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A review of Mössbauer data on trioctahedral micas: Evidence for tetrahedral Fe^{3+} and cation ordering

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Abstract

Over fifty studies on Mössbauer spectroscopy of trioctahedral micas are summarized and reviewed in order to determine reasonable ranges for parameters of different Fe sites. Typical values (in units of mm/s) include Fe^{2+}_{M2}—isomer shift (δ) = 1.13, quadrupole splitting (Δ) = 2.58; Fe^{2+}_{M1}—δ = 1.12 and 1.16, Δ = 2.05 and 2.75; Fe^{3+}_{M1}—δ = 0.40, Δ = 0.55; Fe^{3+}_{M2}—δ = 0.40, Δ = 1.00; Fe^{3+}_{tet}—δ = 0.20, Δ = 0.50. The effects of major-element composition on Mössbauer parameters are assessed and found to be minimal, though the substitution of Li in the octahedral sheet systematically affects the quadrupole splitting of the Fe^{2+}_{M1} doublet. The Mössbauer and compositional data considered together show that tetrahedral Al ↔ Fe^{3+} substitution may be controlled by octahedral cation size and that M2-M1 cation ordering is ubiquitous.

Introduction

When the technique of Mössbauer spectroscopy was initially applied to minerals, biotites were among the first samples to be analyzed (Pollak et al., 1962). Since then a large number of trioctahedral micas have been studied with the Mössbauer effect. This paper evaluates only the room-temperature work done over the past 23 years, as the effects of temperature and dehydroxylation on Mössbauer studies of micas have been reviewed by Heller-Kallai and Rozenson (1981). Three distinct areas of investigation are addressed: (1) What are reasonable ranges for Mössbauer parameters of Fe in the different sites in micas? (2) How do variables such as composition affect Mössbauer results? Are isomer shift (I.S. or δ) and quadrupole splitting (Q.S. or Δ) affected by other cations adjacent to Fe in the mica structure? Is there a difference in peak-area data of igneous vs. metamorphic samples? (3) Is there evidence for cation ordering in micas?

Figure 1 shows a drawing of the mica structure that can be used in the following discussion: details of structural variations in trioctahedral micas are given by Bailey (1984a, 1984b), Guggenheim (1984), and Weiss et al. (1985).

Ranges of Mössbauer parameters

Mössbauer and electron-microprobe data on trioctahedral micas are compiled in the Appendix and plotted in Figure 2. For Fe in oxygen environments, the isomer-shift and quadrupole-splitting values (as calibrated in millimeters per second relative to an Fe-foil spectrum) most commonly fall in the following ranges (Dyar, 1984): Fe^{3+}_{tet}—δ = 0.15–0.30, Δ = 0.30–0.60; Fe^{3+}_{oct}—δ = 0.35–0.50, Δ = 0.40–1.0; Fe^{2+}_{tet}—δ = 0.90–1.0, Δ = 1.5–1.8; Fe^{2+}_{oct}—δ = 1.1–1.2, Δ = 1.8–3.1.

Figure 2 shows a plot of isomer shift vs. quadrupole splitting for all the analyses collected. The data for Fe^{2+} at M2 cluster tightly around Δ = 2.58 and δ = 1.13 mm/s, suggesting that the local geometry about the M2 site is not radically affected by the broad compositional range of these samples. For the data for Fe^{2+} at M1, one group of analyses clusters around Δ = 2.05 and δ = 1.12, and a second, more scattered group falls around Δ = 2.75 and δ = 1.16 mm/s. For Fe^{2+}, lower quadrupole splitting generally implies more distortion around a site (the reverse is true for Fe^{3+}), owing to some combination of the effects of metal-to-oxygen distances and angular components (however, this relationship has never been fully quantified). Therefore there seem to be three types of Fe^{2+} sites: a distorted Fe^{2+} M1 site, the Fe^{2+} M2 site, and a regular Fe^{2+} M1 site.

Mössbauer data for Fe^{3+} sites are less well defined; however, in my opinion the wider range of values may be due to a problem with the fitting procedures and is *not* dependent on compositional effects. Fe^{3+} at M2 and M1 has a similar range of δ = 0.35–0.65 mm/s, although each group has its own range of Δ = 0.11–0.80 and 0.57–1.24 mm/s respectively. Fe^{3+} peaks are almost always less intense than the corresponding Fe^{2+} peaks in the same samples (except in ferri-annites and ferri-phlogopites). In general, fitted Mössbauer doublets are less precise when peak areas are small. The samples in which Fe^{3+} Δ values lie between 0.60 and 1.0 mm/s probably represent spectra in which Fe^{3+} was present at both M2 and M1, but in such small quantities that it was impossible to distinguish them. The resultant single Fe^{3+} doublet in such samples has a Δ that is the average of the Δ values for the two separate sites.

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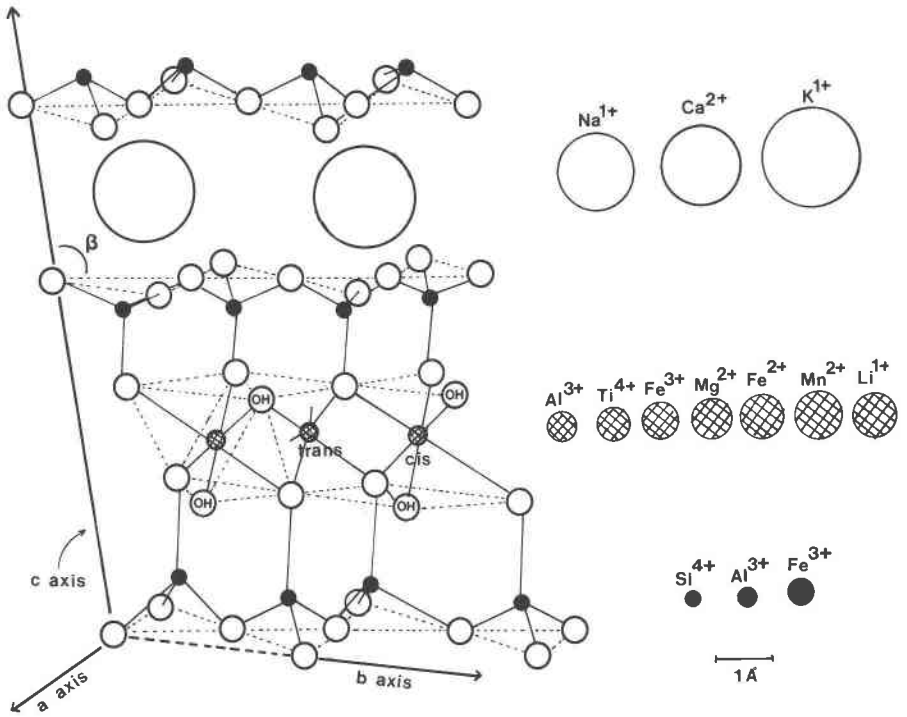

Fig. 1. Scale drawing of a typical trioctahedral mica crystal structure. Ions in the structure are shown schematically; relative (to scale) sizes of the various substituting cations are shown at right.

In the petrologic literature, there has been a consensus that Fe^{3+} does not occur at tetrahedral sites in biotites (Guidotti, 1984), although a few authors have made a case for Fe^{3+}_{tet} when $\Sigma(Si + Al) < 8$ (Foster, 1960; Dawson and Smith, 1977; Delaney et al., 1980; Miyano and Miyano, 1982). However, Mössbauer parameters for tetrahedral Fe^{3+} *are* well-defined by studies of tetra-ferriphlogopite (see sample 87) and clintonites (samples 59–63). Of the Mössbauer data collected in this study, 31 samples contain Fe^{3+}_{tet} with parameters averaging $\delta = 0.20$ and $\Delta = 0.50$ mm/s. Twenty samples are Al-deficient, whereas 11 have excess Al. This observation will be discussed in a later section.

