

MÖSSBAUER STUDY OF MICAS AND THEIR POTASSIUM-DEPLETED PRODUCTS

L. H. BOWEN, S. B. WEED AND J. G. STEVENS
*Departments of Chemistry and Soil Science,
North Carolina State University,
Raleigh 27607.*

ABSTRACT

The Mössbauer spectrum of iron in both dioctahedral and trioctahedral micas can be used to determine nondestructively the ferrous and ferric iron content. Variations in isomer shift and quadrupole splitting among the micas have been correlated with chemical and structural variations. The Mössbauer spectra of potassium-depleted micas are characteristic of the parent structure, except for changes in oxidation state.

INTRODUCTION

The micas form an important class of layered silicates of general formula $KM_2^{3+}AlSi_3O_{10}(OH)_2$ or $KM_3^{2+}AlSi_3O_{10}(OH)_2$. The metal ion M exists in octahedral coordination between tetrahedral layers of SiO_2 . Depending on the fraction of octahedral sites filled, a mica can be classified as dioctahedral ($M = Al^{3+}$ or other trivalent cation) or trioctahedral ($M = Mg^{2+}$ or other divalent cation). Naturally occurring micas usually contain a variety of elements, often including iron in the octahedral layer. The interlayer K^+ can be removed, and a first step in natural weathering of micas is generally considered to be replacement of interlayer K^+ by Mg^{2+} , Ca^{2+} , H_3O^+ , or Al^{3+} , with accompanying hydration and expansion of the crystal structure between the layers. Weathering proceeds at very different rates for the various micas, being slower by several orders of magnitude for dioctahedral than for trioctahedral micas.

The Mössbauer effect (Mössbauer, 1958) has found many applications in solid-state chemistry and physics. In particular, the technology of iron Mössbauer spectroscopy has been developed to a greater extent than that of any other element. Applications to silicate mineralogy have been summarized in recent articles (Bancroft, Maddock, and Burns, 1967; Weaver, Wampler, and Pecuil, 1967). Because the technique enables one to obtain information concerning iron in a solid structure as to oxidation state, coordination geometry, and local electron density, it provides a unique probe for investigating the role of iron in mica weathering and for studying the variation of iron sites in the large variety of naturally occurring micas. The present study was undertaken in order to apply the technique to the chemical problem of mica interlayer alteration, as well as to test the reliability of quantitative determination of ferrous and ferric iron in micas and their potassium-depleted products using Mössbauer spectroscopy.

THEORY

The basic principles of the Mössbauer effect have been well presented in books (see, for example, Wertheim, 1964). To observe the effect one must have a radioactive source of low energy gamma radiation and an absorber containing the same isotope. For iron the source is the 14.4 keV excited state of Fe^{57} , produced by electron capture in 270 day Co^{57} . Natural iron contains 2.2 percent Fe^{57} , so that in principle any iron-containing compound may be used as an absorber. In solids the possibility exists for recoil-free emission and absorption of the 14.4 keV gamma radiation, which is the Mössbauer effect.

Because of the extraordinarily narrow line width (about 10^{-8} eV for Fe^{57}), small interactions between the nucleus and surrounding electron cloud are observable, and these interactions are of primary interest in chemical applications. The interactions are electromagnetic in origin, and cause the 14.4 keV transition in the absorber to be slightly changed in energy. Because of the narrow line width, slight changes in transition energy prevent resonant absorption of the gamma ray. Varying the gamma ray energy externally until resonant absorption is observed allows determination of the changes which have occurred in the absorber transition energy. Although magnetic dipole interactions are important in some materials, this paper will be concerned only with the electric monopole and quadrupole interactions. The first is due to variations in electron density at the nucleus, and is the primary cause of the isomer shift, I.S., which is the energy shift necessary for resonance in a given absorber relative to a standard. In the case of Fe^{57} , the isomer shift depends strongly on the oxidation state of iron and less strongly on the nature of the coordinating anions and degree of covalency. The quadrupole interaction is a splitting of the nuclear levels due to the interaction between the nuclear quadrupole moment and the electric field gradient. For Fe^{57} a nonzero field gradient causes the single line transition to split into two peaks corresponding to $\frac{1}{2}-\frac{1}{2}$ and $\frac{3}{2}-\frac{1}{2}$ nuclear spin transitions. The energy difference between the two peaks, called the quadrupole splitting, Q.S., is determined by the crystal geometry as well as the nature of the coordinating ligands about the iron.

