

A reevaluation of the Mössbauer spectroscopy of calcic amphiboles

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Abstract

The Mössbauer spectra of calcic amphiboles have been reassessed to examine the validity of previous peak assignments. A brief summary of previously-established peak assignments for Mg–Fe, calcic and sodic amphiboles is presented. The Mössbauer spectra of tremolite–actinolites are reinterpreted in terms of Fe²⁺ in the M(1) and M(3) sites (quadrupole splitting, $\Delta \sim 2.8$ mm/sec), the M(2) site ($\Delta \sim 2.2$ mm/sec) and the M(4) site ($\Delta \sim 1.8$ mm/sec). From a number of spectra, these assignments indicate that Fe²⁺ prefers to enter the M(4) site prior to the M(1) and M(3) sites, and it discriminates against the M(2) site. This is the same ordering scheme found in cummingtonite–grunerites. Increasing the Al and Fe³⁺ contents in calcic amphiboles reduces Δ for Fe²⁺ in the M(1), M(2) and M(3) sites from the values in tremolite–actinolites, and separates the M(1) and M(3) doublets. It is suggested that next-nearest-neighbor effects on the already closely-overlapping peaks limit the accuracy of determining site populations from Mössbauer spectra of calcic amphiboles.

Introduction

In a recent study of the electronic absorption spectra of calcic amphiboles, Goldman and Rossman (1977) identified features which they attributed to Fe²⁺ in the Ca-rich M(4) site, and found that these features are characteristic of tremolite–actinolites (TA), Ca₂(Mg,Fe)₅Si₈O₂₂(OH)₂. They also presented a Mössbauer spectrum of a tremolite which is unlike other spectra of calcic amphiboles (DeCoster *et al.*, 1963; Bancroft *et al.*, 1967a; Häggström *et al.*, 1969; Burns and Greaves, 1971; Bancroft and Brown, 1975; Goodman and Wilson, 1976) because it has two well-separated Fe²⁺ quadrupole doublets. As shown in Figure 1, it bears a striking similarity to the Mössbauer spectra of cummingtonite–grunerites (CG), (Mg,Fe)₇Si₈O₂₂(OH)₂, taken as a part of this study. However, the peak assignments for these amphiboles differ greatly. In particular, the inner doublet in CG spectra has been assigned to Fe²⁺ in the M(4) site (Bancroft *et al.*, 1967a,b), whereas it has been assigned to Fe²⁺ in the M(2) site in TA spectra (Burns and Greaves, 1971), and possible contributions from

Fe²⁺ in the M(4) site, in general, have not been considered. The resulting difference in quadrupole splitting, Δ , for Fe²⁺ in the M(2) sites of these amphibole groups is surprisingly large (0.9–1.0 mm/sec), considering the similarity of their first coordination spheres. In addition to the similarity of their Mössbauer spectra, the similarity of their electronic absorption spectra (Fig. 1) suggests that Fe²⁺ occurs in similar types of sites. The arrows point to absorption bands near 1000 nm in β polarization and 2500 nm in α polarization that are assigned to Fe²⁺ in the M(4) site in both samples.

A notable difference exists in the Mössbauer spectra of CG and TA amphiboles when they are examined across their compositional range. CG spectra retain a two-doublet character across their compositional range. The transmission valleys between the inner and outer doublets in tremolite are replaced by resonant absorption at higher iron contents (Burns and Greaves, 1971), and are generally absent in more chemically complex amphiboles, such as hornblendes (Bancroft and Brown, 1975), where an asymmetric Fe²⁺ resonant envelope is typically observed.

This paper (1) summarizes the peak assignments in the Mössbauer spectra of Mg–Fe, calcic and sodic

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Table 1. Electron microprobe analyses

	1	2	3	4	5	6
oxide	weight percent of oxides					
SiO ₂	57.45	51.97	56.99	48.61	54.68	39.82
TiO ₂	0.07	-	0.01	-	0.05	2.18
Al ₂ O ₃	1.31	-	0.92	1.86	2.45	16.06
Cr ₂ O ₃	-	-	0.08	-	0.69	-
MgO	23.62	8.61	20.66	3.83	20.47	14.98
FeO	2.06	36.96	5.48	30.27	5.87	9.09
MnO	-	0.82	0.22	2.22	0.30	0.08
CaO	13.42	1.01	12.15	10.59	12.16	12.43
Na ₂ O	0.61	0.04	0.85	0.26	0.73	2.46
K ₂ O	0.20	-	0.02	0.15	0.06	0.67
Cl	0.04	0.05	0.01	0.04	-	0.02
F	0.21	-	-	-	0.33	-
∑ (-O=F, Cl)	99.09	99.45	97.38	97.88	97.65	97.80
Fe ³⁺ /Fe ^t (Mössbauer)	0.10	n.d.	0.12	0.18	0.08	0.34
	formula proportions*					
Si	7.81	8.00	7.92	7.59	7.66	5.77
Al ^{IV}	0.19	-	0.08	0.34	0.34	2.23
Al ^{VI}	0.02	-	0.07	-	0.06	0.52
Ti	0.01	-	-	-	0.01	0.24
Cr	-	-	0.01	-	0.08	-
Mn	-	0.11	0.03	0.29	0.04	0.01
Fe ²⁺	0.21	4.76	0.56	3.24	0.63	0.72
Fe ³⁺	0.02	-	0.08	0.71	0.06	0.37
Mg	4.77	1.98	4.28	0.89	4.27	3.23
Ca	1.95	0.17	1.81	1.77	1.82	1.93
Na	0.16	0.01	0.23	0.08	0.20	0.69
K	0.03	-	-	0.03	0.01	0.12

1. Tremolite, Mt. Bity, Malagasay Republic (CIT 8038)
 2. Grunerite, Smallwood Mine, Heath Lake, Canada (CIT 7223)
 3. Actinolite, Berkeley, California (CIT 299)
 4. Ferrotremolite, Bwabik iron formation, Babbitt, Minnesota (UCLA-MS2625)
 5. Actinolite, Chester, Vermont (CIT 6191)
 6. Pargasite, Chelan, Washington (CIT 1188)
- * The formula proportions are obtained by normalizing the total positive charge to 46, including both ferrous and ferric iron.

amphiboles, and amphiboles intermediate in composition between calcic and sodic amphiboles; (2) evaluates the peak assignments in TA spectra with particular emphasis on identifying peaks due to Fe²⁺ in the M(4) site, and suggests a new peak assignment scheme that better explains the change in the Fe²⁺ resonant envelope with increasing iron content; and (3) examines the effect of additional chemical complexities on the spectral parameters in calcic amphiboles.

