

⁵⁷Fe Mössbauer spectra of natural and synthetic hastingsites, and implications for peak assignments in calcic amphiboles

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Abstract

In order to test the validity of unique assignments of ⁵⁷Fe Mössbauer spectral peaks to individual crystallographic sites in hornblendes, spectra were collected for six synthetic hastingsites, ideally $\text{NaCa}_2\text{Fe}_4^{2+}\text{Fe}^{3+}\text{Si}_6\text{Al}_2\text{O}_{22}(\text{OH})_2$, and for three natural hornblendes of similar compositions. The synthetic, end-member hastingsites are inferred from compositional constraints to have the M(1), M(2), and M(3) sites filled entirely with iron and to have little or no iron in the M(4) site. Thus, these samples provide a test of peak-to-site correspondence. The areas of the Fe^{2+} doublets in the synthetic samples are not, however, in the same proportions as the abundances of the sites to which they are conventionally assigned, as would be expected if each doublet uniquely represented the contribution from a single site. On the other hand, the fractional areas of the three Fe^{2+} doublets, relative to the total Fe^{2+} absorption normalized to unity, show relatively uniform values of 0.55 ± 0.03 , 0.29 ± 0.03 , and 0.16 ± 0.02 for the outer, intermediate, and inner doublets, respectively, in the synthetic and natural hastingsites from this study, as well as for other hornblendes from the literature exhibiting a range of total iron and Fe^{3+} contents. By inference from their chemical analyses, the natural samples are also considered to contain little or no iron in M(4). These results suggest that the ferrous absorption has a characteristic shape independent of iron concentration and that the ferrous doublets cannot be assigned to sites uniquely to yield accurate site populations for hornblendes. The observed ferrous area fractions cannot be explained by peak broadening due to octahedral next-nearest-neighbor effects, although it is possible that the presence of neighboring tetrahedral aluminum may be a dominant factor in perturbing the areas of the ferrous doublets.

Introduction

One of the principal goals of ⁵⁷Fe Mössbauer spectroscopy of minerals is the resolution of the observed spectrum into its component peaks and their assignment to ferric or ferrous iron in the various crystallographic sites. Of particular interest are the widely occurring calcic amphiboles, including hornblendes, which have been examined in a number of studies (DeCoster and others, 1963; Bancroft and others, 1967; Häggstrom and others, 1969; Burns and Greaves, 1971; Bancroft and Brown, 1975; Goodman and Wilson, 1976; Goldman, 1979). The study of Goldman summarizes all previous work on calcic amphiboles and presents a peak-to-site assignment scheme that is consistent with previously published spectra.

Peak assignments may be evaluated by comparison with infrared, X-ray and electronic absorption data on the same sample, as well as the site distribution inferred from the chemical analysis. An exacting test can be applied if all the potentially iron-bearing sites are nearly or entirely filled with iron. If, in such a case, the peaks of a spectrum have been correctly assigned, the areas of the peaks should be in the same ratio as that of the sites. Unfortunately, the majority of amphiboles for which Mössbauer spectra have been collected contain other cations that substitute for iron and thus this test cannot be applied rigorously. In the present study, Mössbauer spectra were collected on six synthetic hastingsites having the nominal formula $\text{NaCa}_2\text{Fe}_4^{2+}\text{Fe}^{3+}\text{Si}_6\text{Al}_2\text{O}_{22}(\text{OH})_2$, that is, with all octahedral sites filled with iron. In addition, spectra were collected on three natural hastingsites with similar formulas.

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Table 1. Synthesis conditions for hastingsites

Sample	Buffer	T, °C	P, kbars	Duration, hrs (total)
MI322	Iron-quartz-fayalite	680	3000	26
MI321	Iron-wüstite	680	3000	27
MF323	Wüstite-magnetite	680	3000	26
ME339*	Iron-wüstite	680	3000	24
	Fayalite-magnetite-quartz	680	3000	26
ME340*	Iron-wüstite	680	3000	31
	Fayalite-magnetite-quartz	660	3000	13
F193	Wüstite-magnetite	700	3000	6

*Synthesized on iron-wüstite and subsequently annealed on fayalite-magnetite-quartz.

Experimental methods

The synthetic hastingsites were crystallized hydrothermally from an oxide mix at a fluid pressure of 3000 bars, temperatures from 660 to 700°C, and under a range of oxygen fugacities. The conditions of synthesis are given in Table 1. The natural hastingsites are from a variety of localities and were analyzed by electron microprobe as part of this study. The analyses and occurrences are detailed in Table 2.

Mössbauer spectra were collected at room temperature for all samples and at liquid nitrogen-temperature for five samples using a 256-channel analyzer in conjunction with a conventional loud-speaker drive with a moving-source geometry and operated in the constant acceleration mode. Twenty or 15 mCi ^{57}Co -in-Pd sources, kept at room temperature, yielded a minimum line width of 0.29 mm/sec. The velocity increment per channel was about 0.03 mm/sec and was calibrated with iron foil, hematite or a ferrous oxalate-sodium nitroprusside mixture. Samples were hand-ground and mounted in Vaseline in a 1" diameter plastic dish, with total iron concentration ranging from 3–4 mg/cm² for the synthetic samples to about 8 mg/cm² for the natural specimens. Total counts per channel ranged, in different spectra, from about 1×10^6 to over 5×10^6 . The spectra were analyzed using the computer program MOSFT (Dollase, personal communication); the misfit parameter of Ruby (1973) was the primary criterion used to evaluate the goodness of fit.