Finally, different absorbers differ widely in the fraction of gamma rays absorbed without recoil (f). For an appreciable effect, f must approach unity. In general, f increases at low temperatures and for strongly-bonded crystal structures. The wide-spread use of Fe^{57} is due primarily to the large f values at room temperature for many iron-containing solids.

EXPERIMENTAL

Nuclear. The usual method, to vary the gamma energy and trace out the Mössbauer absorption line, is an application of the Doppler effect. Relative motion between source and

absorber adds or subtracts an energy increment $\Delta E = E(v/c)$, where v is the relative speed and c the speed of light. In terms of relative speed, the natural line width of the Fe^{57} resonant peak is about 0.2 mm/sec. Therefore, speeds of several mm/sec are adequate to trace out the absorption spectrum *versus* energy.

Both constant velocity and constant acceleration spectrometers have been used in this work, in conjunction with a 512 channel analyzer and xenon-methane proportional detector. The source was 2 mC Co^{57} diffused in palladium, and all spectra were taken at room temperature.

In order to minimize orientation effects, finely-ground (1–5 μm) micas were mixed with dextrose for uniform distribution over the sample area. The layer structure of a mica such as biotite causes a marked asymmetry between the two peaks of the quadrupole doublet (Pollak, de Coster, and Amelinckx, 1962). Random orientation should equalize the peak intensities except for second-order effects. In this work there was no evidence for asymmetry in the ground micas. One of the biotite flake samples had an intensity ratio of 1.9 to 1, comparable to that of earlier work (Pollak, de Coster, and Amelinckx, 1962). However, the ground sample of the same mica had a completely symmetric doublet (see Fig. 1A).

Typical spectra are shown in Figures 1 and 2. The counts from the 14.4 keV gamma collected per unit time are shown *versus* relative velocity. The units of count rate are arbitrary; the important feature is that a decrease in count rate must be due to resonant absorption by the absorber. Therefore a velocity of minimum observed count rate corresponds to an energy of maximum absorption. These spectra have been analyzed (Figs. 1A and 1B) by a computer program developed in 1966 at Argonne National Laboratory by W. C. Davidson and modified by us for use with an IBM 360/75. This program assumes the spectrum to be a sum of peaks, each having the Lorentzian line shape:

$$y/y_0 = 1 - \alpha/[1 + (4/\beta^2)(x - x_0)^2] \quad (1)$$

where y is the counting rate at velocity x , α the fractional effect, β the width at half maximum, and x_0 the velocity of maximum resonance. The program iterates to find the values of α , β , x_0 and y_0 which best fit the data. The number of peaks must be assumed, and constraints, such as equal values of β , may be imposed.

The typical fit (see Figs. 1A or 1B) has four peaks consisting of two symmetric doublets of equal β . The widely-spaced doublet is due to ferrous iron and the narrow one to ferric (Weaver, Wampler and Pecuil, 1967). The product $\alpha\beta$, or relative intensity, is a measure of the ferrous or ferric iron content. The quadrupole splitting, Q.S., is the velocity difference between the two peaks of a doublet, while the isomer shift, I.S., is the velocity difference between the center of a doublet and a standard. We used the center of the sodium nitroprusside doublet as zero velocity.

Chemical. The micas studied are listed in Table 1. Total chemical analyses of the micas were performed according to the procedures of Shapiro and Brannock (1956). The method of Reichen and Fahey (1962) was used to determine ferrous iron in parent and K^+ depleted micas. Potassium was removed from parent micas by treatment with sodium tetraphenylboron (Reed and Scott, 1962) to form K^+ depleted, *i.e.*, "weathered" products, which were then converted to the Ca^{2+} or Mg^{2+} product.

