

Mössbauer spectroscopy and crystal chemistry of natural Fe–Ti garnets

KENNETH B. SCHWARTZ,¹ DANIEL A. NOLET² 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 trigonal 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 3.015Å, 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 $\text{Fe}^{2+}/\Sigma\text{Fe}$ 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 $\text{Fe}^{3+} > (\text{Al}^{3+}, \text{Ti}^{4+})$ 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; Lehi-jarvi, 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 $\text{Fe}^{2+}/\text{Fe}^{3+}$ 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-

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.

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 $\{\text{X}_3\}[\text{Y}_2](\text{Z}_3)\text{O}_{12}$ per unit cell.³ $\{\text{X}\}$ cations are coordinated by eight oxygens at the vertices of a distorted cube described as an 8-fold triangular dodecahedron (Novak and Gibbs, 1971). $[\text{Y}]$ 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.

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

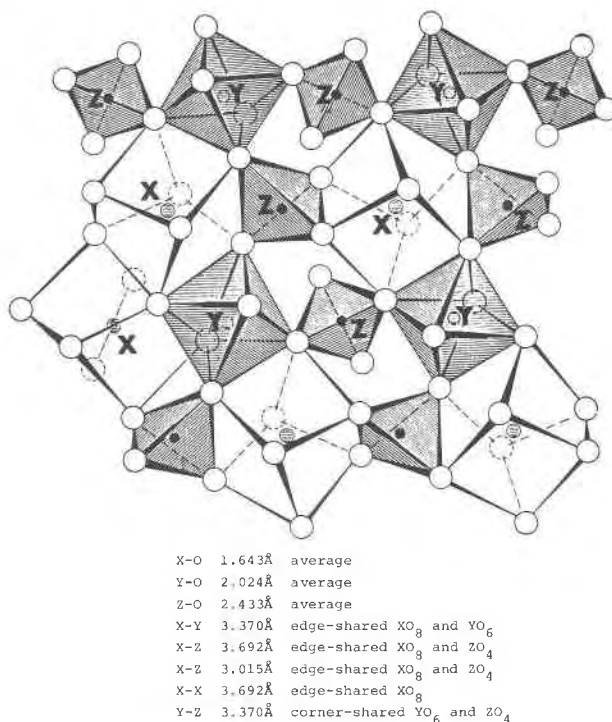


Fig. 1. Portion of the garnet structure projected down the c axis. Note the framework of alternating corner-shared YO_6 octahedra and ZO_4 tetrahedra as well as the chains of alternating edge-shared XO_8 dodecahedra and ZO_4 tetrahedra. Interatomic distances are for andradite, $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$ (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 $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$: $\text{Ca}_3\text{Fe}_2\text{Ti}_3\text{O}_{12}$, 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 $\text{Al} \geq \text{Fe}^{3+} > \text{Ti}^{4+}$.

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

schorlomite 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.

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 $\text{HF}/\text{H}_2\text{SO}_4$ 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 spec-

Table 1. Compositions and sources of the titaniferous garnets

Specimen	1	2	3	4	5	6	7	8
<i>Analyses, wt %</i>								
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
<i>Number of metal ions on the basis of 12 oxygens</i>								
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 $\text{K}_2\text{Cr}_2\text{O}_7$ (see text).

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

trum, 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.

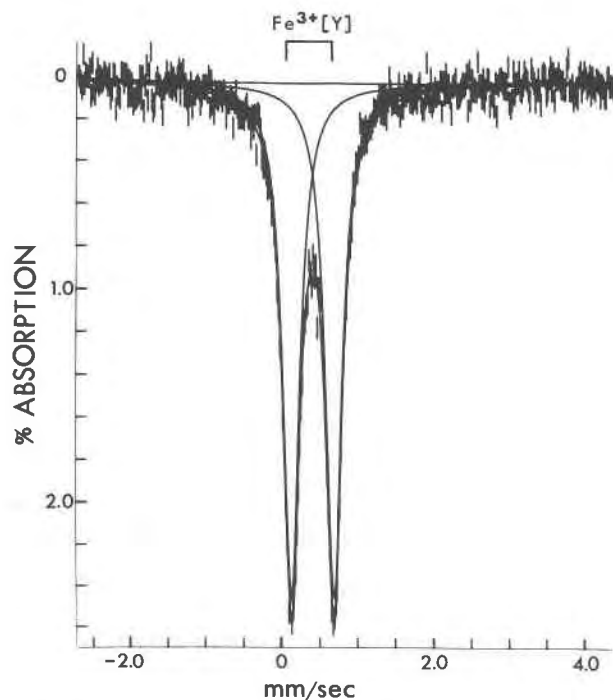


Fig. 2. Mössbauer spectrum of andradite from Semarule, Botswana (#1) fitted to one doublet assigned to $\text{Fe}^{3+}[\text{Y}]$.