Intervalence charge transfer and Mössbauer spectra of biotites

It is well known from optical spectra that charge transfer of electrons can occur between Fe^{2+} and Fe^{3+} in edge-sharing octahedra (Gilkes et al., 1972; Robbins and Strens, 1972; Smith, 1978); biotites are pleochroic because of this intervalence phenomena. However, intervalence charge-transfer doublets do not appear in biotite spectra as they do in ilvaite, magnetite, and many other minerals (Burns, 1981). This issue can be addressed with a brief explanation of the difference between the two types of mixed valence interactions (Nolet and Burns, 1979). The term "charge transfer" is normally applied to dynamic *optical* (phonon) transitions, as have been observed by the workers listed above. Electron delocalization refers to *thermally* activated phenomena as observed in a Mössbauer spectrum. In the case of biotite, the optical transition is easily observed, but the thermal interaction is not observed at room temperature. Possibly the charge transfer in biotite is occurring too rapidly to be measured by the Mössbauer effect.

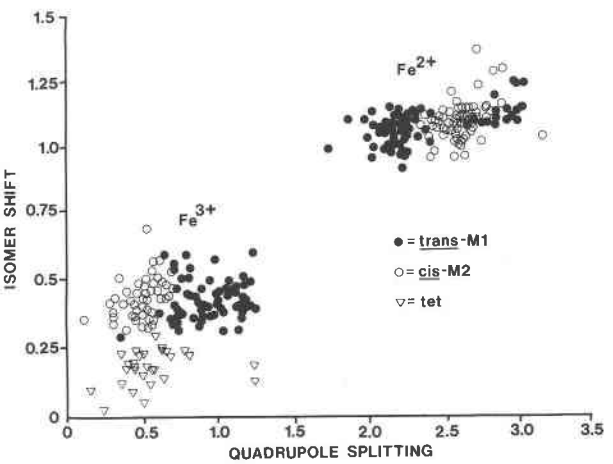

Fig. 2. Plot of isomer shift vs. quadrupole splitting (in mm/s) for all analyses collected (see Appendix). Following the precedent of Bancroft and Brown (1975), the Fe^{3+} doublet with the largest quadrupole splitting is assigned to represent the *trans*-M1 site; the Fe^{3+} doublet with the smaller Δ corresponds to the *cis*-M2 site. For Fe^{2+}, the correspondence is reversed: small Δ is equated to the *trans*-M1 site, and large Δ represents the *cis*-M2 site.

Table 1. Correlation coefficients (r) for Mössbauer and compositional parameters regressed against one another

Al_{iv}	Fe^{3+}_{iv}	Al_{vi}	Ti	Fe^{3+}_{vi}	Mg	Fe^{2+}	Mn	Li	Ca	Na	K	δ1
−0.97	0.04	−0.15	−0.32	0.06	−0.20	0.13	0.11	0.49	−0.88	0.09	0.81	0.25
	−0.27	0.20	0.34	−0.05	0.18	−0.15	−0.14	−0.46	0.82	−0.06	−0.75	−0.21
		−0.22	−0.26	−0.04	0.01	0.17	0.00	−0.23	0.08	−0.12	−0.11	−0.05
			0.03	−0.20	−0.43	−0.02	0.04	0.77	0.23	−0.26	0.00	0.26
				0.38	−0.38	0.25	−0.13	−0.54	0.20	−0.15	−0.01	−0.25
					−0.40	0.36	−0.09	−0.04	−0.20	−0.13	0.11	−0.23
						−0.74	0.01	−0.71	0.29	0.30	−0.30	0.00
							−0.29	−0.44	−0.41	−0.30	0.36	−0.07
								0.77	−0.14	0.18	−0.08	0.04
									−0.43	−0.61	−0.09	0.31
										−0.10	−0.96	−0.38
											0.05	0.21
												0.26

Effects of mica composition on Mössbauer parameters

Heller-Kallai and Rozenson (1981) listed six factors that could affect Mössbauer parameters of Fe at the octahedral sites in phyllosilicates: (1) nature of the octahedral sheets, (2) Fe content of the samples, (3) chemical composition of the octahedral sheets, (4) nature and distribution of next-nearest neighbors, (5) geometry of the sites, and (6) covalency effects.

To investigate possible relationships between composition and Mössbauer parameters, a multiple linear correlation analysis was done on the data in the Appendix. Multiple correlation coefficients (R) were computed for each pair of variables and are listed in Table 1. In addition to analysis of each single variable against every other single variable, correlation coefficients were also calculated for combinations of up to three variables against all other possible combinations (of up to three variables); 8 235 711 combinations were checked.

A few obvious correlations exist; for example, tetrahedral Si and Al have a high correlation ($R = 0.97$) because they often fill the site. Similarly Ca and K ($R = -0.96$) correlate highly. Cations that commonly substitute for each other are strongly related; octahedral Fe^{2+} and Mg have an $R = -0.74$.

As mentioned above, the fact that Fe^{2+}_{M1} Δ values cluster in two groups might be attributed to some compositional effect. Analysis of multiple combinations of variables clearly identifies the source of this effect; regression of Δ of Fe^{2+}_{M1} vs. octahedral Al + Fe^{3+} + Li yields $R = 0.95$. The Δ of Fe^{2+}_{M1} vs. Li content alone is also strongly correlated ($R = 0.87$), though Δ of Fe^{2+}_{M1} vs. Al_{vi} + Fe^{3+}_{vi} is not (R less than 0.70). Possibly the presence of the relatively large Li cation (charge-balanced by Al and Fe^{3+}) in the octahedral layer is accommodated by structural rearrangement or distortion of adjacent oxygens, which is in turn reflected by increased Δ values for Fe^{2+} at M1. Recent work by Weiss et al. (1985) indicates that M1 tends to be most distorted by flattening in those ordered cases where it is occupied by a large cation (such as Li); this argument supports the observed increase in Δ for Li-bearing samples. Unfortunately, Li analyses could be found in the literature for only 19 samples in the data base; perhaps the correlation would be even stronger if more Li data were available.

Site-occupancy data applied to crystal chemistry

Perhaps the most useful aspect of this literature review is that it has yielded a unique set of data on Fe site occupancy for trioctahedral micas. Before exploring the relationships of this complete data set, it is important to add a few cautionary notes on the reliability of site-occupancy data generated by fitting of Mössbauer spectra. Preliminary work on the precision of the Mössbauer technique in simple spectra (as calculated from repeated runs of the same sample) suggests that area data are good to ±3% of the total area. This represents a lower limit on the technique. Furthermore, there is often a problem with preferred orientation of the samples, which is difficult to overcome in micas. Hogg and Meads (1970) suggested that this is not a problem if the particle size in the sample holder is below 5 μm. Careful sample preparation, including mounting the particles with some inert medium to prevent their becoming oriented, is always called for in mica studies. However, in a survey paper such as this,

