represent a segment of the Alpine-Himalayan orogenic chain associated to the closure of the Western Tethyan Ocean.

The Western Alps consist of geological units which suffered a high-P (ca. 15-20 kbar) and relatively low-T (500-550 °C) metamorphism in Cretaceous-Eocene times (from ca. 60-65 Ma to 40-45 Ma) [13, 14]. Ultra High Pressure metamorphic conditions ($P > 35$ kbar; $T > 700$ °C) are also recorded in a continental crust unit (Brossasco-Isasca Unit of Dora Maira massif) [15] and in the oceanic ophiolite unit of Lago di Cignana ($P > 32$ kbar; T ca. 600 °C) [16].

This metamorphic event occurred at high depth in a subduction zone, during the closure of the Tethyan ocean and was followed by a partial re-equilibration process at lower pressure conditions (ca. 5 kbar), during exhumation at shallower crustal levels [17, 18]. During this second metamorphic event, the high pressure mineral assemblages were pervasively re-equilibrated.

T estimates in geological unit marked by high pressure events and followed by retrograde processes can be determined with difficulty using conventional geothermometers, based on the cationic exchange ratio between Fe/Mg-bearing minerals [1].

The purpose of this paper is to present the first systematic application of the Zr-in-rutile thermometer to eclogite - facies rocks from the Western Alps (Italy).

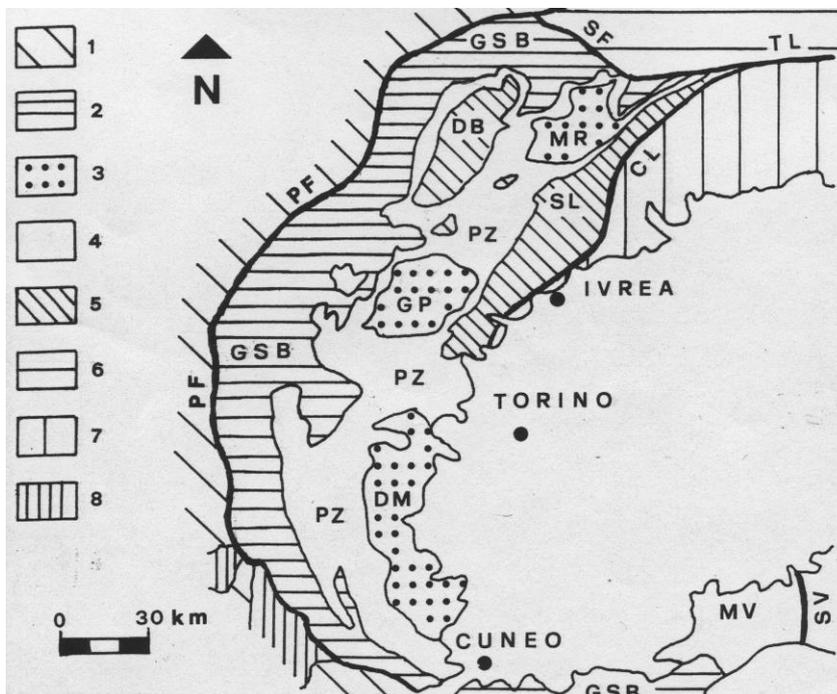


Fig. 1 - Tectonic sketch map of the Western Alps. 1) Helvetic Domain, 2 - 4: Penninic Domain. 2) Grand St. Bernard Nappe (GSB), 3) Internal Penninic Crystalline Nappes (MR = Monte Rosa nappe; GP = Gran Paradiso nappe; DM = Dora-Maira nappe), 4) Metamorphic Oceanic units (PZ = Piedmont Zone; MV = Voltri Massif), 5) Austroalpine Domain (DB = Dent Blanche nappe; SL = Sesia-Lanzo Zone), 6) Lower Penninic nappes of the Ossola - Ticino area, 7) South-alpine Domain, 8) Allocthonous Flysch of Cretaceous to Eocene age. PF = Penninic thrust front; SF = Simplon fault; CL = Canavese Line; TL = Tonale Line; SV = Sestri-Voltaggio Line.

