 **PERIODICO di MINERALOGIA**
established in 1930

An International Journal of

*MINERALOGY, CRYSTALLOGRAPHY, GEOCHEMISTRY,
ORE DEPOSITS, PETROLOGY, VOLCANOLOGY*

and applied topics on *Environment, Archaeometry and Cultural Heritage*

Studying metamorphic microstructures: a brief insight on modern methodological approaches

ALESSANDRO BORGHI^{1,2*} and RICHARD SPIESS^{3,4}

¹ Dipartimento di Scienze Mineralogiche e Petrologiche, Via Valperga Caluso 37, 10125 Torino, Italy

² Istituto di Geoscienze e Georisorse - Sezione di Torino Via Valperga Caluso 35, 10125 Torino, Italy

³ Dipartimento di Mineralogia e Petrologia, Corso Garibaldi 37, 35137 Padova, Italy

⁴ Istituto di Geoscienze e Georisorse - Sezione di Padova, Corso Garibaldi 37, 35137 Padova, Italy

ABSTRACT. — Microstructures evolve in response to processes that rocks undergo during their residence time in the Earth crust and mantle. For a thorough understanding of microstructures all their critical aspects need to be analysed. Much of the recent advances in the comprehension of microstructures and the interrelated processes is linked to the advent of modern instrumental equipments as electron and proton microprobes (EMPA, mPIXE) and to novel analytical techniques as electron backscatter diffraction (EBSD) and orientation contrast imaging (OC). In this review we highlight the basic concepts and the potential applications of such modern analytical tools in microstructural analysis of metamorphic rocks.

RIASSUNTO. — Le microstrutture delle rocce metamorfiche sono le risposte ai processi ai quali le rocce sono sottoposte durante la loro permanenza nella crosta e nel mantello. Una completa comprensione delle microstrutture richiede spesso un'analisi di tutti gli aspetti critici, e molti dei recenti progressi nel meglio intendere le microstrutture sono stati raggiunti perché nuove tecnologie analitiche hanno consentito di evidenziare le interrelazioni tra microstrutture e i processi petrogenetici e dinamici. In questo articolo

affrontiamo in modo conciso le basi concettuali e le potenzialità applicative di alcune nuove tecniche analitiche quali la microsonda protonica (mPIXE), la diffrazione degli elettroni retrodiffusi (EBSD) e l'acquisizione d'immagine per contrasto d'orientazione cristallografica (OC).

KEY WORDS: *microstructures, mPIXE, EBSD, OC, EMPA, trace element distribution*

INTRODUCTION

Microstructures evolve in response to processes that rocks undergo during their residence in the Earth crust and mantle, preserving evidence of their mechanisms. Consequently, microstructures record information on the aspects of reaction kinetics, information on nucleation, growth and deformation mechanisms, or information on kinematics.

Deciphering microstructures requires a thorough analysis of all their aspects. These range from the geometrical shape and mutual arrangement of mineral phases, the presence and form of compositional zoning, the

* Corresponding author, E-mail: alessandro.borghini@unito.it

geometrical arrangement and nature of inclusions, the size distribution of mineral phases, the lack or occurrence of a crystallographic preferred orientation, the geometry and structure of grain- and sub-grain boundaries, etc.. The analysis of these characteristics needs appropriate analytical tools, and much of the recent advances in the understanding of microstructures is linked to the advent of modern technical equipments. Ideal technical tools for microstructural studies must be equipped with imaging systems and analytical routines of high spatial resolution, high precision and accuracy and high versatility. Best examples of standard analytical tools for microstructural analysis are the electron microprobe (EMPA) equipped with wavelength dispersive spectrometers (WDS) and the scanning electron microscope (SEM) equipped with energy dispersive spectrometer (EDS) and backscatter electron (BSE) detector. Proton induced microprobes (mPIXE) and SEM based new techniques as electron backscatter diffraction (EBSD) and orientation contrast imaging (OC) are not yet widespread worldwide, but constitute invaluable analytical support for microstructural analysis.

In this review we highlight the use of such modern analytical tools for the understanding of microstructures. Obviously, this paper will be biased by the analytical experience, the personal view of microstructures and the specific research topics of the two authors.

INSTRUMENTAL TECHNIQUES

Electron microprobe and Scanning Electron Microscope

The development of the electron microprobe analyser (EMPA) in the late 1950's (Castaing, 1951) was a giant step in mineralogy, petrology and microstructural analysis, as EMPA enables major and, under particular instrumental conditions, minor element contents of rock forming minerals to be determined in polished thin sections without destruction.

The much more versatile scanning electron microscope (SEM) was actually developed before the EMPA, but only the arrival of the energy dispersive X-ray analyser (EDS), which enables quick qualitative chemical analysis and thus mineral identification, brought eventually the breakthrough of the SEM in microstructural analysis (Potts *et al.*, 1995; Reed, 1996).

Both EMPA and SEM consist of an electron optical column used to collimate an electron beam and to focus it on a sample contained in the sample chamber. The spatial resolution of EMPA and SEM is controlled by the electron beam diameter (<1-5 mm), and the interaction of the sample with the incident electron beam produces a variety of signals. Among these different signals backscattered electrons (BSE) and X-rays collected at different detectors are widely used for modern microstructural analytical techniques.