Description of the spectra

All of the spectra, both of the natural and synthetic hornblendes, are similar, both in appearance and in the refined hyperfine parameters. They indicate the presence of high-spin ferrous and ferric iron in octahedral coordination with overlapping low ve-

locity ferrous and ferric peaks. There are no transmission valleys or significant inflections except for that between the ferric and ferrous intensities; the absorptions due to ferrous iron, however, are asymmetric with broader inner slopes. Typical spectra are illustrated for a synthetic hastingsite in Figure 1 and for a natural hornblende in Figure 2. The spectra differ primarily in the intensity of the ferric absorption.

All spectra were fitted with four doublets, three for octahedral ferrous and one for octahedral ferric iron, the "correct general fit for calcic amphiboles" of Bancroft and Brown (1975). All peak positions were refined, but each doublet was constrained to be area- and width-symmetric. All ferrous widths were constrained to be equal but different from the ferric width. A 95% Lorentzian–5% Gaussian line shape was assumed in order to account for slight broadening due to sample and instrument effects. No significant misfits were present to suggest problems from the constraints outlined above, preferred orientation or unfitted tetrahedral ferric intensity. The refined hyperfine parameters are given in Table 3.

Table 2. Microprobe analyses and structural formulae of natural hastingsites

	MI3724	MI4671	C-1-11
SiO ₂	37.68	38.71	39.90
Al ₂ O ₃	14.01	11.24	11.87
TiO ₂	1.02	0.52	0.56
Fe ₂ O ₃ *	7.97	6.77	9.48
FeO	20.63	25.96	20.40
MnO	0.66	0.83	0.28
MgO	2.20	0.72	3.75
CaO	9.26	10.81	11.27
Na ₂ O	3.31	1.50	1.08
K ₂ O	2.22	1.86	2.23
Σ	98.96	98.92	100.82
Cations per 23 oxygens			
Si	5.93	6.22	6.14
Al ^{IV}	2.07	1.78	1.86
Al ^{VI}	0.53	0.35	0.29
Ti	0.12	0.06	0.06
Fe ³⁺	0.94	0.82	1.10
Fe ²⁺	2.71	3.48	2.62
Mn	0.09	0.11	0.04
Mg	0.52	0.17	0.86
Ca	1.56	1.86	1.86
Na	1.01	0.47	0.32
K	0.45	0.38	0.44

* Total Fe as FeO from electron microprobe; Fe³⁺/Fe²⁺ from Mössbauer spectroscopy.

Samples: MI3724 Hastings County, Ontario (Royal Ontario Museum collection)
 MI4671 Custer County, Idaho (Royal Ontario Museum collection)
 C-1-11 Feather Falls, California (Compton, 1958)

Hyperfine parameters

Isomer shift

The isomer shifts for octahedral ferrous iron in the room-temperature spectra range from 1.06 to 1.16 mm/sec relative to ^{57}Fe in metallic iron. These values are typical of previously refined spectra for calcic amphiboles (Goldman, 1979). Liquid nitrogen-temperature values range from 1.20 to 1.28 mm/sec. The isomer shifts of the octahedral ferric iron range from 0.37 to 0.49 and 0.39 to 0.57 mm/sec for room-temperature and liquid nitrogen-temperature spectra, respectively. The variation in ferric isomer shifts, and also in ferric quadrupole splittings, is primarily the result of the poorly located low-velocity peak and also of its proximity to the low-velocity component of the inner ferrous doublet. The position of the high-velocity component of the ferric doublet, however, is well known and the total area of the ferric absorption, assuming a symmetric doublet, is thus well determined.

Quadrupole splitting

Like the isomer shifts, quadrupole splittings vary over relatively small ranges and the values for

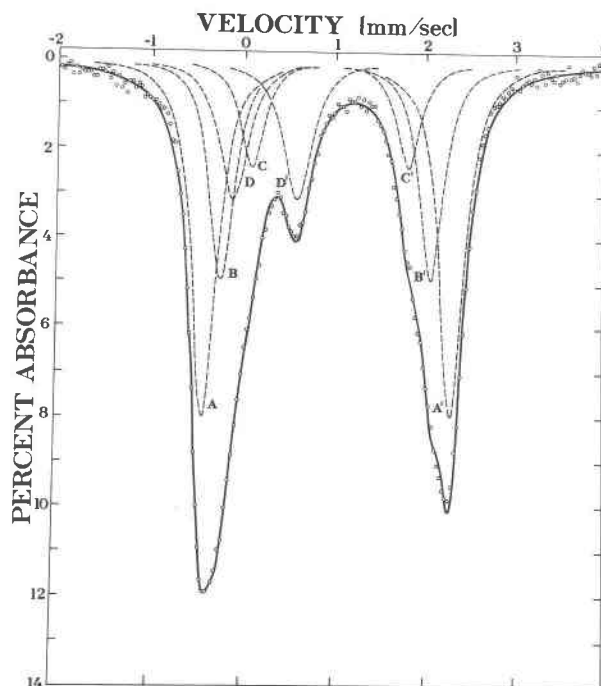


Fig. 2. Mössbauer spectrum of natural hastingsite M14671 taken at room temperature. Doublets AA', BB' and CC' are assigned to Fe^{2+} , and doublet DD' to Fe^{3+} , all in octahedral coordination. Isomer shifts are relative to iron metal.

