Mössbauer spectral study of ferruginous one-layer trioctahedral micas

M. Darby Dyar,* Roger G. Burns

Department of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139

Abstract

A Mössbauer spectral study is described of 15 potassic ferruginous 1M micas representing a wide range of chemical compositions and parageneses. Considerable precaution was taken to alleviate problems due to oxidation and preferred orientation of mica platelets during sample preparation. Biotite Mössbauer spectra were resolved into two Fe^{2+} and two Fe^{3+} doublets assigned to cations in the two cis-M2 and one trans-M1 positions. Deviations of peak areas from the site multiplicity 2:1 ratio demonstrated that Fe^{2+} ions are relatively enriched in cis-M2 positions and that this is accentuated in biotites from metamorphic rocks. Tetrahedral Fe^{3+} ions were confirmed in ferriphlogopite, ferriannites from banded iron formations, and some annites. Annite from the type locality in Massachusetts contains high concentrations of octahedral Fe^{2+} and Fe^{3+} cations in comparable amounts, in accordance with Dana's (1868, *A System of Mineralogy,* 5th edition) original definition of this annite. Of the samples studied, the annite from Pikes Peak, Colorado, approximates most closely Winchell's (1925, *American Journal of Science,* 5th ser., 9, 309–327) classification of annite as the Fe^{2+} endmember analogue of phlogopite.

Introduction

Iron-bearing micas play a prominent role in the earth sciences (Bailey, 1984a). There have been numerous analytical, structural, and spectroscopic measurements of ferruginous micas aimed at identifying coexisting Fe^{2+} and Fe^{3+} ions and their distributions in the crystal structures of several mica polymorphs. However, the literature on iron-rich micas contains inconsistencies concerning the oxidation states, coordination numbers, and site occupancies of iron cations in the mica structure. Many of these ambiguities stem from incorrect interpretations of the Mössbauer spectra. This paper aims to clarify some of the confusion over the crystal chemistry of iron-bearing micas.

Some of the problems that surface upon perusal of the literature on iron-bearing micas include the following:

Nomenclature. The names *ferruginous biotite, annite, lepidomelane, siderophyllite, ferriannite,* and *monrepite* have all been applied to iron-rich micas, often with little regard to historical sequence. The connotations and limitations of each of these names need to be clearly defined.

Cation-site terminology. Most mica structures contain two octahedral and one or two tetrahedral positions, as well as interlayer positions. However, the nomenclature of the two octahedral sites, in particular, is inconsistent and needs to be unified.

Fe^{3+} site occupancy. A fundamental question is whether tetrahedrally coordinated Fe^{3+} ions exist in these micas

when the bulk compositions contain adequate $(Si + Al)$ to fill the tetrahedral sites.

Preferred orientation. The perfect basal cleavage of micas renders them highly vulnerable to preferred orientation of the platelets when specimens are mounted for X-ray diffraction and Mössbauer spectral measurements of powdered specimens. The adverse effects of preferred orientation on relative intensities of peaks in spectrograms need to be eliminated.

Fe^{3+}/Fe^{2+} ratios. Mössbauer spectroscopy has high potential for determining proportions of Fe^{3+} and Fe^{2+} rapidly and nondestructively. However, accuracies may be affected by preferred orientation, oxidation during sample preparation, different recoil-free fractions for Fe^{3+} and Fe^{2+} ions, and problems of peak resolution and assignment.

Atomic substitution. The influence of compositional variations, vacancies, and local charge imbalance induced by the substitution of Fe^{3+}, Ti^{4+}, and Al^{3+} for Fe^{2+} and Mg^{2+} in the octahedral sites needs to be evaluated. Also, effects of replacement of OH^- by F^-, Cl^-, and O^{2-} and influences of nonstoichiometry of K^+, Na^+, Ca^{2+}, etc., in interlayer sites need to be assessed.

Many of these problems are addressed here and in a companion paper (Dyar, ms. in prep.), where the focus is on 1M trioctahedral micas. Following a brief review of the nomenclature of iron-rich micas, essential features of the mica crystal structure are described, and the correct designation of the cation sites is specified. New Mössbauer spectral measurements are then described for a suite of iron-bearing micas representing diverse chemical compositions, crystal chemistries, and parageneses. Results of

---

Table 1. History of nomenclature of iron-rich micas

Term	Reference	Context/Origin
cryophyllite	Cooke, 1867	Fe^{3+}-rich biotite from Cape Ann, Massachusetts
annite	Dana, 1868	Fe^{3+}-rich biotite from Cape Ann, Massachusetts
annite*	Winchell, 1925	hypothetical Fe^{2+} analogue of phlogopite, $KFe_3^{2+}[Si_3AlO_{10}](OH)_2$
lepidomelane	Dana, 1892	black biotite with substantial Fe^{3+}
lepidomelane*	Foster, 1960	$K(Fe_x^{2+}Fe_y^{3+})_{x+y}[Si_3AlO_{10}](OH)_2$ $3.00 > x > 1.50, \ 0 < y < 1.00$
siderophyllite*	Foster, 1960	$K(Fe_x^{2+}Al_z^{3+})_{x+z}[Si_3AlO_{10}](OH)_2$ $3.00 > x > 1.50, \ 0 < z < 1.00$
monrepite	Wahl, 1925	non-aluminous, ferro-ferri mica
ferriannite*	Wones, 1963 Donnay et al., 1964	$KFe_3^{2+}[Si_3Fe^{3+}O_{10}](OH)_2$

*Nomenclature used in the present study

- ● M2 (cis)
- ○ M1 (trans)
- · Si
- ● K
- ○ O
- ◎ OH,F

Fig. 1. Schematic diagram of the mica crystal structure. (left) Projected onto (100) showing the locations of the cation sites and OH^- anions. (right) Projected onto (001), showing the configurations of the cis-M2 and trans-M1 coordination polyhedra.

iron site occupancies are subsequently correlated with structural and bonding features of the mica crystal structure.

NOMENCLATURE

The name *phlogopite* has a precise connotation for the composition $KMg_3[Si_3AlO_{10}](OH)_2$, whereas *biotite* implies atomic substitution primarily of Fe^{2+} for Mg^{2+} in this trioctahedral mica. However, some confusion exists over the nomenclature of iron-rich micas, particularly those containing Fe^{3+} ions, and names that have been proposed are listed in Table 1. Winchell (1925) applied the name *annite* to a hypothetical Fe^{2+} analogue of phlogopite, and this was used by him as one of four components—phlogopite, annite, ferriphlogopite, and ferriannite—to define biotite compositions. However, the name *annite* was originally given by Dana (1868) to a Fe^{3+}-rich biotite from the type locality at Cape Ann, Massachusetts, which had earlier been described, analyzed, and named *cryophyllite* by Cooke (1867). Therefore, the name that Dana gave to a Fe^{3+}-rich mica was misapplied by Winchell to the hypothetical Fe^{2+} mica, which was assumed to contain no Fe^{3+} (Foster, 1960, p. 29). Dana (1892) listed *lepidomelane* as a variety of black biotite characterized by large amounts of Fe^{3+}. Foster (1960, p. 31) pointed out other ambiguities, but recommended applying the name *lepidomelane* to micas having compositions of $K(Fe_x^{2+}Fe_y^{3+})_{x+y}[Si_3AlO_{10}](OH)_2$, where $3.00 > x > 1.50$ and $0 < y < 1.00$. She also recommended (Foster, 1960, p. 30) that the name *siderophyllite* be applied to aluminous biotites having compositions $K(Fe_x^{2+}Al_z)_{x+z}[Si_3AlO_{10}](OH)_2$, where $3.00 > x > 1.50$ and $0 < z < 1.00$.

Note that each of these species names—lepidomelane, siderophyllite, and Dana's original annite—imply that Si and Al fill tetrahedral sites and that Fe^{3+} ions occur in octahedral coordination. The existence of tetrahedrally coordinated Fe^{3+} ions was recognized by Wones (1963) when he described the synthesis of $KFe_3^{2+}[Si_3Fe^{3+}O_{10}](OH)_2$. However, Wones (1963), and later Donnay et al. (1964) in their structure determination of this synthetic iron-rich mica, designated the phase as "ferriannite" and utilized quotation marks because the composition had not yet been found in nature. Wahl (1925), however, had previously described a ferro-ferri-mica from rapakivi granite in Finland with a (nonaluminous) composition paralleling the phlogopite-lepi-
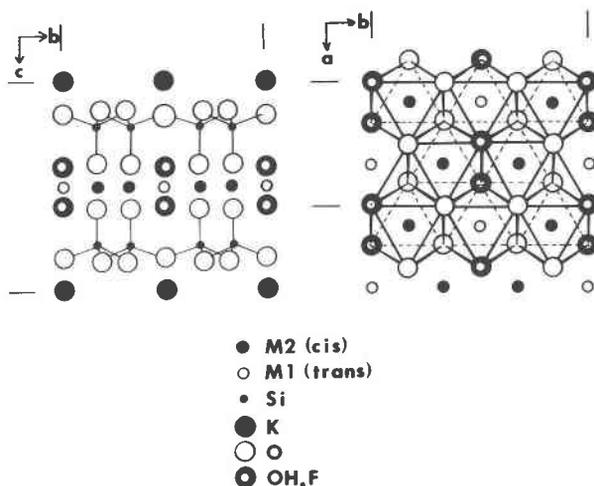
domelane series and had proposed the name *monrepite*. Subsequently, iron-rich, Al-poor micas from West Australian banded iron formations have been described (Miyano and Miyano, 1982; M. J. Gole, unpub. data) and named ferriannites. Tetrahedrally coordinated Fe^{3+} is acknowledged in the species names tetraferriphlogopite and tetraferribiotite (Embrey and Fuller, 1980).