Backscatter electron acquisition images

BSE images show real compositional variations within the analysed objects. BSE images are therefore particularly informative for microstructural analysis as they reveal the distribution of distinct mineral phases within complex fine grained microstructures, and can provide qualitative information on major element distribution within minerals. Minerals imaged in BSE mode show different grey shades, depending upon their average atomic number. Most silicate minerals have low average atomic numbers and appear dark grey in BSE images, whereas ore minerals that have higher average atomic numbers are light grey to white.

X-ray maps

Two-dimensional X-ray compositional maps (XRM) allow to determine carefully the chemical zoning of any material analysed in a microprobe or an SEM. Semi-quantitative X-ray maps are now routinely produced for single elements using different commercial EDS microanalytical systems (Ikeda, 1993; Spear, 1993). Recently, techniques for quantitative X-

ray compositional EDS maps have been developed (Reed, 1995).

WDS quantitative maps are obtained in a microprobe by a network of spot peak counts using a remote stage movement and the spectrometers at fixed positions. The result is a set of numerical matrices, corresponding to the number of elements selected, and containing the net X-ray counts measured at their peak positions, after having subtracted the background counts measured on reference standards at the same analytical conditions.

The results are exported to a PC and then corrected using a dedicated ZAF program (Cossio and Borghi, 1998). The EDS and WDS ZAF correction programs allow to calculate the cationic formula of the mineral on stoichiometric basis, and reject all analytical points which do not respond to the stoichiometric constrains of the selected minerals. The final matrices can be imported into commercial spreadsheets and graphic programs and thus transformed in false-coloured or grey-scale two-dimensional maps, where each colour or grey shade represents a selected concentration range for the analysed element. Additionally, the end-members of the analysed minerals may be displayed as a two-dimensional quantitative map.

Electron backscatter diffraction and orientation contrast imaging

Electron backscatter diffraction (EBSD) and orientation contrast (OC) imaging are novel SEM-based analytical techniques (Dingley 1984; Randle 1992; Day 1993; Prior *et al.*, 1996; 1999) that provide quantitative and qualitative crystallographic information on any crystalline material, irrespective of whether it is optically opaque or isotropic. In Italy both techniques are accessible at the Department of Mineralogy and Petrology of Padova. They can be applied to crystalline material of very fine grain size, since their spatial resolution is on the order of the 1-mm scale. OC images relate to signal contrasts originating from mineral phases showing different crystallographic orientation domains (e.g. sub-grains), whereas

EBSD gives fully quantitative information on the absolute crystallographic orientation of every orientation domain, and on the degree of crystallographic misorientation between domains. The principles of both techniques are briefly outlined below, for a detailed introduction the reader is referred to Prior *et al.*, (1999).

Electron backscatter diffraction. When in an SEM an electronic beam interacts with a crystalline material, then elastically scattered electrons (incident electrons losing little energy) that satisfy the Bragg condition will be diffracted by the lattice planes and may exit the hidden sample. The collection of these backscattered electrons (BSEs) on a phosphor screen results as a network of bands of different intensities (called kikuchi bands). Any of these bands constitutes the projection on the phosphor of a cone of diffracted BSEs that originates from a single lattice plane. Because these diffraction cones have an opening angle close to 180° , the bands corresponding to lattice planes are virtually straight on the phosphor. The intensity of electron diffraction depends on the atomic species that constitute the lattice planes. Therefore, some planes give rise to high intensity diffraction and others to weak diffraction. Intersections of more kikuchi bands result in bright spots on the phosphor screen, and reflect crystallographic zone axes. Crystallographic indexing of any analysed spot is possible, because symmetry elements can be defined directly from the relative position of bands and spots on the diffraction patterns. The quality of the diffraction patterns depends on the crystalline material and on the beam current. Larger beam currents give stronger signals but also correspond to larger probe sizes and therefore reduced spatial resolution. Resolution on the order of 1 μm is possible using a tungsten filament.

Orientation contrast imaging. When in an SEM a crystalline fine grained monomineralic sample is tilted to a high angle relative to the incident electron beam, then variations in the intensity of BSEs collected on a solid-state detector refer to differences in the

crystallographic orientation of the different grains. This effect is known as orientation contrast (OC), crystallographic contrast, or channelling contrast (Joy 1974; Lloyd 1987; Day 1993; Prior *et al.* 1996, 1999). OC images are not quantitative, and the signal intensities revealed as distinct grey shades do not correspond to crystallographic orientation in a simple way. However, sharp changes in grey shades usually correspond to a sharp change in crystallographic orientation (such as a grain boundary or sub-grain boundary), and gradual variations in grey shades usually correspond to gradual variations in crystallographic orientation. Therefore, OC images represent an important base for the quantitative analysis with EBSD. Theoretically, within OC images crystallographic misorientation magnitudes of less than 1° (Prior *et al.*, 2002) can be detected between adjacent orientation domains, and a spatial resolution of less than 1mm is possible depending on the electron emission source.

Secondary ion mass spectrometry and proton induced X-ray emission

Trace elements cannot easily be determined with EMPA and are therefore generally assessed by means of other techniques. For the determination of trace element concentrations on the micron scale two different instruments are potentially suitable: 1) the ion microprobe, or secondary ion mass spectrometer (SIMS), 2) the high resolution proton microprobe (mPIXE).

During ion analysis, the sample surface is bombarded with a beam of focused high-energy ions (generally O^{2-}). This primary ion beam causes the upper atomic layers to be sputtered from the sample. Most of material leaves as neutral atoms or molecules, but a small fraction is ejected as positive or negative secondary ions. These latter are then extracted into a mass spectrometer for energy and mass/charge separation to provide an elemental or isotopic analysis.

