A Mössbauer Study of Coexisting Hornblendes and Biotites: Quantitative Fe^{3+}/Fe^{2+} Ratios

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Abstract

Room temperature ^{57}Fe Mössbauer spectra have been recorded for six hornblendes and seven biotites from the Sierra Nevada Batholith, California. The hornblende spectra have been resolved into three Fe^{2+} doublets due to Fe^{2+} in $M1$, $M2$, and $M3$; and one Fe^{3+} doublet due to Fe^{3+} mainly in $M2$. The biotite spectra have been resolved into two Fe^{2+} and two Fe^{3+} doublets due to Fe^{2+} and Fe^{3+} in both $M1$ and $M2$. Using the areas of the peaks, Fe^{3+}/Fe^{2+} ratios have been derived. For biotites, these are found to be in good agreement with the chemical analysis values; for hornblendes, the constant relating the chemical and Mössbauer Fe^{3+}/Fe^{2+} values is 1.13 ± 0.02. The accuracy of the non-destructive Fe^{3+}/Fe^{2+} analysis is within 2 to 4 percent for most samples. Saturation corrections for such analyses are shown to be negligible.

The ferrous site populations show that Fe^{2+} orders in the $M1$ and $M3$ positions in hornblendes. There is a small amount of ferrous ordering on $M2$ in biotites, which increases as the ferrous content decreases.

Introduction

^{57}Fe Mössbauer spectra have now been widely used to obtain quantitative Fe^{2+} site populations in a large number of silicate minerals (for a review of the results, see Bancroft, 1973). In addition, several authors have suggested that quantitative Fe^{3+}/Fe^{2+} ratios could be obtained from the ^{57}Fe Mössbauer spectra of silicates (Bancroft, 1973; Burns and Greaves, 1971; Annersten, 1974). The agreement between Fe^{3+}/Fe^{2+} ratios from Mössbauer spectra and chemical analyses has been generally semi-quantitative (Bancroft, Burns, and Stone, 1968; Bancroft, 1973; Burns and Greaves, 1971), although for biotites considerable discrepancies between the two methods have been recently noted (Annersten, 1974; Goodman and Wilson, 1973). These latter discrepancies are probably mainly associated with the difficulties in chemically analyzing for Fe^{3+} in the presence of Fe^{2+}.

In this paper, we report the ^{57}Fe Mössbauer spectra for a number of hornblendes and biotites from the Sierra Nevada Batholith (Dodge, Papike, and Mays, 1968; Dodge, Smith, and Mays, 1969). Careful chemical analyses using the conventional methods of Peck (1964) have been made for all but one of the samples studied. We are able to show that the Mössbauer Fe^{3+}/Fe^{2+} ratios are entirely consistent with the chemical analysis values, and that Mössbauer spectroscopy can be used to obtain such analyses non-destructively with an accuracy of a few percent.

Experimental

The hornblendes and biotites were kindly supplied by F. C. W. Dodge and J. J. Papike as 200 mesh samples. The chemical analyses of the hornblendes (SL-18, BCc-13, BP-1, BP-6, BCa-20, MG-1) and biotites (FD-12, FD-20, SL-18, MT-1, BCa-20, MG-1, and BP-1) are described in Dodge *et al* (1968) and Dodge *et al* (1969) respectively. With the exception of hornblende BP-6, all these samples were analyzed by the 'conventional' methods of Peck (1964).

The Mössbauer spectra were obtained using a 50 mCi ^{57}Co in Cu source with both source and absorber at room temperature. From 2×10^6 to 4×10^6 baseline counts were accumulated for each spectrum. Previous results on amphiboles (Burns and Greaves, 1971; Bancroft and Burns, 1969) and biotites (Annersten, 1974) indicate poorer resolution at lower temperatures for both mineral types. Calibration was performed using a 99.99 percent Fe foil, and the scan center method described previously (Bancroft, 1973). All center shifts are quoted with respect to sodium nitroprusside.

To investigate the effects of saturation on the ferric to ferrous ratios, spectra of pure BP-1 hornblende were recorded at different concentrations in two ways. In the first method, 100 mg to 600 mg of pure

mineral were sandwiched between two perspex discs in a holder of cross sectional area 1.76 cm². In the second method, 40 mg to 200 mg of mineral (150 mg except where specified) were mixed with ground sucrose of similar particle size such that the total weight of sample plus sucrose was 600 mg. The mixture was pipetted through a small hole in the top of the perspex sample holder. This technique has previously been found to give randomly oriented samples (Clark, Bancroft and Stone, 1968), and the results in the following section show that random samples were indeed obtained. For BP-1, the percentage of (Fe^{2+} + Fe^{3+}) in the mineral is 11.2 percent, and 100 mg of mineral then corresponds to 6.4 mg Fe per cm². The latter sucrose method was used for all spectra other than the saturation study.