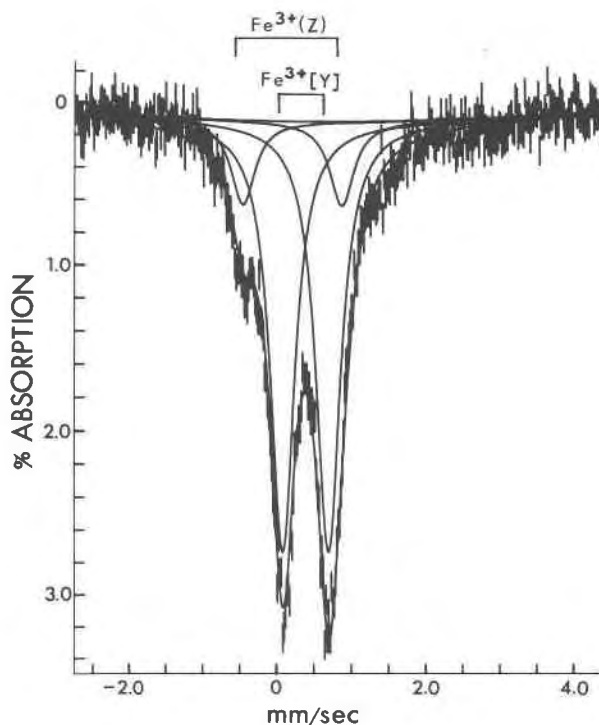


Fig. 3. Mössbauer spectrum of schorlomite from Morocco (#2) fitted to two doublets assigned to $\text{Fe}^{3+}[\text{Y}]$ and $\text{Fe}^{3+}[\text{Z}]$.

Simple, one- and two-doublet spectra allowed resolution of parameters for $\text{Fe}^{3+}[\text{Y}]$ (Fig. 2), $\text{Fe}^{3+}[\text{Z}]$ (Fig. 3), and $\text{Fe}^{2+}[\text{Y}]$ (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 $\text{Fe}^{3+}[\text{Z}]$ and $\text{Fe}^{3+}[\text{Y}]$ peaks separated by 0.18mm/sec (about half the calculated linewidth, Γ) and low-velocity $\text{Fe}^{3+}[\text{Y}]$ and $\text{Fe}^{2+}[\text{Y}]$ separated by 0.27mm/sec ($>3/4\Gamma$).

Specimen 4, shown in Figure 5, displays contributions from three doublets, $\text{Fe}^{3+}[\text{Z}]$, $\text{Fe}^{3+}[\text{Y}]$, and an additional species with a high-velocity peak at $\sim 3.0\text{mm/sec}$. This absorption is due to $\text{Fe}^{2+}[\text{X}]$ 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 $\text{Fe}^{3+}[\text{Y}]$ low-velocity component by 0.20mm/sec ($>1/2\Gamma$). Spectra of

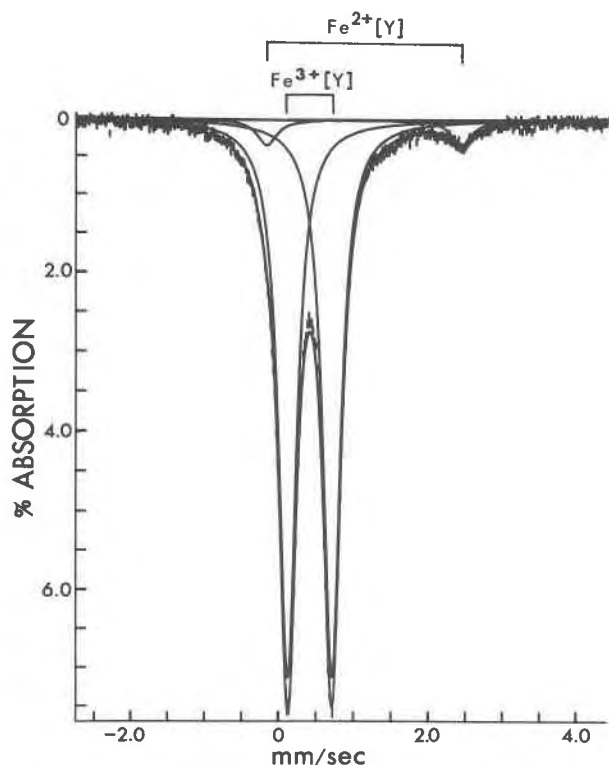


Fig. 4. Mössbauer spectrum of melanite from San Benito County, California (#3) fitted to two doublets assigned to $\text{Fe}^{3+}[\text{Y}]$ and $\text{Fe}^{2+}[\text{Y}]$.