The samples studied were obtained by grinding sheets selected from hand specimens of single mica books. Materials were ground under water, separated into fractions, and the 1–5 μ size fraction taken for study.

RESULTS

Relative intensities. The area under a Mössbauer absorption line is related to the number of absorbing nuclei per unit area in the absorber. For a

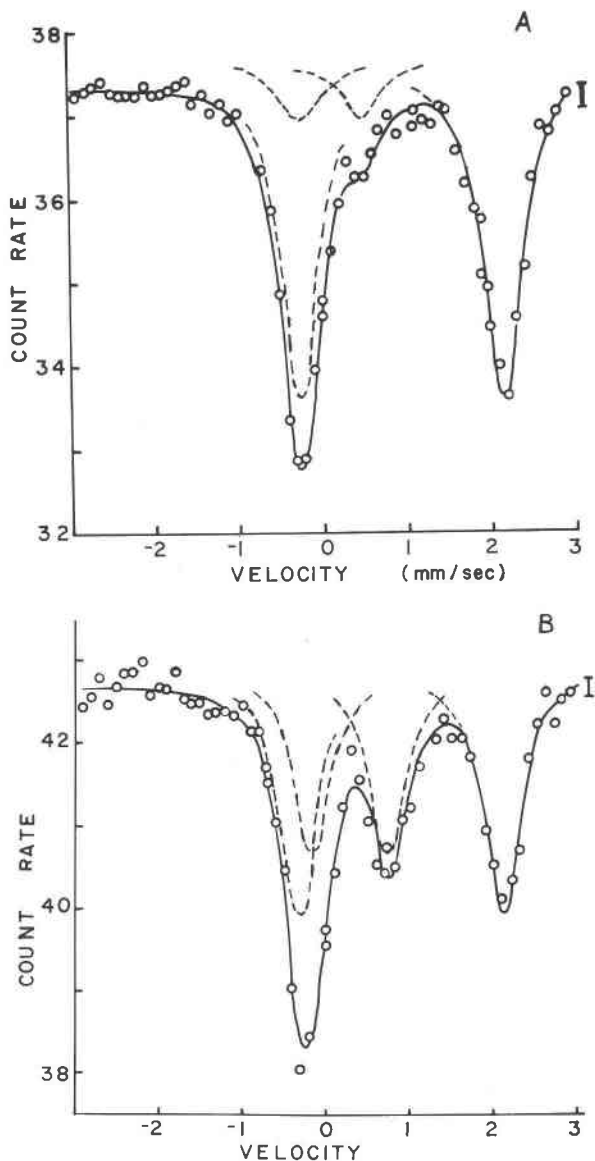


FIG. 1. Mössbauer spectra for (A) untreated and (B) magnesium-saturated biotite B3. Relative count rate *versus* absorber velocity is shown. The solid lines are computer fits to the data. The peak at -0.3 mm/sec is a superposition of both Fe^{2+} and Fe^{3+} lines; the upper halves of the two doublets are well separated. The four individual peaks are indicated by dashed curves. Note the increased intensity of the Fe^{3+} peaks for the magnesium-saturated sample, corresponding to increased oxidation of iron.

