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Mössbauer spectroscopy and crystal chemistry of natural Fe–Ti garnets

KENNETH B. SCHWARTZ,[1] DANIEL A. NOLET[2] AND ROGER G. BURNS

Department of Earth and Planetary Sciences
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Abstract

Anomalies in site occupancy data for iron cations from recent Mössbauer studies of titanian garnets have led to a reassessment of fitting and assignment of doublets in these complex spectra. Component peaks of doublets have been resolved in spectra of a suite of melanites and schorlomites with a significant decrease in the statistical parameters, χ^2 and MISFIT, as well as a decrease in the uncertainty of calculated positions, widths, and intensities. Doublets have been assigned to Fe^{3+} in octahedral [Y] and tetrahedral (Z) sites, Fe^{2+} in 8-fold triangular dodecahedral {X} and octahedral [Y] sites, and $Fe^{2+}\{X\} \rightarrow Fe^{3+}(Z)$ electron delocalization. The latter assignment, which obviates tetrahedral Fe^{2+} replacing Si as suggested in recent studies, is supported by theoretical considerations (ionic radii, crystal field site preference energies, short X–Z separation of 3.015A, edge-shared XO_8 and ZO_4 polyhedra), and correlation with previous optical studies. The absorption band at 5280 cm^{-1}, whose temperature-dependence argues against assignment as a tetrahedral Fe^{2+} crystal field transition, agrees with assignment as $Fe^{2+}\{X\} \rightarrow Fe^{3+}(Z)$ charge transfer. Discrepancies between calculated $Fe^{2+}/\Sigma Fe$ ratios from Mössbauer and wet-chemical analyses indicate the presence of substantial Ti^{3+} in some natural Fe–Ti garnets. Site occupancy data show the relative enrichments in the tetrahedral (Z) site to be $Fe^{3+} > (Al^{3+},Ti^{4+})$ in samples of non-metamorphic origin.

Introduction

The substitution of titanium in garnets of the andradite–melanite–schorlomite series has been known to wreak havoc on garnet crystal chemistry (Zedlitz, 1933, 1935; Kunitz, 1936; Tarte, 1960, 1965; Lehijarvi, 1966; Ito and Frondel, 1967; Isaacs, 1968; Howie and Woolley, 1968; Dowty, 1971). This substitution is associated with a severe Si deficiency in tetrahedral sites and leads to unusual oxidation states and coordination numbers of Fe and Ti (Dowty and Appleman, 1970; Burns and Burns, 1971; Burns, 1972). The presence of Ti^{3+} in titanium-rich specimens was suggested by wet-chemical analyses (Zedlitz, 1933; Howie and Woolley, 1968; Whipple, 1973) and optical absorption spectra (Manning and Harris, 1970; Moore and White, 1971; Burns, 1972), while Mössbauer spectra show absorption due to several Fe^{2+} species and octahedral and tetrahedral Fe^{3+} ions in synthetic and natural specimens (Burns, 1972; Huggins *et al.* 1975, 1976, 1977a,b; Weber *et al.* 1975; Amthauer *et al.*, 1977; Schwartz, 1977).

Current controversy over Fe–Ti garnets centers on quantitative data for proportions and site populations of coexisting Fe^{2+}, Fe^{3+}, Ti^{3+}, and Ti^{4+} (Amthauer *et al.*, 1977; Huggins *et al.*, 1977a,b; Schwartz, 1977). Mössbauer spectroscopy has been used to determine Fe^{2+}/Fe^{3+} ratios and site occupancies of ^{57}Fe cations in minerals containing other substituents which interfere with conventional chemical analyses and crystal structure refinements (Burns, 1972; Bancroft, 1973). Mössbauer spectra of most melanites and schorlomites, however, are extremely complex due to overlapping contributions from several iron species. In addition to predominant octahedral Fe^{3+}, the presence of tetrahedral Fe^{3+}, and of Fe^{2+} in 8-fold, 6-fold, and 4-fold coordination has been suggested. Therefore, as many as five quadrupole dou-

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[1] Present address: Department of Earth and Space Sciences, State University of New York, Stony Brook, New York 11794.

[2] Present address: Material Control and Applied Research, Manufacturing and Engineering, Corning Glass Works, Corning, New York 14830.

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blets (ten component peaks) may contribute to the spectra with varying degrees of overlap.

We have solved complex spectra of a suite of melanites and schorlomites, employing a constrained fitting procedure (Schwartz, 1977). Such constraints are justified by consistency of derived parameters across the suite of specimens, by the reasonable crystal-chemical data generated, and by the near equality of widths and intensities of quadrupole doublets in simpler ^{57}Fe silicate systems (Bancroft *et al.*, 1967; Virgo and Hafner, 1970; Bancroft, 1973; Amthauer *et al.*, 1976; Bancroft, 1979). Quadrupole doublets have been reassigned and most, if not all, of the inconsistencies in crystal-chemical data from recent Mössbauer studies (Huggins *et al.*, 1977b; Amthauer *et al.*, 1977) are resolved.

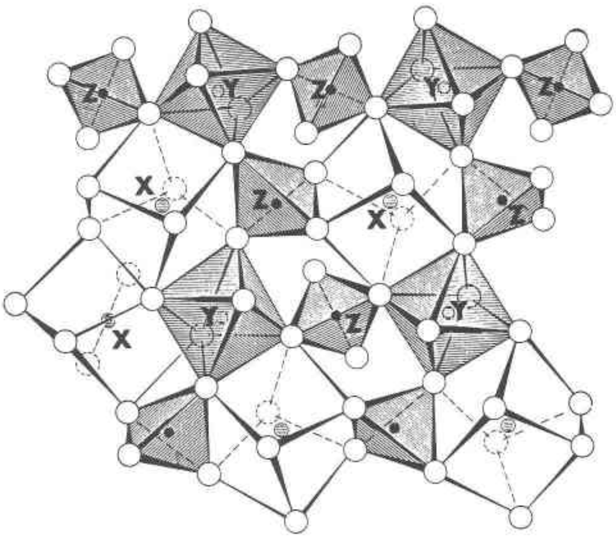
Background

Garnet crystal structure

The orthosilicate, garnet, has eight formula units of the type $\{X_3\}[Y_2](Z_3)O_{12}$ per unit cell.[3] {X} cations are coordinated by eight oxygens at the vertices of a distorted cube described as an 8-fold triangular dodecahedron (Novak and Gibbs, 1971). [Y] cations are octahedrally coordinated and (Z) cations are in tetrahedral coordination, both by oxygens. The structure consists of alternating ZO_4 tetrahedra and YO_6 octahedra (Fig. 1), sharing corners to form a continuous three-dimensional framework. The structure is in the orthosilicate class, as ZO_4 tetrahedra share no corners with each other. YO_6 octahedra also do not share corners with one another, nor do they share edges as in many silicate minerals. The only edge-shared interaction involves XO_8 dodecahedra. Interatomic distances (for andradite) and polyhedral relationships are summarized in Figure 1. Interatomic distances are unlikely to differ significantly in melanite and schorlomite, as cell-edge dimensions vary by less than one percent (Howie and Woolley, 1968).