Table 1. *Continued*

Δ1	δ2	Δ2	δ3	Δ3	δ4	Δ4	δ5	Δ5	% Fe^{2+}	M2/M1	
0.41	0.20	0.46	−0.04	−0.13	−0.61	−0.52	−0.27	−0.32	0.32	−0.20	Si
−0.37	−0.24	−0.45	0.10	0.13	0.75	0.63	0.26	0.28	−0.19	0.18	Al_{iv}
0.01	0.16	0.14	−0.24	−0.03	−0.65	−0.55	−0.05	0.04	−0.37	0.03	Fe^{3+}_{iv}
−0.31	0.18	0.29	−0.30	−0.18	0.14	0.25	−0.02	0.12	0.19	0.14	Al_{vi}
−0.32	−0.49	−0.51	0.15	−0.24	0.23	0.08	−0.59	0.09	0.09	−0.22	Ti
−0.01	−0.26	−0.30	−0.06	−0.03	0.07	−0.08	−0.04	−0.24	−0.11	0.00	Fe^{3+}_{vi}
0.18	0.20	0.21	0.46	0.25	0.01	0.25	0.38	0.21	−0.23	−0.14	Mg
−0.09	−0.18	−0.25	−0.25	−0.35	−0.28	−0.59	−0.45	−0.16	0.27	−0.04	Fe^{2+}
−0.09	−0.28	−0.27	−0.32	0.08	0.27	0.15	0.32	0.09	−0.59	−0.07	Mn
−0.05	0.66	0.87	−0.59	0.29	—	—	—	—	0.24	0.69	Li
−0.40	−0.23	−0.36	0.08	0.25	−0.08	0.11	0.50	0.30	−0.48	0.32	Ca
0.38	0.38	0.27	0.10	0.25	0.43	0.36	0.19	0.12	−0.02	0.07	Na
0.28	0.17	0.32	−0.08	−0.30	0.27	0.20	−0.40	−0.23	0.42	−0.39	K
0.36	0.80	0.40	0.14	−0.03	−0.06	0.06	−0.25	0.32	0.30	0.15	δ1
	0.35	0.30	0.13	0.29	−0.02	−0.19	0.07	−0.19	0.08	−0.07	Δ1
		0.58	0.15	0.09	−0.16	−0.05	0.09	0.08	0.22	0.15	δ2
			−0.12	0.01	−0.51	−0.25	0.07	−0.32	0.19	−0.07	Δ2
				−0.16	0.34	0.34	−0.33	0.17	0.14	−0.27	δ3
					0.47	0.28	0.72	0.52	−0.25	0.51	Δ3
						0.53	−0.92	−0.68	0.26	0.08	δ4
							−0.72	−0.89	0.14	−0.20	Δ4
								0.22	−0.22	0.21	δ5
									−0.04	0.53	Δ5
										−0.17	% Fe^{2+}

it is impossible to determine if anomalous area data are the result of faulty sample preparation.

Another problem with Mössbauer area data hinges on the undetermined value for relative recoil-free fraction in micas. In some minerals, such as garnets, the line strength of Fe^{3+} peaks can be significantly larger than those of Fe^{2+} peaks (Whipple, 1974). In the garnet structure, the Fe^{3+} is held more rigidly at its octahedral site, such that fewer of the Fe^{3+} atoms recoil than than do Fe^{2+} at their eight-coordinated sites. The resultant Mössbauer spectrum appears to have more Fe^{3+} than is actually present, and the resultant area data must be corrected for this differential recoil-free fraction effect. Whipple (1974) examined a phlogopite and a biotite to determine relative line strengths, but unfortunately his results were inconclusive (R_{biotite} was 1.18, $R_{\text{phlogopite}}$ was 0.78, where R = Mössbauer-determined Fe^{3+}/Fe^{2+} ratio divided by the chemically determined Fe^{3+}/Fe^{2+} ratio). Thus it is not known whether differential recoil-free fraction effects are biasing the Mössbauer area data; it is hoped that such effects would be small.

Finally, another problem with the area data for biotites was raised by Mineeva (1978), who interpreted the wide spread of M2/M1 values to be a sign of overfitting; she concluded that only two doublets were present. In my opinion, the area data *are* real, for the following reasons: (1) peak *positions* for the M2 and M1 (both Fe^{3+} and Fe^{2+}) peaks are fairly consistent throughout the 151 samples reviewed here. If two doublets do not really exist, the positions of all the peaks would be more random. (2) As discussed above, Δ values for the Fe^{3+}_{M1} doublet can be explained as a systematic function of octahedral Li, Al, and Fe^{3+} content. If the M1 doublet does not really exist, it is unlikely that such a logical correlation would be found between those variables.

Structural changes based on cation size

The compositional substitutions in mica are firmly based on the principle of maintenance of *charge balance* in the structure. However, as was discussed in the Introduction, the sizes of substituting cations also affect the structure. Hazen and Wones (1972) found a strong correlation between ionic radius of R^{2+} and b_m, which is intuitively obvious when the wide range of cation sizes is considered (see Fig. 1). Tetrahedral rotation may also accommodate size differences between tetrahedral and octahedral sheets. It is known that α is minimized when octahedral-cation radius increases to 0.76 Å (Hazen and Wones, 1972); it is also known that α may be as large as 22° in clintonites, in which the low Si/Al_{tet} ratio compensates for Ca substitution at the A site (Annersten and Olesch, 1978). Data assembled for this review provide yet another important constraint on Si/Al_{tet} as a function of cation size, as follows:

It was noticed that in 11 of the 31 Fe^{3+}_{tet}-bearing samples, Si + Al ≥ 8. Tetrahedral Al is apparently displaced by Fe^{3+}. This does not comply with crystal-chemical expectations; the small Al cation generally should have a greater preference for the smaller tetrahedral site than does the larger Fe^{3+}_{tet}. Contrary to the results of Annersten and Olesch (1978), Figure 3 shows that Si/Al ratios do not particularly *control* this substitutional phenomenon: triangles representing Fe^{3+}_{tet}-bearing samples with Si + Al ≥ 8 are intermixed with the circles for Al-deficient (Si + Al ≤ 8) Fe^{3+} samples (except for the clintonite data,

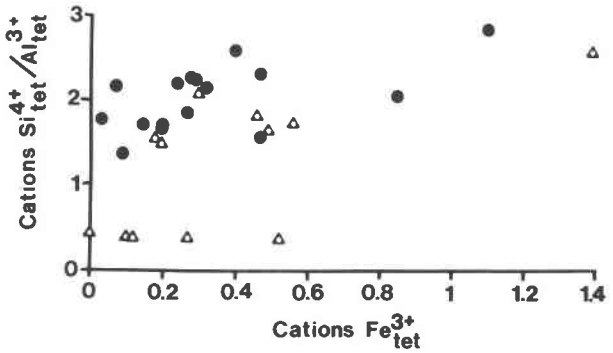

Fig. 3. Si/Al ratio vs. Fe^{3+}_{tet} cations for samples where $Fe^{3+}_{tet} > 0$. Triangles represent data for samples where Si + Al ≥ 8, and circles represent Al-deficient micas. The five lowest triangles are clintonite data from Annersten and Olesch (1974).

which have Si/Al < 1). If Si/Al ratio does not control Fe^{3+}_{tet} in non-Al-deficient samples, what does?

Annersten and Olesch (1978) postulated that the effect of Ca in the interlayer sites was to increase the relative size of the tetrahedra, making it possible for the larger Fe^{3+} cation to enter. As Figure 4 shows, the size of the A site cations does not seem to correlate with Fe^{3+}_{tet} displacing Al. However, Figure 5 demonstrates that the phenomenon does occur when the average size of the octahedral cations is low (<0.68 Å), implying an abundance of 3+ and 4+ cations in the octahedral sheet. Perhaps small cation size can be correlated with the presence of octahedral *vacancies* (needed to charge-balance the smaller, highly charged cations) that would increase the size of the octahedral sheet and necessitate enlargement of the

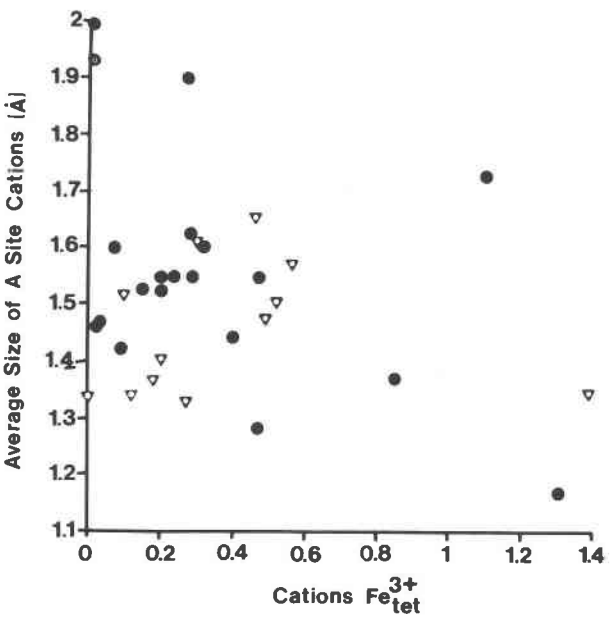

Fig. 4. Average size of the A-site interlayer cations vs. Fe^{3+}_{tet} content, with triangles representing samples with Si + Al > 8. There is no apparent division between triangles and circles (Al-deficient micas).