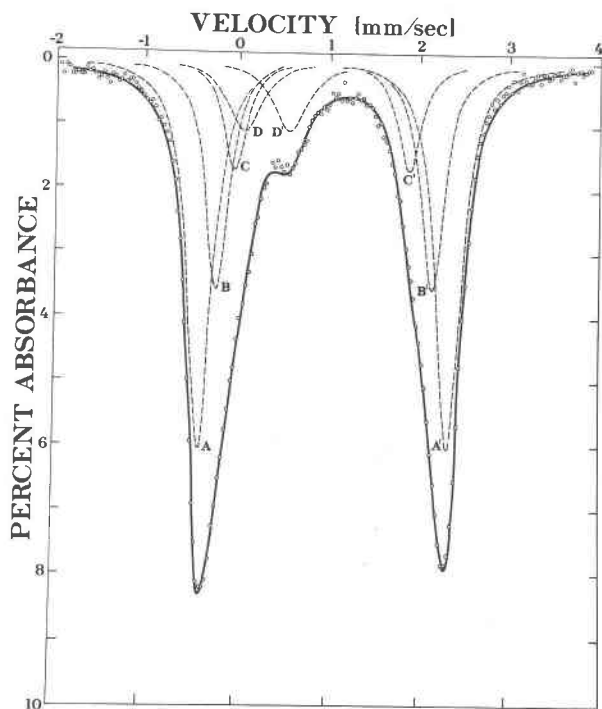


Fig. 1. Mössbauer spectrum of synthetic hastingsite MF323 taken at room temperature. Doublets AA', BB' and CC' are assigned to Fe^{2+} , and doublet DD' to Fe^{3+} , all in octahedral coordination. Isomer shifts are relative to iron metal.

natural and synthetic minerals overlap. The site assignments of these doublets may be tentatively interpreted in light of Goldman's (1979) scheme based on quadrupole splittings. The bulk chemical composition of the oxide mix from which synthetic hastingsites were crystallized as well as the microprobe analyses of the natural minerals indicate that there is no significant contribution to these spectra from Fe^{2+} in the M(4) site. Table 4 lists the ranges of quadrupole splitting for the three ferrous doublets in the synthetic and natural minerals as well as Goldman's ranges for Fe^{2+} in the M(1), M(3), M(2), and M(4) sites of calcic amphiboles. It can be seen that the outer and intermediate doublets in this study can be correlated on the basis of quadrupole splitting with M(1) and M(3) values, whereas the inner doublet values consistently fall below his ranges for M(2). Goldman did suggest, however, that the value of quadrupole splitting for M(1) decreases as the weight percent Fe_2O_3 and Al_2O_3 in the amphibole increases. Goldman did not present a similar plot for variation of M(2) quadrupole splitting with total aluminum content, and for the seven hornblendes he considered, the variation of M(2) is not significant. When the hornblendes from Gold-

Table 3. Mössbauer hyperfine parameters from four-doublet fits for synthetic and natural hastingsites

	Fe ²⁺			Fe ²⁺			Fe ²⁺			Fe ³⁺							
	IS	QS	Area	IS	QS	Area	IS	QS	Area	IS	QS	Area	*/	**/	RMS	Chi	Misfit
MI322	1.12	2.79	0.537	1.11	2.39	0.232	1.10	1.92	0.115	0.37	0.60	0.116	0.33	0.51	1.34	0.135(16)%	
MH321	1.13	2.74	0.495	1.13	2.36	0.261	1.10	1.91	0.126	0.48	0.53	0.118	0.31	0.59	1.28	0.189(21)%	
MF323	1.13	2.73	0.479	1.12	2.37	0.269	1.09	1.92	0.129	0.49	0.50	0.124	0.31	0.46	1.52	0.129(12)%	
ME339	1.14	2.71	0.491	1.14	2.30	0.222	1.12	1.76	0.096	0.42	0.64	0.190	0.31	0.44	1.60	0.116(11)%	
ME340	1.11	2.71	0.419	1.10	2.35	0.258	1.06	1.92	0.107	0.44	0.53	0.216	0.30	0.43	1.42	0.105(12)%	
F193	1.12	2.70	0.469	1.11	2.35	0.276	1.08	1.87	0.134	0.46	0.52	0.121	0.30	0.48	1.25	0.179(24)%	
M13724	1.13	2.74	0.387	1.11	2.36	0.240	1.09	1.82	0.110	0.38	0.69	0.263	0.31	0.38	1.59	0.129(11)%	
M14671	1.12	2.72	0.425	1.09	2.31	0.257	1.12	1.72	0.124	0.40	0.70	0.194	0.32	0.38	1.60	0.125(11)%	
C-1-11	1.16	2.72	0.364	1.12	2.35	0.231	1.12	1.81	0.110	0.41	0.72	0.295	0.32	0.42	2.14	0.203(14)%	

Isomer shifts (IS), quadrupole splittings (QS) and linewidths are in mm/sec. Isomer shifts are relative to metallic iron. Errors in IS, QS and line width are ± 0.03 mm/sec. Estimated standard of the misfit refers to the last digits.