Previous Mössbauer studies

The earliest Mössbauer studies of Ti-rich garnets were reported by Dowty (1971), who measured spectra of six specimens, fitting up to four doublets. Two doublets assigned to octahedral Fe^{3+} were resolved, although the garnet structure contains only one octahedral site, generating some controversy (Burns, 1972; Huggins *et al.*, 1975). The isomer shift for tetrahedral Fe^{3+} was also anomalously low.



X-O	1.643Å	average
Y-O	2.024Å	average
Z-O	2.433Å	average
X-Y	3.370Å	edge-shared XO_8 and YO_6
X-Z	3.692Å	edge-shared XO_8 and ZO_4
X-Z	3.015Å	edge-shared XO_8 and ZO_4
X-X	3.692Å	edge-shared XO_8
Y-Z	3.370Å	corner-shared YO_6 and ZO_4

Fig. 1. Portion of the garnet structure projected down the *c* axis. Note the framework of alternating corner-shared YO_6 octahedra and ZO_4 tetrahedra as well as the chains of alternating edge-shared XO_8 dodecahedra and ZO_4 tetrahedra. Interatomic distances are for andradite, $Ca_3Fe_2Si_3O_{12}$ (after Novak and Gibbs, 1971).

In a study of synthetic titanium garnets with compositions between end-members grossular or andradite and 50 : 50 weight percent $Ca_3Fe_2Si_3O_{12}$: $Ca_3Fe_2Ti_3O_{12}$, Huggins *et al.* (1977a) fitted three Lorentzian peaks to the spectra without constraints on peak parameters. The resulting Fe^{3+} site occupancies led to the inferred preferences for tetrahedral sites in synthetic Fe–Ti garnets of $Al \geq Fe^{3+} > Ti^{4+}$.

A major study of the crystal chemistry of a suite of natural melanites and schorlomites by Mössbauer spectroscopy and wet-chemical and electron microprobe analyses was made by Huggins *et al.* (1977b). They recorded Mössbauer spectra at 77K, attempting to obtain better resolution of Fe^{2+} species and reduce differences between Fe^{2+} and Fe^{3+} recoil-free fractions, significant in the garnet structure at 298K (Whipple, 1973; Amthauer *et al.*, 1977). Spectra were fit only to visually-resolved peaks and with no parameter constraints. Overlapping components were "resolved" into composite peaks and spectra were labeled and assigned as in Figure 7.

Amthauer *et al.* (1977) studied two natural

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[3] This notation was suggested by Geller (1967) and Novak and Gibbs (1971) in respective reviews of garnet crystal chemistry.

schorlomites over a temperature range 15–500K. A simplified fitting procedure similar to that of Huggins *et al.* (1977b) was employed to analyze the spectra, and temperature variations of Mössbauer parameters were discussed in detail for such fits.

Experimental

Plan of approach

The approach used in this study to solve the complex Mössbauer spectra of Ti–rich garnets differs from previous work in two basic assumptions. First, it was assumed that consistency of peak parameters, especially isomer shift and width, over the compositional range of the samples was one primary criterion for judging quality of fits. Since unit-cell dimensions (and hence coordination sphere dimensions) vary by less than one percent with increasing Ti content (Howie and Woolley, 1968), Mössbauer parameters for ^{57}Fe cations of the same valence and coordination should not vary greatly (probably less than 2–3%). This criterion was used to select a hierarchy of specimens of increasing spectral complexity, employing simple, one- and two-doublet spectra to provide accurate initial estimates of parameters in more complex fits.

Table 1. Compositions and sources of the titaniferous garnets

Specimen	1	2	3	4	5	6	7	8
				Analyses, wt %				
SiO_2	36.59	31.35	34.01	35.39	34.63	33.58	26.76	31.85
TiO_2	0.45	8.65	8.44	2.39	2.14	3.96	14.46	7.77
Al_2O_3	4.98	1.44	2.69	6.55	6.89	2.61	5.36	2.23
Fe_2O_3	25.59	23.73	19.24	21.35†	20.59†	24.63	16.90	24.27†
FeO	0.19*	2.00*	2.26*	-	-	1.67*	3.37*	-
MnO	0.35	0.65	0.03	0.25	0.48	0.69	0.70	0.34
MgO	0.87	0.69	0.80	0.61	0.20	0.84	1.43	0.40
CaO	31.06	30.79	32.14	33.07	33.14	30.04	30.91	32.96
Na_2O	-	-	0.12	-	-	-	-	-
K_2O	-	-	0.02	-	-	-	-	-
Total	100.08	99.30	99.75	99.61	98.07	98.02	99.89	100.01
			Number of metal ions on the basis of 12 oxygens					
Si	2.996	2.663	2.818	2.907	2.897	2.859	2.254	2.718
Ti	0.028	0.552	0.526	0.148	0.136	0.254	0.916	0.498
Al	0.481	0.144	0.263	0.635	0.680	0.262	0.532	0.226
Fe^{3+}	1.576	1.517	1.194	1.318	1.295	1.578	1.071	1.563
Fe^{2+}	0.013	0.142	0.156	-	-	0.119	0.237	-
Mn	0.025	0.047	0.002	0.019	0.035	0.050	0.050	0.026
Mg	0.106	0.087	0.099	0.074	0.025	0.107	0.180	0.052
Ca	2.725	2.802	2.853	2.912	2.969	2.741	2.790	3.016
Na	-	-	0.019	-	-	-	-	-
K	-	-	0.002	-	-	-	-	-

† Electron microprobe analyses. All Fe reported as wt. % Fe_2O_3.

* Ferrous iron determined by titration against $K_2Cr_2O_7$ (see text).

1. Andradite, alkali syenite, Semarule, Botswana. Donated by R.A. Howie (specimen 1 in Howie and Woolley, 1968).
2. Schorlomite, carbonatite, Tamazert, Haut Atlas de Midelt, Morocco. Donated by R.A. Howie (specimen 8 in Howie and Woolley, 1968).
3. Melanite, on serpentinite, near Dallas gem mine, San Benito Co., California. Donated by R.A. Howie (specimen 7 in Howie and Woolley, 1968).
4. Melanite, volcanic rock (Frascati, Italy). Obtained from the Dana Collection at Harvard University (specimen no. 87882).
5. Melanite, Monte Somma, Vesuvius, Italy. Obtained from the Dana Collection at Harvard University (specimen no. 85482).
6. Melanite, nepheline syenite, Loch Borolon, Scotland. Donated by R.A. Howie (specimen 4 in Howie and Woolley, 1968).
7. Schorlomite, carbonatite complex, Magnet Cove, Arkansas. Donated by R.A. Howie (specimen 11 in Howie and Woolley, 1968).
8. Schorlomite, nepheline syenite, Kirovsk, Kola Peninsula, U.S.S.R. Obtained from the Dana Collection at Harvard University (specimen no. 103154).

The second assumption was that absorbing ^{57}Fe species occur as quadrupole *doublets* and that constrained fits are justified in order to resolve near-overlapping doublet components. Constraints (on equality of component widths and intensities) are common in Mössbauer fitting (Bancroft, 1979), though it has long been felt that unconstrained fits are inherently superior to constrained ones (Virgo and Hafner, 1970). Our contention is that information derived from resolved doublet components (as opposed to composite peaks) warrants the necessity of appropriate width and intensity constraints. We realize that the burden of proof falls on us to demonstrate both that constrained fits are justified statistically and that crystal-chemical information derived from such fits is significantly different from results derived from simplified fitting procedures. We hope to establish these facts below.