The spectra were fitted using the updated version of the program written by A. J. Stone and methods described in Bancroft (1973). All final spectra were fitted with only linewidth equality constraints. In the hornblende spectra, the final fits were obtained by constraining the Fe^{2+} linewidths to be equal (but allowed to be different from the Fe^{3+} linewidths). In the biotite spectra, the final fits were obtained with *all* Fe^{2+} *and* Fe^{3+} linewidths constrained to be equal. Separate Fe^{2+} and Fe^{3+} linewidth constraints showed no significant difference in the Fe^{2+} and Fe^{3+} line-widths.

After the publication of a paper (Law, 1973) pointing out potential difficulties in fitting eight peaks to one holmquistite spectrum, it seems appropriate to discuss here the statistical and technical reasons why six-peak fits to our hornblende spectra are not satisfactory. Crystal-chemical reasons for the rejection of the six-peak fit will be detailed in the next section. First, there is always a marked decrease in χ^2 (100 ± 20) on going from a six-peak fit to an eight-peak fit. Thus χ^2 for most of our hornblende spectra drops from the 600 range for a six-peak fit to the 500 range for an eight-peak fit. A drop in χ^2 of less than 50 within the statistically acceptable range for *one* spectrum (Law, 1973) need not be strong evidence in favor of the fit with the lower χ^2, but a drop in χ^2 of ~ 100 for a *number* of spectra is compelling evidence for the existence of the extra doublet. Second, a six-peak fit gives inner Fe^{2+} line-widths of 0.40 ± 0.02 mm s⁻¹, which are much larger than those normally observed (0.30 mm s⁻¹) for Fe^{2+} in a single site in silicate minerals (Bancroft, 1973, p. 189). Thus the line widths for a riebeckite [$Na_2Fe^{2+}_3Fe^{3+}_2Si_8O_{22}(OH)_2$; sample 5, Bancroft and Burns (1969)] in which Fe^{2+} can only enter $M1$ and $M3$, are 0.29 mm s⁻¹. These

larger line-widths for six-peak fits strongly suggest a superposition of two peaks. It seems more than coincidental that the eight-peak fit gives Fe^{2+} line-widths of 0.32–0.33 mm s⁻¹ for *every* sample.

Finally, it should be noted that the spectra are not temperature dependent as in some Ca pyroxenes (Williams, Bancroft, Bown, and Turnock, 1971; Dowty and Lindsley, 1973). Thus, site populations derived at 80 K and room temperature for #7 in the previous study (Bancroft and Burns, 1969) were in good agreement. Combined with the crystal-chemical arguments given below, this evidence strongly suggests that the three doublets are due to Fe^{2+} in three structurally distinct positions.

Results and Discussion

Assignment: Amphiboles

Typical spectra of a hornblende and a biotite are shown in Figure 1, and the spectral parameters for all spectra are listed in Tables 1 and 2. The areas of component doublet peaks are very nearly equal and indicate that random samples were obtained. If anything, the low velocity Fe^{2+} peaks are less intense than the high velocity peaks in the biotite spectra.

The χ^2 values generally are statistically acceptable for the hornblende spectra (Table 1), and the center shifts, quadrupole splittings, and half widths are in very good agreement with a similar eight-peak fit to a magnesioriebeckite (#7, in Bancroft and Burns, 1969), but not in as good agreement with the eight-peak fit to a hornblende (#4, Burns and Greaves, 1971, Table 1). These differences, especially in peaks C C′ and D D′, point out one difficulty in fitting these spectra. In the paper by Burns and Greaves, peaks C and D were exchanged, leading to a smaller quadrupole splitting (Q.S.) and larger center shift (C.S.) for the Fe^{2+} peaks and a corresponding larger Q.S. and smaller C.S. for the Fe^{3+} peaks. We have found it possible to fit our hornblende spectra in both ways with very little difference in χ^2. However, because the C.S. usually decreases with decrease in Q.S. for Fe^{2+} minerals (Bancroft, Burns, and Maddock, 1967), we prefer our fits in which the C.S. decreases as the Q.S. decreases. Either fit gives Fe^{3+}/Fe^{2+} ratios and Fe^{2+} site populations equal within the error.