In the present study, we adopt the names *annite, ferriannite, lepidomelane,* and *siderophyllite* as defined sensu stricto in Table 1. *Phlogopite* and *biotite* refer to Mg-rich and intermediate Mg-Fe^{2+} compositions, respectively, and *ferriphlogopite* and *ferribiotite* are used to designate corresponding tetrahedral Fe^{3+}-bearing compositions.

CATION-SITE DESIGNATION

Two different octahedral sites are distinguished by the configuration of the OH^- ions shown in Figure 1. One site, designated *cis*, has the two hydroxyls on adjacent corners of the octahedra; the other site, designated *trans*, has the two hydroxyls on opposite sides of the octahedron. The ratio of cis-octahedra to trans-octahedra is 2:1. In dioctahedral micas (e.g., muscovite), cations are located primarily in the cis-octahedra, whereas both cis- and trans-octahedra are filled in trioctahedral micas. Thus, in the muscovite crystal structure, only one octahedral Al position—the cis-octahedron—is defined, for which the mean Al^{3+}–O distance is about 1.95 Å (Radoslovich and Norrish, 1962; Richardson and Richardson, 1982). The vacant trans-octahedron is much larger in muscovite, having dimensions corresponding to a mean cation–oxygen distance of about 2.20 Å. Following the terminology of Pabst (1955), adopted by Bailey (1975, 1984b), the two octahedral sites in both dioctahedral $2M_1$ and trioctahedral $1M$ polytypes are now designated as the cis-M2 and trans-M1 octahedra. This standardization of octahedral-site nomenclature is important because one ambiguity in mica Mössbauer spectroscopy has arisen from switching of the M1 and M2 site designations.

Numerous structure refinements have been made of 1M trioctahedral micas (Bailey, 1984a), and data relevant to the present study are summarized in Table 2. In phlogopites, biotites, and annites, the average metal–oxygen distances of the cis-M2 and

trans-M1 octahedra are comparable, and the dimensions of both sites increase with rising Fe^{2+} content. The larger dimensions of the tetrahedral sites of ferriphlogopite and ferriannite correlate with Fe^{3+} ions replacing Al^{3+} ions in these sites.

The schematic structural diagram illustrated in Figure 1 also shows that each *trans*-M1 octahedron shares edges with six *cis*-M2 octahedra, whereas each *cis*-M2 octahedron is adjacent to three *cis*-M2 and three *trans*-M1 octahedra. Next-nearest-neighbor distances between cations located in the center of these octahedra are 3.10–3.11 Å in annite, for example (Hazen and Burnham, 1973). Chemical formulae calculated from bulk compositions of trioctahedral micas invariably show a deficiency of cations, and vacancies are assumed to occur in the octahedral sites (in addition to interlayer positions). Recent NMR studies of aluminous biotites (Sanz et al., 1984) have demonstrated that cation vacancies occur in *trans*-M1 sites in trioctahedral micas, by analogy with dioctahedral muscovites in which the *trans*-M1 positions are unoccupied (Radoslovich and Norrish, 1962).

In iron-rich micas approaching annite and ferriannite end-member compositions, the site multiplicity ratio of 2:1 for *cis*-M2 to *trans*-M1 octahedra imposes a constraint for assigning Fe^{2+} and Fe^{3+} doublets in the Mössbauer spectra. Significant departures from this 2:1 ratio for peak area data of intermediate biotite compositions are indicative of cation ordering in the *cis*-M2 and *trans*-M1 positions.

PREVIOUS MÖSSBAUER SPECTRAL MEASUREMENTS

Numerous studies have been made of natural, synthetic, oxidized, heat-treated, and irradiated iron-bearing micas. References to most of the earlier Mössbauer spectral measurements of phyllosilicates are cited elsewhere (Heller-Kallai and Rozenson, 1981; Dyar, ms. in prep.). The Mössbauer spectra of micas usually contain contributions from coexisting Fe^{2+} and Fe^{3+} ions. In most specimens, two Fe^{2+} doublets were resolved, the outer doublet with larger quadrupole splitting generally being assigned to Fe^{2+} in *cis*-M2 sites and the inner doublet with the smaller quadrupole splitting to Fe^{2+} in *trans*-M1 sites for both dioctahedral and trioctahedral micas. However, in some reports (Goodman and Wilson, 1973; Goodman, 1976; Finch et al., 1982), these Fe^{2+}-peak assignments were incorrectly reversed. Wide ranges of Fe^{2+} isomer shift and quadrupole splitting parameters are reported in the literature (see reviews by Heller-Kallai and Rozenson, 1981; Dyar, ms. in prep.), which hint at misfitting of the Mössbauer spectra. An even wider range of parameters has been reported for Fe^{3+} peaks, which often have been resolved into two doublets, the outer (larger quadrupole splitting) doublet usually being assigned to Fe^{3+} in the *trans*-M1 site and the inner doublet to Fe^{3+} in the *cis*-M2 sites (Bancroft and Brown, 1975). Some data fall beyond the range found for octahedrally coordinated Fe^{3+} ions in other silicate and oxide minerals (Dyar, ms. in prep.). Again these inconsistencies suggest incorrect fitting of the Mössbauer spectra.

Peaks attributed to tetrahedrally coordinated Fe^{3+} ions have been suggested for some micas (Annersten, 1974, 1975). Such an assignment is unambiguous for ferriphlogopites and ferriannites because their compositions necessitate substitution of Si^{4+} by Fe^{3+} in the tetrahedral sites. However, in some Al-rich micas containing a surplus of Al^{3+} and Si^{4+} to fill the tetrahedral sites, the parameters obtained from Mössbauer spectra fitted to Fe^{3+} doublets lie beyond the range of isomer shifts for tetrahedrally coordinated Fe^{3+} ions in other minerals (Annersten and Olesch, 1978). Again the fitting of such Mössbauer spectra is suspect and warrants further investigation.

Table 2. Structural data for selected trioctahedral 1M micas

Mineral	Average (Ranges) Metal-Oxygen Distances (Å)			Reference
	cis-M2 octahedra	trans-M1 octahedron	Tetrahedral site	
phlogopite	2.064 (2.063-2.075)	2.076 (2.063-2.076)	1.654 (1.627-1.654)	a
biotite	2.068 (2.004-2.118)	2.086 (2.053-2.102)	1.659 (1.655-1.667)	b
annite	2.101 (2.083-2.112)	2.121 (2.119-2.123)	1.659 (1.653-1.666)	c
oxybiotite	2.059 (1.947-2.142)	2.071 (2.031-2.100)	1.655 (1.650-1.668)	d
ferriphlogopite	2.096 (2.094-2.097)	2.101 (1.975-2.119)	1.681 (1.673-1.694)	e
ferribiotite	2.098	2.111	1.676	f
ferriannite	2.106 (2.075-2.132)	2.107 (2.074-2.123)	1.685 (1.670-1.697)	g

a: Hazen and Burnham, 1973; Rayner, 1974.
b: Takeda and Ross, 1975.
c: Hazen and Burnham, 1973.
d: Ohta et al., 1982.
e: Steinfink, 1962.
f: Semenova et al., 1983.
g: Donnay et al., 1964.

In a thought-provoking paper, Mineeva (1978) has drawn attention to several factors that may complicate the fitting and interpretation of the Mössbauer spectra of biotites. Her calculations of lattice electric-field-gradient (EFG) components for an ideal mica structure indicate that the quadrupole splittings of Fe^{3+} ions in *cis*-M2 and *trans*-M1 sites fall close together, suggesting that only one Fe^{3+} doublet should be resolved. She also suggested that Fe^{2+} cations probably occupy two distinct sites, producing an outer doublet representing Fe^{2+} in an idealized octahedral site and an inner doublet due to Fe^{2+} in sites affected by defects such as vacancies of H^+, clusters including Fe^{3+}, substitution of OH^- by F^-, etc.

EXPERIMENTAL DETAILS

Given the inconsistencies of the published Mössbauer spectral data on micas, this study was conceived to examine a range of specimens in a consistent manner, using the same spectrometer and the same fitting program for all samples. Mica selection was accomplished with two goals: (1) to study well-characterized samples used in earlier spectral and structural measurements so as to establish consistent ranges of Mössbauer parameters for iron cations in each site and (2) to measure a suite of natural annites and ferriannites in order to determine the crystal chemistry of Fe^{3+}.

The chemical compositions and sources of the 15 ferruginous micas used in the present study are summarized in Table 3. Many of the specimens were obtained from samples that had been analyzed previously by wet-chemical or electron-microprobe techniques (specimens 1–4, 9–14). New analyses of specimens 5–8 and 14 were performed at MIT using a MAC-5 electron microprobe with alpha corrections applied to the data.