Samples

Five of the Ti-bearing garnets were donated by Professor R. A. Howie and are specimens used by Howie and Woolley (1968). Published wet-chemical analyses are shown in Table 1. Determination of Fe^{2+} in these samples was difficult, due to their resistance to attack in boiling HF/H_2SO_4 and to the dark color of the resulting solution which made titrimetric endpoints difficult to detect (Howie and Woolley, 1968). Nevertheless, reproducible results were obtained by titration against potassium dichromate. This method measures only the total reducing capacity of the sample, assumed to be due to Fe^{2+}; possible complication due to Ti^{3+} was noted but not quantitatively determined. Additional samples were loaned by the Dana Collection at Harvard University and were analyzed by electron microprobe. Compositions and sources of all eight specimens are given in Table 1.

Experimental apparatus

Mössbauer data were obtained with a constant acceleration spectrometer using 512 channels of a 1024-channel multichannel analyzer. More than 10^6 baseline counts per channel were recorded for each spectrum, using a source of ^{57}Co in a Pd matrix (30–50 mCi). Samples were ground with sucrose under acetone and mounted in a plexiglass holder (2.2cm diameter by 0.1cm thick), adjusting sample weight so that total iron concentrations were approximately 5mg Fe/cm^2. Spectra were calibrated relative to metallic iron foil and were fitted with a program employing the Gauss nonlinear method, assuming Lorentzian shapes, as written by Stone (Stone *et al.,* 1971) and modified by Huggins (1975) and McCammon (1978).

Most spectra were recorded at room temperature (298K), and peak intensities were corrected for differences in Fe^{2+} and Fe^{3+} recoil-free fractions using previously determined correction factors (Sawatzky *et al.,* 1969; Lyubutin *et al.,* 1970; Lyubutin and Dodokin, 1971a,b; Whipple, 1973). Several spectra were also recorded at 77K for comparison with previous studies. No significant increase in resolution was noted in these low-temperature spectra. In fact, while high-velocity peaks did separate somewhat at 77K, overlap in the low-velocity region greatly increased, adding to uncertainties in peak parameters.

Mössbauer spectra and fitting

Final fitted Mössbauer spectra are shown in Figures 2–7. Calculated Mössbauer parameters from final computer fits are summarized in Table 2.

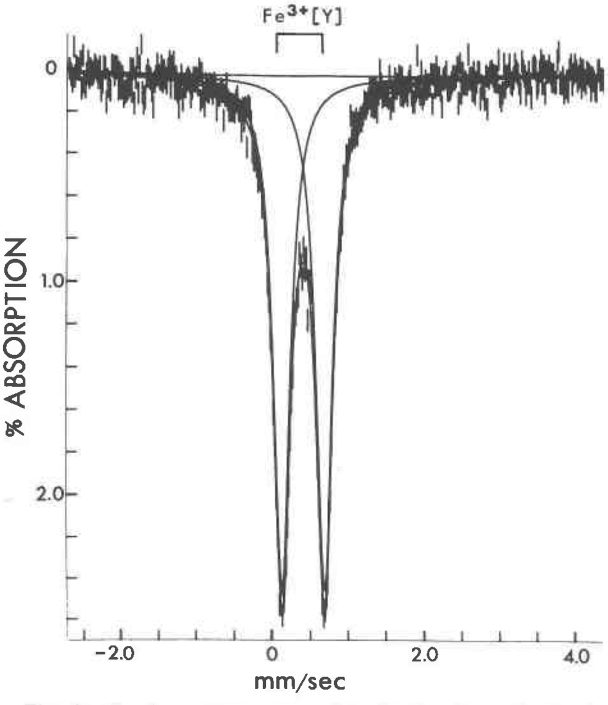

Fig. 2. Mössbauer spectrum of andradite from Semarule, Botswana (#1) fitted to one doublet assigned to Fe^{3+}[Y].

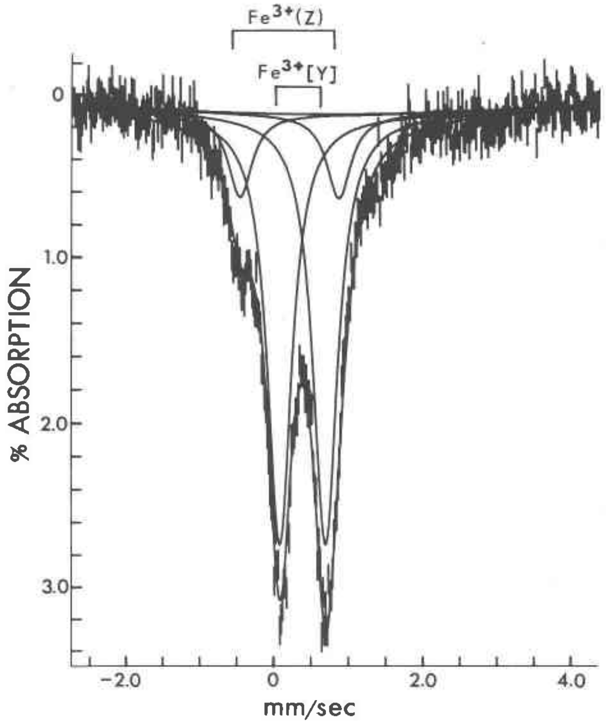

Fig. 3. Mössbauer spectrum of schorlomite from Morocco (#2) fitted to two doublets assigned to Fe^{3+}[Y] and Fe^{3+}(Z).

Simple, one- and two-doublet spectra allowed resolution of parameters for Fe^{3+}[Y] (Fig. 2), Fe^{3+}(Z) (Fig. 3), and Fe^{2+}[Y] (Fig. 4). Parameters obtained for these species were in excellent agreement with other studies (Bancroft *et al.,* 1967; Lyubutin *et al.,* 1970; Huggins *et al.,* 1977b; Amthauer *et al.,* 1976). In each case, doublet components were constrained to be equal in width and intensity, and nearly overlapping peaks were easily resolved by the computer, always converging to the same values despite different initial estimates. In both specimens 2 and 3, resolved components do *not* exactly coincide, with high-velocity Fe^{3+}(Z) and Fe^{3+}[Y] peaks separated by 0.18mm/sec (about half the calculated linewidth, Γ) and low-velocity Fe^{3+}[Y] and Fe^{2+}[Y] separated by 0.27mm/sec ($>3/4\Gamma$).

