

Mössbauer spectroscopy of Zn-poor and Zn-rich rhodonite

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ABSTRACT

Room-temperature Mössbauer spectra of five specimens of typical, Zn-poor rhodonite and five of Zn-rich rhodonite (“fowlerite”) have been obtained to determine whether the spectra reflect structural differences between the two varieties. All Fe is divalent and in the high spin state, and the spectra support the interpretation that Fe is present in all five M sites. Assignment of Mössbauer doublets to specific sites is made principally on the basis of isomer shift values and relationships between quadrupole splitting and polyhedral distortion parameters determined from previously reported crystal-structure refinements. Trends in Mössbauer parameters show correlations with trends in steric details of the sites, both among individual M sites within Zn-rich and Zn-poor varieties and between corresponding M sites of rhodonite and fowlerite. In particular, the Mössbauer parameters for the geometrically similar M1 and M2 sites are similar, and those of M4 and M5 reflect the tendency of the former toward more tetrahedral character and the latter toward less distortion in fowlerite. Iron occupancy is largely a function of polyhedral volume, although there is a secondary preference for octahedral coordination. Structural differences previously determined between rhodonite and fowlerite, which are driven principally by high concentrations of Zn in M4 and Ca in M5, are structurally pervasive and are maintained even when Fe substitutes for Zn or Ca.

Keywords: Rhodonite, fowlerite, Mössbauer spectroscopy, pyroxenoid

INTRODUCTION

The crystal structure of rhodonite [ideally $(\text{Mn} \gg \text{Ca,Fe,Mg})\text{SiO}_3$, $\text{C}\bar{1}$ pyroxenoid, $Z = 20$] contains single tetrahedral chains with a 5-tetrahedron repeat and five independent cation sites (Liebau 1959; Peacor and Niizeki 1963; Pertlik and Zahiri 1999). The structure is illustrated and described in detail in Nelson and Griffen (2005). The nontetrahedral cation sites are designated M1 through M5 (Fig. 1). M1, M2, and M3 are octahedra with differing degrees of distortion; M4 is a quite distorted octahedron with the cation displaced sufficiently from the centroid that several workers have considered it to be 5-coordinated (e.g., Ohashi and Finger 1975; Peacor and Niizeki 1963; Peacor et al. 1978; Pinckney and Burnham 1988); and M5 is usually considered an irregular 7-coordinated site.

Nelson and Griffen (2005) refined the structures of several specimens of both “normal” (Zn-poor) rhodonite from various localities and Zn-rich rhodonite (variety name “fowlerite”) from Franklin, New Jersey, its only known locality. They found that the structural differences between “normal” rhodonite (referred to hereafter simply as rhodonite) and Zn-rich rhodonite (fowlerite hereafter) occur mainly at the M4 and M5 sites. With increasing Zn concentration, M4, which selectively accommodates Zn, becomes more distorted and tends distinctly toward tetrahedral coordination. Concomitantly, M5 becomes more Ca-rich and less distorted in terms of bond lengths (angular distortion being

difficult to quantify for sevenfold coordination). Nelson and Griffen (2005) used site electronegativity values, based on cation distributions constrained by microprobe analyses and electron populations from X-ray site refinements, to conclude that the increase in Zn and Ca in fowlerite, relative to rhodonite, leads to more covalent character for M4 and more ionic character for M5. Their preliminary Mössbauer spectra suggested that Fe is present in all M sites in both rhodonite and fowlerite, although not necessarily equally distributed among those sites.

The only Mössbauer spectra of rhodonite published heretofore are those of Dickson (1975). He resolved the spectra of four specimens into five pure Lorentzian doublets, indicating the presence of Fe in all M sites. Dickson interpreted his results to indicate that Fe distribution in rhodonite is essentially independent of bulk Fe concentration.

Nelson and Griffen (2005) showed that rhodonite and fowlerite exhibit distinct crystal-chemical trends. The present study was undertaken to ascertain whether such differences are reflected in the Mössbauer spectra.