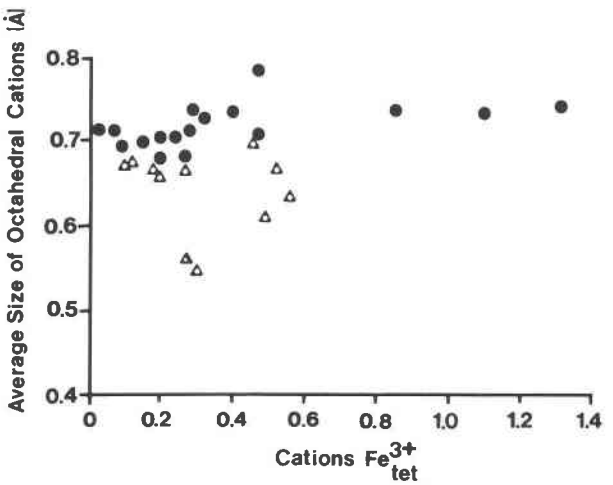

Fig. 5. Average size of the octahedral cations vs. Fe^{3+}_{tet} content. Triangles represent samples where Si + Al > 8. Note that when octahedral-cation size is less than ~0.68 Å, Fe^{3+} substitutes at the tetrahedral position regardless of how much Al is present.

tetrahedra to allow a fit between layers. Enlarged tetrahedra could then easily accommodate Fe^{3+} cations.

Cation ordering

Crystal-structure refinement is the standard method for examination of cation ordering in micas; literature data are summarized in Bailey (1984a). He showed that tetrahedral cation ordering does occur (albeit infrequently) in micas.

On the other hand, octahedral cation ordering is more common. Although early studies found little or no evidence for significant ordering of Mg and Fe in micas (Goodman and Wilson, 1973; Hazen and Burnham, 1973), subsequent workers have suggested that Fe^{2+} prefers M2 (Annersten, 1975), or M1 (Levillain et al., 1981), and that Fe^{2+} in low-grade metamorphic biotites is ordered at M2 (Heller-Kallai and Rozenson, 1981) or M1 (Annersten, 1974). Ohta et al. (1982) postulated that partial cation ordering of Fe^{3+} at M2 may occur, but Fe^{2+} is randomly distributed over the two M2 and one M1 sites in each unit cell.

The Mössbauer effect is of limited use in deciphering site occupancies in micas because it can only describe the location of Fe cations in the structure. The data collected in this study demonstrate that the ratio of Fe cations in the *cis*-M2 : *trans*-M1 sites is rarely 2:1. This suggests that some cation ordering is occurring in the octahedral sheet. It is tempting to assume that only Fe and Mg are ordering; such an assumption would allow development of an equilibrium constant for Fe-Mg exchange at the two sites. However, it is impossible to determine from Mössbauer data alone which of the many cations in the octahedral sheets is ordering (especially in micas with such varied compositions and parageneses).

As can be seen in Table 1, the amount of Fe^{2+} ordering

is not correlated with any of the single compositional variables listed, including $Fe^{2+}/\Sigma Fe$. An attempt was made to correlate $Fe^{2+}_{M2}/Fe^{2+}_{M1}$ ratios with parageneses listed in Appendix Table 4; however there is not enough detailed information to make a worthwhile comparison. A more dedicated study of sample paragenesis vs. ordering of cations among M2 and M1 sites, using a large number of compositionally similar (and simpler) samples, is in progress to determine the systematics of cation-ordering processes. In the context of this literature review, it can only be said that the ratio of Fe^{2+} at the M2 and M1 sites is highly variable (from 0.70 to 5.14) and does not seem to be a simple function of any single compositional variable, including $Fe^{2+}/\Sigma Fe$.

Summary

This review of Mössbauer studies of trioctahedral micas has three principal conclusions:

1. Typical values for Mössbauer parameters of different mica sites are as follows: Fe^{2+}_{M2}—$\delta = 1.13$, $\Delta = 2.58$ mm/s; Fe^{2+}_{M1}—$\delta = 1.12$ and 1.16, $\Delta = 2.05$ and 2.75 mm/s; Fe^{3+}_{M1}—$\delta = 0.40$, $\Delta = 0.55$ mm/s; Fe^{3+}_{M2}—$\delta = 0.40$, $\Delta = 1.00$ mm/s; Fe^{3+}_{tet}—$\delta = 0.20$, $\Delta = 0.50$ mm/s. It is also noteworthy that no Mössbauer evidence for a doublet representing intervalence $Fe^{3+} \rightarrow Fe^{2+}$, delocalized species has been found.

2. The effects of composition on Mössbauer parameters seem to be minimal, although the addition of Li to the octahedral sheet systematically affects quadrupole splitting of the Fe^{2+}_{M1} doublet.

3. The addition of the Mössbauer site-occupancy data to compositional information shows that tetrahedral $Al \leftrightarrow Fe^{3+}$ substitution may be controlled by octahedral cation size and that M2-M1 cation ordering is ubiquitous.

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Appendix Table 1. References used in plots and tables

1	Voitovsky et al., 1975	88	Huggins, 1976
2–3	Shinno and Suwa, 1981	89	Marfunin et al., 1971
4	Levillain et al., 1977	90–92	Tripathi and Lokanathan, 1978
5	Ivanitskiy et al., 1977	93–96	Taylor et al., 1968
6–7	Ishida and Hirowatari, 1980	97–102	Amirkhanov et al., 1980
8	Goncharov et al., 1971	103–104	Tripathi et al., 1978
9	Bagin et al., 1980	105	Goodman and Wilson, 1973
10	Annersten, 1975	106–108	Haggstrom et al., 1969b
11–13	Bowen et al., 1969	109	Yassoglov et al., 1972
14–20	Bancroft and Brown, 1975*	110	Tricker et al., 1976
21	Rice and Williams, 1969	111	Bancroft et al., 1977
22–23	Haggstrom et al., 1969a	112	Chandra and Lokanathan, 1982
24–25	Ivanitskiy et al., 1975a	113	Chandra and Lokanathan, 1977
25–33	Sanz et al., 1978	114–115	Drago et al., 1977
34–35	Ivanitskiy et al., 1975b	116–117	Ericsson et al., 1977
36–41	Annersten, 1974	118–119	Gendler et al., 1978
42	Smith et al., 1980**	120	Ivanitskiy et al., 1975c
43–45	Hogg and Meads, 1970	121	Ivanitskiy et al., 1978
46	Hogg and Meads, 1975	122	Kohno and Kakitani, 1972
47–53	Manapov and Sitdikov, 1974	127	Lefelhocz et al., 1967
54–58	Hogarth et al., 1970	128–129	Manapov and Krinari, 1976
59–63	Annersten and Olesch, 1978	130–132	Pollak et al., 1962
64–71	Levillain et al., 1981	133	Pollak and Bruyneel, 1974
72–84	Dyar, unpublished data	134–144	Pol'shin et al., 1972
85	Astakhov et al., 1975	145	Vertes et al., 1981
86	Herzenberg et al., 1968	146–151	Tripathi and Lokanathan, 1982
87	Annersten et al., 1971		

* Analyses from Dodge et al., 1969.
** Analyses from Smith, 1978.