Specimen 4, shown in Figure 5, displays contributions from three doublets, Fe^{3+}(Z), Fe^{3+}[Y], and an additional species with a high-velocity peak at ~3.0mm/sec. This absorption is due to Fe^{2+} {X} and, employing initial estimates derived from specimens 1 and 2 and width and intensity constraints, a low-velocity component was easily resolved at −0.08mm/sec. This peak is separated from the Fe^{3+}[Y] low-velocity component by 0.20mm/sec ($>\frac{1}{2}\Gamma$). Spectra of

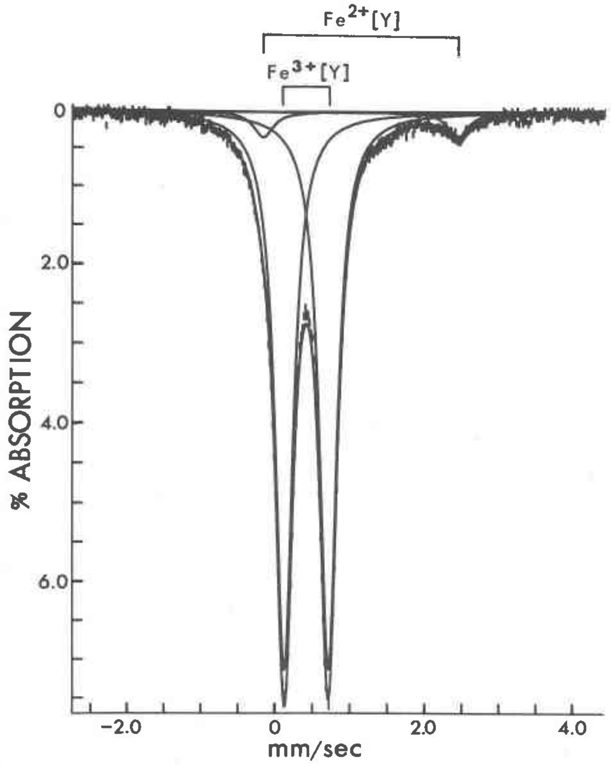

Fig. 4. Mössbauer spectrum of melanite from San Benito County, California (#3) fitted to two doublets assigned to Fe^{3+}[Y] and Fe^{2+}[Y].

specimens 5 and 6 were similarly solved with consistent results (Table 2).

From the located doublets due to Fe^{3+}(Z), Fe^{3+}[Y], Fe^{2+}[Y], and Fe^{2+} {X}, complex spectra of specimens 7 and 8 could be solved. Figure 6 shows a five-doublet, ten-peak fit with species corresponding to the four already resolved and an additional doublet −0.02 and 1.62mm/sec. This doublet corresponds to absorptions assigned by Huggins *et al.* (1977b) and Amthauer *et al.* (1977) to "Fe^{2+}(Z)," ferrous iron substituting into tetrahedral Si sites. Peak parameters of the four previously resolved species remain consistent with those derived from simpler spectra. Specimen 8 could be fit in a similar fashion, again with consistent results.

The inherent crystal-chemical problems associated with the substitution $Fe^{2+} \rightarrow Si^{4+}$ and the unusual temperature variations of "Fe^{2+}(Z)" absorption reported by Amthauer *et al.* (1977) have led to a reexamination of the possibility of cation–cation interactions in the garnet structure.

Electron delocalization in garnet

Electron delocalization (ED) has been observed in the Mössbauer spectra of magnetite (Kundig and Hargrove, 1969), hematite–ilmenite solid solution (Warner *et al.* 1972), and ilvaite (Nolet and Burns, 1979). ED is a thermally activated process as opposed to the dynamic optical transition usually designated charge transfer (CT). ED transitions place electrons in molecular orbitals delocalized over several cation sites. These short-lived electronic states ($\ll 10^{-7}$ sec) are observed as an average of ground and excited states if they occur with sufficient frequency during the nuclear (Mössbauer) transition. In other words, ^{57}Fe nuclei experience the effects of electron densities between $3d^5$ and $3d^6$ when time-averaged over the lifetime of the Mössbauer transition (0.977×10^{-7} sec). Increased thermal vibration increases the frequency of the ED transition and therefore increases absorption associated with ED.

In the classic case of magnetite, an order–disorder transition occurs at 119K (Verwey and Haayman, 1941), which distinguishes between Fe^{2+} and Fe^{3+} crystallographic positions (Hamilton, 1958). This Verwey point complicates the temperature-dependence of ED, introducing a metal → semiconductor

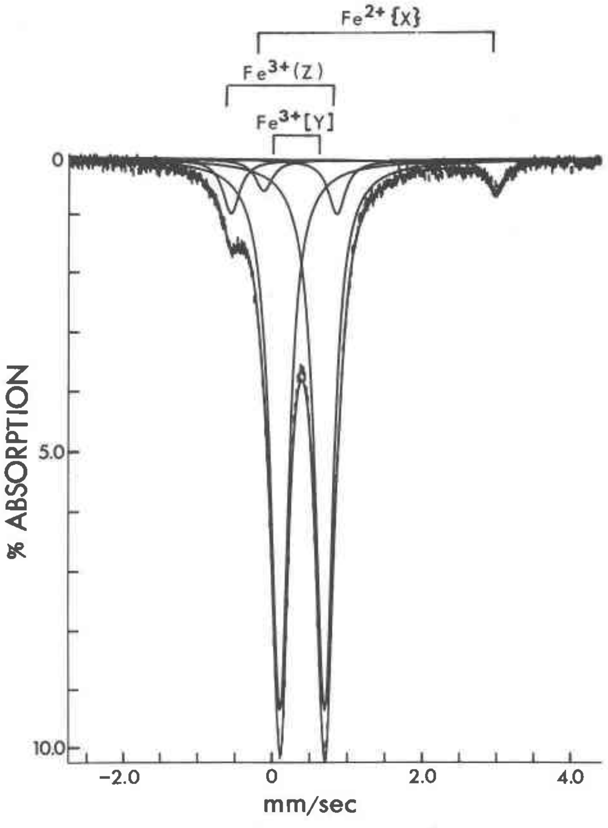

Fig. 5. Mössbauer spectrum of melanite from Frascati, Italy (#4) fitted to three doublets assigned to Fe^{3+}[Y], Fe^{3+}(Z), and Fe^{2+} {X}.

transition. Controversy over modeling the Verwey transition exists between order–disorder models (Verwey and Haayman, 1941; Verwey *et al.*, 1947; Cullen and Callen, 1971) and band or polaron models (Verble, 1974). Further structural studies (Yamada *et al.*, 1968; Samuelson *et al.*, 1968) have failed to resolve the conflict, making magnetite a less than ideal model phase.

Most systems displaying electron delocalization involve Fe^{2+} and Fe^{3+} cations in octahedral coordination and connected by a shared edge. Garnet has no such interactions, but does have one anomalously short cation–cation separation, the {X}–(Z) distance of 3.015A. This is a shared-edge interaction (with suitable possibility for orbital overlap), and the separation is well within the range cited for known $Fe^{2+} \rightarrow Fe^{3+}$ systems (Loeffler *et al.*, 1975; Burns *et al.*, 1976). In such an ED transition involving cations in nonidentical sites, a Verwey-type model is certainly not applicable, nor does the system approach that of either ilvaite (Nolet and Burns, 1979) or hematite–ilmenite solid solution (Warner *et al.*, 1972). Symmetry considerations must be an important factor in assessing the possibility of such ED transitions.

The mechanism for electron delocalization consists of overlapping coordination cluster orbitals mixing to form orbitals delocalized over several cation sites. Such orbitals are populated by thermal activation with short transition lifetimes, but are observable due to high frequencies. Garnet {X}–(Z) cluster overlap could be facilitated by the similar relative energy levels of $t_{2g}(t_2)$ and $e_g(e)$ molecular orbitals in both tetrahedral and dodecahedral coordinations. On the basis of the short {X}–(Z) separation, the correspondence of relative energies of t_{2g} and e_g levels for cubic and tetrahedral coordinations which enhances overlap possibilities, the anomalously high temperature-dependence of the isomer shift and quadrupole splitting for "Fe^{2+}(Z)" (Amthauer *et al.*, 1977), and the classic crystal-chemical radius and charge arguments against the substitution $Fe^{2+} \rightarrow Si^{4+}$, we have assigned "$Fe^{2+}$(Z)" absorptions as $Fe^{2+}\{X\} \rightarrow Fe^{3+}(Z)$ delocalization absorptions.