METHODS AND RESULTS

Mössbauer spectra were obtained for specimens listed in Table 2 of Nelson and Griffen (2005). Localities and microprobe analyses are given in Table 1 of Nelson and Griffen (2005). Material selected for Mössbauer work was ground under acetone and mounted between disks of cellophane tape. Specimen thickness for each sample was ~ 100 mg/cm², corresponding to the ideal Mössbauer thickness (Long et al. 1983).

Data were collected between +4 and –4 mm/s at room temperature in constant acceleration mode using a Mössbauer System I spectrometer manufactured by WEB Research Company. Data were collected to approximately 2 million counts/channel for all spectra. A nominally 25 mCi ⁵⁷Co/Rh source was used, and calibration spectra were collected from Fe metal foil. Data reduction, thickness corrections (Rancourt

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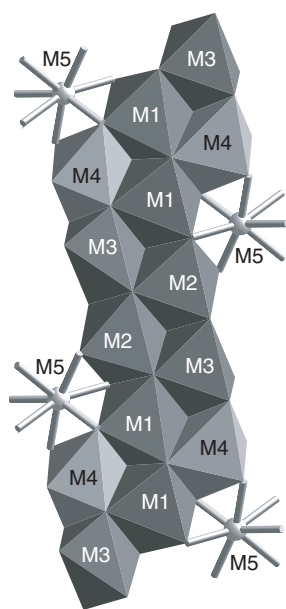


FIGURE 1. The five M sites in rhodonite-fowlerite. Crystallographic data from refinement of specimen 15-4029 (Nelson and Griffen 2005).

et al. 1993), and fitting with Voigt peak shapes (Lagarec and Rancourt 1997) were accomplished with the software package Recoil (Lagarec and Rancourt 1998).

Close examination of the folded spectra revealed evidence for the presence of at least four Mössbauer doublets. We began by fitting four doublets and then, based on the Mössbauer work of Dickson (1975) and the X-ray site refinements of Nelson and Griffen (2005), we split the outermost doublet to obtain a 5-doublet fit. Because of strong correlations, the isomer (chemical, center) shifts, quadrupole splittings, peak widths, and peak areas could not be varied simultaneously for all five doublets, so over several refinement cycles hyperfine parameters were held constant for 2 or 3 sites at a time and varied for the others.

Preliminary results showed that fits for some spectra yielded high χ^2 values (>3.0), and collecting new spectra on different samples of these specimens did not improve the results. We then analyzed the powders used for Mössbauer data collection by X-ray powder diffraction with a Scintag XDS-2000 θ - θ diffractometer (CuK α radiation, solid-state intrinsic Ge detector), and found that in all cases of poor fits, there were non-rhodonite peaks present in the diffractogram. Impurity peaks were present even in samples selected with greater care, so rhodonite specimens 15-4024, 15-4025, and 15-4033, and fowlerite specimens 15-4006 and 15-4027 (Nelson and Griffen 2005, their Table 2) were not used in this study. Additionally, specimen 15-4041 was not used because it is Fe-free.

Adequate fits to complex Mössbauer spectra can be obtained with different combinations of doublet characteristics and numbers of doublets; that is, fitting complex spectra often does not admit of a unique solution. The Si-O bond lengths of the rhodonite and fowlerite structures (Nelson and Griffen 2005) confirm that Fe does not enter the five Si sites. Thus only the five M sites are available for Fe occupancy, and there is no apparent crystal-chemical reason for excluding it from any of them. We therefore maintained the 5-doublet fit throughout, and we show below that it yielded crystallochemically reasonable results.

Table 1 gives isomer shifts (IS) with respect to α -Fe, quadrupole splittings (QS), peak widths (Γ), and peak areas for the five rhodonite and five fowlerite specimens that we used. Specimen numbers are Brigham Young University catalog numbers. All peaks are attributable to Fe²⁺ in the high spin state. There is no clear evidence for Fe³⁺ in either rhodonite or fowlerite, consistent with the work of Dickson (1975). Doublet designations are assigned on the basis of quadrupole splitting, with Doublet A having the smallest and Doublet E the largest. Estimated standard deviations, calculated from the correlation matrices, were typically in the following ranges: IS, <0.02 mm/s; QS, <0.04 mm/s; peak width, <0.02 mm/s; area, $<1\%$. Because only subsets of parameters were refined simultaneously, these uncertainties are underestimated and are thus not provided for each individual parameter in Table 1. Figure 2 shows spectra for a typical rhodonite specimen and for a typical fowlerite specimen.