* Ferrous line widths.

** Ferric line widths.

man (1979) and the more Al- and Fe³⁺-rich samples from the present study are plotted together, the inner, M(2), doublet shows a poorly defined trend of smaller quadrupole splitting with increased total Al and Al + Fe³⁺. In view of the rather high Fe³⁺ and Al content of the hornblendes in this study and the apparent absence of Fe²⁺ in M(4), the inner doublet may be considered as assigned to M(2) and as extending the acceptable range for M(2).

Line widths

Line widths, Γ , that is full widths at half maximum, range from 0.30 to 0.34 mm/sec for Fe²⁺ doublets and 0.38 to 0.59 mm/sec for Fe³⁺ doublets. These values are comparable to those published for other hornblendes (Bancroft and Brown, 1975) and actinolites (Burns and Greaves, 1971), except for the ferric line widths greater than 0.48 mm/s. These are larger than most literature values and are from spectra of the most ferric-poor synthetic hastingsites.

Area fractions and site assignments

In determining the occupancy of various crystallographic sites by ferric or ferrous iron, it is generally assumed that the areas of the resolved Möss-

bauer doublets are in approximately the same proportion as the abundances of the iron atoms responsible for them. Using the chemical analyses determined by electron microprobe and the Fe³⁺/Fe²⁺ ratios from the Mössbauer spectra, site assignments were made for the natural hastingsites in this study. This was done using the four-doublet fit described above and the peak assignment scheme of Goldman (1979), assuming no Fe²⁺ in M(4) in the QS = 1.7–1.9 mm/sec region. Site assignments for these three natural hastingsites produce distributions of cations which are allowed considering the chemical analyses and amphibole stoichiometry. In M14671, a minor underfilling of M(1) and a slight overfilling of M(3) can be explained by errors in the fitting of the spectrum and in the microprobe analysis. In other words, the peak assignment scheme of Goldman (1979), in which the outer, intermediate and inner ferrous doublets are assigned to M(1), M(3) and M(2), respectively, can be applied to these natural hornblendes. It is important to note, however, that the occupancy of the octahedral sites by Fe is not complete, ranging from 75 to 86% of the cations in these sites.

The synthetic hastingsites, by contrast, are inferred to have all M(1), M(3), and M(2) sites filled with iron, but the areas of the ferrous doublets in their spectra are inconsistent with the one-to-one correlation of the outer, intermediate and inner doublets with ferrous iron in M(1), M(3) and M(2), respectively. If such a correlation were valid, the four doublets would exhibit fractional areas, relative to the total area normalized to unity, of 0.40:0.20:(0.40-n):n for the ordered case in which all ferric iron is ordered into M(2) and n is the fractional amount of ferric iron in the particular

Table 4. Quadrupole splitting for hornblendes from this study compared to Goldman's ranges for the M(1), M(3), M(2), and M(4) sites

	Goldman (1979)	This Study	
		Synthetic Hastingsites	Natural Hastingsites
M(1)	2.6–2.8 mm/sec	2.70–2.79 mm/sec	2.72–2.74 mm/sec
M(3)	2.4–2.8	2.30–2.39	2.31–2.36
M(2)	2.0–2.3	1.76–1.92	1.72–1.83
M(4)	<1.85		

Table 5. Ideal and observed area fractions for synthetic hastingsites

Sample	Ideal area fractions								Observed area fractions			
	Ordered [*]				Disordered [†]							
MI322	0.40	0.20	0.28	0.12	0.35	0.18	0.35	0.12	0.54	0.23	0.11	0.12
MH321	0.40	0.20	0.28	0.12	0.35	0.18	0.35	0.12	0.50	0.26	0.13	0.12
MF323	0.40	0.20	0.28	0.12	0.35	0.18	0.35	0.12	0.48	0.27	0.13	0.12
ME339	0.40	0.20	0.21	0.19	0.32	0.16	0.32	0.19	0.49	0.22	0.10	0.19
ME340	0.40	0.20	0.18	0.22	0.31	0.16	0.31	0.22	0.42	0.26	0.11	0.22
F193	0.40	0.20	0.28	0.12	0.35	0.18	0.35	0.12	0.47	0.28	0.13	0.12

* The four columns refer to Fe^{2+} in M(1), M(3) and M(2), and Fe^{3+} in M(2).

† The four columns refer to Fe^{2+} in M(1), M(3) and M(2), and the sum of Fe^{3+} in all sites.

hornblende. For the disordered case in which the ferric iron is assumed to be distributed over all three octahedral sites and the ferric doublet represents Fe^{3+} in all sites, the areas fractions should be $(0.40-0.4n):(0.20-0.2n):(0.40-0.4n):n$. The predicted area fractions for the synthetic hastingsites for these two end-member distributions are given in Table 5. An intermediate state of Fe^{3+} - Fe^{2+} ordering would produce area fractions intermediate between the two given in the table. An examination of the actual area fractions for the synthetic hastingsites shows a significant discrepancy with the predicted values. In particular, the area of the outer doublet is too large, in all cases except ME340, to be the result of Fe^{2+} in M(1) only. To determine whether the anomalous areas are merely the result of poor fitting owing to the presence of ferric iron, the high-velocity portion of the spectrum, which contains absorptions due to ferrous iron only, was fit separately for samples MI322 and ME339. These fits produced, within errors, the same normalized ferrous area fractions relative to the total Fe^{2+} absorption normalized to one, as those determined from the full spectrum.