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

From the located doublets due to $\text{Fe}^{3+}(\text{Z})$, $\text{Fe}^{3+}[\text{Y}]$, $\text{Fe}^{2+}[\text{Y}]$, and $\text{Fe}^{2+}(\text{X})$, 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 " $\text{Fe}^{2+}(\text{Z})$," 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 $\text{Fe}^{2+} \rightarrow \text{Si}^{4+}$ and the unusual temperature variations of " $\text{Fe}^{2+}(\text{Z})$ " 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 \rightarrow semiconductor

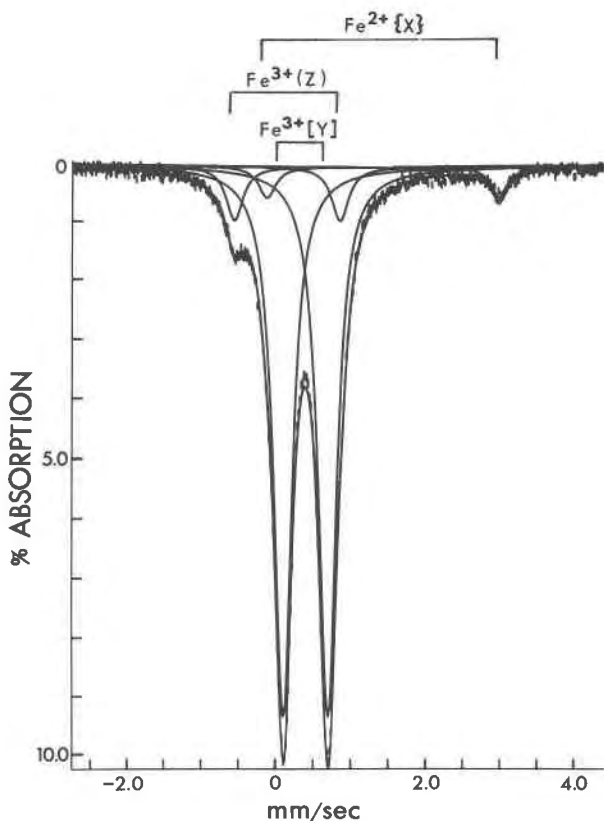


Fig. 5. Mössbauer spectrum of melanite from Frascati, Italy (#4) fitted to three doublets assigned to $\text{Fe}^{3+}[\text{Y}]$, $\text{Fe}^{3+}(\text{Z})$, and $\text{Fe}^{2+}(\text{X})$.

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 3.015Å. This is a shared-edge interaction (with suitable possibility for orbital overlap), and the separation is well within the range cited for known $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ 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 " $\text{Fe}^{2+}(\text{Z})$ " (Amthauer *et al.*, 1977), and the classic crystal-chemical radius and charge arguments against the substitution $\text{Fe}^{2+} \rightarrow \text{Si}^{4+}$, we have assigned " $\text{Fe}^{2+}(\text{Z})$ " absorptions as $\text{Fe}^{2+}\{\text{X}\} \rightarrow \text{Fe}^{3+}(\text{Z})$ 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

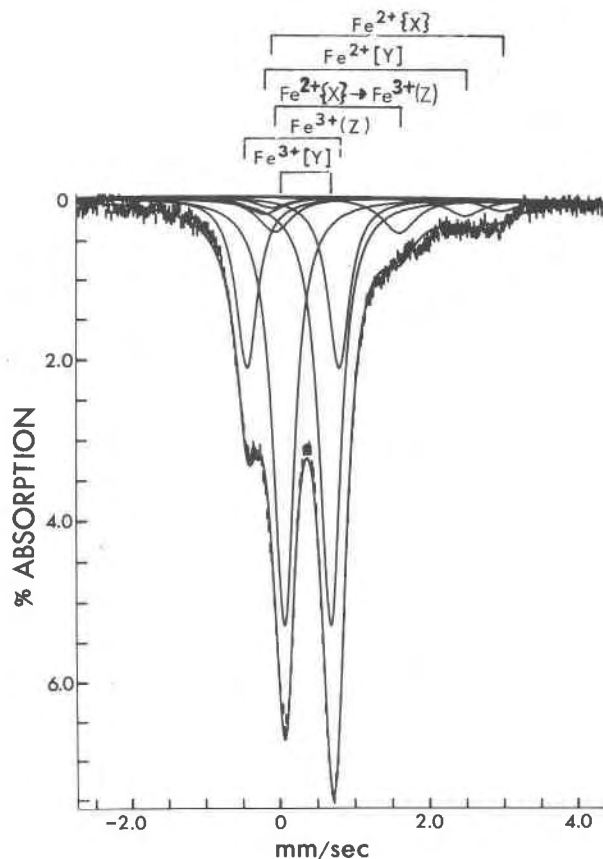


Fig. 6. Mössbauer spectrum of schorlomite from Magnet Cove, Arkansas (#7) fitted to five doublets assigned to $\text{Fe}^{3+}[\text{Y}]$, $\text{Fe}^{3+}(\text{Z})$, $\text{Fe}^{2+}[\text{Y}]$, $\text{Fe}^{2+}\{\text{X}\}$, and $\text{Fe}^{2+}\{\text{X}\} \rightarrow \text{Fe}^{3+}(\text{Z})$ electron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

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.

