EPMA Major and Trace Element Analysis in Garnet and its Petrological Application

Alessandro Borghi1,*, Roberto Cossio2, Filippo Olmi3, Raffaella Ruffini1, and Gloria Vaggelli3

1 Dipartimento di Scienze Mineralogiche e Petrologiche, Via Valperga Caluso 37, Università di Torino, I-10100 Torino, Italy
2 Dipartimento di Scienze della Terra, Via Valperga Caluso 37, Università di Torino, I-10100 Torino, Italy
3 C.N.R. – C. S. per la Minerogenesi e la Geochimica Applicata, Via G. La Pira 4, I-50121 Firenze, Italy

Abstract. A comparison between major and trace element concentrations in garnet performed by electron microprobe (EPMA) technique is reported. Quantitative spot analyses and X-ray maps of major elements (Fe, Mg, Mn, Ca) and the trace element yttrium in garnets from metamorphic rocks are presented. The selected garnet samples come from meta-pelitic and meta-basic specimens belonging to the tectonic unit of the Monte Rosa Nappe (Western Alps).

In the metapelites, the quantitative Y distribution maps display a prominent increase at the core, the Y abundance varying by over two orders of magnitude, from about 80 ppm (rim) to over 2100 ppm (core). The Y profiles show well defined patterns with sharp features that do not correlate with major element distributions. A roughly comparable pattern can be supposed only with Mn. The Y distribution suggests that the diffusion of Y through the garnet is very slow compared to the major elements, thus the Y results are suitable for geothermometric estimates.

In the metabasites, the Y spatial distribution is characterised by an increasing content from the core to the rim, displaying a zoning pattern opposite to the metapelitic garnet. Quantitative EPMA analyses range from 1100 ppm at the rim to values lower than the detection limit at the core.

Therefore, the Y content in the garnet can be related to several chemical and physical variables such as the bulk rock composition and the phase assemblage. In particular, in the xenotime-bearing metapelitic system the Y distribution seems to be correlated with metamorphic peak temperature.

Key words: EPMA; garnet; yttrium; geothermometry.

The chemical composition of rock-forming minerals reflects their crystallisation history and provides information on the temperature and pressure conditions during their formation. Therefore, the chemical and physical changes recorded by minerals during the initial growth or the subsequent re-equilibration can be used to reconstruct either the evolutionary trends of magmas in igneous rocks or the P-T path in metamorphic rocks.

Among metamorphic minerals, the compositional zoning of garnet is a key piece of information in metamorphic petrology because the chemical zoning preserved in the garnet porphyroblasts potentially records the changes in the reaction history of the rock [1]. Accurate interpretation of chemical zoning in garnet leads to significantly improved understanding of P-T paths of metamorphism and hence of the tectonics of mountain belts; therefore, it is essential to develop techniques that elucidate metamorphic processes during garnet growth.

In recent years, many papers have been dedicated to these techniques, discussing their applications and limits [2]. In particular, great interest is devoted to the correct interpretation of garnet zoning in order to evaluate every modification of the original growth zoning due to cationic diffusion [3]. The best way to carefully determine the chemical zoning consists of performing two-dimensional X-ray compositional
maps that represent the spatial distribution of each element within a crystal [4].

In the past only major element compositions could be determined by non-destructive analytical procedures. However, at high temperature major element growth zoning may be significantly modified by intra-crystalline diffusion [5, 6]. Consequently, the study of trace element zoning in garnet, which may be less susceptible to diffusional modification [7], becomes of fundamental importance.

Recent advances in analytical geochemistry provide instruments with the sensitivity and spatial resolution required for determination of trace element concentration by in-situ spot analysis on polished thin sections of rock-forming minerals [8, 9]. In some recent studies, it has been demonstrated that trace element zoning in garnet is more pronounced than major element zoning [10, 11]. This implies that these elements may be more sensitive to P-T change during the metamorphic history of the host rock. In this regard, an inverse correlation between the concentration of yttrium in garnet in the pelitic samples as a function of metamorphic grade has been recently proposed [12]. This coupling is of great advantage as it may be used to calibrate new geothermometers based on exchange equilibria involving trace elements in garnet [13].