In its simplest form, the ion microprobe consists of a source of primary ions, an ion optical column that generates a finely focused primary ion beam, an extraction system which transfers the secondary ion from the surface of the sample to the entrance slit of the mass spectrometer and the mass spectrometer itself. Depending on the polarity of the secondary ion accelerating voltage, either positive or negative ions can be extracted.

Attempts to develop a scheme for quantitative analysis have been hindered by the presence of «matrix effects». The secondary ion intensity of an element in a mineral is not only a function of its concentration but also of the concentration of other elements in the matrix. Therefore, the best way to quantify the ion signals is the empirical approach, which relies on working curves and relative sensitive factors, derived from well-characterized calibration standards.

SIMS detection limits depend upon numerous factors, among which the ionisation potential of the elements, the sputtering rate of the sample, the matrix composition, the presence of interfering ions, the nature of the sample (Ottolini, 2000). However, the detection limits of SIMS are generally very low, on the order of a few tens of ppb or less, up to 1 ppb for LREE. Although this analytical tool is extremely powerful both in terms of detection limit and dwell time, the main disadvantage for microstructural analysis is the dimension of the spot size, which is generally of several tens of μm . For this reason, few papers report analysis performed by SIMS to resolve microstructural problems (e.g. Tribuzio *et al.*, 1995; Franceschelli *et al.*, 2002)

Instead, proton induced X-ray emission microanalysis (micro-PIXE) combines in-situ quantitative determination of trace element concentrations with a high spatial resolution (Fraser, 1990). In addition, micro-PIXE is capable of simultaneous, multielemental analysis, by means of an energy dispersive spectroscopy (EDS) system, with better signal to noise ratio and lower minimum detection limit (MDL) for most elements compared to

EMPA. The major advantage of the proton microprobe mainly lies in its X-ray background, which is lower by several orders of magnitude, leading to MDL around 2 ppm for LILE and HFSE elements. In Italy, two microPIXE facilities are installed, one at the Laboratori Nazionali di Legnaro (LNL) of Istituto Nazionale di Fisica Nucleare (INFN, Padova) and the other at Istituto Nazionale di Fisica Nucleare of Firenze.

In the micro-PIXE of Legnaro (Bollini *et al.*, 1993) a proton beam energy of 2 MeV (Van de Graaf Accelerator), and a proton beam current of 5-8 nA result in a beam of 10 μm diameter, that can be scanned over a 2 x 2 mm² sample area. The system is equipped with an EDS detector.

Because spectra from mineralogical samples are generally dominated by intense major-element lines, a 250 mm thick Al filter is interposed between the sample and the detector. This reduces the intensity of low energy X-rays produced by the major elements, and allows to increase the beam current, so that the detection limits for many trace elements can be improved significantly (Mazzoli *et al.* 2002). The microPIXE analytical spectra are processed by GUPIX dedicated software, developed at University of Guelph - Canada (Maxwell *et al.*, 1989; Campbell *et al.*, 2000).

APPLICATIONS OF NEW TECHNIQUES FOR AN UNDERSTANDING OF MICROSTRUCTURES IN METAMORPHIC ROCKS

Backscatter electron imaging

Corona microstructures are well known in many metamorphic complexes (Messiga & Bettini, 1990; Messiga *et al.*, 1992; Messiga *et al.*, 1995; Borghi *et al.*, 2000). The study of these microstructural features can provide useful information on rates of metamorphic processes and on the geodynamic history of crustal units. Usually, the grain size of these microstructures is too fine to be resolved by

optical microscopy, so that they can only be studied by modern electron beam techniques.

Another example for the invaluable help of SEM based imaging and analytical techniques is shown by Spiess *et al.* (2000) who analysed porphyroblast inclusion trails to determine the interrelationships between metamorphism, deformation and porphyroblast growth. On the basis of geometrical analysis of inclusion trails, episodic porphyroblast growth is usually proposed where porphyroblasts preserve geometrical elements that typically evolve at, or close to, the porphyroblast-matrix interface due to the partitioning of deformation about rigid objects (Bell and Hayward, 1991; Passchier & Speck, 1994). However, unequivocal evidence for episodic porphyroblast growth can only be derived from data indicating that, in coincidence with the geometrical elements outlined above, sudden changes in the intensive variables controlling the metamorphism have occurred. Spiess *et al.* (2000) showed that within an analysed garnet porphyroblast, Fe-Ti solid solution mineral inclusions imaged with the BSE facility in an SEM reveal different reaction microstructures depending on their position within the porphyroblast (Fig. 1). Buddington & Lindsley (1964) have reported that similar reaction microstructures are the result of an increase in oxidation and rate of diffusion. Because the distribution of the microstructures is homogeneous within different garnet growth zones, Spiess *et al.* (2000) have deduced that the oxidation reaction rate of the opaque inclusions was substantially lower than the garnet growth rate. As a consequence, hiatuses in the garnet growth history must have occurred between the evolution from one microstructure to the next. A comparison between the inclusion trail geometry and the microstructural zone boundaries shows a perfect coincidence between these and the sites where inclusion trails become strongly deflected and truncated. This correlation confirms that, in the case studied by the above authors, sharp microstructural boundaries of inclusion trails