It must be emphasized that such delocalization does not place Fe^{2+} in tetrahedral coordination. Delocalization transitions are short-lived relative to the Mössbauer transition, let alone with respect to the relaxation time for the site to adjust to an additional electron. Delocalization is only observed due to the frequency of the transition. Other treatments of electron delocalization are given by Day (1976), Nolet (1978), and Nolet and Burns (1979). Little theoretical work has dealt with the problem of delocalization transitions between nonidentical sites, and highly complex MO calculations are required to resolve the question of nonidentical site ED.

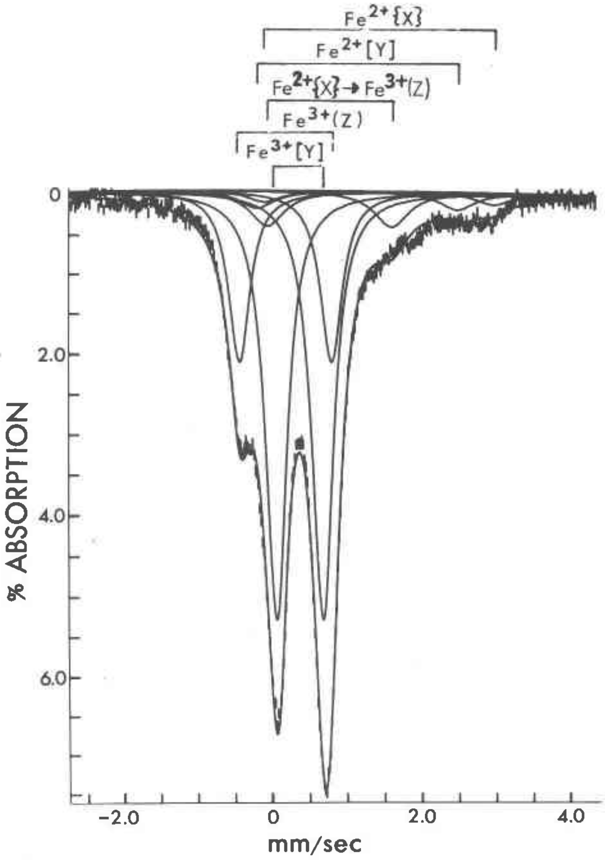

Fig. 6. Mössbauer spectrum of schorlomite from Magnet Cove, Arkansas (#7) fitted to five doublets assigned to Fe^{3+}[Y], Fe^{3+}(Z), Fe^{2+}[Y], Fe^{2+}\{X\}, and $Fe^{2+}\{X\} \rightarrow Fe^{3+}(Z)$ electron delocalization.

$Fe^{2+}/\Sigma Fe$, Ti^{3+}/Ti, and site occupancies from Mössbauer measurements

Final Mössbauer parameters summarized in Table 2 include peak area data from which $Fe^{2+}/\Sigma Fe$ ratios may be calculated. Areas were first corrected for recoil-free fraction differences at 298K by the following relations:

$$f_{Fe^{2+}\{X\}} = 0.78 f_{Fe^{3+}[Y]} = 0.78 f_{Fe^{2+}[Y]} = 0.73_{Fe^{3+}(Z)}$$

These f numbers are based on data by Sawatzky *et al.* (1969) and Whipple (1973). The above relationships imply that Fe^{2+} and Fe^{3+} in octahedral coordination in the garnet structure have similar recoil-free fractions. Areas assigned to $Fe^{2+}\{X\} \rightarrow Fe^{3+}(Z)$ were partitioned equally between tetrahedral Fe^{3+} and

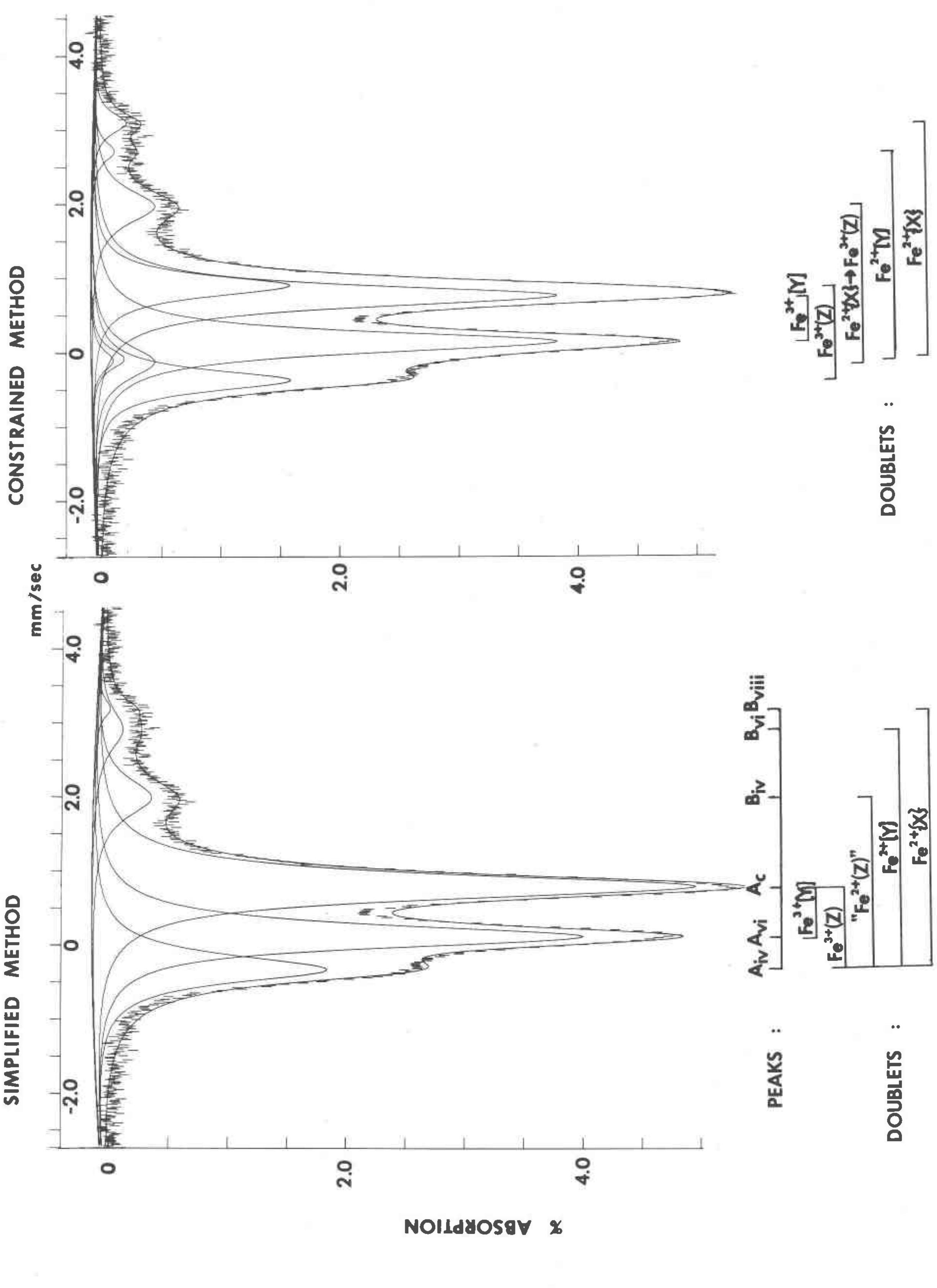

Fig. 7. Comparison of simplified fitting, resolving only visually apparent peaks with no constraints, and constrained fitting, resolving doublet components with width and intensity constraints. Data given in Table 5.

