

⁵⁷Fe-Mössbauer investigation on garnets from the Ivrea-Verbanò Zone

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Abstract

A Mössbauer investigation has been carried out on garnets from the Ivrea-Verbanò zone and the results are compared with those obtained on the same samples by X-ray absorption spectroscopy (XAS). The problem addressed is the precise structural characterisation of the local environment of iron in garnets with Fe/Ca ratio variable between ~3.0 and ~18.0. Ferric iron is octahedrally coordinated and ferrous iron is in the dodecahedral site in all the samples. Mössbauer results are in agreement with those obtained by XAS and show that, at least in the compositional range of the garnets examined (0.1–0.5 calcium atoms p.f.u.), the iron environment is not significantly modified by the larger calcium cations sharing the same dodecahedral site. It is confirmed that the Mössbauer technique is more sensitive than XAS in detecting low percentages of iron, especially when the cation is present in more than one oxidation state and coordination number.

KEYWORDS: Mössbauer spectra, garnets, crystal chemistry, Ivrea-Verbanò zone.

Introduction

THIS work is a contribution to the study of the rock-forming minerals of the Ivrea-Verbanò area. This region is a part of the Hercynian basement of the southern Alps and is a thick exposed section of the upper mantle and the deep crust, originated by underplating of mantle-derived magma onto the base of continental crust (Rivalenti *et al.*, 1984; Voshage *et al.*, 1990; Mazzucchelli *et al.*, 1992).

Of particular interest is the study of the crystal-chemistry of garnets; the general goal is the characterization of the local environment of specific chemical species in the structure, in order to point out the geometrical parameters influencing both the crystal-chemistry of these minerals and the related diffusion mechanisms of major and trace elements in the structure.

To address this problem, investigations by space-averaging XRD techniques should be supported by chemical specific techniques, able to give information on the local environment of a selected element in the presence of other species

sharing the same crystallographic site. A recent X-ray absorption spectroscopy (XAS) investigation at Fe *K*-edge on garnets from the Ivrea-Verbanò zone (Quartieri *et al.*, 1992) showed that the prevalent oxidation state of Fe is 2+ and that the dodecahedral environment of iron atoms seems to be nearly independent of the calcium content of these Fe-rich garnets.

Further investigation on the effective percentage of Fe³⁺ present in these samples are advisable however, because of the difficulties in performing a quantitative analysis of an element present in more than one oxidation state and coordination number, using XAS. A Mössbauer study on the same garnet samples was then planned with the following aims: (1) to detect the presence and the coordination state of Fe³⁺ cations; (2) to verify the influence of Fe/Ca ratio on the site distortion of the Fe²⁺ local environment and (3) to compare the Mössbauer results with those derived from XAS analysis.

Experimental

The samples examined were carefully characterised from the petrologic point of view and were taken from different points of the metamorphic

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sequence (Mazzucchelli *et al.*, 1992; Rivalenti *et al.*, 1984). MP12 and MP18 are large porphyroblastic garnets occurring close to a metasedimentary septum in the UZ unit of the Ivrea-Verbano zone; other than garnets, the host gabbroic rock contains plagioclase, biotite, amphibole, clino and orthopyroxene and abundant magnetite. MP17 is a porphyroblastic garnet occurring in a rock of dioritic composition close to the roof of the complex; the other mineralogical phases present in this sample are mainly quartz, plagioclase and minor orthopyroxene and graphite. MP14 occurs in a depleted granulitic rock of a sedimentary layer at the IZ-UZ transition of the Ivrea-Verbano complex. In all the rocks, garnet is considered to have formed in equilibrium at the liquidus, and to have later re-equilibrated at subsolidus conditions (850 °C and 8 kbar for MP12 and MP18; 850 °C and 4–6 kbar for MP17 and MP14) (Mazzucchelli *et al.*, 1992).

The chemical analysis of the samples performed with SIMS and EMA methods (Mazzucchelli *et al.*, 1992) are reported in Table 1 for major elements.