All the synthetic hastingsites contain small amounts, <5%, of one or two of the phases hedenbergite, fayalite or magnetite, depending on the oxygen fugacity of synthesis and annealing. These impurities decreased during synthesis with continued grinding and rerunning of the charge, but at an ever-decreasing rate. Because of small amount of the charge was lost with each regrinding, the procedure had to be terminated before the sample became too small for effective collection of the Mössbauer spectrum. On the average, each sample was rerun five times except for F193, which is the product of a single crystallization. Visually resolv-

able lines from magnetite, whose peaks do not overlap those of hastingsites, were not observed. For those impurities whose peaks do overlap the hastingsite spectrum, that is, hedenbergite and fayalite, calculations show that the amount of impurities required to account for the anomalous areas are many times greater than the amounts present. Furthermore, the similarity of the spectra to those of impurity-free natural samples, as discussed below, also suggests that the impurities are not perturbing the hastingsite spectra to any great extent.

To compare the ferrous absorptions in the natural and synthetic hornblendes of differing Fe^{3+} contents, the sum of the areas of the ferrous doublets was normalized to 1.0. These normalized values are presented in Table 6. The natural hornblendes chosen for comparison are those from this study and from Bancroft and Brown (1975). The hastingsite from the study of Burns and Greaves (1971, Sample #4) was not used because the chemical analysis suggests that Fe^{2+} is present in M(4). Likewise, the single spectrum from the study of Goodman and Wilson (1976) was not considered, inasmuch as the composition of the hornblende was not reported and the absence of Fe^{2+} in M(4) cannot be assumed. It can be seen that the ferrous peaks in all but two of the hornblendes show similar normalized ferrous area fractions, regardless of the total Fe content or the ferric/ferrous ratio. The average values for the hornblendes in Table 6 are 0.55 ± 0.03 , 0.29 ± 0.03 , and 0.16 ± 0.02 for the outer, intermediate, and inner doublets, respectively. The two most deviant values for the synthetic samples are MI322 and ME339, the former having fayalite impurities and the latter none. Thus, these two extreme values cannot be caused by the minor impurities in the sample.

Table 6. Normalized ferrous doublet area fractions

Sample	Outer	Intermediate	Inner	†	%Fe ³⁺	
Synthetic Hastingsites						
MI322	0.61	0.26	0.13	100	12	*
MI321	0.56	0.30	0.14	100	12	*
MF323	0.55	0.31	0.15	100	12	*
MF339	0.61	0.27	0.12	100	19	*
ME340	0.53	0.33	0.14	100	22	*
F193	0.53	0.31	0.15	100	12	*
Natural Hornblendes						
MI3724	0.53	0.33	0.15	75	26	*
MI4671	0.53	0.32	0.15	86	19	*
C-1-11	0.51	0.33	0.16	75	30	*
C-1-11 (reduced)	0.50	0.34	0.17	75	8	*
BP-1	0.56	0.25	0.18	27	33	**
BP-6	0.54	0.28	0.19	29	28	**
BCc-13	0.58	0.27	0.16	37	34	**
SL-18	0.54	0.29	0.17	37	38	**
BCa-20	0.56	0.27	0.16	32	36	**
MG-1	0.55	0.27	0.18	30	39	**

† Percent octahedral sites occupied by Fe³⁺ + Fe²⁺
 * This study
 ** Bancroft and Brown (1975)

Errors in normalized area fractions are ± 0.03

Also included in Table 6 are the normalized ferrous area fractions for an artificially reduced sample of natural hornblende C-1-11. This hornblende, containing 30% of the iron as Fe³⁺, was annealed hydrothermally for 19 hours at 660°C and 3000 bars fluid pressure with oxygen fugacity controlled by the iron-wüstite buffer. No additional phases were produced by the treatment, but the ferric content of the hornblende was reduced to 8% of the total Fe. The reduction of hydrous iron silicates under low oxygen fugacity (and high hydrogen fugacity) has been frequently observed experimentally (Addison and Sharp, 1962; Semet, 1973, and references contained therein), but the mechanism responsible for it is not fully understood. That the normalized ferrous area fractions show no change between the natural hastingsite with 30% Fe³⁺ and its reduced equivalent with only 8%, implies that either (1) complete Fe³⁺-Fe²⁺ disorder existed in the original hornblende and equal proportions of ferric iron were reduced in all sites or (2) the ferrous absorption has a characteristic shape for hornblendes that is relatively insensitive to site occupancies.

Additional tests of area fractions

The area fractions for the synthetic hastingsites are considered anomalous based on their departure from the expected values for amphiboles with M(1), M(2) and M(3) entirely filled with iron. Peak assign-

ments can also be evaluated by comparison with infrared or X-ray studies. This was done by Burns and Greaves (1971) in their study of actinolites. In their three most Fe-rich samples, the Mössbauer estimate of the ferrous iron in the summed [M(1)+M(3)] sites significantly exceeded, by 24 to 57% relative, the infrared determination; the two methods agreed for the three most Mg-rich samples. For the same six actinolites, the Mössbauer determination of ferrous iron in the summed [M(2)+M(4)] sites was significantly less than the infrared values, by 42 to 84% relative, in all but the most magnesian specimen, for which the two techniques agreed. These data are presented in their Table 6. Burns and Greaves explained the low [M(1)+M(3)] infrared values by the preferential oxidation of Fe²⁺ in M(3) through heating of the sample at 131°C for 10 minutes in air and 10 minutes in vacuum during sample preparation. It is unlikely that such a treatment would cause discrepancies of the magnitude observed, particularly in light of the X-ray evidence discussed below.