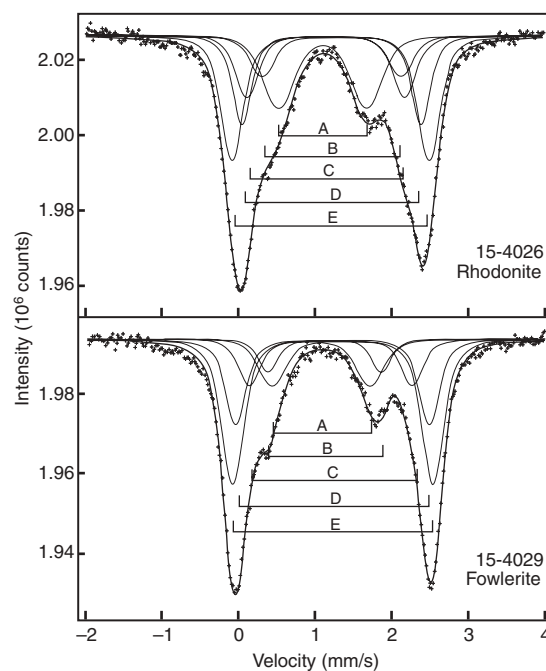


FIGURE 2. Typical Mössbauer spectra for specimens used in this study.

TABLE 1A. Mössbauer parameters for specimens used in this study —rhodonite specimens

Number	15-4034	15-4026	15-4018	15-4030	15-4031
Fe ²⁺ pfu	0.216	0.061	0.038	0.020	0.012
χ^2	2.29	1.33	2.76	1.28	1.34
Doublet A					
IS	1.09	1.10	1.09	1.08	1.05
QS	1.12	1.15	1.31	1.28	1.12
Γ	0.28	0.26	0.22	0.22	0.21
Rel. area	19.3	23.0	25.0	23.0	12.0
Doublet B					
IS	1.19	1.22	1.20	1.20	1.11
QS	1.62	1.81	1.69	1.74	1.36
Γ	0.23	0.22	0.19	0.21	0.18
Rel. area	3.3	11.0	2.4	9.0	11.0
Doublet C					
IS	1.17	1.14	1.15	1.12	1.10
QS	1.91	2.06	2.26	2.17	1.80
Γ	0.28	0.20	0.26	0.21	0.21
Rel. area	17.2	15.6	14.2	11.0	10.0
Doublet D					
IS	1.22	1.22	1.23	1.23	1.21
QS	2.41	2.34	2.44	2.43	2.35
Γ	0.25	0.17	0.25	0.21	0.26
Rel. area	41.0	19.3	22.7	41.0	44.0
Doublet E					
IS	1.21	1.21	1.22	1.20	1.21
QS	2.56	2.57	2.51	2.65	2.61
Γ	0.26	0.20	0.20	0.21	0.19
Rel. area	19.2	31.1	35.2	16.0	23.0

Notes: IS = isomer shift (mm/s); QS = quadrupole splitting (mm/s); Γ = peak width (mm/s); area in %. See text for discussion of errors.

DISCUSSION

Assignment of Mössbauer doublets to cation sites

Figure 3 shows overall positive correlations between IS and QS for both rhodonite and fowlerite, as demonstrated for a wide variety of other rock-forming silicate and oxide minerals by Burns (1994), and for tourmaline by Dyar et al. (1998). He

TABLE 1B. Mössbauer parameters for specimens used in this study—fowlerite specimens