EXPERIMENTAL

The external proton microprobe facility, placed on a beam line of the new 3MV Tandetron accelerator at the LABEC laboratory of INFN in Florence [19] was used for trace elements determination.

The Tandetron accelerator options are: an optical micro-camera system which shows areas of about 1 mm² on a TV screen; a combined beam-scanning and sample-movement up to 25x25 mm²; Si(Li) and Ge detectors; a Backscattering Spectroscopy (BS), and a Particle Induced Gamma-ray Emission (PIGE) equipment [20].

The analytical conditions used are: proton beam energy of 3 MeV; proton beam current of 1-2nA; target (2 mm out of the exit window); He flow; spot size of ~10 µm FWHM; acquisition time of 30 min at counts rate of about 2000 cps, Si(Li) solid angle of 0.1 msr, absorber layer for Ge: Mylar foils 900 µm thick + Al foils 200 µm thick. The detectors were positioned at ~ 135° to the beam. Beam current monitoring: Si X-ray yield of ~ 500 counts per nC. The PIXE analytical spectra and maps were processed by Geopixe II software package [21, 22] <http://www.nmp.csiro.au/GeoPIXE.html>.

With these analytical conditions, the standard deviation (δ) of Zr content as well as the minimum detection limit (MDL) is < 10 ppm. As micro-PIXE analysis is mostly a standardless analytical method, the measured Zr contents have been tested measuring with the same protocol the Zr content in a rutile reference with a well-constrained crystallisation temperature.

For the Zr-geothermometer calibration of [11] it implies a precision better than ± 10 °C at a nominal T of 500 °C. Therefore, it is possible to discriminate temperature estimates for metamorphic peaks of geological units which suffered from similar metamorphic evolution.

RESULTS AND DISCUSSION

The selected rocks comes from well-known geological areas of Western Alps (continental crust: Monte Rosa and Dora Maira Nappes [23, 24, 25] oceanic crust: Piedmont Zone [26, 27]; Fig. 2), where the evolution of pressure and temperature with time is independently constrained by petrological data. In particular, these geological units are characterised by a first metamorphic imprinting of high pressure (12-14 kbar) and low temperature (500-550°C) followed by a second partial re-equilibration event at lower pressure conditions [23, 25, 27].

In these rocks, rutile represents a relict mineral assigned to the high-pressure mineralogical assemblage. Therefore, the temperature estimates based on rutile chemistry can be ascribed to the first high-P metamorphic event. In addition, as the Zr-geothermometer is not pressure dependent,

the temperature estimates can be directly referred to the metamorphic peak without the knowledge of the baric conditions.

Both rutile inclusions in garnet porphyroblasts (Fig. 2a) and rutile grains widespread in the metamorphic-foliated matrix (Fig. 2b) have been analysed. Rutile occurs as very small grains, isolated or in aggregates, ranging from tens to some hundreds micrometers.