Experimental methods

Sample locations and electron microprobe analyses of the six samples used in this study are given in Table 1. Mössbauer, electronic absorption, and electron microprobe data for samples 2 through 6 were taken as part of this study. The data for sample 1 and the experimental methods used to obtain the data have been presented in Goldman and Rossman (1977). All quadrupole splitting and isomer shift values for the

Mössbauer data are room-temperature values unless otherwise specified. All Mössbauer spectra are presented relative to metallic iron. Only the fitted envelopes to the Mössbauer spectra in Figures 1 and 3 are presented, but these spectra were analyzed to obtain Fe²⁺/Fe³⁺ ratios in order to calculate the formula proportions from the electron microprobe data in Table 1. The half-widths of all Fe²⁺ peaks in Figures 4 and 6 were constrained to be equal, and the half-widths of the two ferric peaks were also constrained to be equal. Because of the low Fe³⁺ content of the actinolite sample whose spectrum is shown in Figure 4, it was necessary to specify the half-widths of the ferric peaks and the location of the low-velocity component. All site population data reported or used are obtained directly from the area ratios. X-ray precession photographs of the tremolite sample do not show the presence of an exsolved cummingtonite phase.

Discussion

Table 2 gives the Δ values for Fe²⁺ in the M sites of various amphiboles. Isomer shifts, δ , are typically 1.10–1.15 mm/sec (relative to metallic iron) for Fe²⁺ in these sites. In general, the Δ values for the M(1), M(2), and M(3) sites coincide only in the chemically simple Mg-Fe amphiboles. As the chemistry of the amphibole becomes more complex with the addition of Ca, Na, Al, and Fe³⁺, the Δ values tend to separate. Bancroft *et al.* (1967a) and Häggström *et al.* (1969) suggested that Δ of Fe²⁺ in the M(2) site in actinolite is reduced from the cummingtonite value because of Ca in the adjacent M(4) sites. Next-nearest-neighbor effects involving Ca have been invoked to explain certain anomalies in the Mössbauer spectra of synthetic clinopyroxenes on the hedenbergite (CaFeSi₂O₆)-ferrosilite (Fe₂Si₂O₆) join (Dowty and Lindsley, 1973). They found that the area of the M(2) doublet was larger than expected from the stoichiometry of each specimen [assuming Ca only occurs in the M(2) site] when only one doublet was fitted for each site, and concluded that some of the M(1) intensity overlaps and augments the M(2) peak intensities due to the changing occupancy of the surrounding M(2) sites from Ca to Fe²⁺ across the join. By fitting four M(1) doublets and one M(2) doublet for samples of intermediate composition, M(1)/M(2) ratios were in better, but not exact, agreement with the expected stoichiometry. Consistent with this model, only one M(1) doublet was analyzed in hedenbergite ($\Delta = 2.22$ mm/sec) and ferrosilite ($\Delta = 2.49$ mm/sec). Hence, Δ for Fe²⁺ in the clinopyroxene