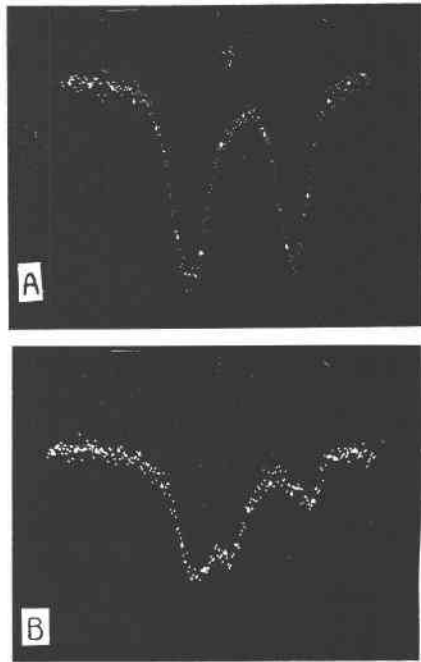


FIG. 2. Mössbauer spectra for (A) untreated biotite B2 and (B) untreated muscovite M6. The large fraction of oxidized iron in the muscovite is readily apparent. The outer two peaks (ferrous doublet) in the muscovite have a larger splitting than in the biotite. These spectra are directly photographed from the oscilloscope trace of relative count rate *versus* multichannel analyzer channel number. The channel number is a linear function of absorber velocity.

Lorentzian line shape, the relationship has been tabulated (Hafemeister and Shera, 1966). In the limit of very thin absorber:

$$A = \frac{1}{2}\pi\Gamma_0\sigma_0ff'w \quad (2)$$

where Γ_0 and σ_0 are the natural line width and absorption cross section, f and f' are recoil-free fractions for source and absorber, and w is the number of absorbing nuclei per unit area. Using parameters for Fe^{57} (Muir, Ando and Cooper, 1966), the relative intensity R.I. ($=\alpha\beta$) for a quadrupole doublet is:

$$\text{R.I.} = (0.027 ff') \times (\text{mg Fe/cm}^2) \quad (3)$$

As the iron content increases, the relative intensity saturates and the line shape is no longer Lorentzian.

For a given absorber containing more than one distinguishable site for iron, the relative intensities of the Mössbauer peaks will give relative site

TABLE 1. STRUCTURAL FORMULAS OF MICAS STUDIED^a

Trioctahedral Micas	
Biotites	
B1	$K_{0.88}Na_{0.04}(Fe^{2+}_{1.11}Fe^{3+}_{0.14}Al_{0.48}Mg_{0.89}Ti_{0.14})(Si_{2.55}Al_{1.45})O_{10}(OH)_{1.92}F_{0.07}$
B2	$K_{0.90}Na_{0.03}(Fe^{2+}_{1.45}Fe^{3+}_{0.24}Al_{0.68}Mg_{0.24}Ti_{0.05})(Si_{2.48}Al_{1.51})O_{10}(OH)_{1.84}F_{0.16}$
B3 ^b	$K(Fe, Mg)_3(AlSi_3)O_{10}(OH)_2$
Phlogopite	
Pl	$K_{0.81}Na_{0.06}(Fe^{2+}_{0.29}Fe^{3+}_{0.08}Al_{0.46}Ti_{0.07}Mg_{2.02})(Si_{2.56}Al_{1.43})O_{10}(OH)_2$
Diocahedral Micas	
Muscovites	
M4	$K_{0.88}Na_{0.06}(Fe^{2+}_{0.16}Fe^{3+}_{0.17}Al_{1.64}Mg_{0.04}Li_{0.06})(Si_{3.05}Al_{0.94})O_{10}(OH)_{1.99}F_{0.01}$
M6	$K_{0.88}Na_{0.05}(Fe^{2+}_{0.16}Fe^{3+}_{0.23}Al_{1.65}Mg_{0.04}Li_{0.03})(Si_{3.04}Al_{0.96})O_{10}(OH)_{1.99}F_{0.01}$
Glaucanite	
G ^b	$K(Fe)_2(AlSi_3)O_{10}(OH)_2$
Nontronite	
N ^b	$Na_{0.67}(Fe)_2(Al_{0.67}Si_{3.33})O_{10}(OH)_2$

^a The biotites B2 and B3, phlogopite, glaucanite, and nontronite were obtained from Wards Natural Science Establishment, Rochester, New York. The other micas were collected in western North Carolina.

^b Specific chemical composition not determined.

populations in a thin absorber. This approach has been used effectively in a number of mineralogical applications (Bancroft, Burns, and Maddock, 1967). However, the variation in f' as the absorbing material is changed generally limits analysis to relative measurements in a single sample.