Four igneous biotites from granitic rocks of the central Sierra Nevada batholith, California (specimens 1–4), were provided by G. M. Bancroft. These biotites are among those described by Dodge et al. (1969), who provided X-ray powder-diffraction and wet-chemical analytical data on the samples. Subsequent Mössbauer analyses of these biotites by Bancroft and Brown (1975) indicated that they contain Fe^{2+} and Fe^{3+} in two octahedral sites, with no evidence of tetrahedral Fe^{3+}. All four biotites studied here have similar compositions (see specimens 1–4, Table 3),

Table 3. Chemical compositions of the ferruginous micas*

	1	2	3	4	5	6	7	8	9	10	11	12	13a	13b	14a	14b	15
SiO_2	36.29	36.34	37.55	36.45	33.92	34.96	35.76	40.88	38.99	33.75	38.44	36.71	33.96	33.92	39.91	33.90	-
Al_2O_3	16.53	15.37	15.49	15.17	19.07	19.91	19.53	9.25	0.90	5.13	5.84	19.82	13.10	11.87	16.73	11.23	-
TiO_2	1.54	2.76	1.70	2.50	2.49	1.39	1.41	0.12	0.00	0.15	0.02	0.55	3.55	3.61	-	3.50	-
Fe_2O_3	4.28	3.64	3.49	4.23	-	*	*	-	12.60	8.11	6.65	-	3.06	-	12.07	-	-
MgO	11.16	9.43	12.23	11.68	9.52	9.53	9.61	23.58	6.07	2.98	11.50	0.04	0.97	0.89	0.62	0.31	-
FeO	15.51	18.37	15.10	15.91	20.61	21.18	20.98	10.25	29.60	34.88	25.15	22.46	32.04	36.42	17.48	34.65	-
MnO	0.84	0.33	0.43	0.41	0.15	0.00	0.06	0.04	0.00	-	0.03	1.60	0.65	0.64	-	0.45	-
CaO	0.57	0.54	0.60	0.57	0.01	0.00	0.00	-	0.37	0.62	0.01	0.01	0.42	0.03	-	-	-
Na_2O	0.30	0.25	0.24	0.21	0.40	0.34	0.27	0.10	0.00	-	0.15	0.16	0.49	0.10	-	0.08	-
K_2O	8.28	9.98	8.53	8.44	8.33	8.11	8.85	10.27	6.56	9.33	8.30	9.66	8.47	8.94	10.66	8.02	-
H_2O^+	3.50	3.10	3.90	3.70	-	-	-	-	-	-	-	-	2.50	-	1.50	-	-
H_2O^-	0.30	0.18	0.32	0.30	-	-	-	-	-	-	-	-	-	-	-	-	-
F^-	0.40	0.28	0.38	0.26	-	-	-	-	-	-	-	3.79	0.82	-	-	-	-
Others	0.04	0.04	0.07	0.05	-	-	-	-	-	-	-	0.01	0.34	-	1.19	-	-
$O=F,Cl$	0.18	0.13	0.18	0.12	-	-	-	-	-	-	-	-	-	-	-	-	-
Total	99.42	100.56	99.89	99.70	94.50	95.42	96.47	94.49	97.99	94.95	96.09	94.81	100.37	96.42	100.16	92.14	-
Si	5.488	5.512	5.637	5.509	5.233	5.317	5.388	6.048	6.490	5.884	6.111	5.946	5.532	5.633	5.040	5.827	6.000
Al_{iv}	2.512	2.488	2.363	2.491	2.767	2.683	2.612	1.613	0.177	1.054	1.094	2.054	2.468	2.324	1.960	2.173	2.000
Fe_{iv}^{3+}	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.333	1.062	0.795	0.000	0.000	0.000	0.000	0.000	0.000
Sum Tet	8.000	8.000	8.000	8.000	8.000	8.000	8.000	7.661	8.000	8.000	8.000	8.000	8.000	7.957	8.000	8.000	8.000
Al_{vi}	0.435	0.260	0.378	0.212	0.701	0.887	0.857	0.000	0.000	0.000	0.000	1.731	0.048	0.000	1.025	0.103	0.000
Ti	0.177	0.318	0.194	0.287	0.292	0.161	0.161	0.013	0.000	0.020	0.002	0.068	0.439	0.455	0.000	0.457	0.000
Fe_{vi}^{3+}	0.487	0.415	0.394	0.481	0.000	0.000	0.000	0.000	0.245	0.002	0.001	0.000	0.375	0.000	1.375	0.000	0.000
Mg	2.515	2.132	2.736	2.631	2.189	2.160	2.158	5.199	1.506	0.774	2.725	0.010	0.235	0.220	0.140	0.079	0.000
Fe^{2+}	1.962	2.330	1.896	2.011	2.659	2.694	2.643	1.268	4.120	5.086	3.344	3.042	4.365	5.058	2.212	4.981	6.000
Mn	0.108	0.042	0.055	0.052	0.020	0.000	0.008	0.005	0.000	0.000	0.004	0.220	0.090	0.090	0.000	0.066	0.000
Sum Oct	5.684	5.497	5.653	5.674	5.861	5.902	5.827	6.485	5.871	5.882	6.076	5.071	5.552	5.780	4.752	5.686	6.000
Ca	0.092	0.088	0.097	0.092	0.002	0.000	0.000	0.000	0.066	0.116	0.002	0.002	0.073	0.005	0.000	0.000	0.000
Na	0.088	0.074	0.070	0.062	0.120	0.100	0.079	0.029	0.000	0.000	0.046	0.050	0.0155	0.032	0.000	0.027	0.000
K	1.597	1.931	1.634	1.627	1.639	1.574	1.701	1.939	1.393	2.075	1.683	1.996	1.760	1.894	2.058	1.759	2.000
Sum A	1.777	2.093	1.801	1.781	1.761	1.674	1.780	1.968	1.459	2.191	1.731	2.048	1.988	1.931	2.058	1.786	2.000

* The formulae of all specimens have been recalculated on an anhydrous basis (oxygens = 22) to facilitate comparisons between microprobe and wet chemical data.
1 Biotite MT-1, in Wheeler Crest Quartz Monzonite, Central Sierra Nevada Batholith (Dodge et al., 1969; Bancroft and Brown, 1975). Analysis includes 0.04% Cl.
2 Biotite SL-18, in granodiorite of Dinkey Creek Type, Central Sierra Nevada Batholith (Dodge et al., 1969; Bancroft and Brown, 1975). Analysis includes 0.07% Cl.
3 Biotite BP-1, in Tinemaha Granodiorite, Central Sierra Nevada Batholith (Dodge et al., 1969; Bancroft and Brown, 1975). Analysis includes 0.07% Cl.
4 Biotite MG-1, in Lamark Granodiorite, Central Sierra Nevada Batholith (Dodge et al., 1969; Bancroft and Brown, 1975). Analysis includes 0.05% Cl.
5-7 Biotites BF9A, BF9E, and BF9G from the amphibolite facies, Rangeley Fm., Bellows Falls, New Hampshire (analyzed and donated by D. Hickmott).
8 Ferriphlogopite, locality unknown (R. M. Hazen, personal communication).
9 Ferriannite SA-2, banded iron formation, Hamersley Range, Western Australia (analysed and donated by M. J. Gole). Contains 1-2% riebeckite and very fine grained hematite.
10 Ferriannite BHD2/448, banded iron formation, Hamersley Range, Western Australia (analysed and donated by M. J. Gole).
11 Ferriannite GE, banded iron formation, Dales Gorge, Hamersley Range, Western Australia (Miyano and Miyano, 1982).
12 Annite (siderophyllite), Lost Creek, Montana (R. A. Robie, personal communication).
13 Annite, B65DS, Devil's Slide, Pikes Peak, Colorado, (Barker et al., 1975; Hazen and Burnham, 1973) (a) Wet chem.; (b) microprobe (Analysis includes 0.34% Cl).
14 Annite (lepidomelane), Cape Ann, Massachusetts, Analysis includes 0.59% Li2O and 0.60% Mn2O3. (a) wet chem (Foster, 1960); (b) microprobe.
15 Synthetic fluorannite (synthesized by J. Munoz; donated by D.R. Wones).

suggesting that their Mössbauer spectra might also be similar. This group of igneous biotites was studied to establish on our spectrometer the range of Mössbauer parameters that might be expected in subsequent analyses of more-complicated micas. Three metamorphic biotites (specimens 5–7) from amphibolite-facies rocks of the Rangeley Formation, Bellows Falls, New Hampshire, were lent by D. Hickmott. Samples 1–7 show a surplus of (Si + Al) over that required to completely fill tetrahedral sites (Table 3). The composition of specimen 8 obtained from R. M. Hazen is deficient in tetrahedral (Si + Al), suggesting that Fe_{tet}^{3+} is present in this ferriphlogopite. Three ferriannites from banded iron formations (specimens 9–11) with compositions indicative of Fe_{tet}^{3+} were provided by M. J. Gole and S. Miyano. Three annite specimens were acquired from granitic rocks at Lost Creek, Montana; Pikes Peak, Colorado; and Cape Ann, Massachusetts. The Lost Creek specimen (sample 12) contributed by D. A. Robie was used by him in calorimetric measurements and has high Al (siderophyllite) and F contents. The Pikes Peak annite (sample 13) donated by F. Barker was used in the crystal-structure re-

finement by Hazen and Burnham (1973). The Cape Ann specimen (sample 14) was collected by us at the type locality near Rockport, Massachusetts. The chemical analysis of this annite indicates a high Fe^{3+} (lepidomelane) content. Sample 15 is a synthetic fluorannite prepared by J. Munoz and lent to us by the late D. R. Wones.