Table 2. Mössbauer parameters for melanites and schorlomites[a]

Specimen	1	2	3	4	5	6	7	8	4[b]	7[b]
Fe^{3+}[Y]										
Isomer Shift	0.420(2)	0.418(3)	0.431(2)	0.417(2)	0.416(2)	0.409(2)	0.393(2)	0.418(2)	0.474(2)	0.471(3)
Quad. Splitting	0.560(1)	0.604(1)	0.589(1)	0.594(1)	0.577(1)	0.590(1)	0.613(2)	0.595(2)	0.585(1)	0.614(2)
Width	0.260(3)	0.328(1)	0.285(1)	0.293(1)	0.280(1)	0.291(1)	0.344(2)	0.333(2)	0.318(1)	0.351(2)
% Area	100.0±0.72	87.9±0.15	94.8±0.19	86.7±0.26	89.3±0.23	87.2±0.28	59.2±0.48	67.3±0.62	86.2±0.25	56.7±0.70
Fe^{3+}(Z)										
Isomer Shift		0.238(3)		0.185(5)	0.176(5)	0.225(5)	0.211(3)	0.218(7)	0.241(5)	0.288(4)
Quad.Splitting		1.300(4)		1.407(6)	1.342(7)	1.357(8)	1.223(4)	1.309(10)	1.401(6)	1.270(4)
Width		0.314(6)		0.273(10)	0.238(12)	0.352(13)	0.344(2)	0.333(2)	0.281(10)	0.351(2)
% Area		12.1±0.15		8.3±0.20	4.9±0.16	8.9±0.24	23.3±0.39	9.4±0.32	8.4±0.20	24.3±0.65
Fe^{2+}{X}										
Isomer Shift				1.465(9)	1.513(11)	1.446(9)	1.457(2)	1.448(2)	1.600(7)	1.530(15)
Quad. Splitting				3.094(11)	3.101(15)	3.063(13)	3.055(19)	2.967(32)	3.204(10)	3.169(3)
Width				0.279(16)	0.401(23)	0.277(17)	0.247(20)	0.474(39)	0.275(14)	0.347(23)
% Area				5.0±0.16	5.8±0.18	3.9±0.13	2.5±0.13	5.2±0.26	5.4±0.16	4.0±0.26
Fe^{2+}[Y]										
Isomer Shift			1.162(9)				1.167(2)	1.149(2)		1.328(24)
Quad.Splitting			2.587(13)				2.660(21)	2.466(32)		2.811(2)
Width			0.327(21)				0.247(20)	0.474(39)		0.347(23)
% Area			5.2±0.19				2.2±0.14	5.5±0.38		2.6±0.22
$Fe^{2+}\{X\}\rightarrow Fe^{3+}(Z)$										
Isomer Shift							.788(36)	0.785(2)		.949(24)
Quad.Splitting							1.734(51)	1.650(45)		2.088(36)
Width							0.885(59)	0.892(82)		0.563(24)
% Area							12.8±0.60	12.6±0.87		12.4±0.45
χ^2	1.06	4.44	1.59	1.63	1.56	2.84	1.55	1.43	1.52	1.69
MISFIT	0.0405 ±0.0404	0.1160 ±0.0058	0.0376 ±0.0054	0.0367 ±0.0051	0.0205 ±0.0031	0.0724 ±0.0052	0.0463 ±0.0072	0.0530 ±0.0098	0.0318 ±0.0050	0.0497 ±0.0066

a - Spectra at 298K except where noted. Isomer Shift, Quadrupole Splitting, and Width parameters in mm/sec, relative to metallic Fe foil and source of $^{57}Co/Pd$.

b - Spectra at 77K.

dodecahedral Fe^{2+}. Wet-chemical ferrous and ferric contents, calculated as cations per formula unit (p.f.u.), and $Fe^{2+}/\Sigma Fe$ ratios by wet-chemistry and Mössbauer methods are given in Table 3. No ferrous iron was resolved in the Mössbauer spectra of specimens 1 and 2, indicating Fe^{2+} contents below the 1% resolution of the spectrometer.

Mössbauer $Fe^{2+}/\Sigma Fe$ ratios show a consistent positive discrepancy from ratios obtained from wet-chemical analyses (Howie and Woolley, 1968), indicating the presence of Ti^{3+} and enabling estimates of Ti^{3+} cation proportions and $Ti^{3+}/\Sigma Ti$ ratios to be made (Table 3). For samples analyzed by electron microprobe, crude estimates of Ti^{3+} and Ti^{4+} were made by charge balance calculations, assuming 12 oxygens per formula unit (Table 4). The data show that up to 23±2% of all Ti is present as Ti^{3+} in one specimen, with an average of 12% and a range of 0–23% over the suite of specimens. Similar results were obtained by Burns (1972) and Huggins *et al.* (1977b).

Iron cation proportions calculated from final Mössbauer data (Table 2) and chemical analyses (Table 1) enabled site occupancy data to be deduced (Table 4). $Fe^{2+}\{X\} \rightarrow Fe^{3+}(Z)$ was again proportioned equally to dodecahedral Fe^{2+} and tetrahedral Fe^{3+}. The remaining cations were distributed under the assumptions:

(1) Si was placed in (Z) positions only. Differences of Si plus tetrahedral Fe^{3+} from 3.000 formula units were filled by (Al^{3+},Ti^{4+}).

(2) Ca was placed in {X} positions, together with dodecahedral Fe^{2+} estimated from Mössbauer data. Deficiencies of Ca plus Fe^{2+} from 3.000 formula units were filled by Mn^{2+} and Mg^{2+}.

(3) Ti^{3+} ions with Al^{3+} and Ti^{4+} not filling the (Z) positions, Mg^{2+} and Mn^{2+} not accomodated in {X} positions, and Fe^{2+} and Fe^{3+} calculated from the Mössbauer data, were allocated to [Y] positions. The sum of ($Fe^{2+} + Fe^{3+} + Ti^{3+} + Ti^{4+} + Al^{3+} + Mg^{2+} + Mn^{2+}$) in [Y] positions was close to 2.000 formula units, ranging from 1.87 to 2.09.