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

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

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

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 $\text{Fe}^{2+}\{\text{X}\} \rightarrow \text{Fe}^{3+}(\text{Z})$ were partitioned equally between tetrahedral Fe^{3+} and

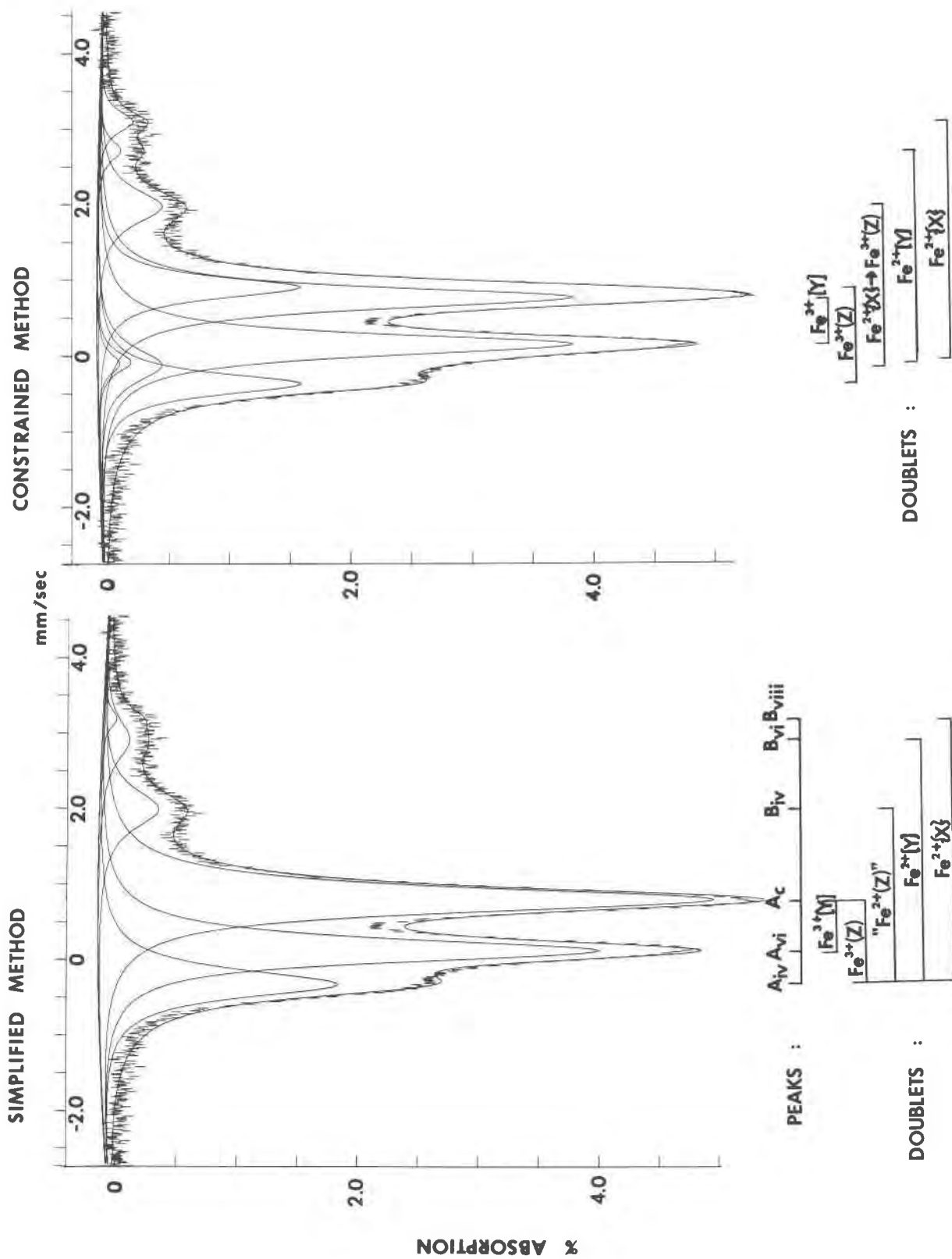


Fig. 7. Comparison of simplified fitting, resolving only visually apparent peaks with no constraints, and constrained fitting, resolving doublet components with width and intensity constraints. Data given in Table 5.