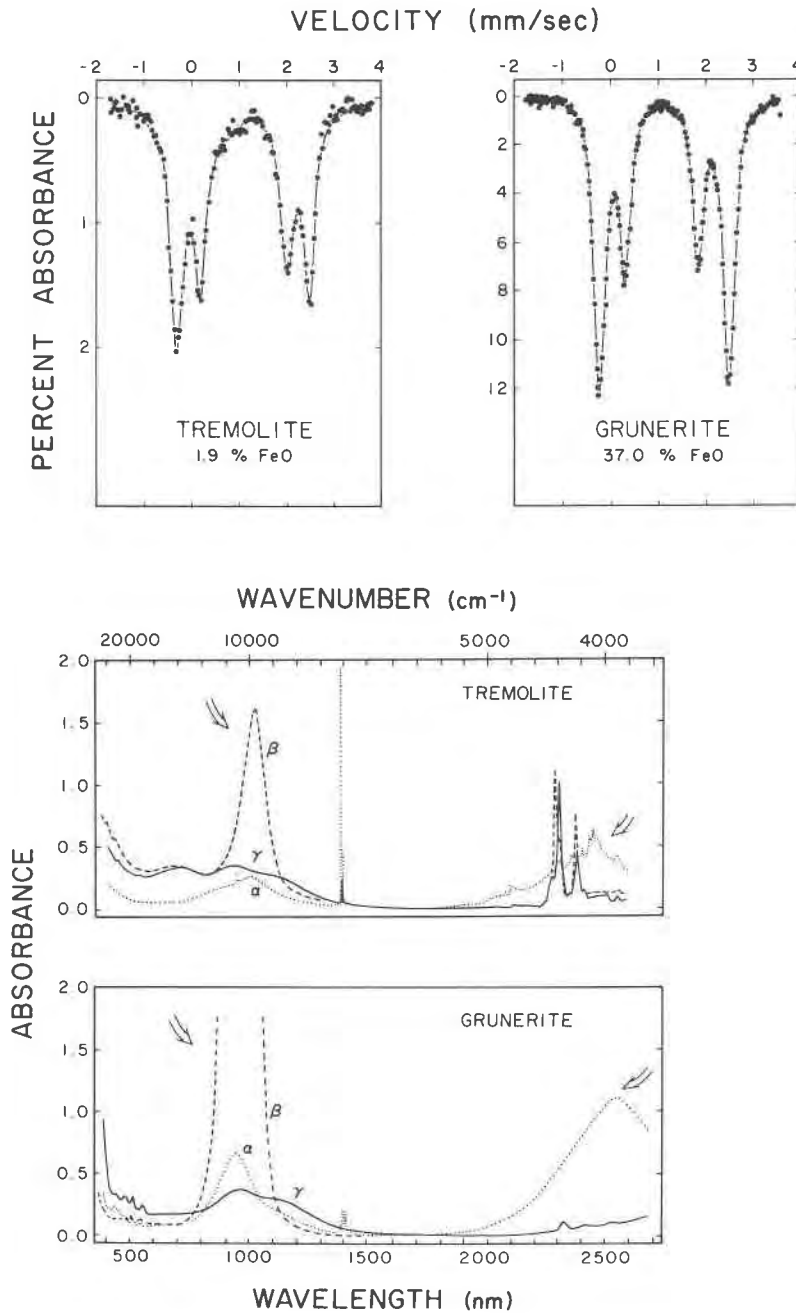


Fig. 1. Mössbauer and electronic absorption spectra of a tremolite (sample 1) from the Malagasy Republic (after Goldman and Rossman, 1977) and a grunerite (sample 2) from Canada taken at room temperature. Fe^{2+} in the M(4) sites of these amphiboles is suggested to produce the intense electronic absorption band near 1000 nm in β polarization and 2500 nm in α polarization, and the inner quadrupole doublet in the Mössbauer spectra. The FeO value represents only Fe^{2+} . The electronic absorption spectra of tremolite and grunerite represent crystal thicknesses of 1.0 and 0.1 mm, respectively.

M(1) site is reduced by about 0.3 mm/sec upon changing the occupancy of the three adjacent M(2) sites from Fe^{2+} to Ca. However, the 0.9–1.0 mm/sec difference in Δ between the inner and outer Fe^{2+} peaks in actinolites is difficult to explain using these

arguments, because the M(2) site only shares two edges with neighboring Ca sites. Considering the close structural (Clark *et al.*, 1969, and others) and topological similarity of the clinopyroxene M(1) and actinolite M(2) sites, it also becomes difficult to ex-

Table 2. Quadrupole splittings of Fe²⁺ in amphiboles

Amphibole	Site				Reference
	M(1)	M(2)	M(3)	M(4)	
cummingtonite-grunerite	2.75-2.85	2.75-2.85	2.75-2.85	1.50-1.80	Bancroft et al. (1967a,b) Hafner and Ghose (1971)
anthophyllite-gedrite	2.70-2.80	2.70-2.80	2.70-2.80	1.84	Seifert (1977)
tremolite-actinolite	2.80-2.90	1.70-1.90	2.20-2.60	n.a.*	Burns and Greaves (1971)
hornblende	2.79	2.01	2.30-2.40	n.a.	Bancroft and Brown (1975)
hornblende	2.84	2.09	2.59	1.70	Goodman and Wilson (1976)
magnesianhastingsite	2.70	2.00	2.70	n.a.	Semet (1973)
sodic amphiboles	2.80	2.00	2.40	n.a.	Bancroft and Burns (1969) Ernst and Wai (1970)

All quadrupole splittings are from room temperature spectra and are presented in mm/sec. Isomer shifts are typically 1.10-1.15 mm/sec (relative to iron metal). *not analyzed.

plain the large difference in Δ to a significant difference in geometric distortion between the two sites. The next-nearest-neighbor (M-M) distances about the Ca sites in actinolite and clinopyroxene are also similar. The M(2)-M(4) distance in actinolite and the analogous M(1)-M(2) distance in diopside are approximately 3.2Å, and the M(1)-M(4) distance in actinolite and the analogous M(1)-M(2) distance in diopside are about 3.5Å (Clark *et al.*, 1969). Note that the M(1) site in actinolite shares one edge with the Ca-rich M(4) site, but its Δ value for Fe²⁺ is not different from the value observed in cummingtonite or anthophyllite, where the adjacent M(4) sites contain only Mg or Fe.

The spectrum of synthetic ferrotremolite (Burns and Greaves, 1971) further supports the reassignment of the intermediate Fe²⁺ doublet in TA spectra ($\Delta = 2.2-2.6$ mm/sec) to the M(2) site. The spectrum is mainly characterized by two Fe²⁺ doublets having Δ values of 2.72 and 2.12 mm/sec³. An assignment of

the inner doublet to Fe²⁺ in the M(2) site is suggested from the similar area ratio with the outer doublet, and is consistent with the Δ value expected from the clinopyroxene model of Dowty and Lindsley (1973). The important point with regard to the synthetic ferrotremolite spectrum is the absence of significant resonance in the innermost doublet region ($\Delta = 1.70-1.90$ mm/sec) in a sample which must contain Fe²⁺ in the M(2) site. All other reported TA spectra have an Fe²⁺ doublet in this region, which has also been assigned to Fe²⁺ in the M(2) site by Burns and Greaves (1971). This apparent inconsistency suggests that the previous assignments are incorrect.

The peaks of the M(2) doublet from the synthetic ferrotremolite spectrum would occur in the transmission valleys between the inner and outer Fe²⁺ doublets in tremolite (Fig. 1), which corresponds to the position of the intermediate doublet previously assigned by Burns and Greaves (1971) to Fe²⁺ in the M(3) site. Based on the synthetic ferrotremolite and clinopyroxene data, I suggest that the intermediate doublet in TA spectra does arise mostly from Fe²⁺ in the M(2) site. This possibility necessitates a reassignment of the other Fe²⁺ resonance. The outer doublet ($\Delta \sim 2.8$ mm/sec) is assigned to Fe²⁺ in the M(1) and M(3) sites, and the inner doublet ($\Delta \sim 1.8$ mm/sec) is assigned to Fe²⁺ in the M(4) site. The basis for these assignments will be discussed in the subsequent sections.