Number	15-4014	15-4029	15-4028	15-4020	15-4040
Fe ²⁺ pfu	0.054	0.042	0.034	0.030	0.026
χ^2	1.19	1.29	1.94	1.70	1.35
Doublet A					
IS	1.08	1.06	1.08	1.07	1.07
QS	1.28	1.28	1.35	1.29	1.34
Γ	0.22	0.23	0.22	0.24	0.21
Rel. area	17.3	15.6	24.4	15.1	21.0
Doublet B					
IS	1.14	1.11	1.19	1.19	1.20
QS	1.84	1.48	1.98	1.91	1.85
Γ	0.21	0.18	0.22	0.23	0.22
Rel. area	7.8	8.5	9.5	9.0	7.0
Doublet C					
IS	1.25	1.19	1.21	1.21	1.22
QS	2.30	2.12	2.39	2.30	2.37
Γ	0.21	0.20	0.22	0.20	0.20
Rel. area	15.9	13.0	15.0	13.6	13.0
Doublet D					
IS	1.20	1.21	1.22	1.22	1.21
QS	2.44	2.53	2.54	2.51	2.57
Γ	0.20	0.19	0.18	0.19	0.18
Rel. area	20.7	22.6	19.0	19.8	33.0
Doublet E					
IS	1.22	1.22	1.21	1.21	1.21
QS	2.71	2.62	2.60	2.61	2.59
Γ	0.20	0.20	0.19	0.20	0.19
Rel. area	38.4	40.5	32.0	42.6	25.0

Notes: IS = isomer shift (mm/s); QS = quadrupole splitting (mm/s); Γ = peak width (mm/s); area in %. See text for discussion of errors.

correlate Mössbauer doublets with cation sites as follows: (1) Because the radius of the Fe nucleus in the excited state is smaller than in the ground state (Parish 1990), the increase in *s* electron density that occurs with decreasing coordination number (CN) lowers the isomer shift. The average isomer shift of Doublet A, 1.08 mm/s, is lower than generally found for octahedrally coordinated sites (e.g., Burns 1994). It is between the 1.11 mm/s for 5-coordinated Fe²⁺ in grandidierite (Seifert and Olesch 1977), and the ~1.00 mm/s for ^{IV}Fe²⁺ in staurolite (Alexander 1989; Dyar et al. 1991). Thus, Doublet A is attributed to Fe²⁺ in M4. (2) Isomer shifts of Doublets C, D, and E fall within the range expected for 6-coordinated Fe²⁺ in silicates (e.g., Bancroft et al. 1967; Burns 1994). These doublets were taken to represent Fe²⁺ in the most to least distorted unambiguously octahedral sites—M3, M2, and M1, respectively—based on the tendency for more regular sites to display higher quadrupole splitting (e.g., Bancroft et al. 1967; Parish 1990). Figure 4 shows quadrupole splitting as a function of quadratic elongation and of octahedral angle variance (Robinson et al. 1971; calculated from data of Nelson and Griffen 2005), and the clustering of data suggests that this assignment (as well as the assignment of Doublet A to M4) is correct. (3) The isomer shifts for Doublet B fall between those of A and C in our fowlerite spectra, and are generally greater than those for C in the rhodonite spectra. Although M5 is considered 7-coordinated, four of the bond lengths are near 2.2 Å, and the others are near 2.5, 2.6, and 2.7 Å, making the site moderately distorted. Dickson (1975) pointed out that a site with this degree of distortion should not be expected to follow trends in isomer shift established by much more regular coordination polyhedra. Moreover, while 7 appears to be a reasonable choice of CN for M5 from bond lengths alone (Nelson and Griffen 2005), the effective coordination number may be different. The bond-valence