Table 2. Mössbauer parameters for melanites and schorlomites^a

Specimen	1	2	3	4	5	6	7	8	4 ^b	7 ^b
	<u>Fe³⁺ [Y]</u>									
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
	<u>Fe³⁺ (Z)</u>									
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
	<u>Fe²⁺ {X}</u>									
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
	<u>Fe²⁺ [Y]</u>									
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
	<u>Fe²⁺ {X} → Fe³⁺ (Z)</u>									
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	0.1160	0.0376	0.0367	0.0205	0.0724	0.0463	0.0530	0.0318	0.0497
	±0.0404	±0.0058	±0.0054	±0.0051	±0.0031	±0.0052	±0.0072	±0.0098	±0.0050	±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 ⁵⁷Co/Pd.

b - Spectra at 77K.

dodecahedral Fe²⁺. Wet-chemical ferrous and ferric contents, calculated as cations per formula unit (p.f.u.), and Fe²⁺/ΣFe 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 Fe²⁺ contents below the 1% resolution of the spectrometer.

Mössbauer Fe²⁺/ΣFe ratios show a consistent positive discrepancy from ratios obtained from wet-chemical analyses (Howie and Woolley, 1968), indicating the presence of Ti³⁺ and enabling estimates of Ti³⁺ cation proportions and Ti³⁺/ΣTi ratios to be made (Table 3). For samples analyzed by electron microprobe, crude estimates of Ti³⁺ and Ti⁴⁺ 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 Ti³⁺ 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). Fe²⁺ {X} → Fe³⁺ (Z) was again proportioned equally to dodecahedral Fe²⁺ and tetrahedral Fe³⁺. The remaining cations were distributed under the assumptions:

- (1) Si was placed in (Z) positions only. Differences of Si plus tetrahedral Fe³⁺ from 3.000 formula units were filled by (Al³⁺, Ti⁴⁺).
- (2) Ca was placed in {X} positions, together with dodecahedral Fe²⁺ estimated from Mössbauer data. Deficiencies of Ca plus Fe²⁺ from 3.000 formula units were filled by Mn²⁺ and Mg²⁺.
- (3) Ti³⁺ ions with Al³⁺ and Ti⁴⁺ not filling the (Z) positions, Mg²⁺ and Mn²⁺ not accommodated in {X} positions, and Fe²⁺ and Fe³⁺ calculated from the Mössbauer data, were allocated to [Y] positions. The sum of (Fe²⁺ + Fe³⁺ + Ti³⁺ + Ti⁴⁺ + Al³⁺ + Mg²⁺ + Mn²⁺) 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. Fe²⁺/ΣFe and Ti³⁺/ΣTi 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 _{Fe³⁺} (p.f.u.)	1.576	1.517	1.194	1.318	1.295	1.578	1.071	1.563
a _{Fe²⁺} (p.f.u.)	0.013	0.142	0.156	-	-	0.119	0.237	-
a _{Fe²⁺/ΣFe} (Chem)	0.008	0.086	0.116	-	-	0.070	0.181	-
b _{Fe²⁺/ΣFe} (Möss)	0.01	0.01	0.052	0.064	0.073	0.050	0.135	0.198
Fe ²⁺ /ΣFe 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⁺ /ΣTi	~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

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⁺	0.004	.148	0.182		.044		.385	.057
Ti ⁴⁺								
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.

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.

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

- (1) Fe³⁺[Y] can be obtained directly from the low-velocity peak, A_{IV}.
- (2) Fe²⁺{X}, Fe²⁺[Y], and "Fe²⁺(Z)" can be obtained directly from the high-velocity peaks B_{VIII}, B_{VI}, and B_{IV}.
- (3) Fe³⁺(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 Fe²⁺ low-velocity components do not exactly coincide with A_{IV} and if Fe³⁺(Z) and Fe³⁺[Y] high-velocity components do not exactly coincide to give A_C, the resultant data can be greatly in error, especially in Fe³⁺(Z) and Fe²⁺/Fe³⁺ ratios. Table 5 compares iron cation proportions derived from the two methods. Even ignoring differences due to the assignment of "Fe²⁺(Z)" as Fe²⁺{X} → Fe³⁺(Z), site populations vary by 10% for Fe³⁺[Y] and 30% for Fe³⁺(Z). Fe²⁺/Fe³⁺ 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 Fe³⁺(Z), Fe²⁺[Y] and Fe²⁺{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 "Fe²⁺(Z)" to the electron delocalization Fe²⁺{X} → Fe³⁺(Z). Classical ionic-radius criteria would rule out the substitution of large Fe²⁺ ions for small Si⁴⁺ ions. Indeed, known Fe²⁺O₄ clusters (spinel, staurolite, akermanite, gillespite) have aver-