The M(2) doublet in the Mössbauer spectra of intermediate and sodic amphiboles has a Δ of approximately 2.0 mm/sec (Bancroft and Burns, 1969; Semet, 1973). This value is approximately 0.2 mm/

³ Burns and Greaves (1971) also assigned a doublet in the synthetic ferrotremolite spectrum with a Δ of 1.37 mm/sec to Fe²⁺ in the M(4) site, and suggested that Ca has displaced Fe²⁺ from some of the smaller M sites. Their inability to fit the spectrum following the assignment scheme used for their other samples, the absence of a visibly-discernible M(4) peak in the low-velocity region, and the absence of electron microprobe data for this sample make it difficult to evaluate the inferred disorder of Ca in the M sites, or possibly the A site. If the inferred Ca disorder is real in this sample and Ca resides in the smaller M sites, the Δ values of Fe²⁺ in the neighboring sites would be expected to be reduced, from the clinopyroxene data of Dowty and Lindsley (1973). However, the outer doublet in the spectrum is at the same position as it is in all other actinolites.

sec smaller than Δ for the proposed M(2) doublet in TA spectra. Table 3 shows that the M(2) site becomes smaller and more distorted in the sequence cummingtonite-actinolite-glaucophane as it accommodates more Al and Fe³⁺ (Papike and Clark, 1969). The relative distortion of the M(2) site in hornblende occurs between actinolite and glaucophane in this sequence (Robinson *et al.*, 1973). Therefore, as more Al and Fe³⁺ enter the calcic amphibole crystal structure, Δ for Fe²⁺ in the M(2) site is expected to be reduced from the TA value.

Fe²⁺ in M(4)

A fundamental assumption used to arrive at peak assignments in calcic amphibole Mössbauer spectra is that Ca, Na, and K occupy most of the M(4) sites and, therefore, peaks due to Fe²⁺ in the M(4) site have not been sought. However, the occurrence of M(4) Fe²⁺ for the actinolites reported by Burns and Greaves (1971) is indicated from their stoichiometry and optical spectra. The sum of Al^{VI}, Ti, Fe³⁺, Fe²⁺, Mg, and Mn ranges from 5.07 to 5.39 for six of seven samples, whereas a total of five M(1), M(2), and M(3) sites are available for these ions. The excess can be accommodated in the M(4) site and the A site. An indication that some of these ions occur in the M(4) site as Fe²⁺ comes from the electronic absorption spectra of their samples 1 and 5 in Burns (1970 p. 101, 102). These spectra have an intense absorption band at 1030 nm in β polarization, which was subsequently shown to be due to Fe²⁺ in the M(4) site by Goldman and Rossman (1977). Note that the large size of the M(4) site also produces an absorption band near 2500 nm in tremolite and grunerite (Fig. 1) and anthophyllite (Mao and Seifert, 1974). In addition to the spectral argument, three of their seven samples (including sample 5) do not contain sufficient Ca, Na, and K to fill the M(4) sites, which suggests that the excess ions from the smaller M sites will occupy the remaining M(4) sites. These results suggest that the inner doublet observed in the Mössbauer spectrum of tremolite is predominantly due to Fe²⁺ in the M(4) site.

The M(4) assignment is supported from CG data (Fig. 2c), which show that Δ for Fe²⁺ in the M(4) site increases from 1.5 to 1.8 mm/sec as the total iron content in the sample decreases. From an extrapolation of these data, a Δ of about 1.8 mm/sec is expected for Fe²⁺ in the M(4) site in tremolite. Note that Δ for the outer CG doublet is not sensitive to compositional change (Fig. 2a). Figure 2b shows that Δ of M(4) Fe²⁺ also decreases as the Fe²⁺ content in

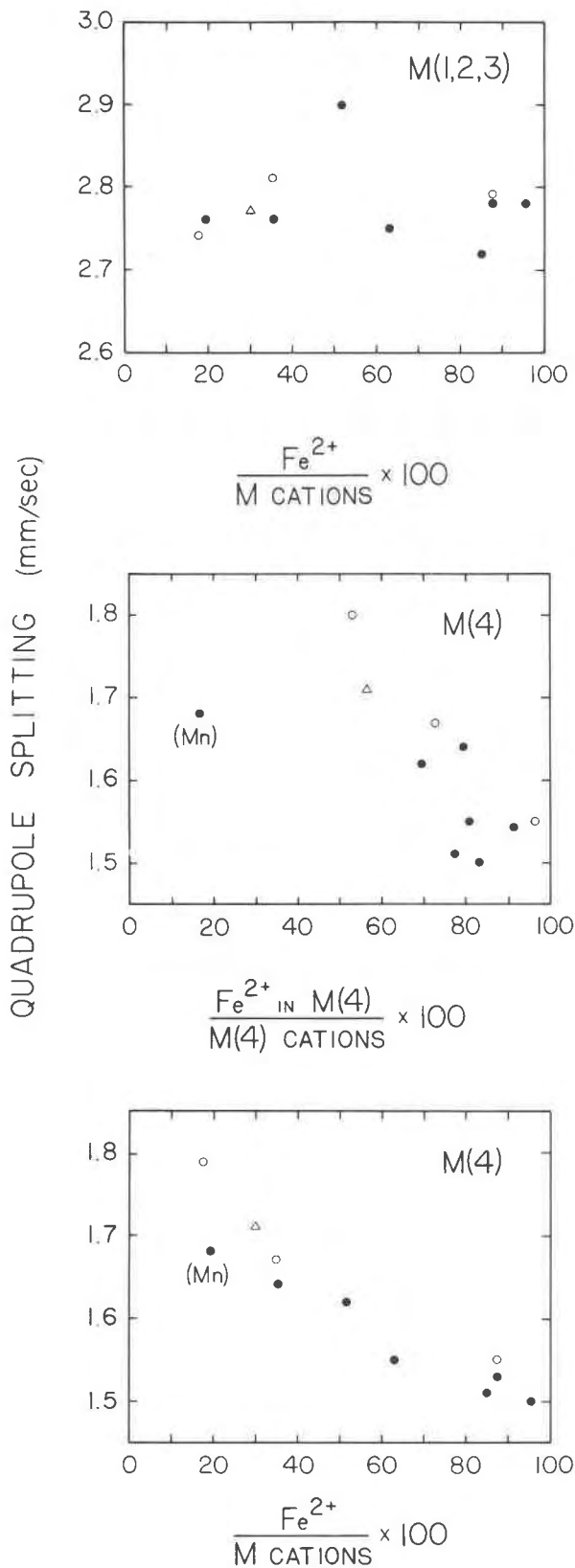
Table 3. Metal-oxygen bond distances for the M sites in amphiboles