Appendix Table 2. Sample origins

4	Massif Central Français
8	metasomatic (ore deposit)
14	monzonite, Sierra Nevada batholith
15–20	granodiorites, Sierra Nevada batholith
21	Bosahan quarry, Falmouth, England
34–35	adjacent to uranium ore
36	high amphibolite facies, gneiss SW Greenland
37	low amphibolite facies, gneiss SW Greenland
38	Revsund granite, Sweden
39	charnockite (granulite facies) Varberg, Sweden
40	metamorphosed iron formation, Sweden
41	titano-ferrous metadiabase, Nordingrd, Sweden
43–46	granites, SW England
47	granulite facies, 2 px-plag mesocratic schist
48	granulite facies, gn-hypersthene gneiss with gn-bi-sill bands
49	granulite facies, silicified gn-bi-sil gn
50	granulite facies, garnet-biotite plagiogneiss
51	amphibolite facies, gn-bi-hb metadiorite
52	amphibolite facies, gn-bi gneiss
53	amphibolite facies, biotite plagiogranite
54–55	intrusive carbonates, Gatineau region, Quebec
56–58	phlogopite-calcite, px vein dikes
59	clintonite with fassaite, grossularite, spinel, perovskite
60	clintonite with fassaite, grossularite, calcite, clinochlore, magnetite
61	clintonite with fassaite, pargasite, chondrodite, calcite, spinel, graphite
62	clintonite with fassaite, calcite, monticellite: contact marble
72	monzonite, Sierra Nevada batholith (same as 15)
73	granodiorite, Sierra Nevada batholith (same as 16)
74	granodiorite, Sierra Nevada batholith (same as 17)
75	granodiorite, Sierra Nevada batholith (same as 18)
76	Pikes Peak granite
77	Lost Creek, Montana granite
78	Cape Ann granite
79	banded iron formation, with riebeckite, hem, mag, qtz, ank, stil
80	banded iron formation, hematite, riebeckite, low grade
81	banded iron formation, "higher grade"
83–84	garnet, sillimanite, muscovite, quartz, plagioclase, rutile
94, 96	banded iron formation, Marquette Iron Range
111	granodiorite, Nova Scotia
118–119	pegmatites of Ukrainian shield

Appendix Table 3. Compositions and Mössbauer data

Sample #	1B	2P	3P	4L	5B	6P	7P	8S	9B	10B	11B	12B	13P	14B	15B	16B	17B	18B	19B	20B	21B
Si^{4+}	5.50	5.89	5.99	7.00	5.14	5.40	6.20	6.00	5.34	4.50	5.10	4.96	5.12	5.60	5.53	5.42	5.37	5.63	5.52	5.62	5.29
Al^{3+}	2.04	1.76	1.68	0.98	2.86	2.20	1.40	2.00	2.10	3.50	2.90	3.04	2.88	2.40	2.47	2.58	2.63	2.37	2.48	2.38	2.22
Fe^{3+}	0.46	0.32	0.28	0.02	-	0.20	0.40	-	0.56	-	-	-	-	-	-	-	-	-	-	-	0.49
Sum Tet	8.00	7.97	7.95	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
Al	1.28	-	-	2.44	0.62	-	-	4.80	1.04	3.00	0.96	1.34	0.90	0.42	0.24	0.67	0.76	0.36	0.48	0.42	1.56
Ti	0.22	0.01	0.03	-	0.24	-	-	0.60	0.20	-	0.28	0.10	0.14	0.29	0.29	0.35	0.36	0.19	0.18	0.32	0.28
Fe^{3+}	0.00	-	-	0.00	0.34	0.20	-	-	0.00	0.16	0.28	0.48	0.16	0.42	0.48	0.44	0.17	0.39	0.49	0.42	0.00
Mg	2.10	5.52	5.49	0.02	1.90	3.40	5.00	-	2.02	-	1.78	0.48	4.04	2.45	2.64	1.22	1.56	2.73	2.53	2.17	1.15
Fe^{2+}	2.36	0.48	0.39	0.42	2.60	-	0.40	0.60	2.16	4.34	2.22	2.90	0.58	2.12	2.02	2.78	2.74	1.89	1.97	2.38	2.34
Mn	0.04	0.01	-	0.05	0.02	2.00	0.60	-	0.02	-	-	-	-	0.05	0.05	0.14	0.06	0.05	0.11	0.04	0.03
Li	0.00	-	-	1.50	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Other	-	-	Cr 0.01	-	-	Ba 0.20	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Sum Oct	6.00	6.02	5.92	6.00	5.72	5.80	6.00	6.00	5.44	6.00	5.52	5.30	5.82	5.75	5.72	5.60	5.65	5.61	5.76	5.75	5.36
Ca	0.10	0.02	0.01	-	0.12	-	-	-	0.10	-	-	-	-	0.03	0.09	0.00	0.00	0.10	0.09	0.09	0.00
Na	0.10	0.10	0.01	0.10	0.22	0.40	-	-	0.10	-	0.08	0.06	0.12	0.07	0.06	0.15	0.13	0.07	0.09	0.08	0.10
K	1.90	1.90	2.01	1.74	1.54	1.60	1.80	2.40	1.80	2.00	1.70	1.80	1.62	1.84	1.63	1.86	1.85	1.63	1.61	1.77	1.76
Other	-	-	-	Rb 0.16	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Sum A	2.10	2.02	2.03	2.00	1.88	2.00	1.80	2.40	2.00	2.00	1.78	1.86	1.74	1.94	1.73	2.01	1.98	1.80	1.79	1.94	1.86
δ1	1.19	1.12	1.12	1.16	1.20	-	1.13	1.17	1.19	1.13	1.11	1.12	1.11	1.12	1.13	1.13	1.14	1.13	1.12	1.13	1.14