For the Mössbauer spectral measurements, samples were finely ground under acetone (to minimize possible oxidation of iron) and mixed with sugar and acetone. This method of sample preparation coats the individual biotite grains with sugar so that each particle is well rounded, thereby alleviating preferred orientation of the mica flakes in the plexiglass sample holder. However, because past studies suggested that preferred orientation affects in Mössbauer spectral profiles are difficult to overcome (Bowen et al., 1969; Annersten, 1975), the experimental technique described above was also tested. Biotite MT-1 was ground dry in the mortar and pestle for 30 min; other aliquots were ground wet (under acetone) for 30 min and for 1 min, and also mounted as the small flakes supplied to us as the mica separate from the

Table 4. Mössbauer parameters for iron-bearing micas

Specimen[*]	Fe_{tet}^{3+}				Fe_{oct}^{3+} (cis-M2)				Fe_{oct}^{3+} (trans-M1)				Fe_{oct}^{2+} (trans-M1)				Fe_{oct}^{2+} (cis-M2)				Misfit	Uncertainty
	δ	Δ	%Area	Γ	δ	Δ	%Area	Γ	δ	Δ	%Area	Γ	δ	Δ	%Area	Γ	δ	Δ	%Area	Γ		
1	-	-	-	-	0.41	0.55	16	0.39	0.42	1.24	11	0.39	1.07	2.22	16	0.39	1.13	2.60	57	0.39	-0.34	-0.05
2	-	-	-	-	0.44	0.47	12	0.39	0.39	1.16	9	0.39	1.10	2.12	22	0.39	1.13	2.57	57	0.39	0.07	0.02
3	-	-	-	-	0.39	0.52	15	0.38	0.41	1.16	12	0.38	1.07	2.15	14	0.38	1.13	2.60	59	0.38	0.04	0.01
4	-	-	-	-	0.46	0.52	15	0.40	0.45	1.17	11	0.40	1.09	2.15	20	0.40	1.12	2.58	54	0.40	-0.03	-0.01
5	-	-	-	-	0.43	0.66	6	0.39	0.49	1.36	4	0.39	1.15	1.87	9	0.39	1.14	2.55	79	0.39	-0.57	-0.08
6	-	-	-	-	0.44	0.28	6	0.37	0.43	1.19	8	0.37	1.13	2.19	14	0.37	1.14	2.63	72	0.37	-0.04	-0.02
7	-	-	-	-	0.44	0.37	5	0.38	0.43	1.20	5	0.38	1.14	2.15	15	0.38	1.14	2.61	75	0.38	0.19	0.03
8	0.19	0.56	62	0.45	-	-	-	-	-	-	-	-	-	-	-	-	1.12	2.63	38	0.38	-0.33	-0.04
9	0.21	0.40	20	0.29	0.36	0.56	6	0.29	-	-	-	-	1.15	2.83	31	0.29	1.13	2.60	43	0.29	0.51	0.05
10	0.20	0.45	18	0.29	-	-	-	-	0.42	1.01	4	0.29	1.16	2.16	19	0.28	1.10	2.55	59	0.28	0.09	0.02
11	0.19	0.39	16	0.28	0.42	0.46	7	0.28	0.39	1.94	5	0.28	1.12	2.82	19	0.37	1.13	2.67	52	0.37	1.01	0.09
12	0.11	0.15	10	0.36	0.34	0.74	10	0.36	-	-	-	-	1.10	2.36	27	0.36	1.14	2.68	53	0.36	-0.17	-0.15
13	-	-	-	-	0.39	0.31	4	0.37	0.43	0.99	7	0.37	1.10	2.06	30	0.37	1.14	2.53	60	0.37	0.26	0.02
14	0.20	0.37	3	0.40	0.37	0.61	30	0.40	0.42	0.98	22	0.40	1.15	1.90	14	0.40	1.12	2.50	32	0.40	0.05	0.01
15	-	-	-	-	-	-	-	-	-	-	-	-	1.15	1.44	31	0.43	1.15	2.17	69	0.43	0.06	0.01

*1 Biotite MT-1; 2 Biotite SL-18; 3 Biotite BP-1; 4 Biotite MG-1; 5 Biotite BF9A; 6 Biotite BF9E; 7 Biotite BF9G; 8 Ferriphlogopite; 9 Ferriannite SA-2; 10 Ferriannite BHD2/448; 11 Ferriannite GE; 12 Annite Lost Creek; 13 Annite Pikes Peak; 14 Annite Cape Ann; 15 Fluorannite synthetic

original rock. Some samples were measured with the plexiglass holder orientated at 54.7° (the "magic angle") to the gamma ray flux to confirm the absence of preferred orientation effects.

Mössbauer spectra were recorded in 512 channels of a constant-acceleration Austin Science Associates spectrometer, using a 100–50 mCi ^{57}Co in a Rh matrix source. Results were calibrated against α-Fe foil (6 μm thick, 99.99% purity). Spectra were transferred to a MINC LSI 11/73 minicomputer, where interactive curve-fitting was executed. Spectra were fit using a Gaussian nonlinear regression procedure with a facility for constraining any set of parameters or linear combination of parameters (Stone et al., 1984). Lorentzian line shapes were used for resolving peaks, as there was no statistical justification for the addition of a Gaussian component to the curve shape used.

Each Mössbauer spectrum was fitted separately with an identical progression of constraints. Because precautions during sample preparation were taken to negate preferred orientation effects, component peaks of each doublet were constrained to have equal areas. Half-widths of all Fe^{2+} doublets were constrained to be equal, as were all F^{3+}-doublet half-widths. Considerable effort was made to approach each analysis in an unbiased fashion, without prior knowledge of the chemical composition and crystal chemistry of the sample. Each spectrum was first fit with one doublet. When that fit had "converged" (or reached a pre-established minimum deviation between the calculated fit and the actual data), a new doublet was added. If the fit converged, additional doublets were added until the statistics of the fit ceased to improve or until it was no longer possible to obtain a "converged" fit. Thus, results that report only two-doublet fits indicate that various three-doublet fits were attempted, but failed. For some samples it was possible to achieve more than one converged fit. The "best fit" to the data for each sample was evaluated on the basis of the statistical parameters calculated by the program, including chi-squared, MISFIT, and the uncertainty of the MISFIT. For comparisons between *different* samples, chi-squared is not useful because it depends on the number of baseline counts of a spectrum (Ruby, 1973). However, MISFIT provides a comparative goodness-of-fit criterion and can be used to evaluate different spectra irrespective of baseline counts (see Ruby, 1973, for details). MISFIT may range from −1 to +1 and is optimal when it is closest to 0. The uncertainty of the MISFIT parameter, which ranges from −∞ to +∞, is also optimal at 0 and represents the probable uniqueness of the fit. Therefore Mössbauer data with low MISFIT and high uncertainties (greater than one) may be viewed as good fits that adequately explain the data set but that may not be unique.

The practical application of these statistical parameters is discussed elsewhere (Dyar, 1984). At best, the precision of the Mössbauer spectrometer and the fitting program is approximately ±0.02 mm/s for isomer shift (δ) and quadrupole splitting (Δ) and ±1.5% for area data for spectra with well resolved, distinct peaks (Dyar, 1984). However, the mica spectra in this study contain several overlapping peaks; the parameters listed in Table 4 are estimated to be ±0.03 mm/s for isomer shift and quadrupole splitting, and at least ±3% for area data. It is important to keep the magnitude of these errors in mind when evaluating the data. Note that these errors are realistic limits not only for this spectrometer, but also for other Mössbauer spectrometers (see Dyar, 1984).

