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

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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 of blueschist and eclogite facies were pervasively re-equilibrated under low pressure conditions, making it difficult to estimate the metamorphic peak P-T conditions.
Rutile [TiO_2] 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 blueschist and eclogite facies rocks of the Western Alps, pervasively re-equilibrated under low-P conditions, is presented in this contribution.
Rutile crystals occurring in metapelites 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 dedicated software package.
The performed Zr-rutile thermometric estimates allowed to better constrain the metamorphic history and T conditions suffered by Alpine metamorphic rocks, 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 peak temperature of high-P metamorphic events suffered by orogenic chains.

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. In very recent years two geothermometers, based on Zr concentration in rutile have been developed [3, 4], 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. In buffered systems by quartz [SiO_2] and zircon [$ZrSiO_4$] occurrence, Zr content in rutile results temperature dependent but not pressure dependent. In this paper, the Zr-geothermometers are applied to rutile crystals coming from various geological units of Western Alps (Italy), which suffered high-P and low-T metamorphic conditions in the Cretaceous age (ca. 60-65 Ma).

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 was used.

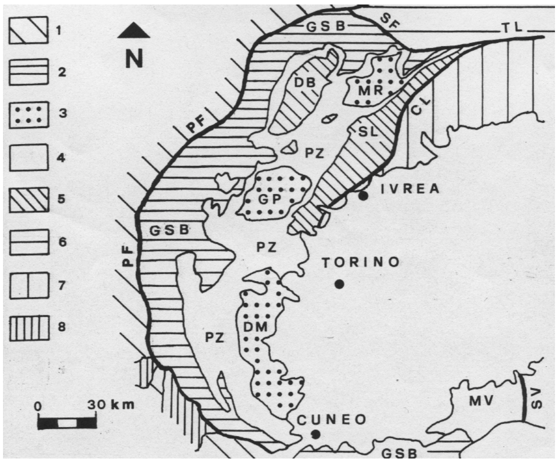

Fig. 1 - Tectonic sketch map of the Western Alps. 1) Helvetic Domain, 2 - 4: Penninic Domain. 2) Grand St. Bernard Nappe (GSB), 3) Internal Penninic Crystalline Nappes (MR = Monte Rosa nappe; GP = Gran Paradiso nappe; DM = Dora-Maira nappe), 4) Metamorphic Oceanic units (PZ = Piedmont Zone; MV = Voltri 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.

The Tandetron accelerator options are: an optical microcamera system which shows areas of about 1 mm^2 on a TV screen; a combined beam-scanning and sample-movement up to 25x25 mm^2; Si(Li) and Ge detectors; a Backscattering Spectroscope (BS), and a Particle Induced Gamma-ray Emission (PIGE) equipment.

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 csp, 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 [5,6] http://www.nmp.csiro.au/GeoPIXE.html.

With these analytical conditions, the standard deviation of Zr content as well as the Limit of Detection is about 10 ppm. For the Zr-geothermometer calibration of [4] 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 studied rutile samples occur in metamorphic rocks from blueschist to eclogite facies rock belonging to both continental and oceanic units of the Western Alps (Italy).

Both rutile inclusions in garnet porphyroblats (Fig. 1a) and rutile grains widespread in the metamorphic-foliated matrix (Fig. 1b) have been analysed. Rutile occurs as very small grains, isolated or in aggregates, ranging from tens to some hundreds micrometers.

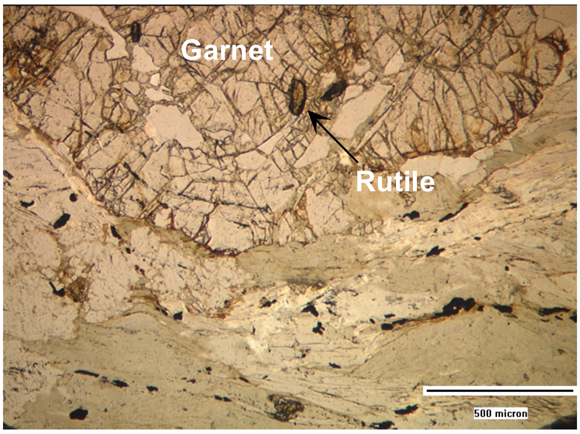

Fig. 2a – Rutile inclusion in garnet porphyroblast, Light polarized microscope

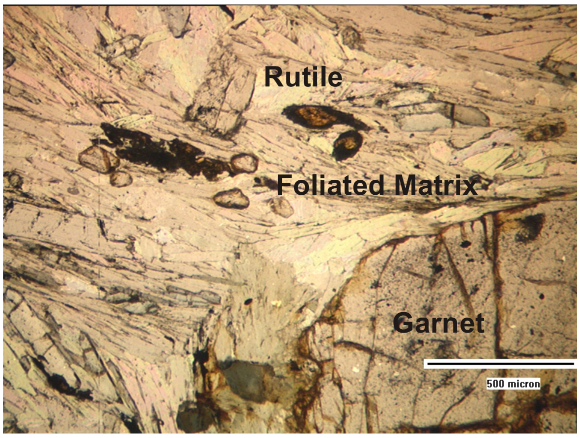

Fig. 2b – Rutile grain occurring in the foliated matrix, Light polarized microscope.