bond	cummingtonite ^a	grunerite ^b	actinolite ^c	glaucophane ^d
M(1)-O(1)	2.07Å	2.082Å	2.090Å	2.078Å
M(1)-O(2)	2.14	2.160	2.115	2.082
M(1)-O(3)	2.10	2.122	2.114	2.100
mean	2.10	2.121	2.105	2.087
max. var.	0.07	0.078	0.025	0.022
M(2)-O(1)	2.14	2.161	2.151	2.038
M(2)-O(2)	2.08	2.128	2.114	1.943
M(2)-O(4)	2.04	2.075	2.022	1.849
mean	2.08	2.121	2.098	1.943
max. var.	0.10	0.086	0.129	0.189
M(3)-O(1)	2.11	2.118	2.100	2.103
M(3)-O(3)	2.08	2.103	2.093	2.077
mean	2.10	2.113	2.098	2.094
max. var.	0.03	0.015	0.007	0.026
M(4)-O(2)*	2.17	2.135	2.388	2.411
M(4)-O(4)	2.02	1.988	2.301	2.337
M(4)-O(6)	2.70	2.757	2.561	2.446
M(4)-O(5)	-	-	2.816	2.798
mean	2.30	2.293	2.517	2.498
max. var.	0.66	0.769	0.515	0.461

a. Fischer (1966); b. Finger (1969); c. Mitchell, Bloss and Gibbs (1971); d. Papike and Clark (1968). * The M(4)-O bond distances in cummingtonite and grunerite represent primarily the position of Fe²⁺, whereas they represent the positions primarily of Ca and Na in actinolite and glaucophane, respectively.

the site decreases. However, additional data from low-iron cummingtonites are required to delineate the trend to lower Fe occupancies of the M(4) site.

Ca generally occupies 85-95 percent of the M(4) sites in calcic amphiboles (Leake, 1968). The M(4) doublet should therefore become relatively less intense as the iron content in the other sites increases. To examine this possibility, the fitted resonant envelope of the tremolite spectrum in Figure 1 can be compared to those of two additional amphiboles of the TA series in Figure 3. These samples have been selected for their different iron contents and the observation of M(4) Fe²⁺ bands in their electronic absorption spectra. The Fe²⁺ content and the locations of the inner Fe²⁺ peaks in tremolite are annotated on each Mössbauer spectrum. These spectra show that, as the Fe²⁺ content increases in the M(1), M(2) and M(3) sites, there is a progressive reduction in the relative intensity of the inner doublet, which is visually distinct in tremolite but barely discernible in ferrotremolite. This observation supports the assignment of the inner doublet to Fe²⁺ in the M(4) site. The reduction in the relative intensity of the M(4) doublet with increasing iron content also provides an explanation for the disappearance of the transmission valley between the inner and outer doublets observed in tremolite. The chemical, Mössbauer, and elec-



tronic absorption data for the samples reported by Burns and Greaves (1971) are consistent with an M(4) assignment for the inner doublet.

Fe²⁺ in M(1) and M(3)

The outer Fe²⁺ doublet ($\Delta \sim 2.7\text{--}2.8$ mm/sec) is interpreted differently for the various amphibole groups. It is assigned to the M(1), M(2), and M(3) sites in CG (Bancroft *et al.*, 1967a,b), to the M(1) and M(3) sites in the intermediate amphiboles (Virgo, 1972; Semet, 1973), and to the M(1) site in sodic amphiboles (Bancroft and Burns, 1969). Absorptions from Fe²⁺ in the M(1) site occur in the outer doublet region in each of these groups. However, there appears to be a progressive separation of the M(3) doublet from the M(1) doublet as more Fe³⁺ and Al enter the crystal structure. The cause of this separation is unlikely to be due to significant differences in geometric distortions of the M(3) site between cummingtonite and glaucophane, because these sites are structurally similar (Table 3). TA have compositions that occur between CG and the intermediate amphiboles in this progression. The outer doublet in TA is therefore assigned to Fe²⁺ in the M(1) and M(3) site, because absorptions from these sites remain superimposed (or nearly superimposed) between CG and the intermediate amphiboles.

It is likely that the separation of the M(1) and M(3) doublets will increase in calcic amphiboles as more Fe³⁺ and Al preferentially enter the adjacent M(2) sites. The separation appears to reach a limiting value of ~ 0.4 mm/sec in glaucophane (Bancroft and Burns, 1969), in which the M(2) site is almost fully occupied by Fe³⁺ and Al. The assignment made above is therefore more safely applied to calcic amphiboles, such as TA, in which these compositional problems are less severe.

Temperature-dependency

The temperature-dependence of Δ is one way by which the proposed peak assignments for TA can be

Fig. 2. Variations in the quadrupole splitting at room temperature in the cummingtonite-grunerite series.

(a) quadrupole splitting of the outer doublet with the total iron content.

(b) quadrupole splitting of the inner doublet with the iron content in the M(4) site.

(c) quadrupole splitting of the inner doublet with the total iron content.