RESULTS

Testing for preferred orientation and sample oxidation

The perfect basal cleavage of micas renders them highly prone to preferred orientation, leading to peak asymmetry in their Mössbauer spectra (Annersten, 1975; Chandra and Lokanathan, 1977). Furthermore, attempts to pulverize micas to extremely small grain sizes to overcome preferred orientation could result in oxidation of Fe^{2+} to Fe^{3+} during sample preparation (Bowen et al., 1969; Gendler et al., 1978). To test these possibilities and to confirm the adequacy of our sample-preparation technique, several Mössbauer spectra were run on biotite MT-1 (sample 1), and the profiles are shown in Figure 2. The spectrum of this biotite when ground under acetone for 30 min (Fig. 2a) is nearly identical to spectra of samples ground for only 1 min (Fig. 2b), or not ground at all (Fig. 2c), but mounted as small flakes sieved through #150 mesh (crystallite diameter 0.5 mm). It appears that the particle size of the biotite that is achieved after only 1 min of grinding is sufficiently small to prevent orientation effects when the sample is mixed with sugar under acetone. However, Figure 2d shows that the spectrum does change slightly when biotite is ground dry for 30 min. The position and intensity of the small peak centered near 0.8 mm/s (attributed to Fe^{3+}) increase, the peak area rising from 22% to 27%. Dry grinding evidently oxidizes the Fe^{2+} to Fe^{3+} ions,
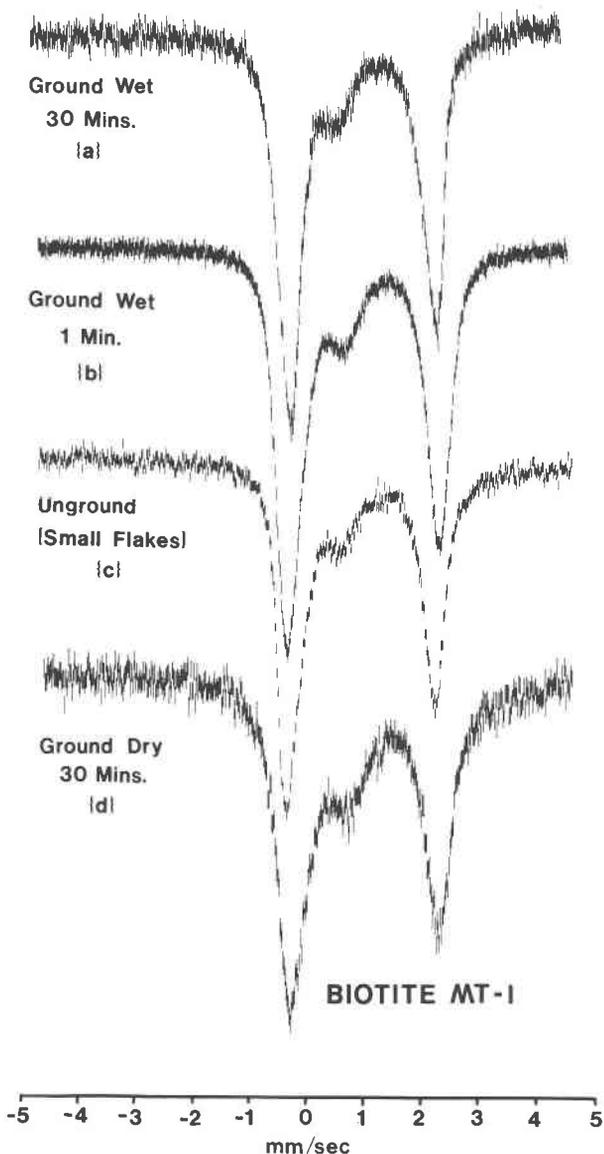
Fig. 2. Mössbauer spectra of biotite MT-1 (specimen 1) prepared in different ways. Spectra (a), (b), and (c) are remarkably similar, but spectrum (d) shows an enlarged Fe^{3+} peak around 1 mm/s resulting from oxidation during dry grinding of the biotite specimen.
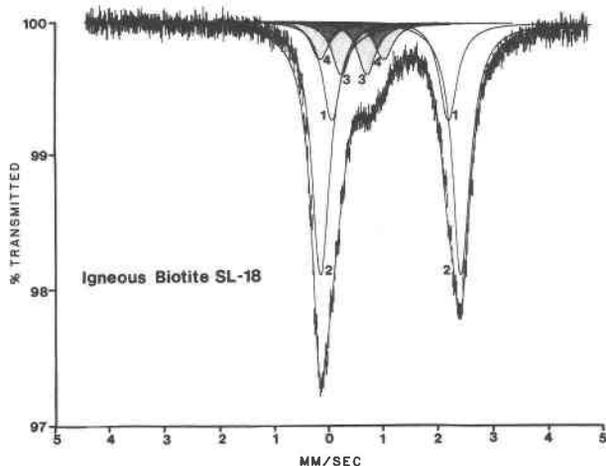

Fig. 3. Mössbauer spectrum of igneous biotite SL-18 (specimen 2); peaks 1-1—Fe^{2+}_{oct} in *trans*-M1; peaks 2-2—Fe^{2+}_{oct} in *cis*-M2; peaks 3-3—Fe^{3+}_{oct} in *cis*-M2; peaks 4-4—Fe^{3+}_{oct} in *trans*-M1.

perhaps coupled with the conversion of OH^- to O^{2-} ions, thereby altering the oxygen ligand characteristics of the *cis*-M2 and *trans*-M1 sites.

The suite of ferruginous micas

The results of extensive curve-fitting of the Mössbauer spectra of the 15 ferruginous micas are presented in Table 4. Representative spectra are illustrated in Figures 3–9. In accord with earlier studies (e.g., Annersten, 1974; Bancroft and Brown, 1975), resolved doublets are assigned to octahedrally coordinated Fe^{2+} and Fe^{3+} ions in the *cis*-M2

and *trans*-M1 sites and to tetrahedrally coordinated Fe^{3+} substituting for Si and Al in the sheets of corner-shared tetrahedra. Note that for most micas the outermost Fe^{2+} doublet (largest quadrupole splitting) originates from *cis*-M2 Fe^{2+} ions, whereas the innermost Fe^{3+} doublet with smaller quadrupole splitting, when resolved, is assigned to Fe^{3+} in *cis*-M2 sites. As noted later, the Fe^{2+} doublets may be reversed in some ferriannites. The choice of two Fe^{3+} doublets is vindicated because the mica structure contains two potential octahedral sites (*cis*-M2 and *trans*-M1) available to Fe^{3+} ions. We also invoked the inverse relationship of quadrupole splitting parameters between Fe^{2+} and Fe^{3+} peaks to assign the octahedral Fe^{3+} doublets.

The spectra of the four igneous biotites (specimens 1–4) are remarkably similar and resemble that of specimen SL-18 shown in Figure 3. Note that the area ratio of Fe^{2+} *cis*-M2/*trans*-M1 in these samples approaches 3:1, which is significantly different from the site multiplicity 2:1 ratio, indicating Fe^{2+} enrichment in the *cis*-M2 positions. The Fe^{3+} *cis*-M2 doublet is only slightly more intense than the Fe^{3+} *trans*-M1 doublet, suggesting that Fe^{3+} ions are relatively enriched in the *trans*-M1 position. The three metamorphic biotites (specimens 5–7) also have similar Mössbauer spectra (e.g., Fig. 4). The Fe^{2+} ions again are very strongly enriched in the *cis*-M2 sites.

The expected occurrence of tetrahedral Fe^{3+} ions in ferriphlogopite (Steinfink, 1962) suggested by the chemical formula of specimen 8 is confirmed by its Mössbauer spectrum illustrated in Figure 5. The spectrum is dominated by the Fe^{3+}_{tet} doublet, with only one other Fe^{2+} doublet being resolved. The parameters of this doublet correlate with those of Fe^{2+} ions in *cis*-M2 sites of the biotites (Table 4, specimens 1–7), suggesting that Fe^{2+} ions are located predominantly in the *cis*-M2 positions of ferriphlogopite. Alternatively, the presence of tetrahedral Fe^{3+} ions in the structure may cause the Fe^{2+} *trans*-M1 and
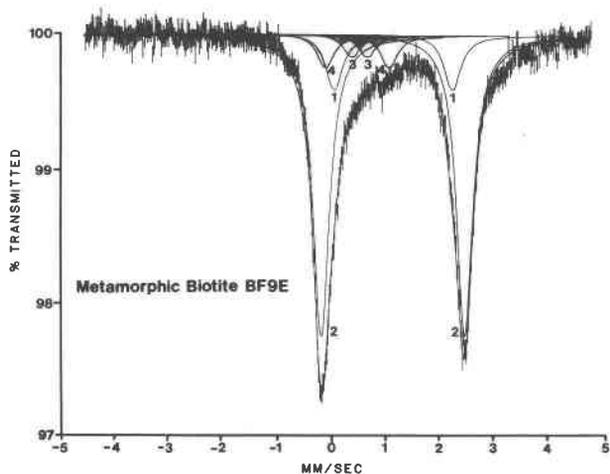
Fig. 4. Mössbauer spectrum of metamorphic biotite BF9E (specimen 6); peaks 1-1—Fe^{2+}_{oct} in *trans*-M1; peaks 2-2—Fe^{2+}_{oct} in *cis*-M2; peaks 3-3—Fe^{3+}_{oct} in *cis*-M2; peaks 4-4—Fe^{3+}_{oct} in *trans*-M1.

Fig. 5. Mössbauer spectrum of ferriphlogopite (specimen 8). The spectrum is dominated by peaks due to tetrahedral Fe^{3+} ions; peaks A-A—Fe^{2+}_{oct}; peaks T-T—Fe^{3+}_{tet}.

cis-M2 doublets to be superimposed in the ferriphlogopite Mössbauer spectrum.

The three ferriannites from banded iron formations (specimens 9–11) also gave Mössbauer spectra that showed the majority of the Fe^{3+} ions to be located in tetrahedral sites. The spectrum of specimen 10 shown in Figure 6 shows a small Fe^{3+}_{oct} doublet, too. Two Fe^{2+} doublets with parameters consistent with Fe^{2+} ions in *cis*-M2 and *trans*-M1 sites are also displayed in the spectrum of specimen 10. The two magnesian ferriannites (specimens 9 and 11) also yielded two Fe^{2+} doublets, but the outermost doublet is less intense and has an unusually large quadrupole splitting (Table 4). By analogy with ferriphlogopite (specimen 8) discussed earlier, the presence of Fe^{3+}_{tet} and Mg^{2+} may influence the parameters of Fe^{2+} in *trans*-M1 positions. Specimens 9 and 11 also have significantly high deficiencies of interlayer cations (Table 3), suggesting that the absence of K^+ ions in A sites could be drastically affecting the Mössbauer spectra of ferriannites. This aspect is discussed further in a companion paper (Dyar, ms. in prep.).