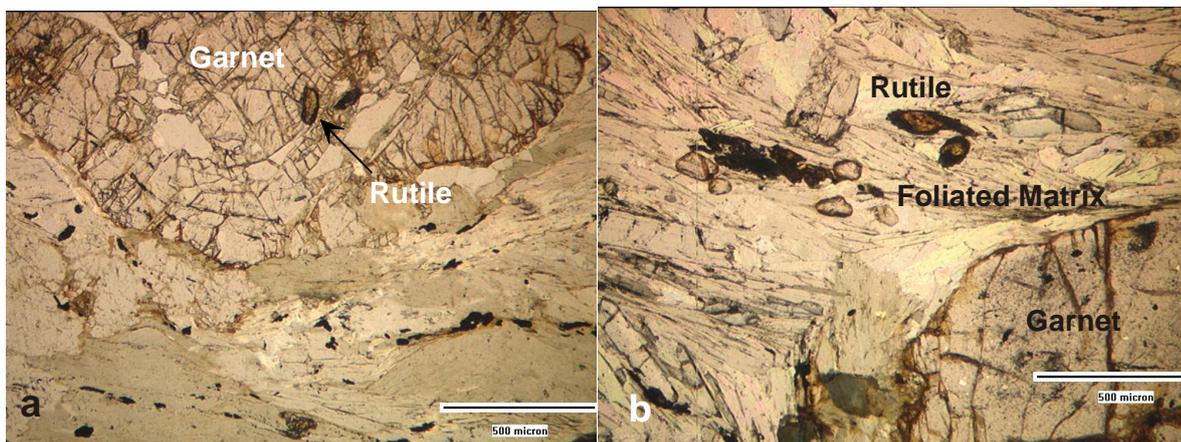


Fig. 2: a – Rutile inclusion in garnet porphyroblast, Light polarized microscope; b – Rutile grain occurring in the foliated matrix, Light polarized microscope.

Before attempting to calculate the temperatures, the nature of Zr distribution within individual rutile grains from the selected samples has to be assessed. Therefore the analyses were performed as maps covering the entire mineral size (Fig. 3). Major (Ti) and trace element (Zr, Fe, Nb) X-ray maps were processed on several samples.

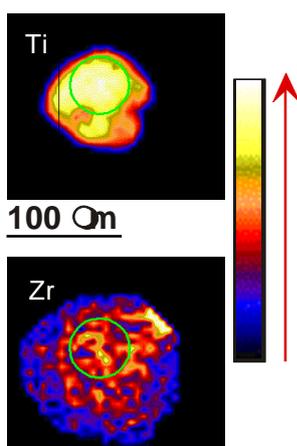


Fig. 3 – X-ray maps of Ti and Zr distribution in rutile from Monte Rosa metapelite rock. The circle indicates the selected area for Zr content determination.

Micro-PIXE analyses allowed to determine the presence and the distribution of Zr and other trace elements (mostly Nb and Fe; Fig. 4).

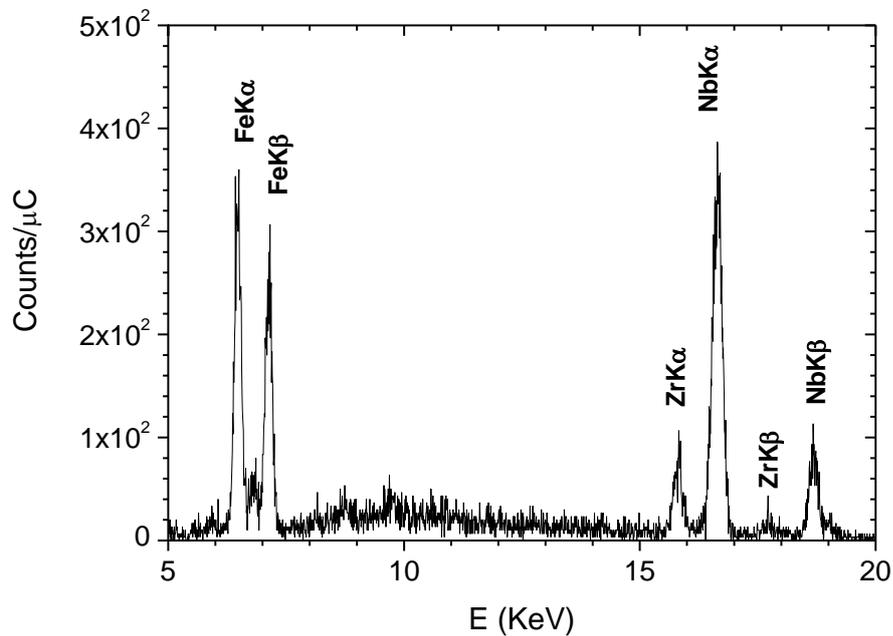


Fig. 4 – PIXE spectrum of rutile from Monte Rosa metapelite rock.

The analytical Zr data, used for the T estimates, come from rutile portions characterized by a homogeneous Zr distribution. The analytical oscillation into a single selected rutile area cannot be interpreted as statistically meaningful and it is considered homogeneous within analytical uncertainty.

The PIXE analytical spectra extracted from the selected mapped areas (ca. 50 μm) were quantitatively processed by Geopixe. Zr contents of representative analyzed rutiles are summarized in Table 1.