The hornblende spectra can be readily assigned as given previously: (Bancroft and Burns, 1969; Greaves and Burns, 1971) peaks A and A′, B and B′, C and C′ to Fe^{2+} in the $M1$, $M3$, and $M2$ positions respectively, and peaks D and D′ to Fe^{3+} in the three positions, although Fe^{3+} is known to predominate in the $M2$
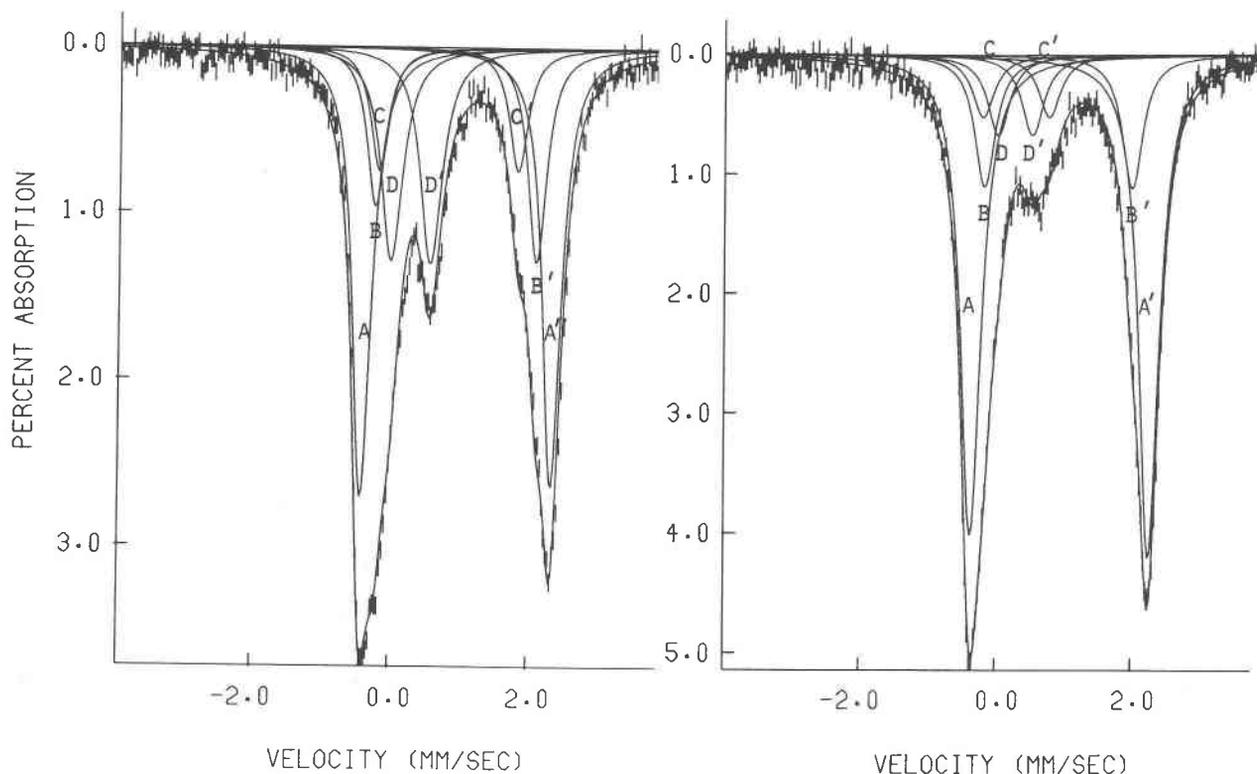
FIG. 1. Mössbauer spectra of (a) BCc-13 hornblende and (b) MT-1 biotite. In the hornblende spectrum peaks A and A', B and B', C and C' are due to Fe^{2+} in the $M1$, $M3$, and $M2$ positions respectively, while peaks D and D' are due to Fe^{3+} in the three positions. In the biotite spectrum, peaks A and A' and B and B' are due to Fe^{2+} in $M2$ and $M1$ respectively, while peaks C and C' and D and D' are due to Fe^{3+} in $M1$ and $M2$ respectively.

position (Bancroft and Burns, 1969; Ernst and Wai, 1970; Papike, Ross, and Clark, 1969). The larger half widths for the Fe^{3+} peaks indicate that peaks D and D' are due to Fe^{3+} ions in more than one position. The $Fe^{3+}/(Fe^{3+} + Fe^{2+})$ values derived from the Mössbauer areas are very similar to, but slightly larger than, those from chemical analyses, with the exception of BP-6 *(vide infra)*.