The Mössbauer spectra of the three natural annites (specimens 12–14) and synthetic fluorannite (specimen 15) each contain two Fe^{2+} doublets with area ratios approximating the 2:1 multiplicity of the *cis*-M2 and *trans*-M1 sites, in agreement with site occupancies in the crystal-structure refinement of specimen 13 (Hazen and Burnham, 1973). The three annites also contain variable proportions of Fe^{3+} iron, a portion of which occurs in tetrahedral coordination in the Lost Creek (Fig. 7) and Cape Ann (Fig. 8) specimens. Of the 15 specimens studied, the Pikes Peak annite with ~11% Fe^{3+}_{oct} and negligible Fe^{3+}_{tet} comes closest to Winchell's (1925) definition of annite as the Fe^{2+} analogue of phlogopite. The Mössbauer spectrum of annite from the type locality at Cape Ann (Fig. 8) shows comparable amounts of Fe^{2+} and Fe^{3+} ions, confirming Dana's (1868) description of this specimen as
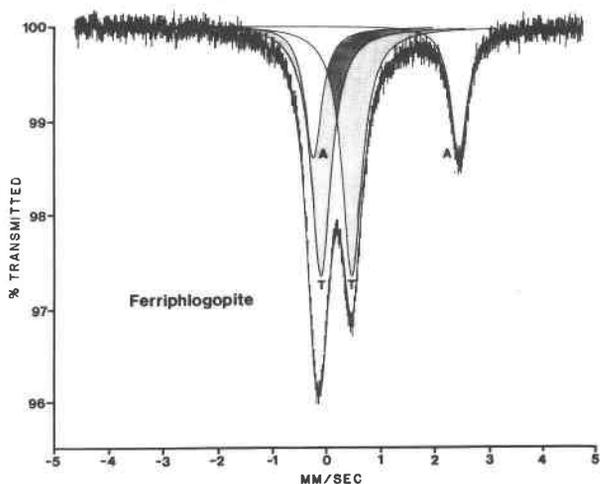
a Fe^{3+}-rich biotite. The annite from Lost Creek (Fig. 7), although containing high concentrations of Al and F, has Mössbauer parameters for the two Fe^{2+} doublets that are comparable to the ranges obtained for the other natural biotite and annite specimens (Table 4). The approximate 2:1 ratio of peak areas for the Lost Creek annite also indicates that Fe^{2+} and Al^{3+} ions are both randomly distributed over *cis*-M2 and *trans*-M1 sites. The fact that F in the Lost Creek annite, and to a lesser extent in the Pikes Peak annite, does not significantly affect their Mössbauer spectra is surprising, since the two well-resolved Fe^{2+} doublets in the synthetic fluorannite spectrum (Fig. 9) have the lowest quadrupole splittings of all ferruginous micas measured (Table 4).
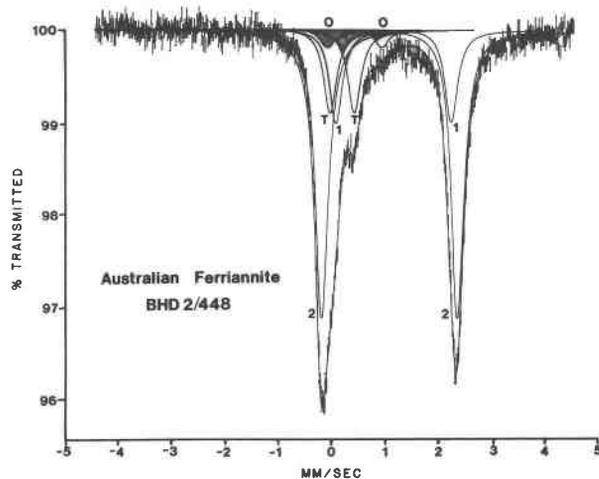

Fig. 6. Mössbauer spectrum of ferriannite BHD2/448 (specimen 10) from a banded iron formation. The majority of Fe^{3+} ions are in tetrahedral sites; peaks 1-1—Fe^{2+}_{oct} in *trans*-M1; peaks 2-2—Fe^{2+}_{oct} in *cis*-M2; peaks T-T—Fe^{3+}_{tet}; peaks 0-0—Fe^{3+}_{oct}.
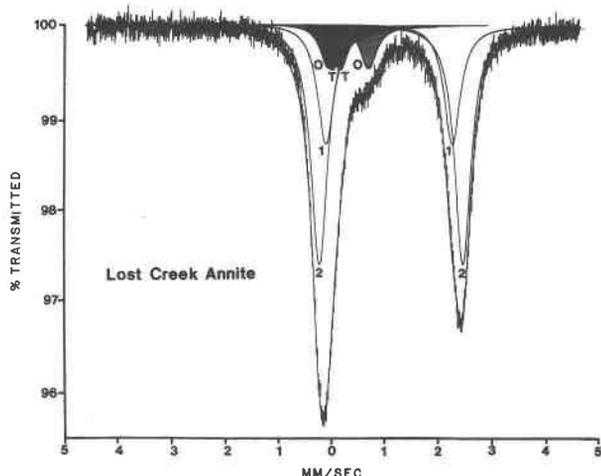
Fig. 7. Mössbauer spectrum of annite from Lost Creek, Montana (specimen 12); peaks 1-1—Fe_{oct}^{2+} in *trans*-M1; peaks 2-2—Fe_{oct}^{2+} in *cis*-M2; peaks T-T—Fe_{tet}^{3+}; peaks 0-0—Fe_{oct}^{3+}.

Fig. 9. Mössbauer spectrum of synthetic fluorannite (specimen 15); peaks 1-1—Fe_{oct}^{2+} in *trans*-M1; peaks 2-2—Fe_{oct}^{2+} in *cis*-M2.

DISCUSSION

This study was conceived to address recurring problems concerning the crystal chemistry of iron in ferruginous micas. Some of the uncertainties raised in the introduction may now be discussed in the light of results obtained in the present study.

Distinguishable iron-cation species

The ease with which the two Fe^{2+} doublets in the Mössbauer spectra of biotites and annites were resolved, coupled with the consistency of their isomer shift and quadrupole splitting parameters, proves that Fe^{2+} ions in the *cis*-M2 and *trans*-M1 positions are readily distinguishable. Furthermore, the approximate 2:1 peak-area ratios of specimens close to endmember annite compositions
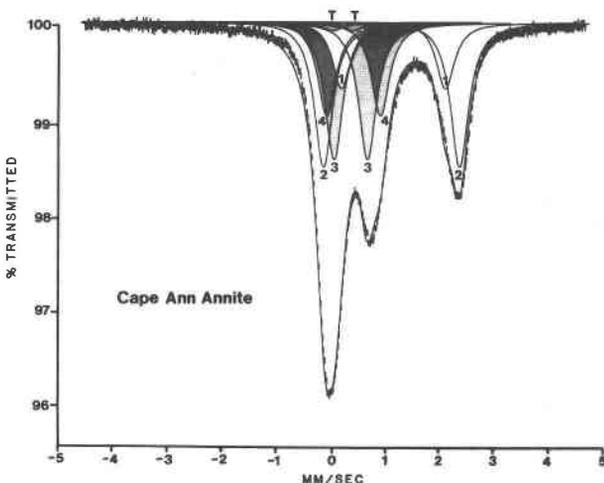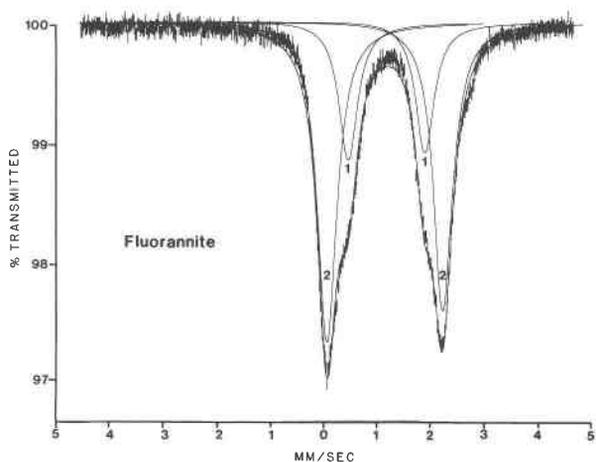

Fig. 8. Mössbauer spectrum of annite from the type locality at Cape Ann, Massachusetts (specimen 14); peaks 1-1—Fe_{oct}^{2+} in *trans*-M1; peaks 2-2—Fe_{oct}^{2+} in *cis*-M2; peaks 3-3—Fe_{oct}^{3+} in *cis*-M2; peaks 4-4—Fe_{oct}^{3+} in *trans*-M1; peaks T-T —Fe_{tet}^{3+}.

confirms the assignment of the outermost and innermost Fe^{2+} doublets to Fe^{2+} ions in the *cis*-M2 and *trans*-M1 sites, respectively. Note that similar peak resolution and assignments apply to Mössbauer spectra of alkali amphiboles (Bancroft and Burns, 1969), in which the amphibole M1 and M3 octahedra have similar hydroxyl anion configurations as the mica *cis*-M2 and *trans*-M1 octahedra, respectively. We conclude, therefore, that so far as octahedral Fe^{2+} ions are concerned, one of Mineeva's (1978) assertions is incorrect; Mössbauer spectra of biotites *do* distinguish between *cis*-M2 and *trans*-M1 sites.

However, in ferriphlogopite and ferriannites, the presence of Fe^{3+} ions in tetrahedral coordination appears to shift peaks, lowering resolution and possibly reversing assignments of the Fe^{2+} doublets. This effect may be augmented by the presence of octahedral Mg^{2+} cations and by severe deficiencies of alkali-metal ions in interlayer positions.