Homogeneous garnet fragments were extracted from the rock matrix and the absence of alterations and inclusions was checked with an optical microscope at a magnification level of 40×. The samples were then powdered finely by hand with an agate mortar and pressed to thin disks.

⁵⁷Fe Mössbauer spectra at 298 K were measured using a 20 MCi ⁵⁷Co source in a Rh matrix. The spectra were recorded over 1024 channels of a multi-channel analyser in the velocity range of ±8 mm/sec. Data from each side of the mirror-imaged spectra were analysed separately and the results given are the average values of the right and left sides. The spectra were fitted with Lorentzian line-shapes by a χ^2 minimization procedure using a modified version of the MOSFUN program.

Because of the low concentration of Fe³⁺ in these samples, the areas and the widths of the

peaks of the Fe³⁺ doublet were always constrained to be equal.

For Fe²⁺ three different fitting models were used: *I*, one quadrupole doublet with equal linewidths and variable intensities; *II*, one quadrupole doublet with both linewidths and intensities variable; *III*, two quadrupole doublets, with equal linewidths and intensities for each doublet.

Results and discussion

The room-temperature Mössbauer spectra of the garnet samples are reported in Fig. 1(a–d). Hyperfine parameters and statistical information on the fits obtained applying model II are reported in Table 2.

Ferrous iron. The most intense contribution to the spectra originates from Fe²⁺ in the dodecahedral site. The isomer shift (IS) (measured with respect to α iron) and the quadrupole splitting (QS) vary between 1.29–1.30 mm/s and 3.54–3.56 mm/s respectively. These values are similar to those found on garnet samples of different composition by other authors (Amthauer *et al.*, 1976; Luth *et al.*, 1990; Geiger *et al.*, 1992). For a comparison, the hyperfine parameters of a synthetic almandine end-member (Geiger *et al.*, 1992) are also reported in Table 2.

The isomer shift and quadrupole splitting values are almost invariable and suggest that the Fe–O distances are nearly the same in all the samples and in the end member, and this is in agreement with the distances found by Fe *K*-edge XAS studies on the same samples (Quartieri *et al.*, 1993). Both spectroscopic techniques suggest that, at least in the range between 0.1 and 0.5 Ca atoms p.f.u., the presence of the larger Ca cation does not modify appreciably the geometry of the dodecahedral sites occupied by iron. This result confirms previous findings by Amthauer *et al.* (1976); these authors measured the Mössbauer spectra of a number of natural Fe-rich garnets with variable Ca content and found close isomer shift values for the Fe²⁺ dodecahedral doublet.

TABLE 1 - Chemical data (based on 12 oxygens) for the garnets in study (Mazzucchelli *et al.*, 1991). The symbols adopted for Ivrea-Verbano samples are from Parenti (1991).

	MP12	MP14	MP17	MP18
Si	2.997	3.004	2.991	3.012
Ti	0.004	0.002	0.003	0.011
Al	1.980	1.951	1.983	1.962
Fe	1.558	1.688	1.965	1.434
Mn	0.040	0.033	0.045	0.048
Mg	0.922	1.136	0.912	1.059
Ca	0.513	0.198	0.114	0.471
Cr	0.001	0.003	0.003	0.000

The calcium local 8-fold coordination geometry in the same garnet samples from Ivrea-Verbano is now being evaluated on the basis of an XAS investigation performed at Ca K-edge (Quartieri

et al., in prep.), to properly characterise the structural changes observed in the join almandine-grossular with Ca content increasing.