Computer analysis of the spectra showed evidence only for single sites containing ferrous or ferric iron. The variations in iron sites may broaden the peaks, but do not cause any appreciable deviation from the Lorentzian shape.

In Table 2 a comparison is made between fractional oxidation of iron determined by the ratio of relative intensities and by chemical means. Throughout a range of total iron content, the present technique yields comparable results with chemical methods. The nondestructive nature of the Mössbauer analysis is a great advantage compared to the usual ferrous iron determination in these materials (Reichen and Fahey, 1962). The precision can be improved by lengthening counting time, or especially by increasing the activity of the source.

In addition to relative measurements, it was of interest to test equation (3) experimentally to see how wide a variation is observed in f' among the micas (f being constant for a given source), and also to see over what range the linear relationship holds. This has been tested from 2 to 30 mg/cm² total iron. The relative intensity is plotted *versus* iron content in Figure 3. Without a background correction, the curve saturates at about 10 mg/cm². Corrected for background the curve remains linear over the range studied, with a least-squares slope of $(9.3 \pm 0.3) \times 10^{-3}$ mm/sec per mg/cm², giving $ff' \sim 0.3$. This corresponds to a reasonably large recoil-free fraction in the micas at room temperature. More important, there appears to be no significant variation in f' among any of the micas studied. As a consequence, not only relative percent oxidation, but absolute

TABLE 2. COMPARISON OF FRACTIONAL OXIDATION OF IRON AS DETERMINED BY RELATIVE INTENSITY AND CHEMICAL METHODS

Sample	Total Fe (%)	Fraction Fe Oxidized	
		Relative Intensity	Chemical
B1	15.5	0.17	0.11
B2	20.3	0.13	0.14
P1	4.7	0.22	0.23
M4	4.5	0.42	0.51
M6	4.5	0.64	0.69

ferric and ferrous iron determination in micas appears practicable by this technique.

In Table 3 is shown the fractional oxidation of iron in samples of artificially "weathered" micas. Potassium was rapidly removed from the trioctahedral micas, 90–100 percent of the initial K⁺ being released within several days. The dioctahedral micas released their K⁺ much less readily; and after several weeks of treatment 20–30 percent of the initial K⁺ remained. Potassium could be reintroduced into the products, which were essentially artificially produced vermiculites, to reproduce the micas or mica-like structure. In all cases the leached samples resaturated with K⁺ exhibited the characteristic 10 Å mica spacing, whereas the Ca²⁺ or Mg²⁺ product showed the 15 Å spacing typical of expanded mica, *i.e.*, vermiculite. The intermediate (48% of original K⁺) in the resaturation of biotite B2 had a basal spacing of 25 Å characteristic of a regular alternation of K⁺ and Ca²⁺ interlayers, whereas that of the phlogopite P1 showed random introduction of K⁺. A large fraction of the original ferrous iron was oxidized in every case except those samples (M6 and G) originally con-

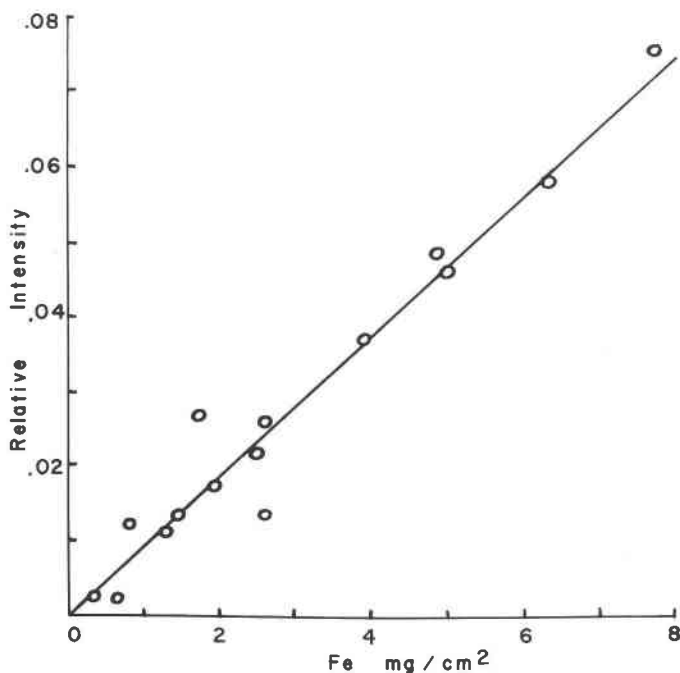
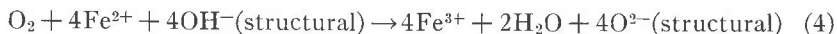