The selected rocks comes from well-known geological areas of Western Alps (continental crust: Monte Rosa and Dora Maira Nappes, oceanic crust: Piedmont Zone; Fig. 2), where the evolution of pressure and temperature with time is independently constrained by petrological data [7]. 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.
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. This new geothermometer represents a quite improvement for T estimates in geological unit marked by high pressure events, where peak temperature can be determined with difficulty using conventional geothermometers, based on the cationic exchange ratio between Fe/Mg-bearing minerals, as these mineralogical phases often suffered from diffusive retrograde processes.
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).

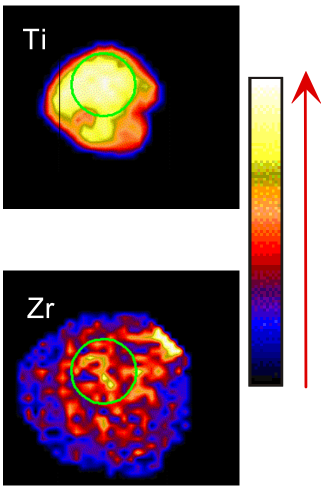

Fig. 3 – X-ray maps of Ti and Zr distribution in rutile from Monte Rosa metapelite rock. The circle indicates the selected area for Zr content determination.

Consequently, the analytical Zr data, used for the T estimates, come from rutile portions characterized by a homogeneous Zr distribution. Micro-PIXE facility allowed to determined the presence of Zr and other high field strength trace elements (mostly Nb) whose petrological importance in rutile is still not well-defined (Fig. 4).
For the continental units two main Zr distribution peaks have been determined. The first ranges between 88-99 ppm 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 68 ppm 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. Zr contents of representative analyzed rutiles are summarized in Table 1.

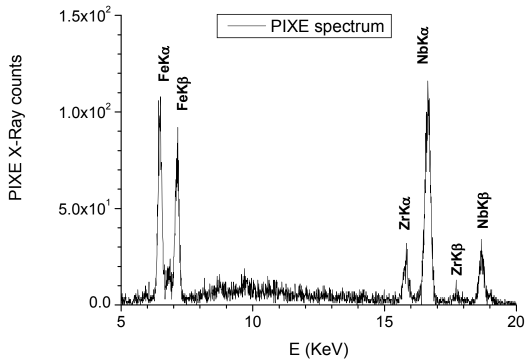

Fig. 4 – PIXE spectrum of rutile from Monte Rosa metapelite rock.

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	68	8	4	536
8	micaschist	62	7	4	530
3	micaschist	59	5	3	527
10	micaschist	55	5	2	522
11	micaschist	74	10	5	541
12	micaschist	67	9	5	535
13	micaschist	93	7	4	556
14	micaschist	86	6	4	551
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

Table 1 – Representative Zr concentration (expressed as ppm) and temperature estimates (expressed as °C and according to [4]) for representative analyses of Monte Rosa (an. 1-6) and Dora Maira (Sample 7÷14) unit. Pre-alpine rutile included in garnet porphyroblast (Sample 15÷17) and from metabasites of the oceanic crust (Sample 18÷20) are also reported.

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 have been measured in rutile inclusions, occurring in relict cores of multi-stage garnet porphyroblasts, which provide T estimates > 600°C. These temperature, incompatible 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.
The oceanic units are characterised by Zr contents ranging between 104 and 140 ppm, 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.
As micro-PIXE analysis is mostly a standarless analytical method, the measured Zr contents have been finally tested both using a rutile reference with a well-constrained crystallisation temperature and measuring Y content in host garnets and applying the corresponding Y-geothermometer [8]. All our results seem to provide T estimates consistent with Y-geothermometer.
In conclusions, the performed Zr-rutile thermometric estimates allowed to better constrain the metamorphic history and T conditions suffered by Alpine metamorphic rocks, respect to phase relations and conventional geothermometry, indicating that determination of Zr concentration in rutile by the micro-PIXE technique is a useful tool to reconstruct metamorphic peak temperatures of high-P metamorphic events suffered by orogenic chains.

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