age Fe–O distances significantly larger than the garnet Si–O distances of 1.643Å (Novak and Gibbs, 1971). Crystal field site preference energies would also prohibit the introduction of Fe²⁺, normally stabilized by distorted sites of ionic character, into isolated, symmetric, highly covalent Si⁴⁺ tetrahedra. Fe²⁺ → Si⁴⁺ 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 Fe²⁺ would have a smaller preference for the symmetric tetrahedral sites than coexisting Fe³⁺, particularly in the presence of high concentrations of octahedral Fe³⁺ in titanian andradites. This is not the case in specimens OL, SB, ML, and Ar of Huggins *et al.* (1977b), where Fe²⁺ occupancies derived for the Z position are larger than Fe³⁺. 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 → ⁵T₂ in tetrahedral Fe²⁺ (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)} → Fe^{3+(Z)} electron delocalization in Mössbauer spectra of Fe–Ti garnets.

Garnet site occupancies derived from the above fitting and assignment scheme show strong enrich-

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

Simplified Method			Constrained Method			
Peaks	mm/sec ^b	σ	Positions ^a			
			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)} →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)} →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)}→Fe^{3+(Z)};
5-7, Fe^{3+(Z)}; 4-6, Fe^{3+(Y)}

b - Calibration is relative to metallic Fe foil and source of ⁵⁷Co/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 χ² = 1.2 and MISFIT = .03 ± 01.

ment of Fe³⁺ in tetrahedral (Z) sites not filled by Si⁴⁺. While our study has not investigated the relative enrichment of Al³⁺ and Ti⁴⁺ in Z sites, Huggins *et al.* (1977a) suggest that Al³⁺ is enriched relative to Ti⁴⁺, yielding the trend Fe³⁺ > Al³⁺ ≥ Ti⁴⁺. 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 $\text{Fe}^{3+}(\text{Z})$ 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 " $\text{Fe}^{2+}(\text{Z})$ " absorption to $\text{Fe}^{2+}(\text{X}) \rightarrow (\text{Z})$ 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 $\text{Fe}^{2+}(\text{Z})$ over $\text{Fe}^{3+}(\text{Z})$ 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 $\text{Fe}^{2+}/\Sigma\text{Fe}$ ratios indicates the presence of Ti^{3+} in melanites and schorlomites. $\text{Ti}^{3+}/\Sigma\text{Ti}$ 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 $\text{Fe}^{3+} > (\text{Al}^{3+}, \text{Ti}^{4+})$, contrary to that found by Huggins *et al.* (1977a).

Acknowledgments

This research was made possible to a great extent by the generous donation by Professor R. A. Howie of chemically analyzed melanites and schorlomites. Useful discussions were held with Professor J. A. Tossell, Professor G. M. Bancroft, Dr. G. Waychunas, Professor G. Rossman, B. M. Loeffler, K. M. Parkin, M. D. Osborne. We thank Drs. F. E. Huggins, D. Virgo, and S. Hafner for providing preprints of their manuscripts. We are grateful to Margaret Johannets, Jamie Mac Eachern, and Francis Doughty for preparation of the manuscript. The research was supported by grants from NASA (NGR 22-009-551, NSG 7338 and NSG-7604).