For one sample (Burns and Greaves, 1971 #6), the site populations were also determined from a crystal structure refinement by Mitchell and others (1971). By comparison with the X-ray technique, the Mössbauer determinations of ferrous iron are too high, by 25% relative, for M(1) and too low, by 37% relative, for M(2). Thus, it appears that in moderately Fe-rich actinolites, as well as in Fe-rich hornblendes, the area fractions associated with the outer doublet are too large and those with the inner doublet, too small, to be consistent with a simple peak-to-site assignment scheme.

Comparison with other amphiboles

The spectra of other iron-rich amphiboles do not show the same problems associated with those of the hornblendes. The spectra of two nearly end-member natural riebeckites (Bancroft and Burns, 1969, sample #5; Ernst and Wai, 1970, sample #L0-1) exhibit peak areas that are consistent with a one-to-one peak assignment scheme. Likewise, the spectrum of the most iron-rich natural grunerite from the study of Bancroft and others (1967) shows expected areas, although in this case M(1), M(2) and M(3) are not resolved and only their summed intensity can be compared with the M(4) absorption. Finally, the spectrum of a synthetic ferritorichterite (Virgo, 1972) displays the expected area fractions of 3:2 for the unresolved [M(1)+M(3)] absorption *versus* the resolved, and summed, ab-

Table 7. Mössbauer hyperfine parameters from three-doublet fits for synthetic and natural hastingsites

	Fe ²⁺			Fe ²⁺			Fe ³⁺			*/	**/	RMS	Chi	Misfit
	IS	QS	Area	IS	QS	Area	IS	QS	Area					
MI322	1.12	2.74	0.671	1.10	2.14	0.217	0.40	0.54	0.112	0.38	0.49	1.76	0.227(21)%	
MH321	1.13	2.67	0.658	1.11	2.10	0.231	0.46	0.54	0.111	0.36	0.52	1.76	0.351(30)%	
MF323	1.13	2.66	0.647	1.11	2.11	0.234	0.48	0.51	0.119	0.36	0.44	2.22	0.270(18)%	
ME339	1.14	2.66	0.617	1.11	2.08	0.193	0.46	0.57	0.190	0.36	0.45	2.58	0.296(19)%	
ME340	1.11	2.64	0.580	1.08	2.11	0.208	0.42	0.56	0.212	0.36	0.44	2.25	0.254(18)%	
F193	1.12	2.61	0.675	1.09	2.03	0.209	0.46	0.54	0.116	0.36	0.47	1.73	0.336(33)%	
MI3724	1.13	2.65	0.556	1.12	2.00	0.190	0.36	0.72	0.254	0.37	0.38	2.52	0.317(18)%	
MI4671	1.12	2.64	0.576	1.13	1.94	0.239	0.36	0.78	0.185	0.39	0.37	2.66	0.340(19)%	
C-1-11	1.16	2.63	0.500	1.15	2.00	0.212	0.38	0.79	0.288	0.37	0.41	2.90	0.365(19)%	

Isomer shifts (IS), quadrupole splittings (QS) and line widths are in mm/sec. Isomer shifts are relative to metallic iron. Errors in IS, QS and line width are ± 0.03 mm/sec. Estimated standard errors these misfits refer to the last digits.

* Ferrous line widths.

** Ferric line widths.

sorptions for ferrous and ferric iron in M(2). Ernst's (1966) synthetic ferroactinolite (originally termed ferrotremolite) apparently contained some Fe²⁺ in M(4) (Burns and Greaves, 1971) and thus may have been off-composition; as a result, its spectrum cannot be evaluated. It is important to note that (1) in the grunerite the M(1), M(2) and M(3), and in ferrorichterite the M(1) and M(3), ferrous absorptions were not resolved, and (2) in the completely ordered riebeckites only M(1) and M(3) Fe²⁺ absorptions were resolved and explained by presuming that M(2) is almost entirely occupied by Fe³⁺. Thus, there exists no spectrum of an amphibole having >90% of the octahedral sites filled with iron in which three ferrous doublets have been resolved and which show the area fractions expected for one-to-one peak assignment.