To further substantiate our eight-peak fits, as well as the assignment both for alkali amphiboles general-ly and for actinolites (Greaves and Burns, 1971), we briefly review the crystal chemistry of these minerals,

TABLE 1. Mössbauer Parameters—Hornblende Samples (295 K)[†]

Sample	χ^2	Peaks AA' (M1)			Fe^{2+} Absorptions Peaks BB'(M3)			Peaks CC' (M2)			Fe^{3+} Absorption Peaks DD' (M1,M2,M3)			$Fe^{3+}/(Fe^{2+} + Fe^{3+})$	
		C.S.	Q.S.	H.W.	C.S.	Q.S.	H.W.	C.S.	Q.S.	H.W.	C.S.	Q.S.	H.W.	Moss.	Chem[*]
		mm s^{-1}			mm s^{-1}			mm s^{-1}			mm s^{-1}				
BP-6	563	1.40	2.81	0.33	1.37	2.39	0.33	1.31	1.99	0.33	0.75	0.53	0.38	0.215	0.223
BCc-13	760	1.39	2.76	0.32	1.38	2.35	0.32	1.26	2.02	0.32	0.72	0.57	0.38	0.251	0.222
BP-1	518	1.38	2.79	0.32	1.35	2.40	0.32	1.29	2.01	0.32	0.72	0.54	0.37	0.251	0.231
SL-18	585	1.39	2.76	0.32	1.37	2.37	0.32	1.28	2.01	0.32	0.72	0.56	0.37	0.278	0.252
BCa-20	545	1.39	2.79	0.32	1.37	2.39	0.32	1.30	2.01	0.32	0.71	0.57	0.38	0.262	0.241
MG-1	601	1.39	2.79	0.32	1.36	2.41	0.32	1.28	2.04	0.32	0.71	0.58	0.38	0.283	0.262
Burns #4[**]	634	1.36	2.71	0.32	1.32	2.30	0.32	1.35	1.72	0.32	0.63	0.65	0.41	0.246	0.211

[†]   Errors in C.S., Q.S. and H.W. are ±0.02 mm s^{-1}.
     The C.S. values are quoted relative to sodium nitroprusside at room temperature.
     Subtract 0.16 mm s^{-1} to convert to stainless steel; subtract 0.26 mm s^{-1} to convert to iron metal.
[*]   Chemical analyses values taken from Dodge, Papike and Mays, (1968).
[**] Sample #4 in Burns and Greaves, (1971).

TABLE 2. Mössbauer Parameters—Biotite Samples (295 K)[†]

Sample	x^2	Peaks AA' (M2)			Fe^{2+} Absorptions Peaks BB' (M1)			Peaks CC' (M1)			Fe^{3+} Absorptions Peaks DD' (M2)			$Fe^{3+}/(Fe^{2+} + Fe^{3+})$	
		C.S.	Q.S.	H.W.	C.S.	Q.S.	H.W.	C.S.	Q.S.	H.W.	C.S.	Q.S.	H.W.	Moss.	Chem.[*]
		mm s^{-1}			mm s^{-1}			mm s^{-1}			mm s^{-1}				
BP-1															
a 6 peak fit	643	1.38	2.67	0.36	1.35	2.26	0.36				0.76	0.65	0.45	0.175	0.172
b 70 mg. 8 peak fit	616	1.38	2.62	0.35	1.35	2.18	0.35	0.75	1.05	0.35	0.73	0.59	0.35	0.174	0.172
c 150 mg. 8 peak fit	614	1.39	2.65	0.36	1.35	2.20	0.35	0.75	1.03	0.35	0.75	0.52	0.35	0.173	0.172
MG-1	1015	1.39	2.62	0.37	1.36	2.15	0.37	0.73	1.05	0.37	0.75	0.50	0.37	0.197	0.193
MT-1	676	1.38	2.61	0.35	1.35	2.17	0.35	0.75	1.00	0.35	0.74	0.52	0.35	0.190	0.199
FD-12	770	1.39	2.57	0.37	1.37	2.06	0.37	0.74	1.00	0.37	0.78	0.47	0.37	0.126	0.137
BCa-20	570	1.38	2.62	0.40	1.36	2.13	0.40	0.72	1.00	0.40	0.71	0.42	0.40	0.170	0.166
SL-18	730	1.39	2.61	0.36	1.37	2.14	0.36	0.77	1.05	0.36	0.77	0.51	0.36	0.153	0.151
FD-20	770	1.40	2.62	0.40	1.39	2.15	0.40				0.86	0.57	0.40	0.047	0.059