FIG. 3. Relative intensity *versus* iron content for micas. Both dioctahedral and trioctahedral micas are included, and both Fe^{2+} and Fe^{3+} peaks. A background counting correction has been made. Within experimental error the data fall onto a single straight line up to 30 mg/cm^2 . Only the lower portion is shown.

taining more Fe^{3+} than Fe^{2+} . Resaturation with K^+ left essentially unchanged the ratio of Fe^{3+} to Fe^{2+} observed in the expanded material. The amount of oxidation appears to be independent of total iron content, type of mica, or total layer charge. In trioctahedral micas, according to Newman and Brown (1966), iron oxidation occurs independently of other effects of interlayer alteration, requiring only expansion of the interlayer spacing to allow atmospheric oxygen to reach the iron sites and react according to:



The oxidation observed by Mössbauer spectroscopy is in agreement with this mechanism and with Newman and Brown's chemical studies of the alteration process. According to the above, once the interlayers have been expanded and the iron oxidized, there should be no further change in the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio upon reintroducing K^+ and collapsing the layers, in agreement with the present observations.

TABLE 3. MÖSSBAUER DETERMINATION OF IRON OXIDATION IN ALTERED MICAS

Sample ^a	Total Fe (%)	Fraction Original K ⁺ ^b	Fraction Fe Oxidized
B1 (untreated)	15.5	1.00	0.17
B2 (untreated) ^c	20.3	1.00	0.13
VB2 (Ca)		0.07	0.41
VB2 (Ca/K)		0.48	0.44
VB2 (K)		0.87	0.37
B3 (untreated)	12.4	1.00	0.16
VB3 (Mg)		0.24	0.43
P1 (untreated) ^c	4.7	1.00	0.22
VP1 (Ca)		0.04	0.37
VP1 (Ca/K)		0.61	0.36
VP1 (K)		0.89	0.33
M4 (untreated)	4.5	1.00	0.42
VM4 (Ca)		0.35	0.66
M6	4.5	1.00	0.64
VM6 (Ca)		0.19	0.70
G (untreated)	14.0	1.00	0.91
VG (Ca)		0.21	1.00

^a V refers to micas treated for K⁺-removal. Symbols in parentheses refer to added saturating cations.

^b The fraction of original K⁺ remaining or added is indicated.

^c K⁺ was replaced by reversing the alteration process.

Isomer shifts and splittings. Table 4 gives the isomer shifts and quadrupole splittings observed in this work. The most striking features are the constancy within a mica group and the ease of distinguishing by means of the quadrupole splitting among trioctahedral micas, muscovites, and glauconite.

The isomer shifts for both Fe²⁺ and Fe³⁺ are essentially the same for all the micas studied and are characteristic of ionic compounds. Interlayer cation substitution did not affect the isomer shift except possibly for a slight increase in the case of M6. Since these minerals are ionic, it is expected that interlayer processes should not appreciably change the *s*-electron density at the iron nucleus, and thus the isomer shift should remain constant.