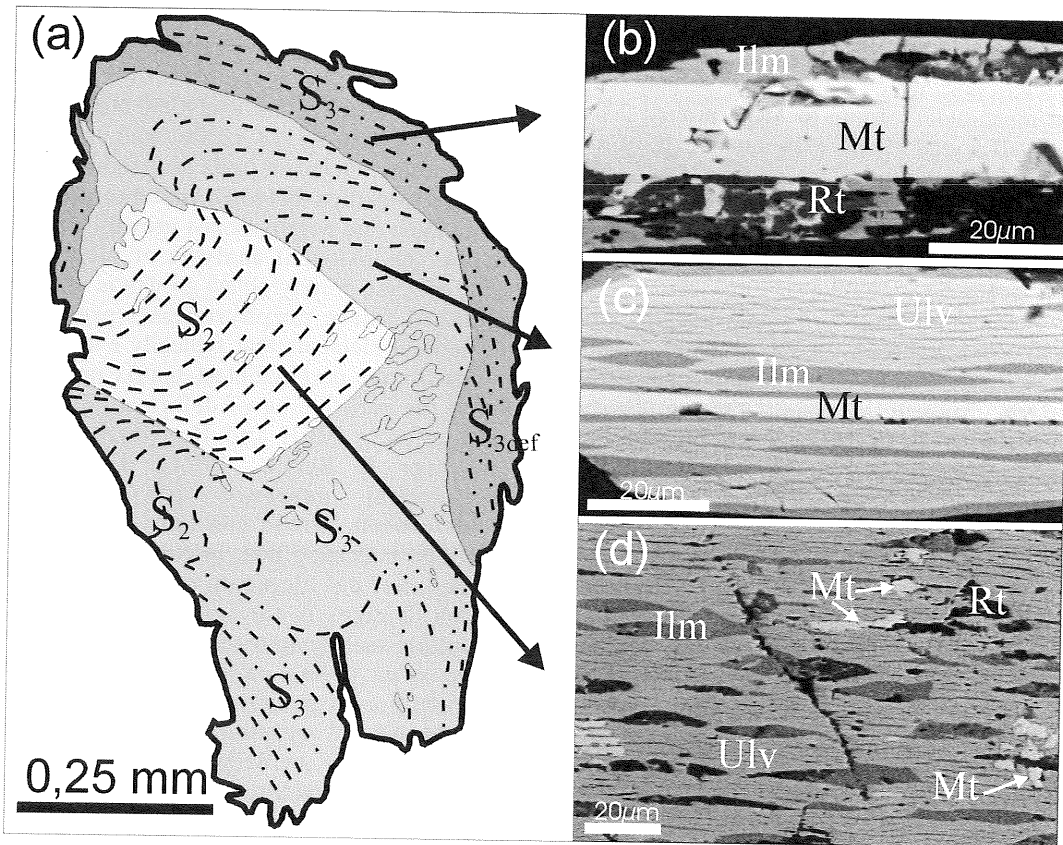


Fig. 1 – (a) Line drawing shows garnet porphyroblast with complex inclusion trails as seen in the optical microscope. (b), (c) and (d) are BSE images of reaction microstructures preserved within Fe-Ti solid solution mineral inclusions revealing that different reaction microstructures characterise distinct garnet growth zones (distinguished by different grey shades in (a)). The reaction microstructures relate to ulvöspinel breakdown at increasing rates of diffusion and oxidation, and their homogeneous distribution throughout the distinct garnet growth zones suggests that hiatuses in garnet growth must have occurred between the evolution of each reaction microstructure. (Ilm = imenite, Mt = magnetite, Rt = rutile, Ulv = ulvöspinel).

coincide with growth hiatuses and point to episodic garnet formation during metamorphism at distinct P-T conditions and due to distinct metamorphic reactions.

Trace element distribution revealed by microprobe analysis and X-ray mapping

Recently an analytical approach that allows the detection of trace elements in the ppm range was developed for modern electron

microprobes (Cousens *et al.*, 1997; Robinson *et al.*, 1998; Reed, 2000). The approach consists in the use of a high accelerating voltage, a high probe current, long counting times, and background points that are near the peak and without interference. Taking into account these recommendations, Borghi *et al.* (2002a) performed a comparison between major and trace element concentrations in garnet coming from metapelitic specimens of the Monte Rosa Nappe (Western Alps). In particular,

quantitative spot analyses and X-ray maps of yttrium distribution are presented and compared with the spatial variation of Fe, Mg, Ca and Mn.

The quantitative Y distribution profile shows a prominent decrease from the core to the rim. In particular Y abundance reaches almost two orders of magnitude ranging from about 80 ppm at the rim to almost 2000 ppm at the core (Fig. 2). This pattern is in agreement with what was found by Pyle & Spear (2000) for metapelite garnets of low to medium grade metamorphic conditions, where a negative correlation between the Y concentration and temperature is reported.

From the comparison between the well defined Y pattern distribution and the smooth profiles shown by major elements (Fig. 2), no correlation can be supposed. This contrast in major vs. trace element distribution attests to the considerable difference in diffusivities between Fe, Mg, Mn and Y. The sharp and steep gradients in the Y distribution suggest that the diffusion of Y through the garnet must be very slow compared to the major elements, which were strongly modified by diffusion at high temperature. The much slower diffusivity

of Y prevents significant modification of the original growth zoning pattern, allowing thus to reconstruct the thermal history experienced by the host rock, and the recognition of events that would remain unrecorded by major elements.