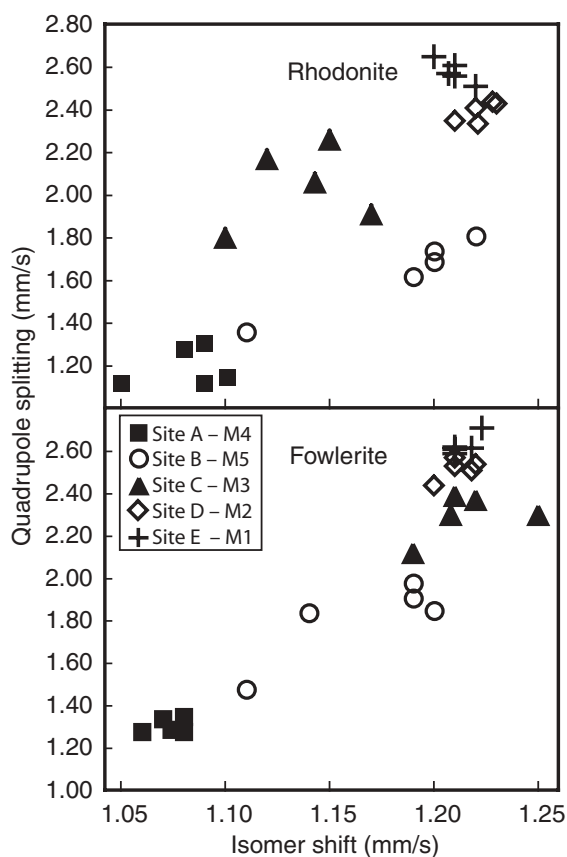


FIGURE 3. Isomer shift vs. quadrupole splitting in rhodonite (top) and fowlerite (bottom). Symbols in box apply to both rhodonite and fowlerite.

sums (Brown and Altermatt 1985) at M5 calculated using only the nearest six oxygen neighbors essentially satisfy the charge at M5. Further, the method of Chiari (1990) for evaluating the CN of Ca based on polyhedral volumes indicates that 6 is an unambiguously better choice than 7 for the effective coordination number of the mainly Ca-containing M5 of fowlerite. Similar calculations for the rhodonite specimens also yield 6 as the best choice of effective coordination number, although Ca is not the dominant cation in M5 of rhodonite, so the calculation may be less relevant to rhodonite than it is to fowlerite. These results suggest that the relatively low IS for M5 may be due to the combined effects of polyhedral distortion and a lower-than-assumed effective CN. The clustering of QS values as a function of quadratic elongation (Fig. 4) suggests that the assignment of Doublet B to M5 is valid.

These site assignments, in terms of relative positions of the peaks, are the same as those postulated by Dickson (1975). The clustering of data in Figure 4 is reasonable circumstantial evidence that doublets have been correctly assigned to crystallographic sites. One must be careful with this interpretation, inasmuch as the doublet designations are based on quadrupole splitting. Nevertheless, if the site assignments were incorrect, one might not expect such a clean clustering of points when Mössbauer parameters were plotted against structural data.