[†] Errors in C.S., Q.S. and H.W. are ± 0.02 mm s^{-1}
     C.S. values are quoted relative to sodium nitroprusside.
[*] Chemical analyses values taken from Dodge, Smith and Mays, (1969).

concentrating particularly on the $M2$ position. In previous Mössbauer studies of alkali amphiboles (Bancroft and Burns, 1969; Ernst and Wai, 1970), with one exception the minerals have an (Fe^{3+} + Al^{3+}) content greater than 1.77 atom p.f.u. For samples 1–5 studied by Bancroft and Burns (1969), (Fe^{3+} + Al^{3+}) totalled over 1.90 p.f.u. Since it is generally recognized that Fe^{3+} and Al^{3+} enter the $M2$ position, very little Fe^{2+} would be expected to enter $M2$. In the actinolites studied recently (Greaves and Burns, 1971), there is very little Fe^{3+} + Al^{3+} (usually less than 0.50 p.f.u.), and we would thus expect a large amount of Fe^{2+} in $M2$. Our present samples have ~0.7 (Fe^{3+} + Al^{3+}) p.f.u., and we would thus expect a considerable amount of Fe^{2+} to enter $M2$.

Our spectra (and the actinolite spectra) are entirely consistent with the above crystal chemistry. Consider first the site populations. For glaucophane and riebeckite (Bancroft and Burns, 1969) where little, if any Fe^{2+} is expected in $M2$, two *narrow* Fe^{2+} doublets were observed which were assigned to Fe^{2+} in $M1$ and $M3$ (Q.S. 2.8 mm s^{-1} and 2.3 mm s^{-1} respectively). This assignment was confirmed by the excellent agreement between X-ray and Mössbauer results for the Fe^{2+} site populations for the glaucophane (Bancroft and Burns, 1969; Papike and Clark, 1968). Since considerable Fe^{2+} is expected to enter $M2$ in actinolites, it is not unexpected to see in these spectra a new resolved doublet (Q.S. < 2.0 mm s^{-1}) which was assigned not surprisingly to Fe^{2+} in $M2$. Our samples would be expected to have a

doublet C and C' (Fe^{2+} in $M2$) intermediate in intensity between the glaucophane-riebeckite and actinolite spectra, and this is in fact observed.

To further support the above assignment, our quadrupole splittings are consistently in good agreement with those quoted above for Fe^{2+} in the three positions (Table 1). Thus, our $M1$, $M2$, and $M3$ Q.S. vary from 2.76 − 2.81 mm s^{-1}, 2.35 − 2.40 mm s^{-1}, and 1.99 − 2.04 mm s^{-1} respectively. (The somewhat larger $M2$ Q.S. is due to the choice of the fit mentioned earlier.) A six-peak fit to alkali amphiboles with significant Fe^{2+} in $M2$ (#7, Bancroft and Burns, 1969; # S.C., Ernst and Wai, 1970; and *all* our spectra) gives inner Fe^{2+} Q.S. of <2.15 mm s^{-1}.

Finally, the consistency of the site populations discussed later is yet another strong argument in favor of the eight-peak fits.

Taken together, the above evidence leaves no doubt that the eight-peak fit is the correct *general* fit to calcic and sodic amphiboles. The magnitude of the errors associated with the peak areas (and thus the site populations) are still disputable, however. These errors will be discussed in the next section.

To avoid instrumental and other errors when reporting new spectra, it is imperative first, to take a number of spectra of related minerals; second, to use justifiable constraints which are necessary to obtain reasonable parameters; and third, to check the consistency of all the results. Law (1973) did none of the above, and thus his site populations cannot be evaluated. For example, his line-widths for the three

Fe^{2+} doublets vary from 0.22 mm s^{-1} to 0.37 mm s^{-1}. *Both* values are outside the range for Fe^{2+} widths for *all* silicate minerals with Fe^{2+} in a single site.