Orientation contrast imaging and electron backscatter diffraction

Microstructures are always then difficult to interpret when the geometrical aspects of the microstructures are ambiguous, and a more quantitative database is required to constrain interpretations. Collecting a quantitative data base is not always an easy task, particularly when we deal with isotropic minerals as garnet. An example of such a situation constitutes the garnet porphyroblasts that occur within the Schneeberg Complex of the Eastern Alps (Fig. 3). These porphyroblasts show microstructural features that have been attributed to a deformational origin (Helbig and Schmidt, 1978), but use of novel SEM-based analytical tools as EBSD and OC allows to recognise that they formed by a mechanism that implies multiple nucleation, coalescence and grain-boundary energy driven rotation (Spiess *et al.*, 2001).

Two different types of garnet porphyroblast occur in the Schneeberg Complex of the Eastern Alps (Fig. 3). **Type 1** is restricted to the lowest part of the Schneeberg Complex and forms ellipsoidal pods with small garnet grains in the centre, and large garnet grains at the margin. Orientation contrast (OC) imaging shows that the larger marginal garnet grains comprise a number of orientation sub-domains (Fig. 3). Individual garnet grains without sub-domains are small and idioblastic. Sub-domains of larger garnet grains are similar in size to the individual, small garnet grains.

Type 2 porphyroblasts occur within the higher structural levels of the Schneeberg Complex and form single ellipsoidal garnet crystals, showing with OC small sub-domains in the centre and larger sub-domains at the margin (Fig. 3).

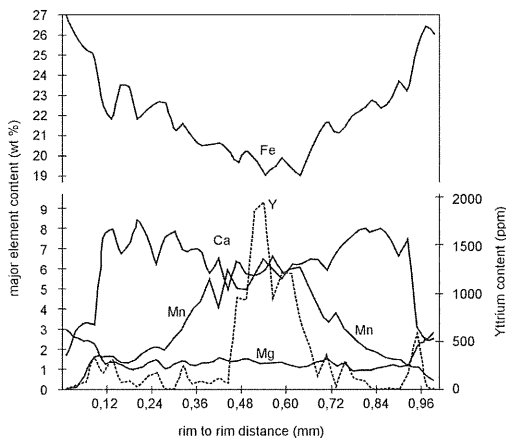


Fig. 2 – Representative concentration profile of zoned garnet (Monte Rosa Nappe, Western Alps). Porphyroblast diameter = 1 mm.

garnet orientation (Fig. 3). Within **Type 2** garnet porphyroblasts all sub-domains irrespective of their size have a strong preferred crystallographic orientation.

The only explanation that fits all observational data is that Schneeberg garnet porphyroblasts formed by simultaneous, multiple nucleation, followed by growth and amalgamation of individual garnet grains. Individual garnet grains rotated towards coincident orientations once they came into contact with each other during coalescence. This process was driven by the reduction of sub-domain boundary energy associated with misorientation loss. The range of individual garnet and garnet sub-domain sizes can be explained by a faster growth rate at the porphyroblast margin than in the centre. The differentiation between **Type 1** and **Type 2** porphyroblasts relates to the reactions kinetics that controlled the settling up of growth rate differentials within the ellipsoidal porphyroblast growth sites (Dobbs *et al.*, 2003).

Proton induced X-ray emission

In the past only major element composition could be determined easily by electron probe microanalysis (EMPA). However, at high temperature mineral growth zoning of major elements may have been significantly modified by intra-crystalline diffusion (Florence & Spear, 1995).

Consequently, determining the distribution of those elements that are least susceptible to diffusional modifications becomes of fundamental importance. Because some trace elements satisfy this condition (Schwandt *et al.*, 1996), and because their partitioning between mineralogical phases is controlled by the physical, chemical and kinetic characteristics of metamorphic and/or magmatic differentiation processes, techniques allowing their determinations with high spatial resolution and low detection limits have become extremely important. MicroPIXE is such a technique,

although it has been rarely applied by geologists (Ryan *et al.*, 1990; Sie, 1993).

We here report a study conducted by Vaggelli *et al.*, (2003) at the microPIXE facility of Legnaro. Other microPIXE applications are reported in Borghi *et al.* (2002b) and Mazzoli *et al.* (2002). In Vaggelli *et al.* (2003), strongly zoned garnet porphyroblast from metapelites of the Western Alps (Italy) metamorphosed under eclogite facies conditions were selected. The garnet in the BSE images of Fig. 4 has an idioblastic core that crystallized during the eclogitic event and a rim that grew during the subsequent amphibolite facies event. The garnet crystal shows a well-defined compositional zoning. The Y distribution is strongly enriched in the core, but is flat at the rim (Fig. 4). The abrupt decrease of Y concentration occurs precisely in correspondence to the core/rim boundary which is outlined by the distribution of small quartz inclusions. The distribution of major elements is instead characterized by a smooth and concentric variation from core to rim.

The quantitative profile performed with mPIXE along the garnet crystal shows the same Y concentration trend as the X-ray map (compare Figs 4 and 5). The overall distribution is characterised by a narrow Y-rich layer in correspondence to the boundary between the core and the rim of the garnet. In the major element X-ray distribution maps, this feature cannot be recognised. A comparison of the Y pattern with the smooth profiles of the major elements reveals no correlation (Fig. 5), except a weak similarity between Mn and Y.

The formation of the above oscillatory zoning can be explained by garnet re-absorption and contemporaneous back-diffusion of Y into the garnet core, followed by rim accretion with a different Y-concentration (Pyle & Spear, 1999; Lanzirotti, 1995). This interpretation is in agreement with our microstructural observation, which suggest the development of two garnet generations under different metamorphic conditions.