The open circles, filled circles, and triangles represent data from Hafner and Ghose (1971), Bancroft *et al.* (1967a,b), and Buckley and Wilkins (1971), respectively. The sample labeled Mn has 23.7 mole percent Mn²⁺.

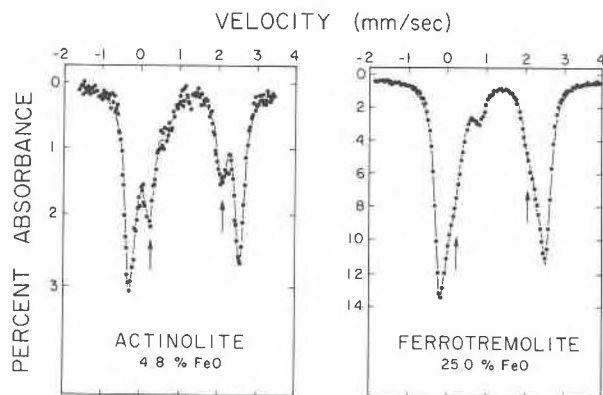


Fig. 3. Mössbauer spectra of an actinolite from California and a ferrotremolite from Minnesota taken at room temperature, which show that as the Fe^{2+} content (given as FeO) increases, the relative intensity of the inner Fe^{2+} doublet is reduced. The arrows mark the locations of the inner Fe^{2+} peaks in the tremolite spectrum in Fig. 1.

evaluated. Hafner and Ghose (1971) showed that Δ for Fe^{2+} in the CG M(1), M(2), and M(3) sites increases from 2.8 to about 3.1 mm/sec as the temperature decreases to 77 K, whereas Δ for Fe^{2+} in the M(4) site remains nearly constant. The Mössbauer spectrum of an actinolite taken at 77 K is presented in Figure 4, to examine the temperature-dependency of the three Fe^{2+} doublets⁴. The stoichiometry (Table 1) and electronic absorption spectra of this sample indicate the presence of Fe^{2+} in the M(4) site. The outer doublet has a Δ of 3.10 mm/sec, which is 0.3 mm/sec larger than its typical room-temperature value. A similar Δ at 77 K was found for the outer doublet in synthetic ferrorichterite, which was assigned to Fe^{2+} in the M(1) and M(3) sites (Virgo, 1972). The intermediate Fe^{2+} doublet in Figure 4 has a Δ of 2.50 mm/sec, which is about 0.3 mm/sec larger than the room-temperature value of the proposed M(2) doublet in synthetic ferrotremolite (Burns and Greaves, 1971). The similarity in the temperature-dependency of the outer and intermediate doublets in TA Mössbauer spectra to that found for the outer doublet in CG spectra supports their assignment to Fe^{2+} in the M(1) and M(3) sites and the M(2) site, respectively. The inner Fe^{2+} doublet in Figure 4 has a Δ of 1.86 mm/sec, which can be compared to the room-temperature

value of 1.84 mm/sec determined for the inner doublet in tremolite (Goldman and Rossman, 1977). The lack of a temperature-dependence for the inner doublet in TA spectra supports its assignment to Fe^{2+} in the M(4) site, based on the CG data. Although Bancroft and Burns (1969) indicated that Δ for Fe^{2+} in the sodic amphibole M(2) site does not appear to have a significant temperature-dependency, it must be remembered that this site is much more distorted than the TA M(2) site (Table 3), and a comparison between these groups is likely to be less valid.

Site preferences

The observation from Figure 1 that Fe^{2+} is nearly equally distributed between the M(4) site and the other sites in tremolite suggests that Fe^{2+} will attempt to occupy available M(4) sites prior to Mg. The presence of a transmission valley between the M(1) and M(3) doublet and the M(4) doublet suggests that Fe^{2+} discriminates against the M(2) site. These observations indicate that Fe^{2+} prefers to enter the M(4) site prior to the M(1) and M(3) sites, and discriminates against the M(2) site. This is the same ordering scheme found in cummingtonite (Ghose, 1961; Fischer, 1966) and grunerite (Ghose and Hellner, 1959; Finger, 1969) from X-ray studies. In addition, this ordering scheme is consistent for a suite of TA as shown in Figures 1 and 3 and from the spectra in Burns and Greaves (1971). These interpretations provide an additional reason for the disappearance of the transmission valleys between the inner and outer

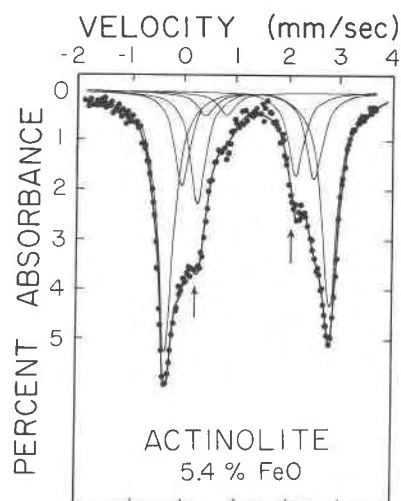


Fig. 4. Mössbauer spectrum of an actinolite from Vermont taken at 77 K, showing the increased peak separation. The FeO content represents only Fe^{2+} , and the arrows mark the locations of the inner Fe^{2+} peaks in the tremolite spectrum in Fig. 1.

⁴ The computed values for Δ , δ , and the relative area of each Fe^{2+} doublet are: 3.10, 1.26 mm/sec, 52.1 percent; 2.50, 1.26 mm/sec, 20.0 percent; 1.86, 1.23 mm/sec, 20.2 percent. The values for the Fe^{3+} doublet are: 0.41, 0.64 mm/sec, 7.8 percent. The ferrous and ferric half-widths are 0.36 and 0.46 mm/sec, respectively, and χ^2 for the 200 channels analyzed is 274.

doublets as the iron concentration increases. The change in the appearance of the Fe^{2+} envelope involves a progressively less intense M(4) doublet and a continuously more intense M(2) doublet as the iron concentration increases.