Assignment: Biotites

The χ^2 values for the biotite spectra are generally higher than those for the hornblendes, although our values are substantially lower than those reported in two recent studies (Goodman and Wilson, 1973; Annersten, 1974). Our values for the Q.S., C.S., and widths for the four doublets are in substantial agreement with those reported in the previous studies.

There has been some disagreement as to the assignment of biotite spectra. Annersten (1974) assigned the peaks as follows: outer and inner Fe^{2+} doublets to the $M2$ and $M1$ positions respectively, and outer and inner Fe^{3+} doublets to $M1$ and $M2$ positions respectively. However, Goodman and Wilson (1973) made the opposite assignment. Our data, together with the results of recent crystal-structure refinements of trioctahedral micas (Hazen and Burnham, 1973) strongly support the former assignment, namely, peaks A and A' to Fe^{2+} in $M2$, peaks B and B' to Fe^{2+} in $M1$; peaks C and C' to Fe^{3+} in $M1$; and peaks D and D' to Fe^{3+} in $M2$. The usual distortion criteria (Bancroft, 1973) for assigning Fe^{2+} peaks cannot be readily applied to biotites since the two sites are very similar both in size and in distortion from octahedral symmetry (Hazen and Burnham, 1973). The similarity of the sites and the Fe^{2+} site populations determined by crystal structure refinement for annite (Hazen and Burnham, 1973) indicate that there should be very little ordering of Fe^{2+} or Fe^{3+} in either site. The above assignment of the Fe^{2+} and Fe^{3+} peaks usually leads to little ordering of either cation (Table 6), whereas the reverse assignment would result in a large amount of ordering of both cations on the $M1$ sites. The above assignment is also consistent with the reversal of relative quadrupole splittings for Fe^{2+} and Fe^{3+} (Bancroft, 1973). The more distorted site leads to a smaller Fe^{2+} quadrupole splitting and a larger Fe^{3+} quadrupole splitting.

Saturation Effects

To examine the effect of saturation on the derived $Fe^{3+}/(Fe^{2+} + Fe^{3+})$ ratios, we ran a number of spectra on BP-1 hornblende as described in the experimental section. These results are summarized in Table 3. In the pure samples (100 mg to 600 mg), there appears to be a trend indicating small saturation corrections, although it is hardly outside the estimated error (Table 2). The spectra of the three

TABLE 3. Thickness Effects in BP-1 Hornblende

Mg. hornblende* in sample	Sample type	$Fe^{3+}/(Fe^{2+} + Fe^{3+})$**	χ^2
100	Pure	0.240	567
250	Pure	0.251	501
400	Pure	0.268	578
600	Pure	0.267	474
40	***	0.255	540
70	***	0.247	513
150	***	0.251	518

* 100 mg of this hornblende contains 11.2 mg $(Fe^{2+} + Fe^{3+})$. 100 mg then corresponds to 6.4 mg Fe per cm^2 (surface area of holder is 1.76 cm^2).
** Estimated error, ± 0.008
*** Total weight of sample plus sucrose is 600 mg.

samples mixed with sucrose give very consistent results for the $Fe^{3+}/(Fe^{2+} + Fe^{3+})$ ratio which are in close agreement with the chemical analysis value. These results strongly suggest that saturation corrections can be neglected for such samples. Because the mineral particles are well spread out in the sucrose, the true thickness for these samples should be less than that for the neat samples. Yet, the $Fe^{3+}/(Fe^{2+} + Fe^{3+})$ ratios for the neat samples—even up to 600 mg—are not far outside the sucrose value of 0.251. These results, along with all the Fe^{2+} site populations derived previously, strongly indicate that the large saturation corrections calculated by Stone (1973) are not applicable to granular samples with no correction for background.

The two results for biotites BP-1 (Table 2, top) also suggest that saturation corrections can be neglected. There is no significant change in the $Fe^{3+}/(Fe^{2+} + Fe^{3+})$ ratio between the 70 mg and 150 mg samples, and the derived Mössbauer ratios are in excellent agreement with the chemical analysis values. Once again, these results very strongly suggest that saturation corrections can be ignored.

Fe^{3+}/Fe^{2+} Ratios

The Fe^{3+}/Fe^{2+} values derived from the Mössbauer areas for hornblendes and biotites are given in Tables 4a and 4b respectively along with the chemical analyses. From the reproducibility of the results, we suggest that our Mössbauer Fe^{3+}/Fe^{2+} values are accurate to ± 0.006 or ~2 percent for hornblendes, but 3 percent for most biotites to ~12 percent for FD-20 biotite. These are only qualitative error estimates but the excellent consistency of the results discussed below strongly indicates that this is a reasonable error.