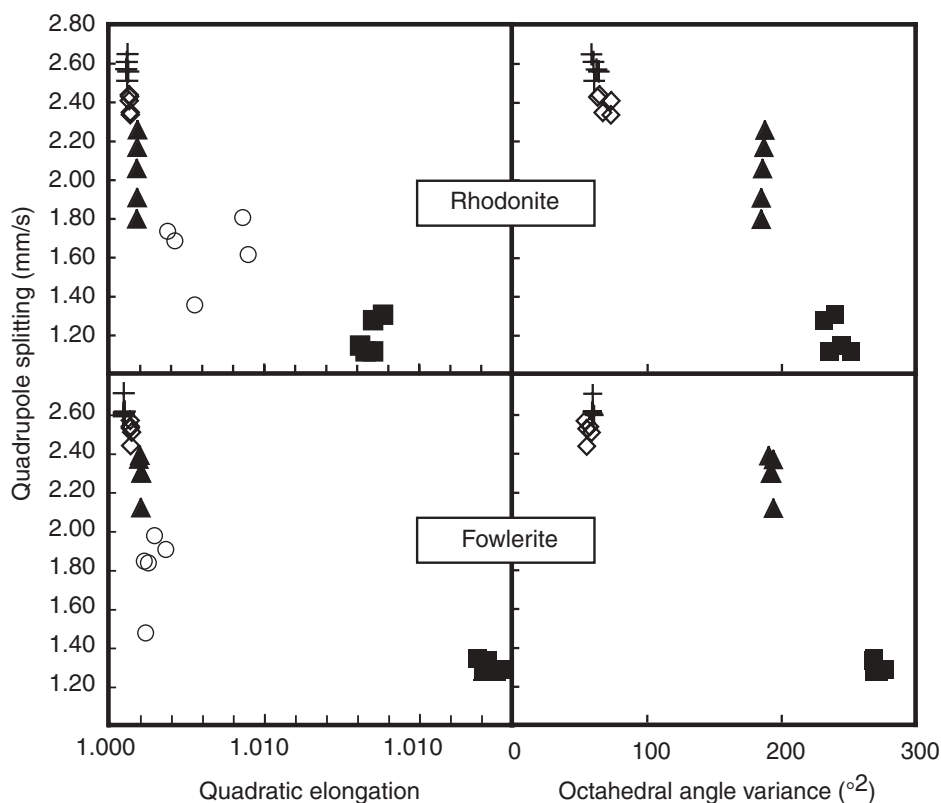


FIGURE 4. Quadrupole splitting as a function of distortion parameters (quadratic elongation and octahedral angle variance). Note that M4 was considered an octahedron for comparison purposes, and that angle variance was not calculated for M5 because of its irregular coordination. Symbols as in Figure 3.

Comparison of Mössbauer data for rhodonite and fowlerite

Mössbauer parameters and polyhedral distortions. Figures 3 and 4 show the IS–QS clusters and QS–distortion clusters for most M sites to be tighter for fowlerite than for rhodonite. This is consistent with the comparisons of chemical and crystallographic variables made by Nelson and Griffen (2005), which show variability within the population of their fowlerite specimens to be generally less than that within the population of their rhodonite specimens. Mössbauer parameters for M1 and M2 of rhodonite and fowlerite are very much alike, which mirrors the similarities found in stereochemical details of these sites by crystal structure refinement. Even at the scale of Figure 1, the geometrical similarities between M1 and M2, and the differences between them and the other M sites, are apparent.

The IS of M4 is smaller, on average, for fowlerite than for rhodonite. The calculation of quadratic elongation and of octahedral angle variance, plotted in Figure 4, is based on consideration of M4 as a distorted octahedral site. This was done to make comparison of distortions with M1, M2, and M3 straightforward. Figure 5 shows that octahedral and tetrahedral angle variances for M4 in both rhodonite and fowlerite are antipathetically related, suggesting that as the site becomes a “poorer” (more distorted) octahedron, it becomes a “better” (less distorted) tetrahedron. M4 in fowlerite is decidedly a “poorer” octahedron and a “better” tetrahedron than is M4 in rhodonite. This is consistent with the tendency toward tetrahedral coordination in the M4 site of fowl-

erite, as determined by crystal structure refinements (Nelson and Griffen 2005), and explains the lower IS of M4 in fowlerite.

M5 of fowlerite displays less variation in bond lengths than M5 in rhodonite (Nelson and Griffen 2005), as reflected by quadratic elongation values in Figure 4. Both Figure 4 and Table 1 also show that the range in QS values for M5 is shifted about 0.2 mm/s lower for rhodonite than fowlerite, as might be expected from the greater site distortion.

Figure 3 shows a clear contrast between the IS values for M3 in fowlerite and those in rhodonite. The IS values for M3 in fowlerite place that site just where one would expect it on the plot, given the trend established by the other sites. For rhodonite, the IS values of M3 seem to be too small. The measures of distortion, considered as averages or ranges, are not significantly different for the two. Given the strong preferences of Zn for M4 and Ca for M5 in fowlerite (Nelson and Griffen 2005), the occupancies of the M3 sites in fowlerite and rhodonite cannot differ by much and must involve mostly Mn. Moreover, one might expect an error in curve-fitting to affect perhaps one or two specimens, but not all of the rhodonite specimens and none of the fowlerite specimens. We are thus left without explanation for the difference.

Site preferences for Fe²⁺. Table 1 reveals similar Fe²⁺ site preferences in rhodonite and fowlerite: (1) The bulk of the Fe resides in M1 and M2, although these peak areas vary more-or-less antipathetically about relatively constant values. This variation could be real, or it could result from mutually compensating errors