Peak variations

I suggested earlier that the substitution of Al and Fe^{3+} into the calcic amphibole crystal structure produces a separation of the M(1) and M(3) doublets, and reduces Δ for Fe^{2+} in the M(2) site. The Mössbauer spectra of the hornblendes studied by Bancroft and Brown (1975) are likely examples of this process. The stoichiometry of most of their samples (Dodge *et al.*, 1968) suggests that there is not sufficient Fe^{2+} in the M(4) site to be an important contribution to the Mössbauer spectra. This is also indicated from the electronic absorption spectra of two of those samples taken as a part of this study. The Δ values for the doublets assigned to Fe^{2+} in the M(1), M(3), and M(2) sites are approximately 2.8, 2.4, and 2.0 mm/sec, respectively. The possibility that hornblendes may also have Fe^{2+} in the M(4) site suggests that four Fe^{2+} doublets may be required for certain samples, such as those reported by Goodman and Wilson (1976). However, such fits should be viewed with caution without supporting evidence from chemical and electronic absorption data for the occurrence of Fe^{2+} in the M(4) site. Nevertheless, the observation of a distinct inner Fe^{2+} peak or shoulder in a calcic amphibole Mössbauer spectrum probably signifies the presence of Fe^{2+} in the M(4) site.

It is also possible that Al and Fe^{3+} influence the peak parameters for the outer Fe^{2+} doublet in hornblendes. As shown in Figure 5, the Mössbauer data for the hornblendes reported by Bancroft and Brown (1975) correlate with the Al and Fe^{3+} contents of these samples (Dodge *et al.*, 1968; Burns and Greaves, 1971). These trends show that Δ for the outer doublet decreases with increasing Al, Fe^{3+} , and (Al + Fe^{3+}). Similar trends have been reported for Fe^{2+} in the smaller M sites in anthophyllite-gedrite spectra by Seifert (1977). Although variations in the Na content of the M(4) site may be involved in these correlations, the spectrum of a low-Fe richterite (Goldman, unpublished data) is nearly identical to the tremolite spectrum in Figure 1, which indicates that significant variations of the Na content in the M(4) site do not affect the peak positions of Fe^{2+} in the M(1), M(3), or M(4) sites.

The trends in Figure 5 also suggest that two different mechanisms are responsible for producing the

variation in Δ , because the Al in these samples is mostly in tetrahedral coordination and bonding occurs through one Al-O-(Fe,Mg) bridge, whereas the Fe^{3+} is most likely in octahedral coordination and bonding with adjacent octahedral sites occurs by sharing a common edge. An indication that the amount of tetrahedral Al is the dominant factor comes from the Mössbauer and structural data for the intermediate and sodic amphiboles. In glaucophane, the M(2) site is almost fully occupied by Al and Fe^{3+} (Papike and Clark, 1968) and there is very little tetrahedral Al, but Δ of the outer peaks is about 2.8 mm/sec (Bancroft and Burns, 1969). In synthetic magnesiohastingsite less than half of the M(2) sites could be occupied by Al and Fe^{3+} , but there is significant tetrahedral Al. Δ of the outer peaks is about 2.7 mm/sec (Semet, 1973). It appears likely that the amount of tetrahedral Al affects the fit of the octahedral and tetrahedral chains. The fit of the octahedral and tetrahedral chains in response to changing Fe/Mg compositions was discussed by Hafner and Ghose (1971) as a possible cause for the variation in Δ of Fe^{2+} in the M(4) site in CG spectra.

Regardless of the mechanisms responsible for producing the trends in Figure 5, the result would be a progressive "collapse" of the Fe^{2+} envelope, if the locations of the inner peaks remain about the same. This can be seen in the Mössbauer spectrum of a pargasite in Figure 6⁵. This pargasite was selected because its electronic absorption spectra indicate the presence of Fe^{2+} in the M(4) site. The Δ values for the outer, intermediate, and inner doublets are 2.59, 2.26, and 1.88 mm/sec, respectively. The smaller Δ of the outer doublet does result in a "collapse" of the Fe^{2+} envelope, because the inner doublet remains at about the same position as in tremolite (Fig. 1, $\Delta = 1.84$ mm/sec). This produces a much closer overlap of all Fe^{2+} peaks, and therefore the ability to determine accurate site distributions by assuming that one peak represents Fe^{2+} in only one site is further impaired.

It was found that convergence in the computer fitting of the pargasite spectrum in Figure 6 was obtained, using only half-width constraints, only if all of the Fe^{2+} peaks in the low-velocity region occurred at lower velocities than the Fe^{3+} peaks. The positioning of the inner Fe^{2+} peak and the low-velocity Fe^{3+}

⁵ The computed values for Δ , δ , and the relative area of each Fe^{2+} doublet are: 2.59, 1.15 mm/sec, 30.6 percent; 2.26, 1.14 mm/sec, 23.0 percent; 1.88, 1.10 mm/sec, 12.6 percent. The values for the Fe^{3+} doublet are: 0.55, 0.61 mm/sec, 33.8 percent. The ferrous and ferric half-widths are 0.31 and 0.49 mm/sec, respectively, and χ^2 for the 210 channels analyzed is 240.