Peak resolution and assignment of the Fe^{3+} doublets is not clear-cut. On the one hand, tetrahedral Fe^{3+} ions, which are readily identified in the Mössbauer spectra of ferriphlogopite and ferriannite specimens, yield just one Fe^{3+} doublet that is unambiguously assigned to Fe^{3+} ions substituting for Si and Al in the silicate layers of the 1M mica structure. On the other hand, the assignment of octahedral Fe^{3+} doublets remains controversial. In this study, two doublets with isomer shifts consistent with Fe_{oct}^{3+} ions could be resolved in all biotites and in some annite and ferriannite specimens. Although such two-Fe^{3+}-doublet fits for these specimens are statistically superior to a one-Fe^{3+}-doublet fit, the quadrupole splitting parameters display a range of values owing to acute problems of resolving two Fe_{oct}^{3+} doublets in the heavily overlapping region of the spectrum near zero velocity where the more intense low-velocity Fe^{2+} peaks occur. Mineeva (1978) suggested that Fe^{3+} ions in mica *cis*-M2 and *trans*-M1 octahedra cannot be distinguished and implied that two-Fe^{3+}-doublet fits

Table 5. Formula proportions for ferruginous micas, based on analytical and Mössbauer data

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Si	5.466	5.492	5.608	5.489	5.201	5.271	5.356	5.942	6.507	5.846	6.060	5.856	5.508	5.491
Al_{iv}	2.534	2.508	2.392	2.511	2.799	2.729	2.644	1.286	0.177	1.048	1.086	1.844	2.492	2.145
Fe^{3+}_{iv}	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.772	1.316	1.106	0.854	0.300	0.000	0.364
Sum Tet	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000
Al_{vi}	0.402	0.231	0.335	0.182	0.648	0.810	0.804	0.299	0.000	0.000	0.000	1.884	0.012	0.000
Ti	0.176	0.317	0.193	0.286	0.290	0.160	0.160	0.013	0.000	0.019	0.002	0.067	0.437	0.431
Fe^{3+}_{vi}	0.659	0.574	0.615	0.646	0.264	0.374	0.263	0.000	0.167	0.238	0.296	0.300	0.566	2.253
Mg	2.505	2.124	2.722	2.621	2.176	2.141	2.145	5.108	1.509	0.769	2.702	0.010	0.235	0.074
Fe^{2+}	1.781	2.160	1.663	1.838	2.379	2.297	2.364	0.473	4.221	4.766	2.956	2.396	4.152	2.159
Mn	0.107	0.042	0.054	0.052	0.020	0.000	0.008	0.005	0.000	0.000	0.004	0.217	0.089	0.062
Sum Oct	5.630	5.448	5.582	5.625	5.777	5.782	5.744	5.898	5.897	5.792	5.960	4.874	5.491	4.979
Ca	0.092	0.088	0.096	0.092	0.002	0.000	0.000	0.000	0.067	0.115	0.002	0.002	0.073	0.000
Na	0.088	0.073	0.069	0.061	0.119	0.099	0.079	0.028	0.000	0.000	0.046	0.049	0.154	0.025
K	1.591	1.924	1.625	1.621	1.630	1.560	1.691	1.905	1.396	2.062	1.669	1.966	1.752	1.658
Sum A	1.771	2.085	1.790	1.774	1.751	1.659	1.770	1.933	1.463	2.177	1.717	2.107	1.979	1.683
$Fe^{3+}/\Sigma Fe$	0.27	0.21	0.27	0.26	0.10	0.14	0.10	0.62	0.26	0.22	0.28	0.20	0.12	0.52
cis M2														
Fe^{3+}	0.390	0.328	0.342	0.373	0.159	0.160	0.131	0.000	0.056	0.000	0.173	0.200	0.206	1.284
Fe^{2+}	1.391	1.558	1.344	1.341	2.136	1.923	1.970	0.299	2.453	3.605	2.165	1.587	2.768	1.252
trans M1														
Fe^{3+}	0.268	0.246	0.273	0.273	0.106	0.214	0.131	0.000	0.111	0.238	0.123	0.100	0.360	0.969
Fe^{2+}	0.390	0.601	0.319	0.497	0.243	0.374	0.394	0.000	1.768	1.161	0.791	0.809	1.384	0.907
Fe^{3+} cis M2/trans M1	1.455	1.333	1.253	1.366	1.500	0.748	1.000	-	0.504	-	1.406	2.000	0.572	1.325
Fe^{2+} cis M2/trans M1	3.567	2.592	4.213	2.698	8.790	5.142	5.000	-	1.387	3.105	2.737	1.962	2.000	1.380

could represent differences of next-nearest-neighbor environments induced by vacancies, cation clustering, etc., in adjacent cis-M2 and trans-M1 sites. Therefore it remains unclear whether the two doublets actually represent two sites or whether they represent different defect distributions independent of site occupancies.

Proportions of Fe^{3+}

Although Mössbauer spectroscopy provides a nondestructive technique for identifying coexisting Fe^{2+} and Fe^{3+} ions in minerals, the task of estimating accurately the proportions of Fe^{2+} and Fe^{3+} still present formidable problems so far as micas are concerned. Effects of oxidation during sample preparation, preferred orientation of the mica flakes, and different recoil-free fractions of the cations may all bias the peak-area data toward spuriously high percentages of Fe^{3+} ions. This study has confirmed that reproducible Fe^{3+}/Fe^{2+} ratios for micas can be obtained provided adequate precautions are taken when mounting pulverized mica crystals prior to a Mössbauer spectral measurement. However, it is worth noting that samples are usually supplied to the mineral spectroscopist as sieved mineral separates of uniform grain size. Oxidation of Fe^{2+} may have occurred beforehand during comminution of a bulk rock sample to particle sizes amenable to mineral beneficiation by hand-picking, heavy liquid, and magnetic separation techniques.

Cation ordering

The structural data for a variety of trioctahedral 1M micas summarized in Table 2 indicate that the cis-M2 and trans-M1 octahedra have comparable dimensions and distortions. The average metal–oxygen distances of the cis-M2 octahedra are perhaps marginally smaller than those of the trans-M1 octahedra. As noted earlier, the most noticeable differences between the two octahedral sites are the configurations of the two hydroxyl anions constituting the coordination polyhedra and the arrangements of next-nearest-neighbor cation sites. Therefore, structural characteristics alone provide little insight into predicting preferred cation site occupancies. The Mössbauer spectral data, however, provide direct evidence of Fe^{2+} and Fe^{3+} site occupancies and, in some cases, indirect evidence of Mg^{2+}, Al^{3+}, and Ti^{4+} site enrichments.

Table 5 summarizes the chemical formulae of the naturally occurring mica specimens studied here, recalculated from the data in Table 3 by using the Fe^{3+} and Fe^{2+} cation proportions determined from the Mössbauer spectral peak-area data. The recalculated formula proportions show that the cis-M2/trans-M1 ratio data for Fe^{2+} in Table 5 generally exceed the ideal 2:1 site multiplicity ratio, indicating that Fe^{2+} ions are relatively enriched in the cis-M2 positions. This observation confirms results obtained earlier (Bancroft and Brown, 1975) for biotites from igneous rocks. Our results for metamorphic biotites indicate that Fe^{2+}

ions are even more highly enriched in *cis*-M2 octahedra than they are in igneous biotites. Whether the surplus of Fe^{2+} ions in *cis*-M2 positions is induced by vacancies in *trans*-M1 positions or is caused by cation ordering of Mg^{2+}, Al^{3+}, and Ti^{4+} ions in *trans*-M1 sites is impossible to evaluate from the Mössbauer spectral data for biotites. The closeness of the *cis*-M2/*trans*-M1 ratio to 2:1 for the Lone Creek annite (specimen 12 containing high Al^{3+}_{oct}) and the Pikes Peak annite (specimen 13 containing high Ti^{4+}) may suggest that Al^{3+} and Ti^{4+} have no strong site preferences in these Fe^{2+}-rich specimens. Therefore, it is probably Mg^{2+} ions that are relatively enriched in the *trans*-M1 positions of biotites, and this factor contributes to Fe^{2+} enrichments in *cis*-M2 positions of these specimens. Strong Mg^{2+} ion enrichments in *trans*-M1 positions are also suggested by the Mössbauer spectral data of ferriphlogopite and two ferriannites (specimens 8, 9, and 11).

Tetrahedral Fe^{3+}

This study demonstrates for the first time by Mössbauer spectroscopy that Fe^{3+} ions occur in tetrahedral coordination in naturally occurring ferriannites. Wones (1963) had earlier synthesized and established the stability field of ferriannite. He predicted that similar mica compositions might occur naturally in rocks devoid of Al, such as iron formations and evaporite deposits. Subsequently, Miyano and Miyano (1982) and M. J. Gole (pers. comm.) described such ferriannites in metamorphosed iron formations. These authors deduced from microprobe analytical data that tetrahedrally coordinated Fe^{3+} is present in these metamorphic ferriannites because there is insufficient (Si + Al) to completely fill the tetrahedral sites in the phyllosilicate layers. The Mössbauer spectral data for specimens 9–11 confirm the presence of tetrahedral Fe^{3+} ions in naturally occurring ferriannites and correlate with previous measurements of ferriphlogopite (Steinfink, 1962; Annersten, 1975).

The occurrence of small proportions of tetrahedral Fe^{3+} ions in the Lone Creek and Cape Ann annites is unexpected, since both of these specimens contain a surplus of (Si + Al) to fill the tetrahedral sites. The occurrence of some Fe^{3+} ions in the tetrahedral layer may be rationalized by polyhedral distortion criteria (Bailey, 1984a; Hazen and Wones, 1972). The high Fe^{2+} content of annite induces expansion of the octahedral (hydroxyl) layer that may be compensated for by enlargement of the tetrahedral (silicate) layer. This can be achieved by accommodating the larger (i.e., relative to Si^{4+} and Al^{3+}) Fe^{3+} cations in the tetrahedral sites (Hazen and Wones, 1972).

CONCLUSIONS

Nomenclature. Annite from the type locality at Cape Ann, Massachusetts, is a Fe^{3+}-rich mica as originally defined by Dana (1868). The Fe^{3+} ions, however, occur mostly in octahedral sites with small amounts in tetrahedral coordination. The annite from Pikes Peak, Colorado, comes closest to Winchell's (1925) concept of annite as

the Fe^{2+} analogue of phlogopite. Ferriannite, hitherto known as a synthetic phase (Wones, 1963), is confirmed to be a naturally occurring mineral in metamorphosed iron formations (e.g., Miyano and Miyano, 1982; M. J. Gole, pers. comm.) by the positive identification of tetrahedral Fe^{3+} ions by Mössbauer spectroscopy.