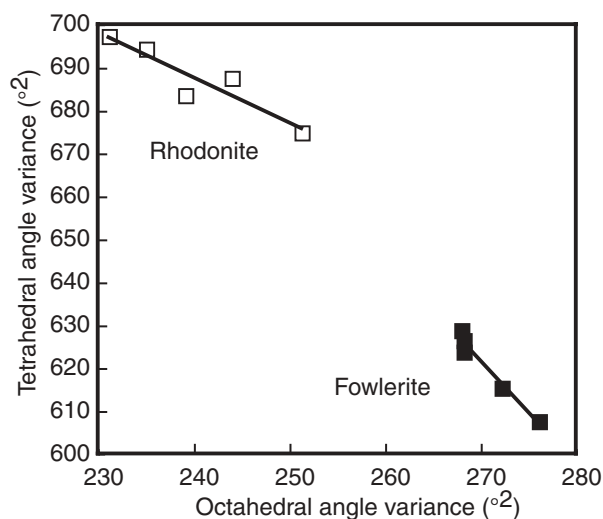


FIGURE 5. Octahedral angle variance vs. tetrahedral angle variance for M4.

in the peak fits. (2) M5 contains a smaller proportion of Fe^{2+} than any of the other sites. (3) M3 and M4 contain intermediate amounts of Fe^{2+} , although more is consistently in M4 than in M3.

Site preference for Fe^{2+} in rhodonite-fowlerite is apparently based, in part, on the sizes of sites available. Figure 6 shows the average percent of Fe in a site as a function of the mean octahedral volume of the site. [Note that (1) M4 has been considered as an octahedron in Fig. 6 for the purposes of comparisons, and (2) the total Fe percentage does not sum to 100% for either rhodonite or fowlerite because the Fe in M5 is not included in the figure.] Clearly, for M1–M4 there is a direct correlation between polyhedral volume and Fe concentration.

Size is apparently not the only factor of importance governing Fe site preference. M5, which is the largest of the M sites, contains the smallest amount of Fe. M5, at 19.3 \AA^3 (CN = 7) or 15.9 \AA^3 (CN = 6), is not too large for Fe^{2+} , as the volume of the {X} site in almandine is 20.9 \AA^3 (Novak and Gibbs 1971). Nor are the smaller sites too small, given the volumes of the M1 (12.6 \AA^3) and M2 (13.2 \AA^3) octahedra in fayalite (Hazen 1977), and of the tetrahedrally coordinated Fe^{2+} site in staurolite (4.1 \AA^3 , Alexander 1989). Thus, Fe^{2+} site preference for M1 through M4 appears to be controlled primarily by the sizes of the polyhedra, with the paucity of Fe in M5 being at odds with that trend.

Although Fe exhibits similar site preferences in rhodonite and fowlerite, the Mössbauer parameters reflect some of the important structural differences found in previous X-ray work. ^{57}Fe Mössbauer spectroscopy is a probe of the specific local environments of Fe nuclei. Nelson and Griffen (2005) found the structural differences between rhodonite and fowlerite to depend on high concentrations of Zn in M4 and Ca in M5 in fowlerite. We have shown these differences to be reflected in the Mössbauer parameters, which are obviously insensitive in any direct way to Zn and Ca. We conclude, therefore, that high concentrations of Zn in M4 and Ca in M5 drive pervasive structural adjustments that are maintained locally even if Fe^{2+} (or presumably any other substituent) is present in a given site.

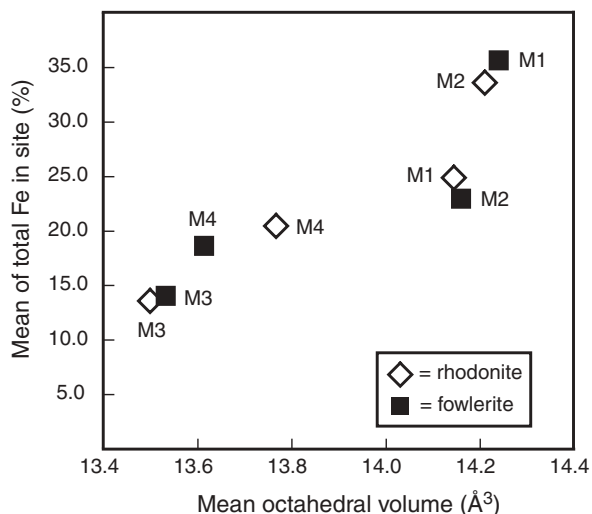


FIGURE 6. Average Fe occupancy of M1–M4 as a function of mean volume of the coordination polyhedron. Note that M4 was considered an octahedron for purposes of comparison with M1–M3.

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