References

- Amthauer, G., H. Annersten and S. S. Hafner (1976) The Mössbauer spectrum of ^{57}Fe in silicate garnets. *Z. Kristallogr.*, **143**, 14-55.
- , ———, and ——— (1977) The Mössbauer spectrum of ^{57}Fe in titanium-bearing andradites. *Phys. Chem. Miner.*, **1**, 399-413.
- Bancroft, G. M. (1973) *Mössbauer Spectroscopy: An Introduction for Inorganic Chemists and Geochemists*. McGraw-Hill, London.
- (1979) Mössbauer spectroscopic studies of the chemical state of iron in silicate minerals. *J. de Phys.*, **40**, C2-464-C2-471.
- , A. G. Maddock and R. G. Burns (1967) Applications of the Mössbauer effect to silicate mineralogy: I. Iron silicates of known crystal structure. *Geochim. Cosmochim. Acta*, **31**, 2219-2246.
- Burns, R. G. (1972) Mixed valencies and site occupancies of iron in silicate minerals from Mössbauer spectroscopy. *Can. J. Spectrosc.*, **17**, 51-59.
- and V. M. Burns (1971) Study of the crystal chemistry of titaniferous garnets by Mössbauer spectroscopy (abstr.). *Geol. Soc. Am. Abstracts with Programs*, **3**, 519-520.
- , K. M. Parkin, B. M. Loeffler, I. S. Leung and R. M. Abu-Eid (1976) Further characterization of spectral features attributable to titanium on the moon. *Proc. Lunar Sci. Conf.*, **7th**, 2561-2578.
- Cullen, J. R. and E. Callen (1971) Band theory of multiple ordering and the metal-semiconductor transition in magnetite. *Phys. Rev. Lett.*, **26**, 236-238.
- Day, P. (1976) Mixed valence chemistry and metal chain compounds. In H. J. Keller, Ed., *Low Dimensional Cooperative Phenomena*, p. 191-214. Plenum Press, New York.
- Dowty, E. (1971) Crystal chemistry of titanium and zirconium garnet: I. Review and spectral studies. *Am. Mineral.*, **56**, 1983-2009.
- and D. E. Appleman (1970) X-ray refinement and Mössbauer study of Ti-Zr garnets: tetrahedral Fe^{2+} ? *Geol. Soc. Am. Abstracts with Programs*, **7**, 541.
- Geller, S. (1967) Crystal chemistry of the garnets. *Z. Kristallogr.*, **125**, 1-47.
- Hafner, S. S., D. Virgo and D. Warburton (1971) Oxidation state of iron in plagioclase from lunar basalts. *Earth Planet. Sci. Lett.*, **12**, 159-166.
- Hamilton, W. C. (1958) Neutron diffraction study of the 119°K transition in magnetite. *Phys. Rev.*, **110**, 1050-1057.
- Howie, R. A. and A. R. Woolley (1968) The role of titanium and the effect of TiO_2 on the cell size, refractive index and specific gravity in the andradite-melanite-schorlomite series. *Mineral. Mag.*, **36**, 775-790.