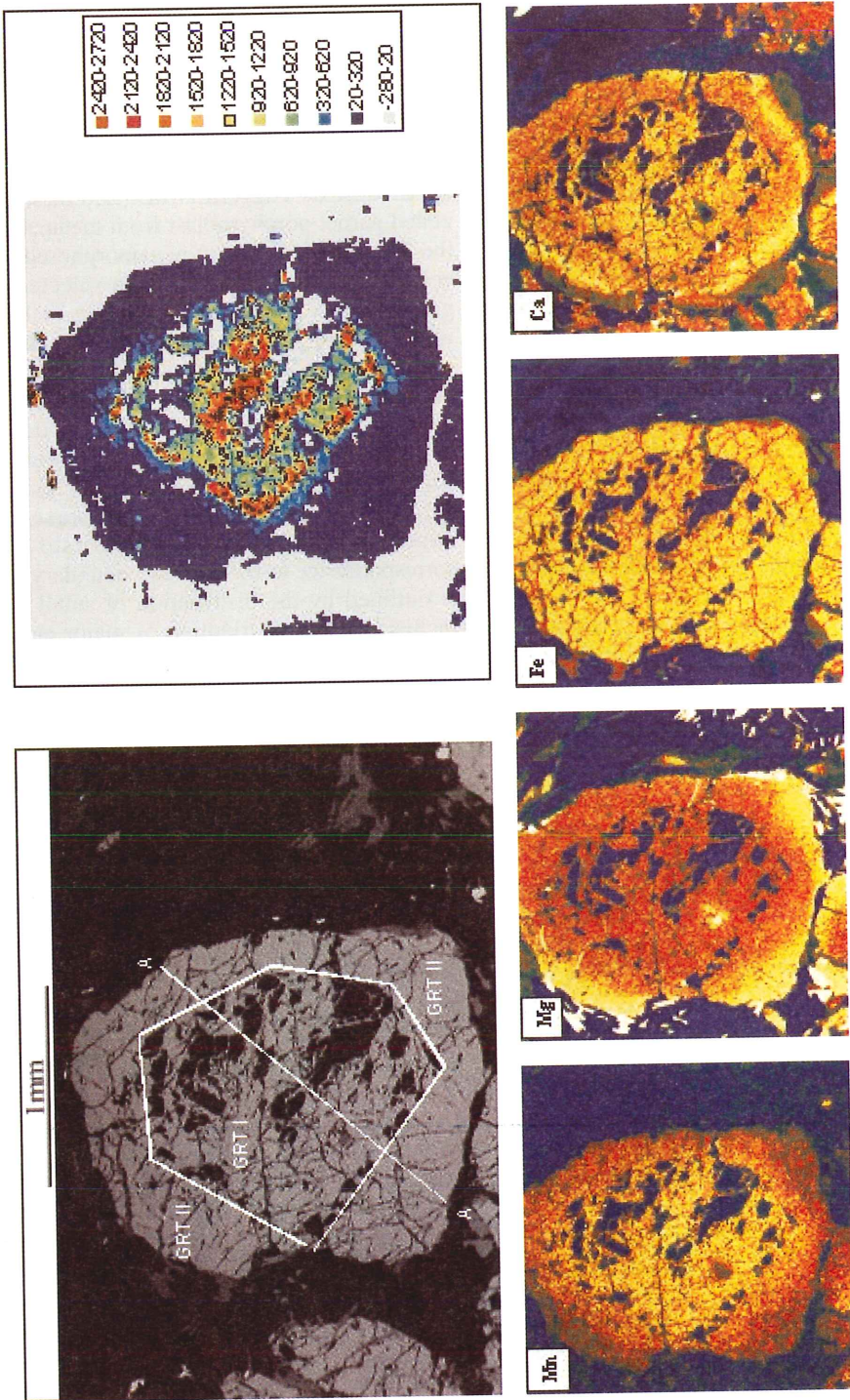


Fig. 4 – (Upper left) SEM backscattered digitized images of garnet sample. Quartz inclusions define two garnet generations boundary. GRT I = first garnet generation; GRT II = second garnet generation. Line A-A traces compositional profile shown in Fig. 5. (Upper right) Quantitative compositional maps of Yttrium (Y) expressed as ppm. (Lower row) Qualitative compositional maps of major chemical elements (Mn, Mg, Fe, Ca) expressed as wt% oxide.

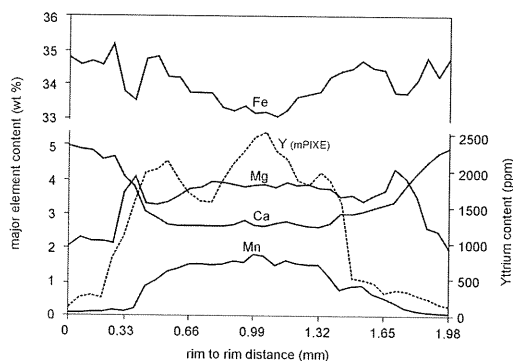


Fig. 5 – Representative concentration profile of metapelite garnet. Major element contents (Fe, Mg, Mn, Ca) expressed as wt% oxide. Yttrium content acquired by micro-PIXE facility expressed as ppm.

ACKNOWLEDGMENTS

A. Borghi thanks Murst ex 60% and R. Spiess thanks Progetto di Ateneo (2003) dell'University of Padova. The reviews of Stefano Poli (Milan) and Kurt Stüwe (Graz) are greatly acknowledged.