An alternate peak assignment

The spectra of the natural and synthetic hornblendes in this study were also fitted by three doublets, two ferrous and one ferric. All other details were the same as for the four-doublet fits. The hyperfine parameters for these fits are given in Table 7. As shown by the misfit parameter, these three-doublet fits are less good than the corresponding four-doublet fits, which was the reason for preferring the latter originally. Inspection of the area fractions reveals that, within the errors, the inner doublet has a constant value of 0.20 in the spectra of the synthetic hastingsites. This is the area fraction that would be expected if these hastingsites have all Fe³⁺ ordered into (M2) and the inner doublet is assigned to M(3). In this scheme, the outer doublet would represent the unresolved absorptions of Fe²⁺ in M(1) and M(2). In addition, such an assignment scheme is consistent with the

chemical analyses of the natural hornblendes in this study. Although M(1) and M(2) both have formal symmetry 2 and M(3), 2/m, there is much X-ray and Mössbauer evidence to suggest that M(1) and M(3) are more similar to each other than to M(2), should have similar quadrupole splittings, and should have the least easily resolved doublets. This reassignment is probably not applicable to other than aluminous calcic amphiboles: the ferrorichterite spectrum (Virgo, 1972) is not compatible with it and the nearly end-member riebeckites (Bancroft and Burns, 1969; Ernst and Wai, 1970) are consistent with it only if the M(3) doublet can have a quadrupole splitting of approximately 2.3 mm/sec. Finally, the spectrum of Ernst's (1966) ferroactinolite collected by Burns and Greaves (1971) suggests that the M(2) absorption overlaps that of M(3) and not M(1). The evidence presented here is not conclusive enough to suggest the use of a new peak assignment scheme for calcic amphiboles. Nonetheless, it is striking that a wide range of difficulties with the spectra of these iron-rich end-members can be solved merely by changing peak assignments.

Liquid nitrogen-temperature spectra

Liquid nitrogen-temperature spectra were collected for three synthetic and two natural hornblendes in this study. Inasmuch as low-temperature Mössbauer spectra of amphiboles are more poorly resolved than their room-temperature equivalents (Bancroft and Brown, 1975), the additional information obtainable from them is limited. The outer and intermediate ferrous doublets are, in general, more overlapped than in the room-temperature spectra, whereas the intermediate and inner ferrous doublets may be more or less overlapped or have the same separation. The areas are not constant in the four-

doublet fits at the two temperatures, with corresponding values differing by one to eleven times the estimated standard deviations of the areas.

The uncertainties in the peak parameters are greater in the liquid nitrogen spectra than in the room-temperature spectra, due to both the poorer quality of the spectra produced by shorter counting times, and to the increased overlap of the peaks. Nonetheless, the lack of constancy of the peak areas in the four-doublet fits further suggests that these peaks do not represent individual sites, or at least that the correspondence between the peak areas and the site populations is poor, a conclusion that is consistent with the evaluation of the room-temperature spectra presented in preceding sections.

Discussion

Causes for the apparently anomalous Mössbauer area fractions can be of two types. (1) The errors associated with the area fractions may be sufficiently large that determined values of areas do not differ from the expected ones within the errors. (2) The area fractions are in fact different from the expected values and require an explanation other than a simple one-to-one peak assignment scheme with all ferrous recoil-free fractions assumed to be equal.

It is well known that the uncertainties associated with Mössbauer spectral parameters increase with increasing overlap of the individual peaks (Bancroft, 1970; Dollase, 1975). At separations less than 0.6 Γ there is a rapid decline in the precision with which all the peak parameters can be determined; in addition, the weaker the peak, the greater the uncertainty for a given degree of overlap (Dollase, 1975). Using Dollase's method for estimating the errors associated with Mössbauer parameters yields average uncertainties in the peak areas, for the synthetic hastingsites, of 4–9%, and for the natural hornblendes, of 2–7%. If the expected ratios for the synthetic minerals are compared to those observed, the following deviations are seen: for M(1), +34% to +5% (with all but one $> +17\%$), for M(3), +38% to +11%, and for M(2), –60% to –42%. Similar deviations are seen from the infrared and X-ray values for Burns and Greaves' (1971) more Fe-rich actinolites, as explained above. Finally, it should be noted that the sign of the deviations is the same in all cases. It would seem, then, that the observed area fractions are significantly different from the expected values.

Two categories of physically based explanations

may be considered. The first is that the peaks are correctly assigned to sites, but the recoil-free fraction for Fe^{2+} in each octahedral site is sufficiently different to account for the observed anomalies. This explanation is contrary to much of the evidence from Mössbauer investigations of silicates (see, for example, Bancroft, 1970) and is not corroborated by independent evidence such as temperature factors determined from X-ray studies (Hawthorne and Grundy, 1973a, 1973b, 1977; Mitchell *et al.*, 1971; Papike, *et al.*, 1969; Robinson *et al.*, 1973).

The second category involves the assumption of nearly equal recoil-free fractions, but assumes that the three resolved ferrous doublets cannot be assigned to sites on a one-to-one basis. Dowty and Lindsley (1973) found that fitting ferrosilite–hedenbergite (pyroxene) spectra with two ferrous doublets, one each for the M(1) and M(2) sites, did not yield the expected area fractions. These authors found that they could obtain more explicable areas by dividing the M(1) doublet into three or four doublets reflecting the various next-nearest-neighbor configurations of M(1). In their analysis, the excess area associated with M(2) in the two-doublet fit arose from the inclusion of some of the broadened M(1) intensity in the M(2) peak.