Cation-site terminology. Since the two octahedral sites are so clearly distinguished by the configuration of the hydroxyl anions, there is no longer cause for confusing them with the designated *cis*-M2 and *trans*-M1 positions having a site multiplicity ratio of 2:1.

Cations distinguishable in a Mössbauer spectrum. The annite and fluorannite spectra demonstrate that octahedral Fe^{2+} in *cis*-M2 and *trans*-M1 positions may be resolved as the outermost and innermost Fe^{2+} doublets, respectively. The doublet representing tetrahedral Fe^{3+} is also characterized in ferriphlogopite and ferriannite Mössbauer spectra. However, the poor resolution of doublets attributed to octahedral Fe^{3+} ions in micas containing low concentrations of Fe^{3+} may not belay the ambiguity of peak assignments in biotite Mössbauer spectra (Mineeva, 1978).

Oxidation and preferred orientation. Having confirmed that Mössbauer spectra are adversely affected by oxidation during grinding and by alignment of mica crystallites in holders, this study demonstrates that these problems can be reduced or eliminated through use of adequate precautions during sample preparation. Mixing the mica separate with sugar, grinding wet under acetone, and sprinkling the sugar-coated powder into holders is the procedure recommended for Mössbauer spectral studies of micas.

Cation-site occupancy. The clear distinction between Fe^{2+} ions in *cis*-M2 and *trans*-M1 positions enables confirmation to be made of the relative enrichment of Fe^{2+} in *cis*-M2 positions of biotites (Bancroft and Brown, 1975), particularly in specimens in metamorphic rocks. If the assignment of the Fe^{3+} doublets in biotite Mössbauer spectra is correct, Fe^{3+} ions are slightly enriched in *trans*-M1 positions. Mg, and not necessarily Al or Ti, appears to be enriched in *trans*-M1 positions, particularly in ferriphlogopite and ferriannite. This may be induced by tetrahedral Fe^{3+} and deficiencies of K^+ in interlayer positions.

References

Annersten, H. (1974) Mössbauer studies of natural biotites. American Mineralogist, 59, 143–151.

—— (1975) Mössbauer study of iron in natural and synthetic biotites. Fortschritte der Mineralogie, 52, 583–590.

Annersten, H., and Olesch, M. (1978) Distribution of ferrous and ferric iron in clintonite and the Mössbauer characteristics of ferric iron in tetrahedral coordination. Canadian Mineralogist, 16, 199–203.

Bailey, S.W. (1975) Cation ordering and pseudosymmetry in layer silicates. American Mineralogist, 60, 175–187.

—— (1984a) Crystal chemistry of the true micas. In S.W. Bailey, Ed. Micas. Reviews in Mineralogy, 13, 13–60.

—— (1984b) Review of cation ordering in micas. Clays and Clay Minerals, 32, 81–92.

Bancroft, G.M., and Brown, J.R. (1975) A Mössbauer study of coexisting hornblendes and biotites: Quantitative Fe^{3+}/Fe^{2+} ratios. American Mineralogist, 60, 265–272.

Bancroft, G.M., and Burns, R.G. (1969) Mössbauer and absorption spectral study of alkali amphiboles. Mineralogical Society of America Special Paper 2, 137–148.

Barker, F., Wones, D.R., Sharp, W.N., and Desborough, G.A. (1975) The Pikes Peak batholith, Colorado Front Range, and a model for the origin of the gabbro-anorthosite-syenite-potassic granite suite. Precambrian Research, 2, 97–160.

Bowen, L.H., Weed, S.B., and Stevens, J.G. (1969) Mössbauer study of micas and their potassium depleted products. American Mineralogist, 54, 72–84.

Chandra, R., and Lokanathan, S. (1977) Electric field gradient in biotite mica. Physica Status Solidi, (b), 83, 273–280.

Cooke, J.P., Jr. (1867) On cryophyllite, a new mineral species of the mica family, with some associated minerals in the granite of Rockport, Mass. American Journal of Science, 2nd series, 43, 217–230.

Dana, E.S. (1892) The system of mineralogy, 6th edition. Wiley, New York.

Dana, J.D. (1868) A system of mineralogy, 5th edition. Wiley, New York.

Dodge, F.C.W., Smith, V.C., and Mays, R.E. (1969) Biotites from granitic rocks of the central Sierra Nevada batholith, California. Journal of Petrology, 10, 250–271.

Donnay, G., Morimoto, N., Takeda, H., and Donnay, J.D.H. (1964) Trioctahedral one-layer micas. I. Crystal structure of a synthetic iron mica. Acta Crystallographica, 17, 1369–1373.

Dyar, M.D. (1984) Precision and interlaboratory reproducibility of measurements of the Mössbauer effect in minerals. American Mineralogist, 69, 1127–1144.

Embrey, P., and Fuller, J.P. (1980) A manual of new mineral names 1892–1978. Oxford University Press, London, 468 p.

Finch, J., Gainsford, A.R., and Tennant, W.C. (1982) Polarized optical absorption and ^{57}Fe Mössbauer study of pegmatitic muscovite. American Mineralogist, 67, 59–68.

Foster, M.D. (1960) Interpretation of the composition of trioctahedral micas. Geological Survey Professional Paper 354-B, 68 p.

Gendler, T.S., Daynyak, L.G., and Kuz'min, R.N. (1978) Parameters of the Mössbauer spectrum of Fe^{3+} ions in biotite, and continuity of biotite-oxybiotite transition at 300–900 K. Geochemistry International, 15, 17–22.

Goodman, B.A. (1976) The Mössbauer spectrum of a ferrian muscovite and its implications in the assignment of sites in dioctahedral micas. Mineralogical Magazine, 40, 513–517.

Goodman, B.A., and Wilson, M.J. (1973) A study of the weathering of biotite using the Mössbauer effect. Mineralogical Magazine, 39, 448–454.

Hazen, R.M., and Burnham, C.W. (1973) The crystal structure of one-layer phlogopite and annite. American Mineralogist, 58, 889–900.

Hazen, R.M., and Wones, D.R. (1972) The effect of cation substitutions on the physical properties of trioctahedral micas. American Mineralogist, 57, 103–129.

Heller-Kallai, L., and Rozenson, I. (1981) The use of Mössbauer spectroscopy of iron in clay mineralogy. Physics and Chemistry of Minerals, 7, 223–238.

Mineeva, R.M. (1978) Relationship between Mössbauer spectra and defect structure in biotites from electric field gradient calculations. Physics and Chemistry of Minerals, 2, 267–277.

Miyano, T., and Miyano, S. (1982) Ferri-annite from the Dales Gorge Member iron-formations, Wittenoon area, Western Australia. American Mineralogist, 67, 1179–1194.

Ohta, T., Takeda, H., and Takeuchi, Y. (1982) Mica polytypism: Similarities in the crystal structures of coexisting 1M and $2M_1$ oxybiotite. American Mineralogist, 67, 298–310.

Pabst, A. (1955) Redescription of the single layer structure of the micas. American Mineralogist, 40, 967–974.

Radoslovich, E.W., and Norrish, K. (1962) The cell dimensions and symmetry of layer-lattice silicates. I. Some structural considerations. American Mineralogist, 47, 599–616.

Rayner, J.H. (1974) The crystal structure of phlogopite by neutron diffraction. Mineralogical Magazine, 39, 850–856.

Richardson, S.M., and Richardson, J.W. (1982) Crystal structure of a pink muscovite from Archer's Post, Kenya: Implications for reverse pleochroism in dioctahedral micas. American Mineralogist, 67, 69–75.

Ruby, S.L. (1973) "Why Misfit when you already have χ^2?" In I.J. Gruverman and C.W. Seidel, Eds. Mössbauer effect methodology 8, 263–276. Plenum Press, New York.

Sanz, J., de la Calle, C., and Stone, W.E.E. (1984) NMR applied to minerals. V. The localization of vacancies in the octahedral sheet of aluminous biotites. Physics and Chemistry of Minerals, 11, 235–240.

Semenova, T.F., Rozhdestvenskaya, I.V., Frank-Kamenetskii, V.A., and Pavlishin, V.I. (1983) Crystal structure of tetraferriphlogopite and tetraferribiotite. Mineralogical Zhurnal, 5, 41–49 (in Russian).

Steinfink, H. (1962) Crystal structure of a trioctahedral mica: Phlogopite. American Mineralogist, 47, 886–896.

Stone, A.J., Parkin, K.M., and Dyar, M.D. (1984) STONE: A program for resolving Mössbauer spectra. DEC User's Society Program Library, #11-720, Marlboro, Massachusetts.

Takeda, H., and Ross, M. (1975) Mica polytypes: Dissimilarities in the crystal structures of coexisting 1M and $2M_1$ biotite. American Mineralogist, 60, 1030–1040.

Wahl, W. (1925) Die Gesteine des Wiborger Rapakiwigebietes. Fennia (Geographical Society of Finland Bulletin), 45, 87.

Winchell, A.N. (1925) Studies in the mica group. American Journal of Science 5th series, 9, 309–327.

Wones, D.W. (1963) Phase equilibria of "ferriannite," $KFe_3^{2+}Fe^{3+}Si_3O_{10}(OH)_2$. American Journal of Science, 261, 581–596.