The widths and areas of the peaks of the Fe^{2+}

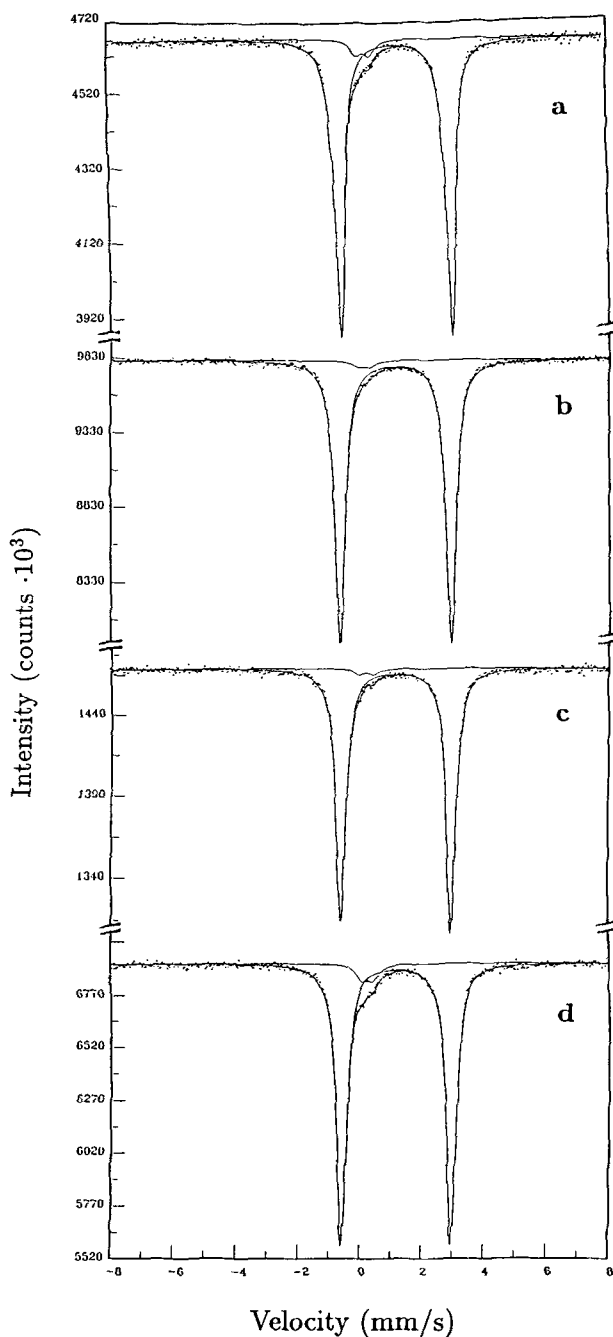


FIG. 1. ^{57}Fe Mössbauer spectra of MP12(a), MP14(b), MP17(c), MP18(d) garnet samples. Small doublet is Fe^{3+} .

quadrupole doublet show in all samples a small but clearly measurable asymmetry: the low-velocity line is wider than the high-velocity line in all the samples; moreover the area is also greater. This can be quantified by an asymmetry parameter (AS in Table 2) ranging between 3.9 and 8.0%.

Due to peak asymmetries, the model using constrained widths for the lines of the ferrous doublet (model I) gives reasonable fits only if some ferric iron is assumed to be in a tetrahedral coordination. The low reliability of this hypothesis will be discussed below in more detail.

Similar asymmetries in the areas and widths of the peaks have already been observed in garnet samples by other authors (Amthauer *et al.*, 1976; Murad and Wagner, 1987; Luth *et al.*, 1990; Geiger *et al.*, 1992) and have been ascribed to four phenomena: (i) preferred orientation in the absorber; (ii) magnetic relaxation effects

(Amthauer *et al.*, 1976); (iii) overlap of two or more doublets (Murad and Wagner, 1987); (iv) anisotropic recoil-free fraction (Goldanskii-Karyagin effect; Geiger *et al.*, 1992).