REFERENCES

- BELL T.H. and HAYWARD N. (1991) — *Episodic metamorphic reactions during orogenesis: the control of deformation partitioning on reaction sites and duration*. *J. Metam. Geol.*, **9**, 619-640.
- BOLLINI D., CERVELLERA F., EGENI G.P., MAZZOLDI P., MOSCHINI G., ROSSI P. and RUDELLO V. (1983) — *The microbeam facility of the AN-2000 accelerator of the Laboratori Nazionali di Legnaro*. *Nucl. Instr. Meth.*, **328**, 173-176.
- BORGHI A., AGNELLA D., BELLUSO E., COSSIO R. and RUFFINI R. (2000) — *Multiple electron beam analyses applied to eclogite from the Western Alps*. *Mikrochim. Acta*, **132**, 479-487.
- BORGHI A., COSSIO R., OLMI F., RUFFINI R. and VAGGELLI G. (2002a) — *EPMA major and trace element analysis in garnet and its petrological application*. *Mikrochim. Acta*, **139**, 17-25
- BORGHI A., COSSIO R. and MAZZOLI C. (2002b) — *A mineralogical application of micro-PIXE technique: Yttrium zoning in garnet from metamorphic rocks and its petrologic meaning*. *Nucl. Instr. Meth.*, **189**, 412-417.
- BUDDINGTON A.F. and LINDSLEY D.H. (1964) — *Iron-titanium oxide minerals and synthetic equivalents*. *J. Petrol.*, **5**, 310-357.
- CAMPBELL W.J.L., HOPMAN T.L., MAXWELL J.A. and NEJEDLY Z. (2000) — *The Guelph PIXE software package III: Alternative proton database*. *Nucl. Instr. Meth.*, **170**, 193-204.
- CASTAING R. (1951) — *Application des sondes électroniques: une méthode d'analyse ponctuelle chimique et cristallographique*. Ph.D. Thesis.
- COSSIO R. and BORGHI A. (1998) — *PETRMAT: MS-DOS software package for quantitative processing of X-ray maps of zoned minerals*. *Comp. Geosci.*, **24**, 805-814.
- COUSENS D.R., RASCH R. and RYAN C.G. (1997) — *Detection limits and accuracy of the electron and proton microprobe*. *Micron*, **28**, 231-239.
- DAY A. (1993) — *Developments in the EBSD technique and their application to grain imaging*. Ph.D. dissertation, University of Bristol.
- DINGLEY D.J. (1984) — *Diffraction from sub-micron areas using electron backscattering in a scanning electron microscope*. *Scann. Electr. Micr.*, **2**, 569-575.
- DOBBS H.T., PERUZZO L., SENO F., SPIESS R. and PRIOR D.J. (2003) — *Unravelling the Schneeberg garnet puzzle: a numerical model of multiple nucleation and coalescence*. *Contrib. Mineral. Petrol.*, **146**, 1-9.
- FLORENCE F.P. and SPEAR F.S. (1995) — *Intergranular diffusion kinetics of Fe and Mg during retrograde metamorphism of a pelitic gneiss from the Adirondack Mountains*. *Earth Planet. Sci. Lett.*, **134**, 329-340.
- FRANCESCHELLI M., MEMMI I., OTTOLINI L. and VANNUCCI R. (2002) — *Trace- and major-element zoning in garnet: A case study in the pelitic schists of NE Sardinia (Italy)*. *Neues Jb. Miner. Monat.*, **8**, 337-351.
- FRASER D.G. (1990) — *Applications of the high-resolution scanning proton microprobe in the Earth Sciences: An overview*. *Chem. Geol.*, **83**, 27-37.
- HELBIG P. and SCHMIDT D. (1978) — *Zur Tektonik und Petrogenese am W-Ende des Schneebergerzuges (Ostalpen)*. *Jb. Geol.*, **121**, 177-217
- IKEDA T. (1993) — *Compositional zoning patterns of garnet during prograde metamorphism from the Yanai district, Ryoke metamorphic belt, southwest Japan*. *Lithos*, **30**, 109-121.
- JOY D.C. (1974) — *Electron channelling patterns in the SEM*. in Holt, D.B., Muir, M.D., Boswarva, I.M., and Grant, P.R. *Quantitative Scanning Electron Microscopy*, Academic Press, New York.
- LANZIROTTI A. (1995) — *Yttrium zoning in metamorphic garnet*. *Geochim. Cosmochim. Acta*, **59**, 4105-4110.
- LLOYD G.E. (1987) — *Atomic number and*