Applying the experimental Zr-geothermometer calibration of Watson et al. [11] a precision better than ± 10 °C for a nominal T of 500 °C is reached. Therefore, it is possible to discriminate temperature estimates for metamorphic peaks of geological units (portions/blocks) which suffered from similar metamorphic evolution.

For the continental units two main Zr distribution peaks have been determined. The first ranges between 90-100 ppm (sample 1÷) which corresponds to a T range 550÷560 °C and is related to rutiles from North-West units of Monte Rosa Massif.

The second one corresponds to a Zr variation from 55 to 70 ppm (sample 9÷14) which corresponds to a T range 525÷535 °C and is referred to rutiles coming from Dora Maira Massif outcropping in the central portion of Western Alps.

Therefore, for these continental units outcropping in separate zones of Western Alps, two slightly different thermal peaks for the same metamorphic event have been calculated and, the T estimates, obtained with conventional geothermometers suggesting T range of 500-550 °C, are now better constrained.

Moreover, higher Zr values (320-390 ppm; sample 15÷17) have been measured in rutile inclusions, occurring in relict cores of multi-stage garnet porphyroblasts, which provide T estimates > 600°C. These temperature, incompatible with respect to Alpine metamorphic evolution, may be inferred to the pre-alpine metamorphic event of Variscan age (ca. 350 Ma) developed under amphibolite-facies conditions [28].

The oceanic units are characterised by Zr contents ranging between 105 and 140 ppm, (sample 18÷20) implying T estimates of 565÷585 °C for the alpine metamorphic peak, slightly higher than the continental units. This result may be interpreted as a difference either in the alpine metamorphic evolution and/or in the bulk-rock composition.

Table 1 – Representative Zr concentration (expressed as ppm) and temperature estimates (T expressed as °C according to [11] calibration) for representative analyses of Monte Rosa (an. 1-8) and Dora Maira (Sample 9÷14) units. Pre-alpine rutile included in garnet porphyroblast (Sample 15÷17) and from metabasites of the oceanic crust (Sample 18÷20) are also reported.

Sample	Rock-type	Zr	MDL	δ	T
1	micaschist	95	10	6	557
2	micaschist	88	10	5	552
3	micaschist	99	9	6	560
4	micaschist	92	8	5	555
5	micaschist	96	6	4	558
6	micaschist	89	6	3	553
7	micaschist	93	7	4	556
8	micaschist	86	6	4	551
9	micaschist	68	8	4	536
10	micaschist	62	7	4	530
11	micaschist	59	5	3	527
12	micaschist	55	5	2	522
13	micaschist	74	10	5	541
14	micaschist	67	9	5	535
15	micaschist	358	9	9	657
16	micaschist	323	8	8	648
17	micaschist	383	8	8	663
18	metabasite	123	9	7	575

19	metabasite	140	8	6	584
20	metabasite	104	9	7	563

CONCLUSIONS

In conclusions, the performed Zr-rutile thermometric estimates allowed to better constrain the metamorphic history and T conditions suffered by Alpine metamorphic rocks, with respect to phase relations and conventional geothermometry. Therefore, the determination of Zr concentration in rutile by micro-PIXE technique is a useful tool to reconstruct metamorphic peak temperature of high-P metamorphic events suffered by orogenic chains.

- Indeed, the continental units outcropping in separate zones of Western Alps, show two slightly different thermal peaks ($T_{\text{mean}}=530 \pm 10$ and $T_{\text{mean}}=555 \pm 10$ °C) for the same metamorphic event. The T estimates, obtained with conventional geothermometers suggesting T range of 500-550 °C, are now better constrained.
- The oceanic units provide T_{mean} estimates of 575 ± 10 °C for the alpine metamorphic peak, slightly higher than the continental units. This result may be interpreted as a difference in the alpine metamorphic evolution of oceanic crust with respect to continental one.

Acknowledgements

This study was carried out with the financial support of MIUR (Italy) and CNR-IGG U.O of Torino (Italy). P.A. Mandò and G. Pratesi (University of Firenze) are thanked for providing PIXE facility and Geopixe licence, respectively.