Discussion

Comparison of fitting procedures

A comparison of peak parameters from Huggins *et al.* (1977b) and Amthauer *et al.* (1977) can be made

Table 3. $Fe^{2+}/\Sigma Fe$ and $Ti^{3+}/\Sigma Ti$ ratios for natural Fe–Ti garnets

Specimen	1	2	3	4	5	6	7	8
^{a}Ti (p.f.u.)	0.028	0.552	0.526	0.148	0.136	0.254	0.916	0.498
$^{a}Fe^{3+}$ (p.f.u.)	1.576	1.517	1.194	1.318	1.295	1.578	1.071	1.563
$^{a}Fe^{2+}$ (p.f.u.)	0.013	0.142	0.156	-	-	0.119	0.237	-
$^{a}Fe^{2+}/\Sigma Fe$ (Chem)	0.008	0.086	0.116	-	-	0.070	0.181	-
$^{b}Fe^{2+}/\Sigma Fe$ (Möss)	0.01	0.01	0.052	0.064	0.073	0.050	0.135	0.198
$Fe^{2+}/\Sigma Fe$ difference (Chem-Möss)	∼0	∼0.076	0.064	-	-	0.020	0.046	-
Ti^{3+} (p.f.u.)	∼0	0.126	0.086	0.005[c]	0.021[c]	0.034	0.060	0.110
$Ti^{3+}/\Sigma Ti$	∼0	0.23	0.16	0.03	0.15	0.13	0.07	0.22

[a] From Table 1.
[b] Obtained from calculated peak areas corrected for recoil-free fraction differences.
[c] Obtained from charge balance calculations of electron microprobe data.

with those of our study. Discrepancies in the low-velocity region of the earlier studies indicate the potential for serious error in Mössbauer-derived crystal-chemical data. In order to compare statistics and data derived from the two fitting procedures, a 77K spectrum of specimen 7 was fit by both methods, with resultant spectra shown in Figure 7 and data summarized in Table 5. Significant statistical improvement over the Huggins *et al.* (1977b) method can be seen as χ^2 decreases from 2.883 to 1.668 and MISFIT (Ruby, 1973) decreases from 0.1418±0.0101 to 0.0497±0.0066 by adopting a constrained fit resolving component doublets. These figures may be compared to those for a typical iron-foil calibration with χ^2 about 1.2 and MISFIT 0.03±0.01.

Table 4. Cation distributions in natural Fe–Ti garnets[a]

Specimen	1	2	3	4	5	6	7	8
Si	2.996	2.663	2.818	2.907	2.897	2.859	2.254	2.718
Fe^{3+}		.189		.101	.059	.141	.361	.225
Al^{3+} Ti^{4+} }	0.004	.148	0.182		.044		.385	.057
ΣZ	3.000	3.000	3.000	3.008	3.000	3.000	3.000	3.000
Ti^{3+}		.126	.086	.005	.021	.034	.060	.110
Ti^{4+} Al^{3+} }	0.505	.422	.521	.778	.751	.482	1.003	.557
Fe^{3+}	1.589	1.470	1.280	1.133	1.141	1.472	.770	1.029
Fe^{2+}			.070				.029	.084
Mg^{2+}				0.074	0.025		.168	0.052
Mn^{2+}				.015	0.035		0.026	
ΣY	2.095	2.018	1.957	2.005	1.973	1.988	2.030	1.858
Ca^{2+}	2.725	2.802	2.853	2.912	2.969	2.741	2.790	3.016
Fe^{2+}				.084	.095	.084	.148	.225
Mg^{2+}	0.106	0.087	0.099			0.107	.012	
Mn^{2+}	0.025	0.047	0.002	.004		0.050	0.050	
Na^{+}			0.019					
K^{+}			0.002					
ΣX	2.856	2.936	2.975	3.000	3.064	2.982	3.000	3.241

[a] Based on chemical analyses (Table 1) and Mössbauer peak areas corrected for recoil-free fraction differences.

Crystal-chemical data were derived from the Huggins *et al.* (1977b) fits by assuming as do those authors that:

(1) $Fe^{3+}[Y]$ can be obtained directly from the low-velocity peak, A_{VI}.

(2) $Fe^{2+}\{X\}$, $Fe^{2+}[Y]$, and "$Fe^{2+}(Z)$" can be obtained directly from the high-velocity peaks B_{VIII}, B_{VI}, and B_{IV}.

(3) $Fe^{3+}(Z)$ can be calculated (from overlapping species) by $\frac{1}{2}[(A_{IV} - B_{IV} - B_{VI} - B_{VIII}) + (A_C - A_{VI})]$.

Clearly, if the Fe^{2+} low-velocity components do not exactly coincide with A_{IV} and if $Fe^{3+}(Z)$ and $Fe^{3+}[Y]$ high-velocity components do not exactly coincide to give A_C, the resultant data can be greatly in error, especially in $Fe^{3+}(Z)$ and Fe^{2+}/Fe^{3+} ratios. Table 5 compares iron cation proportions derived from the two methods. Even ignoring differences due to the assignment of "$Fe^{2+}(Z)$" as $Fe^{2+}\{X\} \rightarrow Fe^{3+}(Z)$, site populations vary by 10% for $Fe^{3+}[Y]$ and 30% for $Fe^{3+}(Z)$. Fe^{2+}/Fe^{3+} ratios, assuming Huggins *et al.* (1977b) assignments, are 0.258 for the simplified fit and 0.235 for the constrained one, a difference of 10%.

Another critical improvement in the constrained fits can be seen in the decrease of the error (standard deviation) of the resultant areas. This is due to errors in positions and widths, which are reduced upon resolution of doublet components. Areas of $Fe^{3+}(Z)$, $Fe^{2+}[Y]$ and $Fe^{2+}\{X\}$ all have errors in excess of 10% associated with them in simplified fitting. These errors are also purely statistical and take no account of the errors associated with the basic assumptions, for example, that ferrous low-velocity peaks exactly coincide with A_{IV}. The statistical superiority of constrained fits which resolve component doublets is clear.

Assignment of Mössbauer absorption

A fundamental difference between earlier work and the present study of Ti-rich garnets is the assignment of "$Fe^{2+}(Z)$" to the electron delocalization $Fe^{2+}\{X\} \rightarrow Fe^{3+}(Z)$. Classical ionic-radius criteria would rule out the substitution of large Fe^{2+} ions for small Si^{4+} ions. Indeed, known $Fe^{2+}O_4$ clusters (spinel, staurolite, akermanite, gillespite) have average Fe–O distances significantly larger than the garnet Si–O distances of 1.643A (Novak and Gibbs, 1971). Crystal field site preference energies would also prohibit the introduction of Fe^{2+}, normally stabilized by distorted sites of ionic character, into isolated, symmetric, highly covalent Si^{4+} tetrahedra. $Fe^{2+} \rightarrow Si^{4+}$ substitution might be facilitated in sites of high effective distortion with coordinated vacancies or other defects [*e.g.* lunar plagioclase (Hafner *et al.*, 1971)]. Such substitution, however, has yet to be demonstrated in any phase with a symmetric Si site.

Assignment of electron delocalization absorption as "Fe^{2+}(Z)" yields puzzling crystal-chemical data. From ionic radius and crystal field site preference considerations, it would be predicted that Fe^{2+} would have a smaller preference for the symmetric tetrahedral sites than coexisting Fe^{3+}, particularly in the presence of high concentrations of octahedral Fe^{3+} in titanian andradites. This is not the case in specimens OL, SB, ML, and Ar of Huggins *et al.* (1977b), where Fe^{2+} occupancies derived for the Z position are *larger* than Fe^{3+}. Such anomalies are indicative of incorrect fitting and assignments.