Δ1	2.62	2.65	2.65	2.62	2.86	-	2.52	2.52	2.58	2.54	2.47	2.51	2.44	2.62	2.62	2.57	2.62	2.65	2.61	2.61	2.56
δ2	1.17	-	-	1.18	1.17	-	-	-	1.19	1.18	-	-	-	1.10	1.10	1.11	1.13	1.09	1.09	1.11	1.15
Δ2	2.24	-	-	2.99	2.29	-	-	-	2.13	2.00	-	-	-	2.13	2.15	2.06	2.15	2.20	2.17	2.14	2.63
δ3	-	-	-	-	0.43	0.34	-	-	-	0.40	-	-	-	0.46	0.47	0.48	-	0.49	0.49	0.51	-
Δ3	-	-	-	-	1.12	1.02	-	-	-	0.76	-	-	-	1.00	1.05	1.00	-	1.03	1.00	1.05	-
δ4	-	-	-	-	0.46	-	-	-	-	-	0.54	0.54	0.44	0.45	0.49	0.52	0.60	0.49	0.48	0.51	-
Δ4	-	-	-	-	0.62	-	-	-	-	-	0.60	0.80	0.90	0.42	0.50	0.47	0.57	0.52	0.52	0.51	-
δ5	0.20	0.20	0.24	0.25	-	0.26	0.15	-	0.14	-	-	-	-	-	-	-	-	-	-	-	-0.03
Δ5	1.23	0.52	0.47	0.35	-	0.62	0.63	-	1.23	-	-	-	-	-	-	-	-	-	-	-	0.24
$Fe^{2+}/\Sigma Fe$	0.84	0.60	0.58	0.96	0.88	0.00	0.50	1.00	0.79	0.96	0.89	0.86	0.78	0.83	0.81	0.86	0.94	0.83	0.81	0.85	0.17
M2/M1 Fe^{2+}	-	-	-	1.91	2.14	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Sample #	22B	23A	24B	25B	26P	27P	28P	29B	30B	31B	32B	33B	34B	35B	36B	37B	38B	39B	40B	41B	42B
Si^{4+}	5.63	6.00	5.60	5.60	6.18	6.08	5.68	5.42	5.48	5.48	6.00	6.00	5.28	5.59	5.25	5.39	5.50	5.45	5.92	5.20	5.44
Al^{3+}	2.37	2.00	2.40	2.40	1.82	1.92	2.32	2.58	2.52	2.52	2.00	1.76	2.73	2.41	2.75	2.61	2.50	2.35	2.05	2.33	2.56
Fe^{3+}	-	-	-	-	-	-	-	-	-	-	-	0.24	-	-	-	-	-	0.20	0.03	0.47	0.00
other																					
Sum Tet	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.01	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
Al	0.02	2.00	0.62	1.60	0.18	0.08	0.18	0.50	1.20	0.36	0.12	-	-	0.86	0.33	0.36	0.18	0.00	0.00	0.00	0.88
Ti	0.46	-	0.21	-	0.34	0.26	0.26	0.34	0.26	0.10	0.04	0.12	0.10	0.25	0.37	0.23	0.40	0.67	0.12	0.65	0.16
Fe^{3+}	0.75	1.95	0.41	0.60	0.04	0.09	0.18	0.09	0.34	0.02	0.03	0.06	1.52	0.46	0.32	0.50	1.21	0.38	0.13	2.06	0.73
Mg	0.48	-	2.07	1.60	3.80	3.20	2.04	2.16	0.92	5.10	5.46	5.36	3.73	1.61	2.39	2.30	0.46	2.27	4.30	0.52	2.34
Fe^{2+}	3.97	4.05	2.48	2.00	1.50	2.08	2.88	2.52	2.48	0.32	0.34	0.32	0.27	2.04	1.94	2.11	2.95	2.31	1.27	3.36	1.54
Mn	0.05	-	-	-	0.02	0.10	0.08	0.06	0.08	-	0.02	-	0.02	0.02	0.02	0.02	0.05	0.01	0.05	0.03	0.08
Li	-	-	-	-	0.18	0.10	0.08	0.04	0.38	0.01	0.03	-	-	-	-	-	-	-	-	-	-
Other	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Sum Oct	5.73	6.00	5.78	5.80	6.06	5.91	5.70	5.71	5.66	5.91	6.04	5.86	5.64	5.24	5.37	5.52	5.25	5.64	5.87	6.62	5.73
Ca	-	-	0.20	-	0.16	0.02	0.04	0.04	0.03	0.10	0.06	0.02	0.04	-	-	-	-	-	-	-	0.00
Na	-	-	-	0.20	0.14	0.18	0.12	0.06	0.10	0.12	0.08	0.02	0.08	0.17	-						
K	1.88	2.00	1.80	1.80	1.88	1.88	1.96	1.86	1.88	1.70	1.90	1.90	1.74	1.82	1.78	1.73	1.89	1.89	1.79	1.60	1.89
Other	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Sum A	1.88	2.00	2.00	2.00	2.18	2.08	2.12	1.96	2.01	1.92	2.04	1.94	1.86	1.99	1.78	1.76	1.92	1.90	1.84	1.60	1.89
δ1	1.13	1.15	1.14	1.15	1.14	1.15	1.14	1.15	1.13	1.12	1.12	1.13	1.19	1.18	1.06	1.07	1.06	1.06	1.05	1.05	1.04
Δ1	2.56	2.56	2.61	2.66	2.61	2.60	2.60	2.66	2.59	2.56	2.60	2.65	2.66	2.66	2.56	2.62	2.60	2.56	2.58	2.57	2.60
δ2	1.11	1.11	1.13	1.14	1.12	1.10	1.10	1.12	1.12	1.12	1.13	-	1.18	1.18	1.03	1.05	1.01	1.02	1.03	1.05	1.01
Δ2	2.17	2.18	2.10	2.29	2.20	2.16	2.17	2.23	2.17	2.22	2.20	-	2.28	2.18	2.10	2.19	2.20	2.13	2.21	2.12	2.23
δ3	0.55	0.54	0.46	0.46	0.54	0.57	0.50	0.51	0.49	0.61	0.61	-	0.54	0.50	0.41	0.50	0.43	0.41	0.51	0.50	0.48
Δ3	0.55	0.52	0.85	1.00	0.60	0.56	0.69	0.65	0.60	0.98	0.97	-	0.76	1.11	1.02	0.72	0.93	0.74	1.17	0.88	0.78
δ4	-	-	-	-	-	-	-	-	-	-	-	-	-	0.52	0.43	0.52	0.40	0.39	0.46	0.54	0.46
Δ4	-	-	-	-	-	-	-	-	-	-	-	-	-	0.64	0.50	0.57	0.50	0.57	0.65	0.34	0.32
δ5	-	-	-	-	-	-	-	-	-	-	-	0.26	-	-	-	-	-	-	-	-	-
Δ5	-	-	-	-	-	-	-	-	-	-	-	0.45	-	-	-	-	-	-	-	-	-
$Fe^{2+}/\Sigma Fe$	0.84	0.68	0.86	0.78	0.90	0.95	0.82	0.89	0.96	0.88	0.88	0.71	0.87	0.79	0.86	0.81	0.71	0.86	0.91	0.62	0.68
M2/M1 Fe^{2+}	2.78	1.58	1.96	2.00	0.74	0.88	1.15	1.19	1.35	0.70	1.00	1.00	2.11	2.04	1.03	0.80	1.64	1.39	0.75	1.31	2.09