Using the usual formulation for area ratios (Bancroft, 1973), it is convenient to write:

TABLE 4a. Fe^{3+}/Fe^{2+} Ratios and Calculation of
C for Hornblendes

		Fe^{3+}/Fe^{2+}		
Sample	Mössbauer[†]	Chemical[*]	C	
BP-1 40 mg	0.329	0.300	1.10	
70 mg	0.341	0.300	1.13 } 1.12
150 mg	0.335	0.300	1.12	
BCa-20	0.355	0.318	1.12	
MG-1	0.394	0.356	1.11	
BP-6	0.280	0.288	0.97	
BCc-13	0.336	0.285	1.17	
SL-18	0.384	0.337	1.14	
		Average [††]	1.13 ± 0.02	

† Estimated error, ± 0.006
* From Dodge, Papike and Mays, (1968). Note that
   BP-6 was not analyzed by Peck's method
†† Not including BP-6

$$\frac{A_{Fe^{3+}}}{A_{Fe^{2+}}} = C \frac{N_{Fe^{3+}}}{N_{Fe^{2+}}}$$

where A represents Mossbauer absorption peak areas, and N represents chemical analysis values, and

$$C = \frac{\Gamma_{Fe^{3+}} f_{Fe^{2+}} G(X)_{Fe^{3+}}}{\Gamma_{Fe^{2+}} f_{Fe^{2+}} G(X)_{Fe^{2+}}}$$

where Γ is the line-width, f is the Mössbauer recoil-free fraction, and $G(X)$ is the saturation correction. The C values quoted on the right hand side of Table 4 are just the ratio of the Mössbauer Fe^{3+}/Fe^{2+} values to the chemical analysis Fe^{3+}/Fe^{2+} values.

For biotites, C is very close to 1.00 for all but FD-20 for which there is a comparatively large error in both the chemical analyses and Mössbauer ratios due to the very small Fe^{3+} content. The average of 0.98 ± 0.04 for C suggests that Fe^{3+}/Fe^{2+} values can be obtained directly from Mössbauer areas with no corrections. The line-widths, $\Gamma_{Fe^{2+}}$ and $\Gamma_{Fe^{3+}}$ are equal (Table 2), and since nearly the same proportionate amount of Fe^{2+} and Fe^{3+} enter the $M1$ and $M2$ sites, the average f value for both Fe^{2+} and Fe^{3+}

TABLE 4b. Fe^{3+}/Fe^{2+} Ratios and Calculation of
C for Biotites

	Fe^{3+}/Fe^{2+}		
Sample	Mössbauer[†]	Chemical[*]	C
BP-1 70 mg	0.207	0.208	1.00
150 mg	0.213	0.208	1.02
MG-1	0.243	0.239	1.02
MT-1	0.232	0.248	0.94
FD-12	0.142	0.158	0.90
BCa-20	0.197	0.199	0.99
SL-18	0.180	0.178	1.01
FD-20	0.049	0.063	0.78
		Average[††]	0.98±0.04

† Estimated error, ±0.006
* From Dodge, Smith, and Mays (1969)
†† Not including FD-20

should be very similar. The C value further supports our conclusion that saturation corrections can be neglected.

For hornblendes, the constant C is 1.13 ± 0.02, and the consistency of the C values is excellent except for BP-6, which was not analyzed by 'conventional methods.' We have not included the C value for BP-6 in our average C value. The larger C value is consistent with Fe^{3+} ordering in the smaller $M2$ positions, while Fe^{2+} preferentially orders in the larger $M1$ and $M3$ positions. We would expect that the smaller Fe^{3+} sites would result in $f_{Fe^{3+}}$ being larger than $f_{Fe^{2+}}$ giving rise to $C > 1$. In addition, it is apparent that $\Gamma_{Fe^{3+}} > \Gamma_{Fe^{2+}}$. For hornblendes and alkali amphiboles, the true chemical Fe^{3+}/Fe^{2+} ratio can now be obtained by dividing the Mössbauer value by 1.13.

The above results indicate that accurate Fe^{3+}/Fe^{2+} chemical analyses can be obtained for any other silicate mineral from Mössbauer area ratios after a calibration procedure similar to that given above. For minerals such as biotites in which Fe^{3+} and Fe^{2+} enter the same sites in similar relative amounts, the chemical Fe^{3+}/Fe^{2+} values can be obtained directly from the Mössbauer area ratios.