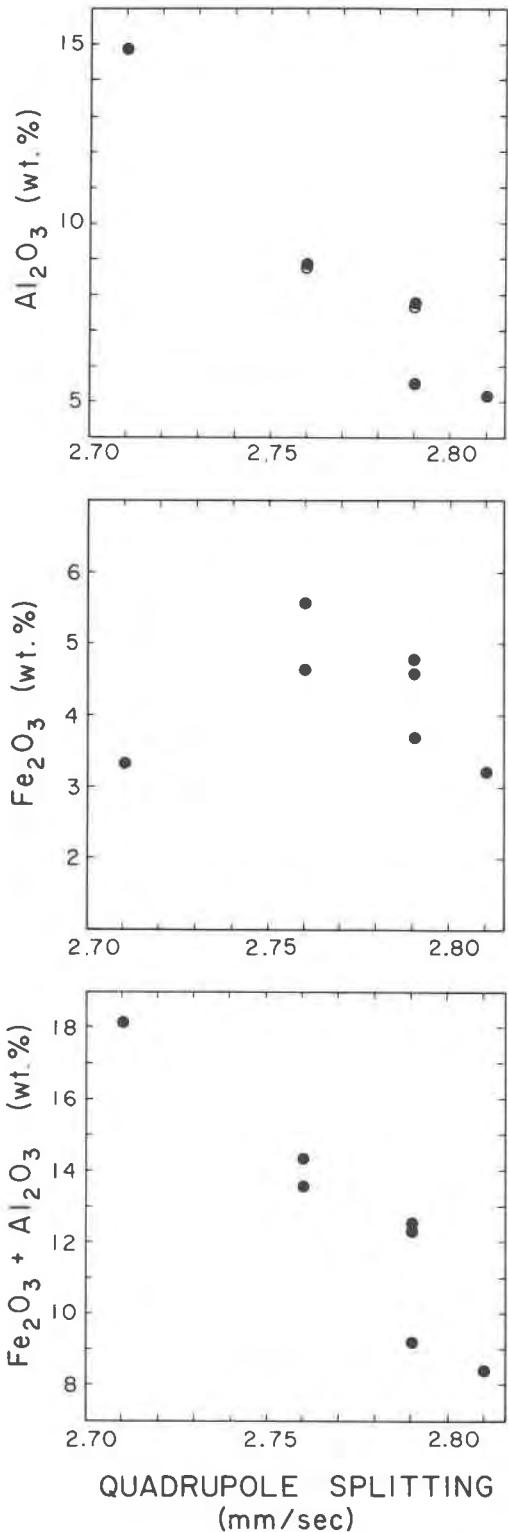


Fig. 5. Correlations between the quadrupole splitting of the outer Fe^{2+} doublet and the Al_2O_3 and Fe_2O_3 contents in the hornblendes reported by Bancroft and Brown (1975). Chemical data are from Dodge *et al.* (1968) and Burns and Greaves (1971).

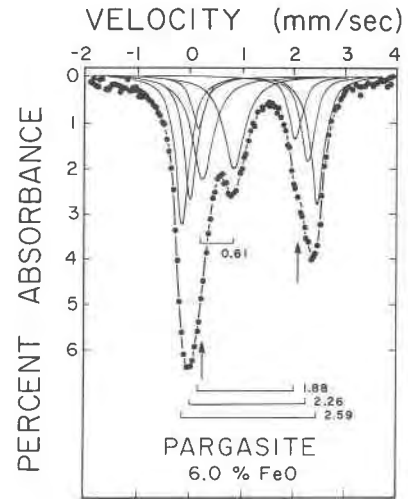


Fig. 6. Mössbauer spectrum of a pargasite from Washington taken at room temperature. The FeO content represents only Fe^{2+} , and the arrows mark the locations of the inner Fe^{2+} peaks in the tremolite spectrum in Fig. 1. The electronic absorption spectra of this sample indicate the presence of Fe^{2+} in the M(4) site.

peak in this region is similar to the fits for hornblendes in Bancroft and Brown (1975), but reversed from the fits for actinolites in Burns and Greaves (1971). Bancroft and Brown (1975) preferred their placement of these peaks, because it resulted in decreasing δ values as the Δ decreases for the Fe^{2+} peaks. It is true that, as Δ for Fe^{2+} in the M(4) site in cummingtonite-grunerites decreases, δ also decreases (Bancroft *et al.*, 1967a,b). However, the δ values for the inner and outer doublets for tremolite in Figure 1

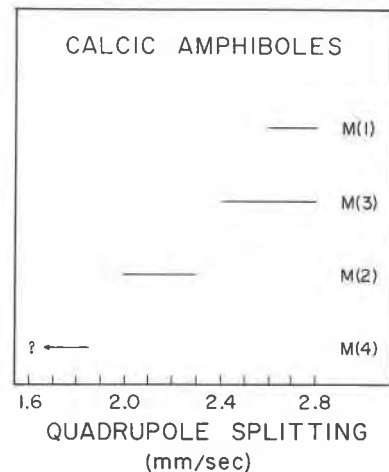


Fig. 7. Summary of the values of quadrupole splitting for Fe^{2+} in calcic amphiboles. The lower values in each range for Fe^{2+} in the M(1), M(2) and M(3) sites represent samples having more Al and Fe^{3+} .

show just the reverse, being 1.17 and 1.14 mm/mm/sec, respectively (Goldman and Rossman, 1977). Δ for the inner doublet in Figure 6 is sufficiently close to the expected value for M(4) Fe^{2+} based on the tremolite spectrum that it was felt that imposing additional constraints to reverse the M(4) and Fe^{3+} peaks in the low-velocity region was unnecessary.

The effect of next-nearest-neighbor chemical variations in calcic amphiboles has been discussed in terms of reducing Δ for Fe^{2+} in the M(1), M(2), and M(3) sites as more trivalent ions enter the crystal structure. It is realized that Fe^{2+} in a particular site may experience a variety of next-nearest-neighbor environments within a crystal structure, which would tend to broaden the spectral region in which it absorbs. Fitting one peak to this broadened region for iron in that site will lead to erroneous site distributions, as shown for synthetic clinopyroxenes by Dowty and Lindsley (1973). Because of the chemical complexities characteristic of calcic amphiboles, and the large number of sites available for Fe^{2+} , these problems may always be inherent to the method. Hence, a compromise between the number of peaks that can be fitted to a complex Mössbauer spectrum and the ability to decipher the origin of each peak must be reached. Figure 7 summarizes the conclusions regarding the site assignments for calcic amphibole Mössbauer spectra.

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