These authors discussed in detail the specific influence of these effects. Murad and Wagner (1987), Luth *et al.* (1990) and Geiger *et al.* (1992) rule out the first two hypothesis while some debate exists on the role of the latter two. Geiger *et al.* (1992) clearly demonstrated that the asymmetry of the peak areas in the almandine end-member can be quantitatively explained by the Goldanskii-Karyagin effect. The anisotropic recoil-free fraction of Fe^{2+} in garnets is attributed to the strong anisotropic vibrational behaviour of this cation in the eight-coordinated site of the cubic garnet structure. This assumption is also confirmed by the recent X-ray absorption studies performed on the same samples (Quartieri *et al.*, 1993): the Debye-Waller factors derived from the

Table 2 - Mossbauer data from 298 K spectra (*); fits obtained by model II.

Ferrous doublet							
Sample	A(LV) %	A(HV) %	HW(LV)	HW(HV)	IS	QS	AS
MP12	49.5	46.6	.197	.182	1.291	3.56	7.8
MP14	49.2	48.3	.198	.191	1.296	3.54	3.9
MP17	49.2	48.9	.190	.180	1.295	3.54	5.4
MP18	48.7	46.6	.194	.183	1.289	3.55	6.0
ALML00 §	50.9	49.1	.260	.240	1.280	3.50	8.0

Ferric doublet					
Sample	A%	HW	IS	QS	chi2
MP12	3.9	.223	.367	0.41	1.211
MP14	2.5	.250	.295	0.32	1.526
MP17	1.9	.185	.331	0.50	1.215
MP18	4.7	.240	.359	0.39	1.419

* IS = isomer shift relative to metallic iron at room temperature (± 0.005 mm/s)
 QS = quadrupole splitting (± 0.05 mm/s)
 HW(LV) = half width of the low velocity line (± 0.005 mm/s)
 HW(HV) = half width of the high velocity line (± 0.005 mm/s)
 A(LV)% = resonant absorption area of the low velocity line (± 0.5 %) referred to the total resonant absorption area = 100
 A(HV)% = resonant absorption area of the high velocity line (± 0.5 %) referred to the total resonant absorption area = 100

$$AS = \text{asymmetry} = 2 * \frac{HW(LV) - HW(HV)}{HW(LV) + HW(HV)} * 100$$

§ Geiger *et al.* (1992)

XAS analysis indicate a higher degree of disorder on the four longer Fe–O bond distances, in comparison with the other four shorter distances of the eighth-coordinated iron cation.

The third hypothesis mentioned above, i.e. the presence of more than one ferrous quadrupole doublet which could originate from a mixed site occupancy in the dodecahedra—cannot be excluded in chemically complex samples; this model could also explain better the observed line-width asymmetry between the low- and high-velocity peaks. We have therefore fitted the spectra also with model III, which considers two quadrupole doublets with different total areas and linewidths: in this case the fit is as good as that obtained by model II and the peak widths of the doublets converge towards a common equal value. The values of χ^2 and of the hyperfine parameters (isomer shift and quadrupole splitting averaged over the two doublets are very close to those obtained from model II.

In the frame of model II, the asymmetry of the line intensities can, as mentioned above, be interpreted as due to a Goldanskii–Karyagin effect (Geiger *et al.* 1991). We have thus derived the ratio R_q between the intensities of the two lines of the ferrous iron quadrupole doublet. The R_q values obtained range from 1.01 to 1.06 in reasonable agreement with the one of the almandine end-member (1.03 from Geiger *et al.* (1991)). We have also evaluated the R_q ratios on the basis of the crystallographic data (Oberti, pers. comm.) which provide values for the mean-square vibrational amplitudes parallel and perpendicular to the principal axis of the electric field gradient. From the difference ($\langle x_{\parallel}^2 \rangle - \langle x_{\perp}^2 \rangle$), following the standards procedure described by Gonser (1975), we have obtained for our samples an average value of $R_q^{calc} = 1.06$, which compares quite well with the range obtained from the Mössbauer spectra.

Ferric iron. Ferric iron is present in octahedral coordination in all samples. The hyperfine parameters are in the ranges: IS = 0.29–0.37 mm/s and

QS = 0.32–0.51 mm/s. The quadrupole splitting values are consistent with a medium degree of distortion of the octahedral site in these garnets.