Appendix Table 3.—*Continued*

Sample #	43P	44B	45Z	46B	47B	48B	49B	50B	51B	52B	53B	54P	55P	56P	57P	58P	59C	60C	61C	62C	63C
Si^{4+}	5.60	5.30	6.92	5.88	5.51	5.35	5.25	5.11	5.14	5.23	5.38	5.96	6.10	5.65	5.69	5.61	2.41	2.41	2.73	2.35	2.23
Al^{3+}	2.40	2.70	1.08	2.12	2.49	2.47	2.56	2.89	2.77	2.77	2.62	1.69	1.83	2.08	2.30	2.38	5.49	5.47	5.27	5.38	5.25
Fe^{3+}	-	-	-	-	-	0.18	0.20	-	0.09	-	-	0.29	0.07	0.27	0.01	0.01	0.10	0.12	-	0.27	0.52
Sum Tet	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	7.94	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
Al	0.16	0.39	2.31	1.81	0.11	0.52	1.09	0.68	0.00	0.55	0.30	0.00	0.00	0.00	0.00	0.00	1.44	1.53	1.13	1.70	1.40
Ti	0.23	0.38	0.03	0.04	0.48	0.47	0.18	0.23	0.44	0.27	0.27	0.02	0.02	0.12	0.15	0.13	-	-	-	-	-
Fe^{3+}	0.03	0.54	0.09	0.24	0.21	0.05	0.19	0.35	0.54	0.40	0.33	0.00	0.05	0.22	0.16	0.14	0.00	0.03	0.00	0.03	0.08
Mg	5.07	2.18	0.04	0.11	2.70	3.22	2.01	2.15	1.94	2.37	2.61	5.59	5.13	5.19	4.25	5.31	4.42	4.39	4.80	4.20	4.45
Fe^{2+}	0.37	2.05	0.66	2.14	2.18	1.41	2.17	2.30	2.76	2.13	2.16	0.49	0.69	0.16	1.04	0.15	0.10	0.07	0.17	0.05	0.00
Mn	0.00	0.00	0.68	0.04	0.02	0.00	0.01	0.04	0.03	0.01	0.04	0.01	0.00	0.01	0.01	0.00	-	-	-	-	-
Li	-	-	2.29	0.91	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Other	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Sum Oct	5.86	5.54	6.10	5.29	5.70	5.67	5.65	5.75	5.71	5.73	5.71	6.11	5.89	5.70	5.61	5.73	5.96	6.02	6.10	5.98	5.93
Ca	0.07	0.19	0.02	0.21	0.05	0.07	0.03	0.03	0.20	0.03	0.09	0.03	0.01	0.00	0.00	0.00	1.99	1.98	1.96	1.97	2.23
Na	0.36	0.14	0.07	0.10	0.02	0.01	0.08	0.05	0.03	0.02	0.04	0.13	0.13	0.67	0.86	0.63	0.24	0.00	0.02	0.00	0.00
K	1.55	1.46	1.83	1.80	1.69	1.64	1.66	1.76	1.58	1.78	1.83	1.80	1.88	1.82	1.78	1.89	0.02	0.00	0.00	0.00	0.00
Other	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Sum A	1.98	1.79	1.92	2.21	1.76	1.72	1.77	1.84	1.81	1.83	1.96	1.96	2.02	2.49	2.64	2.52	2.25	1.98	1.98	1.97	2.23
δ1	1.10	1.07	1.15	1.13	1.13	1.13	1.15	1.15	1.13	1.13	1.14	1.18	1.19	1.14	1.17	1.15	1.08	-	1.13	1.08	-
Δ1	2.56	2.58	2.65	2.44	2.57	2.44	2.65	2.62	2.57	2.65	2.61	2.76	2.76	2.62	2.79	2.76	2.48	-	2.46	2.39	-
δ2	1.08	1.06	-	1.13	1.09	1.10	1.13	1.14	1.12	1.10	1.11	1.28	1.29	1.24	1.28	1.14	1.04	1.09	1.15	-	-
Δ2	2.24	2.14	-	2.74	2.19	2.07	2.18	2.19	2.17	2.22	2.21	2.97	2.95	2.82	3.01	2.97	1.72	2.11	1.85	-	-
δ3	0.47	0.39	0.40	0.38	0.63	0.59	0.63	0.60	0.63	0.60	0.60	-	0.64	0.53	0.54	0.50	0.52	0.52	-	-	0.49
Δ3	0.80	0.72	0.89	0.83	0.64	0.57	0.64	0.57	0.78	0.57	0.57	-	1.22	0.94	1.15	1.06	1.05	1.20	-	-	1.08
δ4	-	-	-	-	0.38	-	-	-	-	-	0.35	-	-	-	-	-	-	-	-	-	-
Δ4	-	-	-	-	0.57	-	-	-	-	-	0.50	-	-	-	-	-	-	-	-	-	-
δ5	-	-	-	-	-	0.06	0.13	-	0.10	-	-	0.19	0.21	-	-	-	0.27	0.24	-	0.26	0.24
Δ5	-	-	-	-	-	0.50	0.36	-	0.43	-	-	0.44	0.44	-	-	-	0.62	0.68	-	0.65	0.80
$Fe^{2+}/\Sigma Fe$	0.90	0.81	0.83	0.89	0.80	0.84	0.85	0.83	0.82	0.83	0.80	0.74	0.86	0.82	0.94	0.81	0.35	0.26	1.00	0.24	-
M2/M1 Fe^{2+}	1.65	1.24	-	3.50	1.20	2.19	1.93	1.54	2.15	2.04	1.96	-	-	-	-	-	4.63	-	3.23	-	-

Sample #	64L	65Z	66Z	67Z	68S	69S	70S	71S	72B	73B	74B	75B	76B	77B	78A	79A	80A	81A	82P	83B	84B
Si^{4+}	7.40	5.68	5.39	5.67	4.98	5.14	5.19	3.99	5.47	5.49	5.61	5.49	5.56	5.86	5.49	6.06	6.51	5.85	5.94	5.27	5.36
Al^{3+}	0.60	2.32	2.61	2.33	3.02	2.86	2.81	4.01	2.53	2.51	2.39	2.51	2.29	1.84	2.15	1.94	0.18	1.05	1.59	2.73	2.64
Fe^{3+}	-	-	-	-	-	-	-	-	-	-	-	-	0.15	0.30	0.36	0.85	1.31	1.10	0.47	-	-
Sum Tet	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
Al	2.13	2.42	2.35	2.29	2.16	2.24	2.18	1.84	0.40	0.23	0.34	0.18	0.00	1.88	0.00	0.00	0.00	0.00	0.00	0.81	0.80
Ti	-	-	-	-	-	-	-	-	0.18	0.32	0.19	0.29	0.30	0.07	0.43	0.00	0.00	0.02	0.01	0.16	0.16
Fe^{3+}	0.00	0.00	0.18	0.33	0.03	0.16	0.26	0.21	0.66	0.57	0.62	0.65	0.60	0.30	2.25	0.30	0.17	0.24	0.30	0.37	0.26
Mg	-	-	-	-	-	-	-	-	2.51	2.12	2.72	2.62	0.22	0.01	0.07	2.70	1.51	0.77	5.11	2.14	2.15
Fe^{2+}	0.45	1.58	1.45	1.25	2.55	2.18	2.13	3.96	1.78	2.16	1.66	1.84	4.39	2.40	2.16	2.96	4.22	4.77	0.47	2.30	2.36
Mn	-	-	-	-	-	-	-	-	0.11	0.04	0.05	0.05	0.09	0.22	0.06	0.00	0.00	0.00	0.01	0.00	0.01
Li	3.53	2.09	2.09	2.04	1.30	1.31	1.25	0.00	-	-	-	-	-	-	-	-	-	-	-	-	-
Other	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Sum Oct	6.11	6.09	6.07	5.91	6.04	5.89	5.82	6.01	5.64	5.44	5.58	5.63	5.60	4.88	4.97	5.96	5.90	5.80	5.90	5.78	5.74
Ca	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.09	0.09	0.10	0.09	0.01	0.00	0.00	0.00	0.07	0.12	0.00	0.00	0.00
Na	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.09	0.07	0.07	0.06	0.03	0.05	0.03	0.05	0.00	0.00	0.03	0.10	0.08
K	1.78	1.81	2.02	1.90	2.05	2.02	1.97	1.96	1.59	1.92	1.63	1.62	1.87	1.97	1.66	1.67	1.40	2.06	1.91	1.56	1.69
Other	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Sum A	1.78	1.81	2.02	1.90	2.05	2.02	1.97	1.96	1.77	2.08	1.80	1.77	1.91	2.02	1.69	1.72	1.47	2.18	1.94	1.66	1.77
δ1	1.17	1.13	1.17	1.14	1.16	1.17	1.13	1.14	1.13	1.13	1.13	1.12	1.13	1.14	1.12	1.13	1.13	1.10	1.12	1.14	1.14
Δ1	2.63	2.42	2.57	2.66	2.36	2.51	2.64	2.55	2.60	2.57	2.60	2.58	2.53	2.68	2.50	2.67	2.60	2.55	2.63	2.63	2.61
δ2	1.18	1.13	1.18	1.15	1.15	1.17	1.14	-	1.07	1.10	1.07	1.09	1.10	1.10	1.15	1.12	1.15	1.16	-	1.13	1.14
Δ2	2.96	2.77	2.90	2.93	2.69	2.83	2.90	-	2.22	2.12	2.15	2.15	2.06	2.36	1.90	2.82	2.83	2.16	-	2.19	2.15
δ3	-	-	0.40	0.42	-	0.38	0.48	0.34	0.42	0.39	0.41	0.45	0.43	0.34	0.42	0.39	0.36	0.42	-	0.43	0.43
Δ3	-	-	0.61	0.88	-	0.69	0.98	0.39	1.24	1.16	1.16	1.17	0.99	0.74	0.98	0.94	0.56	1.01	-	1.19	1.20
δ4	-	-	-	0.38	-	-	0.35	-	0.41	0.44	0.39	0.46	0.39	-	0.37	0.42	-	-	-	0.44	0.44
Δ4	-	-	-	0.54	-	-	0.52	-	0.55	0.47	0.52	0.52	0.31	-	0.61	0.46	-	-	-	0.28	0.37
δ5	-	-	-	-	-	-	-	-	-	-	-	-	-	0.11	0.20	0.19	0.21	0.20	0.19	-	-
Δ5	-	-	-	-	-	-	-	-	-	-	-	-	-	0.15	0.37	0.39	0.40	0.45	0.56	-	-
$Fe^{2+}/\Sigma Fe$	1.00	1.00	0.91	0.79	0.00	0.93	0.89	0.95	0.73	0.79	0.73	0.74	0.88	0.80	0.52	0.72	0.74	0.78	0.38	0.86	0.90
M2/M1 Fe^{2+}	4.88	1.56	1.43	1.27	1.73	1.53	1.78	-	3.57	2.59	4.21	2.70	2.00	1.96	2.28	2.74	1.39	3.23	-	5.14	5.00