Fe^{2+} Site Populations

Assuming that $C = 1$, the ferrous site populations for hornblendes and the ferrous and ferric site populations for biotites can be readily calculated (Tables 5 and 6). The estimated errors are comparatively large (footnote, Tables 5 and 6) because the peaks closely overlap. No site populations from X-ray diffraction measurements on these samples are available for comparison with our Mössbauer results. The standard deviations in the areas for amphiboles (derived from our least-squares fitting procedure) are never larger than 10 percent of the areas (typically 4% for $M1$, 8% for $M3$ and 10% for $M2$). Because of the assumptions in the treatment (equal linewidths, and $C = 1$), we give an error which is normally much larger than these standard deviations. The reproduci-

TABLE 5. Fe^{2+} Site Populations in Hornblende
Samples per Formula Unit

Sample	Total Fe^{2+} p.f.u.[†]	Fe^{2+} per formula unit[*]			Age[**] (in millions of years)
		M1	M2	M3	
BP-1	1.35	0.76	0.25	0.34	150
BP-6	1.43	0.77	0.27	0.39	170
BCc-13	1.85	1.05	0.29	0.51	92
SL-18	1.86	1.01	0.31	0.54	91
BCa-20	1.61	0.90	0.26	0.44	87
MG-1	1.50	0.82	0.27	0.41	84

† From Dodge, Papike, and Mays (1968).
* Estimated errors ± 0.05
** K-A measurements; Kistler, Bateman and Brannock (1965)

TABLE 6. Calculation of Ferric and Ferrous Site Populations in Biotites per Formula Unit

Sample		Fe/formula* unit		Site Populations								Age**
				Fe^{2+}				Fe^{3+}				
		Fe^{2+}	Fe^{3+}	$4M2^\dagger$	M2	$2M1^\dagger$	M1	$4M2^\dagger$	M2	$2M1^\dagger$	M1	m.y.
BP-1	70 mg	1.89	0.39	1.46	0.36	0.43	0.22	0.30	0.08	0.09	0.05	78
	150 mg	1.89	0.39	1.37	0.34	0.52	0.26	0.25	0.06	0.14	0.07	78
MG-1		2.02	0.48	1.43	0.36	0.59	0.29	0.29	0.07	0.19	0.10	77
MT-1		1.97	0.49	1.55	0.39	0.42	0.21	0.31	0.08	0.18	0.09	81
FD-12		2.78	0.44	1.93	0.48	0.85	0.43	0.31	0.08	0.13	0.07	80-90
BCa-20		2.12	0.42	1.42	0.35	0.70	0.35	0.22	0.06	0.20	0.10	85
SL-18		2.38	0.42	1.68	0.42	0.70	0.35	0.29	0.07	0.13	0.07	82
FD-20		2.74	0.17	1.87	0.47	0.87	0.43	not resolved				80-90

*   From Dodge, Smith and Mays, (1969).
$\dagger$ Estimated error, $\pm$ 0.10
**   Kistler, Bateman and Brannock(1965);   Dodge, Smith and Mays(1969).

bility of the results, combined with the similarity of the site populations for samples with the same relative age and location (Table 5), suggests our errors are reasonable.

The results for hornblendes (Table 5) show immediately that Fe^{2+} orders in the $M1$ and $M3$ positions, and that there is little ordering between $M1$ and $M3$. These results are entirely consistent with the results for other alkali amphiboles (Bancroft and Burns, 1969). Because there is no background experimental work on equilibrium site populations of alkali amphiboles at different temperatures, it is difficult to comment at this stage on the relative ordering in the different age groups.

In most biotites in this study, Fe^{2+} orders in the $M2$ position—as found generally by Annersten (1974). Because of the small amount of Fe^{3+} and the relatively large errors in their site populations, there is no evidence in this work that Fe^{3+} orders in one position. Our results show that the two biotites with lowest Fe^{2+} contents (BP-1 and MT-1) are the most ordered, indicating that they were formed at the lowest temperature and/or cooled the most slowly. It is interesting that all the other samples are nearly disordered, indicating a higher temperature of formation and/or a more rapid rate of cooling. Obviously, more thermodynamic and kinetic data on ordering in biotites is needed for a more complete interpretation of the above results.

Acknowledgments

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