In this communication we report a comparison between major and trace element concentrations in metamorphic rock minerals performed by electron probe microanalysis using higher counting times and beam current in respect to routine analysis conditions in order to reach very low detection limits.

In particular, quantitative spot analyses and X-ray maps of yttrium distribution in garnet crystals, one of the most common minerals in metamorphic rocks, are presented here. The selected samples come from meta-pelitic and meta-basitic specimens belonging to the tectonic unit of the Monte Rosa Nappe (Western Alps).

**Experimental**

**WDS Microprobe Analysis**

WD spectrometers have the advantage that they record only one wavelength at a time and thus are not swamped by major element peaks when a high beam current is used to maximise the intensity of trace element peaks [14]. However, the presence of X-ray continuum limits the detectability of small peaks as defined by statistical criteria.

The elemental detection limit depends on counting statistics. Therefore, appropriate instrumental conditions, such as high beam current and long counting times, are needed in order to analyse elemental concentrations of the order of some tens of ppm. In addition, for trace analysis the optimum line/crystal combination is that which gives the maximum P X/P/B [14].

Taking into account all these recommendations, the following instrumental conditions were applied.

Major and trace element analyses were performed by a JEOL JXA 8600 microprobe equipped with 4 wavelength dispersive spectrometers. Si and Al data were collected using Kα1 order X-ray lines in order to prevent the detector saturation. The yttrium data were acquired by measuring the YLα X-ray line with a PET analyser.

Analytical conditions include an accelerating potential of 15 kV, a Faraday cup current of 500 nA and acquisition times (at the peak position) of 120 s for Y, 10 s for Si and Al, and 5 s for the other major elements. The same times were used for background counting. With these analytical conditions the minimum detection limit (MDL) for Y is lower than 50 ppm.

More sensitive analyses are in progress using a proton induced X-ray emission (PIXE) facility at the Instituto Nazionale di Fisica Nucleare (INFN) of Legnaro (Padua, Italy) [15].

Natural or synthetic silicates and oxides were used as primary standards. In particular, for quantitative yttrium analyses synthetic YAG (Y3Al5O12) was used as standard. This has a high Y content (Y2O3 = 57.06 wt%), and is characterised by a matrix similar to that of natural garnet samples.

As reported by Reed [14], there is little benefit in using as standard for a trace element a material in which the relevant element is present in a similarly low concentration because this has the disadvantage that the standard measurement is then subject to the inaccuracies associated with measuring small peaks. In addition, uncertainty in the matrix corrections is reduced if the standard resembles the sample in composition. It is therefore reasonable to use the same standards for trace elements as for major elements, though the beam current must be relatively low to avoid excessive count-rates.

Quantitative analyses were performed using the ZAF matrix correction routine by the TN-5600 Tracer-Northern software package.

**X-Ray Maps**

All maps were collected using a JEOL JXA 8600 microprobe by means of an automated mapping program. A network of spot peak counts using remote stage movement with spectrometers at fixed positions was collected. Operating conditions for map collection include an accelerating potential of 15 kV, a Faraday cup current of 2 μA, a defocused beam spot of 10 μm and a dwell-time of 2 s/pixel with step size of 10 μm/pixel. For a spatial resolution of 128 × 128 pixel a total acquisition time of about 48 h was needed. The maximum number of elemental maps for each acquisition set is limited by the number and type of available spectrometers (4).

The results consist of a set of numerical matrices, corresponding to the number of selected elements and containing the X-ray counts collected at their peak positions. Each raw peak count is corrected by subtracting the background counts calculated using the correction method reported in [16]. This method consists of an estimation of background level based on average atomic number measured on major constituents. The net peak counts are then computed by means of PETROMAP, a PC-pedicated software program, that allows a quantitative ZAF correction for K-lines [17]. In this way, each pixel of the map represents a ZAF – processed WDS quantitative analysis, with its own precision and accuracy. The output matrices can be loaded into common commercial spreadsheet programs. The compositional range between the maximum and the minimum value may be divided into a selected number of classes.