The amphiboles have more sites and hence more next-nearest-neighbor configurations than the pyroxenes. In the case of complete disorder of Fe^{3+} over all the octahedral sites, each M(1) and M(3) site has eighteen possible next-nearest-neighbor configurations and each M(2) has fifteen, although some are of low probability. The completely ordered case with all Fe^{3+} in M(2) is more easily evaluated, and partial or complete ordering is probably a more realistic model for amphiboles. In the completely ordered case for end-member hastingsite, each M(1) and M(3) site has three possible next-nearest-neighbor configurations, all of which have a high probability of occurrence in amphiboles containing approximately 10 to 30% Fe^{3+} . The M(2) site has, however, only one next-nearest-neighbor configuration, inasmuch as this site shares edges with two M(4) sites, filled only with Ca, and one M(3) and two M(1) sites, all filled with Fe^{2+} only. Table 5 shows that, for the synthetic hastingsites, the inner doublet, assigned to M(2), is much less intense than expected. This is opposite to what is predicted by Dowty and Lindsley's (1973) model. The M(2) intensity would be low only if part of its intensity were being donated to the M(3) doublet

through next-nearest-neighbor broadening, but M(2) is the only site which, in the ordered case, has only one next-nearest-neighbor configuration and thus would not be broadened. Furthermore, the M(3) doublet would be expected to be broadened and donate part of its intensity to the inner, or M(2), doublet. Thus if next-nearest-neighbor broadening were occurring, the inner doublet, if its assignment to M(2) is correct, would have a greater-than-expected intensity rather than the significantly lower-than-expected intensity that is observed. The natural hornblendes, in which octahedral Mg, Al, Mn and Ti could also contribute to next-nearest-neighbor effects, have spectra with a ferrous absorption of essentially the same shape as those of the synthetic amphiboles. This also suggests that octahedral next-nearest-neighbor effects are not perturbing the spectra in the way suggested by Dowty and Lindsley (1973) for the pyroxenes.

Goldman (1979) has suggested that the spectra of calcic amphiboles are progressively more collapsed, that is, the ferrous doublets are more overlapped, with increasing amounts of ferric iron and tetrahedral aluminum, the latter being more important. He does not, however, suggest any specific mechanism other than Al-influenced misfitting of the tetrahedral and octahedral chains. Seifert (1977) also recognized a similar effect of Al on the spectra of anthophyllites. In addition, the consideration of tetrahedral Al and Si as next-nearest-neighbors of octahedral iron will greatly increase the number of possible environments for Fe^{2+} . In particular, M(2), as well as M(1), shares corners with both tetrahedral sites, T(1) and T(2), and thus may experience a wide variety of next-nearest-neighbor configurations. If the tetrahedral cations can perturb the Mössbauer spectrum of octahedral Fe^{2+} there is opportunity for the broadening of the M(2) absorption and possible reduction in intensity of the inner ferrous doublet. Consistent with Goldman's (1979) suggestion that tetrahedral Al may affect the spectra, it can be noted that Al-free, Fe-rich amphiboles discussed in a previous section exhibit spectra with expected, although sometimes summed, area fractions.

With the evidence presented above, it is tempting to suggest an explanation in which the observed Mössbauer spectrum represents absorption by iron in a continuum of sites consisting of the formal crystallographic sites modified by a variety of next-nearest-neighbor configurations involving the tetrahedral cations. The differing intensity of the absorp-

tion with velocity (energy) reflects the distribution of iron across this continuum. Defects could provide a variety of Fe^{2+} environments, especially in the synthetic samples, but the similarity of their spectra with those of the natural minerals, for which defects are possible but less likely, argues against this explanation. As with the model of discrete, distinguishable sites, this model does not specifically explain the relatively constant nature of the normalized ferrous area fractions with differing amounts of octahedral iron. If the inner doublet represents a range of sites, or a single site, that is least favorable for Fe^{2+} , this doublet should be smaller for low-Fe hornblendes and larger for the all-Fe hornblendes in which iron occupies all available octahedral sites. Table 6 shows that this is not the case.

Conclusions

The Mössbauer spectra of minerals in which all potentially iron-bearing sites are completely filled with iron provide a test of the one-to-one assignment of the spectrum peaks to individual crystallographic sites. The areas of the three Fe^{2+} doublets in the spectra of end-member synthetic hastingsites are not in the same proportion as the sites to which they are conventionally assigned. The differences between the observed and expected areas are too large to be explained solely by the uncertainties in the refined peak parameters of overlapped doublets. This result suggests that either the conventional assignment is incorrect or that doublets cannot be assigned to sites on a one-to-one basis to yield accurate site populations, at least for the calcic amphiboles. Similar deviations have been observed in natural Fe-Mg actinolites in which the Mössbauer doublet areas are different from the expected areas predicted by infrared and X-ray studies (Burns and Greaves, 1971).

Comparison of natural and synthetic hornblendes reveals that the spectra of both exhibit ferrous doublets with relatively uniform normalized area fractions over a wide range of total iron concentrations. If the doublet areas accurately reflected site occupancies, the area fractions should change with iron concentration. A Dowty and Lindsley (1973) type analysis cannot explain the anomalous peak areas if only octahedral next-nearest-neighbor effects are considered. On the other hand, the primary perturbing influence on the spectra of calcic amphiboles, especially hornblendes, may be the presence of tetrahedral aluminum as a next-nearest

neighbor as suggested by Goldman (1979). Indeed, the spectra of iron-rich amphiboles having no tetrahedral Al do not exhibit the anomalous areas associated with the spectra of calcic amphiboles. Finally, the Fe^{2+} site populations derived from Mössbauer spectra of amphiboles containing tetrahedral aluminum must be considered inaccurate regardless of the total amount of iron in the octahedral sites.

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