B = Biotite P = Phlogopite L = Lepidolite S = Siderophyllite Z = Zinnwaldite A = Annite C = Clintonite

*Mössbauer parameters are corrected using standard values of reference points as tabulated by Gettys and Stevens (1981); data are quoted relative to the midpoint and velocity gradient of a metallic Fe foil spectrum to allow direct comparison of all results.

Appendix Table 4. Data from papers with no compositional information

Sample #	85L	86Z	87P	88P	89P	90P	91P	92P	93L	94B	95B	96B	97B	98B	99B	100B	101B	102B	103B	104B	105B	106B	107B
δ1	1.06	1.08	-	1.00	1.41	1.02	1.09	1.09	1.11	1.16	1.14	1.11	1.10	1.11	1.19	1.12	1.12	1.19	1.12	1.11	1.13	1.15	1.12
Δ1	2.73	3.13	-	2.62	2.70	2.42	2.56	2.56	2.40	2.60	2.45	2.50	2.66	2.64	2.60	2.62	2.66	2.67	2.42	2.54	2.64	2.48	2.48
δ2	1.06	-	-	-	1.15	-	1.05	0.96	-	-	-	-	1.10	1.10	1.18	1.14	1.09	1.17	-	1.10	1.11	-	-
Δ2	2.38	-	-	-	2.20	-	2.17	2.21	-	-	-	-	2.21	2.21	2.32	2.25	2.36	2.29	-	2.07	2.19	-	-
δ3	-	-	-	-	0.31	0.35	-	0.48	-	-	0.39	0.39	-	-	-	0.58	-	-	0.45	0.43	0.38	-	0.46
Δ3	-	-	-	-	0.36	0.87	-	1.11	-	-	0.95	0.95	-	-	-	0.80	-	-	0.86	1.14	0.89	-	1.16
δ4	-	-	-	-	0.49	-	0.49	0.39	0.46	0.51	0.41	0.36	0.56	0.58	0.61	-	0.39	0.73	-	0.44	-	0.49	-
Δ4	-	-	-	-	1.32	-	0.39	0.43	0.50	0.60	0.30	0.30	0.69	0.57	0.60	-	0.44	0.52	-	0.44	-	0.55	-
δ5	-	-	0.17	0.19	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Δ5	-	-	0.50	0.57	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$Fe^{2+}/\Sigma Fe$	-	-	-	-	-	0.17	0.76	0.26	-	-	-	-	-	-	-	-	-	-	-	0.82	0.57	0.81	0.74
M2/M1 Fe^{2+}	-	-	-	-	-	-	1.92	2.25	-	-	-	-	-	-	-	-	-	-	-	3.56	1.71	-	-

Sample #	108B	109B	110B	111B	112B	113B	114B	115B	116B	117B	118B	119B	120B	121B	122G	123B	124B	125B	126B	127B	128B	129B	130B
δ1	1.18	-	1.11	1.11	1.11	1.04	1.08	1.12	1.11	1.12	1.13	1.19	1.11	1.13	1.09	1.12	1.15	1.21	1.25	1.10	1.13	1.14	1.27
Δ1	2.48	-	2.58	2.53	2.54	2.59	2.63	2.43	2.58	2.56	2.62	2.58	2.67	2.60	2.34	2.33	2.40	2.57	2.53	2.50	2.57	2.61	2.71
δ2	-	1.04	1.08	1.08	1.10	1.03	1.07	-	1.08	1.10	1.11	1.19	1.12	1.09	-	-	-	-	-	-	1.12	1.13	1.08
Δ2	-	2.02	2.15	1.98	2.07	2.09	2.22	-	2.24	2.09	2.24	2.13	2.10	2.23	-	-	-	-	-	-	2.17	2.21	2.32
δ3	-	0.43	0.43	0.51	0.43	0.34	-	-	0.57	0.60	-	-	0.42	-	-	0.36	0.37	0.36	0.37	-	0.63	-	-
Δ3	-	0.91	0.71	0.17	1.13	1.70	-	-	0.71	0.71	-	-	1.81	-	-	0.70	0.72	0.70	0.71	-	0.78	-	-
δ4	0.38	0.42	-	0.51	0.44	0.38	-	-	-	0.48	-	-	0.42	0.54	0.47	-	-	-	-	-	-	0.60	-
Δ4	0.11	0.52	-	0.54	0.44	0.45	-	-	-	0.46	-	-	0.52	0.59	0.67	-	-	-	-	-	-	0.57	-
δ5	-	-	-	-	-	-	-	-	-	-	-	0.14	-	-	-	-	-	-	-	-	0.10	0.25	-
Δ5	-	-	-	-	-	-	-	-	-	-	-	1.23	-	-	-	-	-	-	-	-	0.43	0.50	-
$Fe^{2+}/\Sigma Fe$	0.82	-	0.70	0.83	0.83	-	-	-	0.91	0.89	-	-	0.86	-	-	-	-	-	-	-	0.82	0.80	-
M2/M1 Fe^{2+}	-	-	3.13	-	3.61	-	-	-	1.22	2.30	-	-	1.45	-	-	-	-	-	-	-	2.15	1.96	-

Sample #	131B	132B	133B	134B	135B	136B	137B	138B	139B	140B	141B	142B	143B	144B	145B	146B	147B	148B	149B	150B	151B
δ1	1.33	1.34	1.12	1.15	1.15	1.16	1.16	1.16	1.16	1.16	1.17	1.17	1.18	1.19	1.13	1.00	1.05	1.10	1.10	1.11	1.12
Δ1	2.81	2.87	2.66	2.61	2.68	2.67	2.70	2.70	2.65	2.67	2.60	2.70	2.80	2.64	2.56	2.55	2.57	2.54	2.54	2.58	2.51
δ2	1.14	1.14	1.13	1.11	1.12	1.15	1.11	1.14	1.13	1.15	1.11	1.14	1.17	1.14	1.01	1.00	1.02	1.10	1.08	1.13	1.07
Δ2	2.41	2.47	2.20	2.16	2.22	2.22	2.26	2.24	2.16	2.22	2.16	2.23	2.40	2.20	2.20	2.01	2.24	2.07	2.16	2.02	2.23
δ3	-	-	0.40	-	-	-	-	-	-	-	-	-	-	-	-	0.48	0.43	0.43	0.34	-	0.34
Δ3	-	-	0.96	-	-	-	-	-	-	-	-	-	-	-	-	0.61	1.14	1.14	1.02	-	1.13
δ4	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.44	0.44	0.46	-	0.46
Δ4	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.48	0.48	0.51	-	0.52
δ5	-	-	0.13	-	-	-	-	-	-	-	-	-	-	-	0.32	-	-	-	-	-	-
Δ5	-	-	0.54	-	-	-	-	-	-	-	-	-	-	-	0.58	-	-	-	-	-	-
$Fe^{2+}/\Sigma Fe$	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.38	0.46	0.83	0.75	1.00	0.53
M2/M1 Fe^{2+}	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.45	2.54	3.61	2.41	3.16	2.79