The existence of intervalence transitions in titanian garnets is further supported by optical spectral studies. The near infrared spectra of titanian garnets show an absorption band at 5,280 cm^{-1}, originally assigned to the crystal field transition $^5E \rightarrow {}^5T_2$ in tetrahedral Fe^{2+} (Manning, 1967; Manning and Harris, 1970). Dowty (1971) and Huggins *et al.* (1977b) adopted this assignment to support the resolution of "Fe^{2+}(Z)" in Mössbauer spectra of titanian garnets. However, Moore and White (1971) found that the temperature-dependence of the 5,280 cm^{-1} band, which decreases in intensity with rising temperature, was not consistent with crystal field transitions, and speculated that the band might represent a CT transition. Recent studies (Smith and Strens, 1976; Smith, 1977) demonstrate that CT bands in other minerals also have inverse temperature-dependence. Additionally, Moore and White performed electrical conductivity measurements on garnets and found that andradite is an insulator but becomes a semiconductor as the Ti content increases. The activation energy for conduction was calculated to be about 0.47 eV or 3,800 cm^{-1}, in agreement with the energy of the CT band. These results support the assignment of $Fe^{2+}\{X\} \rightarrow Fe^{3+}(Z)$ electron delocalization in Mössbauer spectra of Fe–Ti garnets.

Table 5. Comparison of computed Mössbauer parameters from simplified and constrained fitting procedures

Simplified Method				Constrained Method			
Positions[a]							
Peaks	mm/sec[b]	σ		Peaks	mm/sec[b]	σ	
A_{IV}	-.304	.004		1	-.054	.011	
A_{VI}	.148	.003		2	-.077	.017	
A_C	.817	.003		3	-.095	.035	
B_{IV}	2.002	.010		4	.164	.003	
B_{VI}	2.916	.088		5	-.347	.004	
B_{VIII}	3.201	.042		6	.778	.003	
				7	.924	.004	
				8	1.993	.008	
				9	2.734	.017	
				10	3.115	.011	
Widths							
Peaks	mm/sec	σ		Peaks	mm/sec	σ	
A_{IV}	.455	.008		Fe^{2+}	.347	.023	
A_{VI}	.380	.008		Fe^{3+}	.351	.002	
A_C	.403	.002		$Fe^{2+}\{X\} \rightarrow Fe^{3+}(Z)$	.563	.024	
B_{IV}	.656	.036					
B_{VI}	.694	.163					
B_{VIII}	.312	.219					
Areas							
Peaks	% Area	σ		Peaks	% Areas	σ	% Error
A_{IV}	17.90	.32		$Fe^{2+}\{X\}$	4.00	.26	6.40
A_{VI}	31.19	.40		$Fe^{2+}[Y]$	2.64	.22	8.33
A_C	40.64	.27		$Fe^{2+}\{X\} \rightarrow Fe^{3+}(Z)$	12.38	.45	3.62
B_{IV}	6.39	.37		$Fe^{3+}(Z)$	24.26	.65	2.67
B_{VI}	3.16	1.48		$Fe^{3+}[Y]$	56.74	.70	1.24
B_{VIII}	0.72	.97					
Site Populations							
Cation	% in Site[c]	σ	% Error	Cation	% in Site[d]	σ	% Error
$Fe^{2+}\{X\}$	1.44	1.93	134.31	$Fe^{2+}\{X\}$	10.19	.34	3.34
$Fe^{2+}[Y]$	6.32	2.97	46.96	$Fe^{2+}[Y]$	2.64	.22	8.33
$Fe^{3+}(Z)$	17.08	1.90	11.12	$Fe^{3+}(Z)$	20.45	.69	2.25
$Fe^{3+}[Y]$	62.38	.81	1.29	$Fe^{3+}[Y]$	56.74	.70	1.24
"$Fe^{2+}(Z)$"	12.78	.74	5.81				
χ^2 [e]	1404.06/487 = 2.883			χ^2 [e]	825.43/489 = 1.688		
MISFIT[e]	.1418 ± .0101			MISFIT[e]	.0497 ± .0066		

a - Positions for the constrained method refer to peaks assigned as follows:

1-10, $Fe^{2+}\{X\}$; 2-9, $Fe^{2+}[Y]$; 3-8, $Fe^{2+}\{X\} \rightarrow Fe^{3+}(Z)$;

5-7, $Fe^{3+}(Z)$; 4-6, $Fe^{3+}[Y]$

b - Calibration is relative to metallic Fe foil and source of $^{57}Co/Pd$.

c - Calculated by method of Huggins et al. (1977b).

d - Corrected for electron delocalization.

e - Statistical parameters may be compared to average values for Fe foil calibration with χ^2 = 1.2 and MISFIT = .03 ± 01.

Garnet site occupancies derived from the above fitting and assignment scheme show strong enrichment of Fe^{3+} in tetrahedral (Z) sites not filled by Si^{4+}. While our study has not investigated the relative enrichment of Al^{3+} and Ti^{4+} in Z sites, Huggins *et al.* (1977a) suggest that Al^{3+} is enriched relative to Ti^{4+}, yielding the trend $Fe^{3+} > Al^{3+} \geq Ti^{4+}$. This trend may be biased somewhat by the compositions of natural garnets studied; further work on synthetic samples is in progress to verify the trend.

Conclusions

Constrained fitting of Mössbauer spectra of Ti-rich garnets is warranted by:

(1) Decrease of statistical parameters χ^2 and MISFIT on resolving doublet components in constrained fits.

(2) Decrease in the standard deviations of area data from the Mössbauer fits, increasing the accuracy of the derived site populations.

(3) Consistency of derived Mössbauer parameters as expected from small crystallographic variations. Isomer shifts for Fe^{3+}(Z) vary from 0.16 to 0.28mm/sec in Huggins *et al.* (1977b) compared with variation of <0.06mm/sec in our study.

(4) Non-coincidence of resolved doublet components, separated in most cases by $>1/2\Gamma$, yielding crystal-chemical data lacking the anomalies and inconsistencies of previous studies.

Assignment of "Fe^{2+}(Z)" absorption to Fe^{2+} {X} → (Z) electron delocalization is justified on the grounds:

(1) Substitution of Fe^{2+} for Si^{4+} is not observed in other silicates, nor is it to be expected from ionic radius or crystal field site preference considerations.

(2) Elimination of anomalous preference of Fe^{2+}(Z) over Fe^{3+}(Z) in several specimens.

(3) Resolution of CT bands in optical spectra (Moore and White, 1971) with appropriate temperature-dependencies and with energies corresponding to the garnet semiconduction activation energy.

(4) Electrical conductivity studies of titanian garnets classed as semiconductors as opposed to the insulating character of andradite (Moore and White, 1971).

(5) Structural correlations of theoretical factors affecting electron delocalization, *i.e.* short cation–cation distance, shared edge connection, and possibility of cation overlap facilitated by similar relative energies of $t_{2g}(t_2)$ and $e_g(e)$ molecular orbitals in tetrahedral and dodecahedral coordinations.

Other significant conclusions can be drawn from the cation-distribution data. A consistent discrepancy between Mössbauer and wet-chemical $Fe^{2+}/\Sigma Fe$ ratios indicates the presence of Ti^{3+} in melanites and schorlomites. $Ti^{3+}/\Sigma Ti$ ratios range from 0.00 to 0.23 across the suite of samples. Site occupancies in the Z positions show strong enrichment of Fe^{3+} in tetrahedra not filled by Si. In high-temperature garnets (from nepheline syenites, carbonatites, and volcanic rocks) excluding samples from serpentized peridotites, the enrichment trend from this study is $Fe^{3+} > (Al^{3+},Ti^{4+})$, contrary to that found by Huggins *et al.* (1977a).

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