A tentative interpretation of the spectra based on the fit where the areas of the ferrous peaks were constrained to be equal (model I), resulted in the apparent presence in some samples of Fe^{3+} in tetrahedral coordination. This model is, however, inconsistent both with the chemical analyses, especially the high Si content of all the samples (Table 1), and with the X-ray absorption results (Quartieri *et al.*, 1993): the absence in the XAS spectra of the intense pre-edge feature typical of the tetrahedral Fe^{3+} , rules out the hypothesis of the presence in our samples of iron substituting for Si in the tetrahedral site. A similar shortcoming was noted by Luth *et al.* (1990) for a series of mantle-derived garnets and is thought to be an artefact due to the use of constrained areas for the peaks of the ferrous iron doublet.

As discussed by Amthauer *et al.* (1976), and more recently by De Grave and Van Alboom (1991), the Mössbauer recoilless fraction values for Fe^{3+} are somewhat overestimated with respect to those of Fe^{2+} . The Fe^{3+} Mössbauer fractions were therefore corrected by the reduction factor (0.78) specifically calculated by Amthauer *et al.* (1976) for garnets.

The percentages of octahedral Fe^{3+} obtained by Mössbauer spectroscopy, ranging between 1.9 and 4.7%, are compared in Table 3 with those determined on the same samples by single crystal X-ray diffraction (Oberti, pers. comm.) and by XAS (Quartieri *et al.*, 1993). For comparison, the data relative to a garnet sample much richer in Fe^{3+} (BRIC, Basso *et al.*, 1981) are also reported in Table 3. It is evident that the percentages of Fe^{3+} found by Mössbauer in the Ivrea–Verbano garnets are below the limit of XAS sensitivity. These garnet samples, where the absorbing element is present in two oxidation states and different coordination geometries, are therefore particularly difficult to characterise in detail using XAS. This sensitivity problem in XAS was found

Table 3 - Fe^{3+} percentages determined by Mössbauer spectroscopy, single crystal X-ray diffraction and XAS spectroscopy.

	MP12	MP14	MP17	MP18	ERIC
MOSS. (a)	3.9	2.5	1.9	4.7	87.5
XRD (b)	1.9	3.0	2.5	3.0	85.3
XAS (c)	0	0	0	0	94.0

(a) this work (b) Oberti, pers. comm.

(c) Quartieri *et al.*, 1992

to be even more dramatic in more complex low symmetry structures (Brown *et al.*, 1988; Artioli *et al.*, 1991; Artioli and Geiger, 1992).

Conclusions

Ferrous iron is present in the dodecahedral site in all the garnet samples; Mössbauer results confirm that in the compositional range of the garnet examined (0.1–0.5 Ca atoms p.f.u.) the average geometric environment of Fe²⁺ is not significantly modified by the different amounts of the larger calcium cations sharing the dodecahedral site. This result is in agreement with that obtained by XAS investigations and suggests that in the studied compositional range, the Ca cations might be in an eight-coordinated arrangement whose geometry is different from that assumed in the grossular end-member.

This study establishes that the examined garnets contain octahedrally coordinate Fe³⁺, ranging between 1.9 and 4.7%, which is undetected by XAS analysis. The higher sensitivity of Mössbauer spectroscopy in discriminating the oxidation state of iron in mixed-valence minerals is thus confirmed.

Acknowledgements

Italian CNR, MURST and INFM are acknowledged for financial support. Prof. Basso (University of Genova) Prof. Rivalenti and Dr Mazzucchelli (University of Modena) kindly supplied the garnet samples. A particular acknowledgment is due to Dr. Oberti (University of Pavia) for the single crystal X-ray diffraction measurements. Computing time was made available by CICAIA (University of Modena).

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[Manuscript received 8 September 1992;
revised 7 December 1992]