- Huggins, F. E. (1975) *Mössbauer Studies of Iron Minerals under Pressure of up to 200 Kilobars*. Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, Massachusetts.
- , D. Virgo and H. G. Huckenholz (1976) The crystal chemistry of melanites and schorlomite. *Carnegie Inst. Wash. Year Book*, 75, 705–711.
- , ———, and ——— (1977a) Titanium-containing silicate garnets. I. The distribution of Al, Fe³⁺, and Ti⁴⁺ between octahedral and tetrahedral sites. *Am. Mineral.*, 62, 475–490.
- , ———, and ——— (1977b) Titanium-containing silicate garnets. II. The crystal chemistry of melanites and schorlomite. *Am. Mineral.*, 62, 646–665.
- , ———, E. Holz and H. G. Huckenholz (1975) Distribution of Al, Fe³⁺, and Ti⁴⁺ between the octahedral and tetrahedral sites in garnets between Ca₃Al₂Si₃O₁₂ and Ca₃Fe₂Ti_{1.416}Si_{1.584}O₁₂. *Carnegie Inst. Wash. Year Book*, 74, 579–585.
- Isaacs, T. (1968) Titanium substitutions in andradites. *Chem. Geol.*, 3, 219–222.
- Ito, J. and C. Frondel (1967) Synthetic zirconium and titanium garnets. *Am. Mineral.*, 52, 773–781.
- Kundig, W. and R. S. Hargrove (1969) Electron hopping in magnetite. *Solid State Comm.*, 7, 223–227.
- Kunitz, W. (1936) Magmatic associations—the role of titanium and zirconium in rock-forming silicates. *Neues Jahrb. Mineral. Geol., Beil.-Bd. 70A*, 385–466.
- Lehijarvi, M. (1966) On the zoning of titaniferous andradite garnets. *Geologi*, 18, 102–103.
- Loeffler, B. M., R. G. Burns and J. A. Tossell (1975) Metal→metal charge transfer transitions: interpretation of visible-region spectra of the moon and lunar materials. *Proc. Lunar Sci. Conf., 6th*, 2663–2676.
- Lyubutin, I. S. and A. P. Dodokin (1971a) Temperature dependence of the Mössbauer effect for tetrahedral iron atoms in garnets. (trans.) *Sov. Phys. Crystallogr.*, 15, 936–938.
- and ——— (1971b) Temperature dependence of the Mössbauer effect for Fe²⁺ in dodecahedral coordination in garnets. (trans.) *Sov. Phys. Crystallogr.*, 15, 1091–1092.
- , ——— and I. M. Belyaev (1970) Temperature-dependence of the Mössbauer effect for octahedral iron atoms in garnets. (trans.) *Sov. Phys. Solid State*, 12, 1100–1102.
- Manning, P. G. (1967) The optical absorption spectra of some andradites and the identification of the ⁶A₁→⁴A₁ ⁴E(G) transition in octahedrally bonded Fe³⁺. *Can. J. Earth Sci.*, 4, 1039–1047.
- and D. C. Harris (1970) Optical absorption and electron microprobe studies of some high Ti-andradites. *Can. Mineral.*, 10, 260–271.
- McCammon, C. A. (1978) *A Study of the Oxidation and Thermal Decomposition of Vivianite using Mössbauer and Optical Absorption Spectroscopy*. S. B. Thesis (Physics), Massachusetts Institute of Technology, Cambridge, Massachusetts.
- Moore, R. K. and W. B. White (1971) Intervalence electron transfer effects in the spectra of the melanite garnets. *Am. Mineral.*, 56, 826–840.
- Nolet, D. A. (1978) Electron delocalization observed in the Mössbauer spectrum of ilvaite. *Solid State Comm.*, 20, 719–722.
- and R. G. Burns (1979) Ilvaite: a study of temperature-dependent electron delocalization by the Mössbauer effect. *Phys. Chem. Minerals*, 4, 221–234.
- Novak, G. A. and G. V. Gibbs (1971) The crystal chemistry of the silicate garnets. *Am. Mineral.*, 56, 791–825.
- Ruby, S. L. (1973) Why MISFIT when you already have χ^2 ? In J. Gruverman, Ed., *Mössbauer Effect Methodology* 8, p. 263–276. Plenum Press, New York.
- Samuelsen, E. J., E. J. Bleeker, L. Dobrzynski and T. Riste (1968) Neutron scattering from magnetite below 119°K. *J. Appl. Phys.*, 39, 1114–1115.
- Sawatzky, G. A., F. van der Woude and A. H. Morrish (1969) Recoilless-fraction ratios for ⁵⁷Fe in octahedral and tetrahedral sites of a spinel and a garnet. *Phys. Rev.*, 183, 383–386.
- Schwartz, K. B. (1977) *Mössbauer Spectroscopy and Crystal Chemistry of Natural Fe-Ti Garnets*. M.S. Thesis, Massachusetts Institute of Technology, Cambridge, Massachusetts.
- Smith, G. (1977) Low-temperature optical studies of metal→metal charge transfer transitions in various minerals. *Can. Mineral.*, 15, 500–507.
- and R. G. J. Strens (1976) Intervalence-transfer absorption in some silicate, oxide, and phosphate minerals. In R. G. J. Strens, Ed., *Physics and Chemistry of Minerals and Rocks*, p. 583–612. Wiley, New York.
- Stone, A. J., H. J. Augard and J. Fenger (1971) General constrained non-linear regression for Mössbauer spectra. *Publ. Danish Atomic Energy Comm., RISO-M-1348*.
- Tarte, P. (1960) Infrared spectra of silicates. II. Determination of the structural role of Ti in certain garnets. *Silicate Industry*, 25, 171–175.
- (1965) Experimental study and interpretation of infrared spectra of silicates and germanates. Applications of these structural problems relative to the solid state. I. and II. *Acad. Roy. Belg. Cl. Sci., Mem. Coll. in 8°*, 35, 4a and 4b.
- Verble, J. L. (1974) Temperature-dependent light scattering studies of the Verwey transition and electronic disorder in magnetite. *Phys. Rev. B9*, 5236–5248.
- Verwey, E. J. and P. W. Haayman (1941) Electronic conductivity and transition point of magnetite (“Fe₃O₄”). *Physica*, 8, 979–987.
- , ——— and F. C. Romeijn (1947) Physical properties and cation arrangement of oxides with spinel structures. II Electrical conductivity. *J. Chem. Phys.*, 15, 181–187.
- Virgo, D. and S. S. Hafner (1970) Fe²⁺, Mg order-disorder in natural orthopyroxenes. *Am. Mineral.*, 55, 201–223.
- Warner, B. N., P. N. Shive, J. L. Allen and C. Terry (1972) A study of the hematite-ilmenite series by the Mössbauer effect. *J. Geomag. Geoelectr.*, 24, 353–367.
- Weber, H. P., D. Virgo and F. E. Huggins (1975) A neutron diffraction and ⁵⁷Fe Mössbauer study of a synthetic Ti-rich garnet. *Carnegie Inst. Wash. Year Book*, 74, 575–579.
- Whipple, E. R. (1973) *Quantitative Mössbauer Spectra and Chemistry of Iron*. Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, Massachusetts.
- Yamada, T., K. Suzuki and S. Chikazumi (1968) Electron microscopy of orthorhombic phase in magnetite. *Appl. Phys. Lett.*, 13, 172–174.
- Zedlitz, O. (1933) Lime-iron garnets rich in titanium. *Zentr. Mineral. Geol., A*, 225–239.
- (1935) Titaniferous calcium-iron garnets. II. *Zentr. Mineral. Geol., A*, 68–78.