REFERENCES

- [1] Spear FS. Relative thermobarometry and metamorphic P-T paths. In *Evolution of metamorphic belts*, Daly JF, Cliff RA, Yardley BWD (eds) Geological Society of London, Special Publication, 1989; 43: 63-81.
- [2] F.P. Florence FP, Spear FS. *Earth and Planetary Science Letters* 1995; 134: 329-340.
- [3] Schwandt CS, Papike JJ, Shearer CK. *American Mineralogist* 1996; 81: 1195-1207.
- [4] Hickmott DD, Shimizu N. *Contrib. Mineral. Petrol.* 1990; 104- 619.
- [5] Norman MD, Griffin WL, Pearson NJ, Garcia MO, O'Reilly SY. *Journal of Analytical Atomic Spectrometry* 1998; 13, 477-482.
- [6] Gao S, Xiaomin L, Yuan H, Hattendorf B, Günther D, Chen L, Hu S. *Geostandards Newsletter* 2002; 26, 181-196.
- [7] Ryan CG, Cousens DR, Sie SH, Griffin WL, Suter GF. *Nucl Instr and Meth B* 1990; 47: 55-71.

- [8] Sie, SH. *Nucl Instr and Meth B* 1993; 75: 403-410
- [9] Koepke J, Falkenberg G, Rickers K, Dietrich O. *Eur. J. Min.* 2003; 15: 883-892.
- [10] Zack T, Moraes R, Kronz A. *Contrib. Mineral. Petrol* 2004; 148: 471-488.
- [11] Watson EB, Wark DA, Thomas JB. *Contrib. Mineral. Petrol.* 2006; 151: 413-433.
- [12] Bohlen SR, Wall WJ, Boettcher AL. *American Mineralogist* 1983; 86: 10049-1058.
- [13] Ernst WG, Dal Piaz GV. *American Mineralogist* 1978; 63: 621-640.
- [14] Fry N, Barnicoat AC. *Journal of Geological Society of London* 1987; 144: 653-659.
- [15] Chopin C. *Contrib. Miner. Petrol.* 1984; 86: 107-118.
- [16] Reinecke T. *Eur. J. Mineral.* 1991; 3: 7-17.
- [17] Borghi A, Compagnoni R, Sandrone R. *Eclogae Geol. Helv.* 1996; 89: 345-367.
- [18] Droop GTR, Lombardo B, Pognante U. Formation and distribution of eclogite facies rocks in the Alps. In *Eclogite Facies Rocks*, Carswell DA (ed). Blackie: New York, 1990; 225-259.
- [19] Massi M, Giuntini L, Chiari M, Gelli N, Mandò PA. *Nucl.Instr. and Meth.B* 2002; 190: 276-282.
- [20] Giuntini L, Massi M, Calusi S. *Nucl.Instr. and Meth.A* 2007; 576: 266-273
- [21] Ryan CG, Van Achterbergh E, Mark G, Yeats CJ, Drieberg SL, McInnes BM, Win TT, Cripps G, Suter GF, *Nucl. Instr. Meth.* 2002; 188: 18-27.
- [22] Ryan CG, Van Achterbergh E, Yeats CJ, Win TT, Cripps G. *Nucl. Instr. Meth. B.* 2002; 189: 400-407.
- [23] Pognante U, Sandrone R. *Mineralogy and Petrology* 1989; 40: 57-71.
- [24] Engi M, Sherrer NC, Burri T. *Schweiz. Mineral. Petrogr. Mitt.* 2001; 81: 305-328.
- [25] Chopin C, Moniè P. *Contrib. Mineral. Petrol.* 1984; 87: 388-398.
- [26] Bucher K, Fazis Y, De Capitani C, Grapes R. *American Mineralogist* 2005 ; 90 : 821-835.
- [27] Cartwright I, Barnicoat AC. *J. Metamorph. Geol.* 2002; 20: 263-281.
- [28] Sandrone R, Borghi A. *Eur. J. Miner.* 1992; 4: 465-474.