- crystallographic contrast images with the SEM: A review of backscattered techniques. *Mineral. Mag.*, **51**, 3-19.
- MAXWELL J.A., CAMPBELL J.L. and TEESDALE W.J. (1989) — *The Guelph PIXE software package*. *Nucl. Instr. Meth.*, **43**, 218-230.
- MAZZOLI C., HANCHAR J.M., DELLA MEA G., DONOVAN J.J. and STERN R.A. (2002) — *mPIXE analysis of monazite for total U-Th-Pb age determination*. *Nucl. Instr. Meth.*, **189**, 394-399.
- MESSIGA B. and BETTINI E. (1990) — *Reaction behaviour during kelyphite and symplectite formation: a case study of mafic granulites and eclogites from the Bohemian Massif*. *Eur. J. Mineral.*, **2**, 125-144.
- MESSIGA B., TRIBUZIO R. and SCAMBELLURI M. (1992) — *Mafic eclogites from the Valosio crystalline massif (Ligurian Alps, Italy)*. *Schweiz. Mineral. Petrogr. Mitt.*, **72**, 365-377.
- MESSIGA B., SCAMBELLURI M. and PICCARDO G.B. (1995) — *Chloritoid-bearing assemblages in mafic system and eclogite-facies hydration of alpine Mg-Al metagabbros (Erro-Tobbio Unit, Ligurian Western Alps)*. *Eur. J. Mineral.*, **7**, 1149-1167.
- OTTOLINI L.P. (2000) — *Understanding the History of rocks by the use of microbeam analysis techniques*. *Mikrochim. Acta*, **132**, 467-478.
- PASSCHIER C.W. and SPECK J.H.R. (1994) — *The kinematic interpretation of obliquely-transected porphyroblasts: an example of the Trois Seigneurs Massif, France*. *J. Struct. Geol.*, **16**, 971-984.
- POTTS P.J., BOWLES J.F.W., REED S.J.B. and CAVE M.R. (1995) — *Microprobe technique in the Earth Sciences*. Chapman & Hall, London. 419 pp.
- PRIOR D.J., TRIMBY P.W., WEBER U.D. and DINGLEY D.J. (1996) — *Orientation contrast imaging of microstructures in rocks using forescatter detectors in the scanning electron microscope*. *Mineral. Mag.*, **60**, 859-869.
- PRIOR D.J., BOYLE A.P., BRENKER F., CHEADLE M.C., DAY A., LOPEZ G., PERUZZO L., REDDY S., SPIESS R., TIMMS N.E., TRIMBY P., WHEELER J. and ZETTERSTRÖM L. (1999) — *The application of electron backscatter diffraction and orientation contrast imaging in the SEM to textural problems in rocks*. *Am. Mineral.*, **84**, 1741-1759.
- PRIOR J.P., WHEELER J., PERUZZO L., SPIESS R. and STOREY C. (2002) — *Some garnet microstructures: an illustration of the potential of orientation maps and misorientation analysis in microstructural studies*. *J. Struct. Geol.*, **24**, 999-1011.
- PYLE J.M. and SPEAR F.S. (1999) — *Yttrium zoning in garnet: coupling of major and accessory phases during metamorphic reactions*. *Geol. Mat. Res.*, **1**, 49 pp.
- PYLE J.M. and SPEAR F.S. (2000) — *An empirical garnet (YAG) - xenotime thermometer*. *Contrib. Mineral. Petrol.*, **138**, 51-58.
- RANDLE V. (1992) — *Microtexture determination and its applications*. The Institute of Materials, London, 174 pp.
- REED S.J.B. (1995) — *Electron microprobe microanalysis*. In: P. J. Potts, J. F. W. Bowers, S. J. B. Reed & M. R. Cave eds, *Microprobe Technique in the Earth Sciences*, Chapman & Hall, London, 49-90.
- REED S.J.B. (1996) — *Electron microprobe analysis and scanning electron microscopy in geology*. Cambridge University Press, Cambridge. 201 pp.
- REED S.J.B. (2000) — *Quantitative trace analysis by wavelength dispersive EPMA*. *Microchim. Acta*, **132**, 145-151
- ROBINSON B.W., WARE N.G. and SMITH D.W.G. (1998) — *Modern electron microprobe trace-element analysis in mineralogy*. In: Modern approaches to ore and environmental mineralogy (eds. Cabri L.J. and Vaughan D.J.). *Mineral. Ass. Can.*, short course **27**, 153-180.
- RYAN C.G., COUSENS D.R., SIE S.H., GRIFFIN W.L., SUTER G.F. and CLAYTON E. (1990) — *Quantitative PIXE: microanalysis of geological material using the CSIRO proton microprobe*. *Nucl. Instr. Meth.*, **47**, 55-71.
- SCHWANDT C.S., PAPIKE J.J. and SHEARER C.K. (1996) — *Trace element zoning in pelitic garnet of the Black Hills, South Dakota*. *Am. Mineral.*, **81**, 1195-1207
- SIE S.H. (1993) — *Progress of quantitative micro-PIXE applications in geology and mineralogy*. *Nucl. Instr. Meth.*, **75**, 403-410.
- SPIESS R., BERTOLO B., BORGHI A., CHINELLATO M. and TINOR CENTI M. (2000) — *Microtextures of opaque inclusions: their use as indicators for hiatuses during garnet porphyroblast growth*. *J. Metam. Geol.*, **18**, 591-603.
- SPIESS R., PERUZZO L., PRIOR D.J. and WHEELER J. (2001) — *Development of garnet porphyroblasts by multiple nucleation, coalescence and boundary driven rotations*. *J. Metam. Geol.*, **19**, 269-290.
- SPEAR F.S. (1993) — *Metamorphic Phase Equilibria and Pressure - Temperature - Time Paths*. Mineralogical Society of America, Monograph **1**, Washington, 799 pp.
- TRIBUZIO R., RICCARDI M.P. and OTTOLINI L. (1995) — *Trace-element redistribution in high-temperature deformed gabbros from east ligurian ophiolites (northern apennines, italy) - constraints on the origin of syndeformation fluids*. *J. Metam. Geol.*, **13**, 367-377

- VAGGELLI G., BORCHI A., COSSIO R., MAZZOLI C. and OLMI F. (2003) — *Comparison between major and trace element concentrations in garnet performed by EPMA and micro-PIXE techniques.* Spectrochim. Acta, **58**, 699-709.