In addition, the quadrupole splittings were not affected by interlayer substitution, with the possible exception again of a muscovite, M4. This result was unexpected, due to the wide variation in the rates of K⁺removal and X-ray patterns of the intermediates, and indicates that not only the *s*-electron density, but the charge distribution about the iron sites is insensitive to chemical alteration of the interlayers. A marked variation in

TABLE 4. ISOMER SHIFTS AND QUADRUPOLE SPLITTINGS OF
MICA SAMPLES AND THEIR ALTERED PRODUCTS

Isomer shifts are relative to sodium nitroprusside. All values are in mm/sec. Values in parenthesis have greater statistical error due to low intensity of the peak.

Sample	Fe ²⁺		Fe ³⁺	
	I.S.	Q.S.	I.S.	Q.S.
B1	1.37	2.47	(0.8)	(0.6)
B2	1.38	2.51	(0.8)	(0.8)
VB2 (Ca)	1.35	2.50	0.70	0.86
VB2 (Ca/K)	1.36	2.48	0.71	0.90
VB2 (K)	1.38	2.44	0.66	1.01
B3	1.37	2.42	(0.6)	(0.6)
VB3 (Mg)	1.34	2.42	0.76	0.88
P1	1.37	2.44	(0.7)	(0.9)
VP1 (Ca)	1.40	2.46	0.63	0.93
VP1 (Ca/K)	1.39	2.44	0.60	0.86
VP1 (K)	1.37	2.50	0.70	0.86
Average, Trioctahedral	1.37±0.02	2.46±0.03	0.68±0.05	0.90±0.05
M4	1.35	2.89	0.64	0.69
VM4 (Ca)	1.36	3.12	0.55	0.67
M6	1.39	2.87	0.64	0.70
VM6 (Ca)	1.48	2.85	0.66	0.68
Average, Muscovite	1.39±0.06	2.93±0.12	0.62±0.05	0.68±0.02
G	(1.5)	(2.3)	0.62	0.45
VG (Ca)	—	—	0.61	0.42
Nontronite (Na)	—	—	0.62	0.38

quadrupole splitting was observed among the various micas, however. The muscovite samples show a splitting for Fe²⁺ considerably larger than the trioctahedral micas. The difference is large enough to be an easily distinguishable feature of the Mössbauer spectra of these materials. The splittings for Fe³⁺ fall into three groups. Once again the muscovites and trioctahedral micas are easily distinguished, but the trioctahedral splittings are the larger. Glauconite and nontronite appear to form a separate group with the smallest Fe³⁺ splittings. Unfortunately, neither of these latter samples had enough Fe²⁺ to classify the ferrous splitting.

Reports have been made recently of shifts and splittings for certain micas. In comparisons the isomer shifts have been adjusted to the nitroprusside standard (Muir, Ando, and Cooper, 1966). Biotite spectra have been reported by several workers (Weaver, Wampler, and Pecuil, 1967; Herzenberg and Toms, 1966; Pollak, de Coster, and Amelinckx, 1962). The two earlier reports assumed two sites of equal population for ferrous

iron in biotite, primarily because of the asymmetric spectra obtained. We have observed that the asymmetry disappears when the biotite is powdered and randomly oriented. Reasonably narrow peak widths (about 0.5 mm/sec) were observed in all the micas. Adding more peaks in the computer analysis did not improve the fit. The conclusion is that there is only one iron site in biotite distinguishable by Mössbauer spectroscopy. The present values for the Fe^{2+} I.S. and Q.S. agree within experimental error with the adjusted ones of Weaver *et al.* (1967) (I.S. = 1.41, Q.S. = 2.40). They report a somewhat smaller splitting (0.60) for Fe^{3+} in a naturally weathered biotite. The computer analysis in the present work provides more precision than graphical methods for overlapping peaks, and may account for small differences.

Weaver, Wampler, and Pecul (1967) also report values for nontronite (Fe^{3+} I.S. = 0.56, Q.S. = 0.6) and glauconite (Fe^{3+} I.S. = 0.61, Q.S. = 0.64; Fe^{2+} I.S. \sim 1.4, Q.S. \sim 2.2). Hofman, Fluck and Kuhn (1967) report Fe^{3+} I.S. = 0.72, Q.S. = 0.57 for glauconite. Malden and Meads (1967) have determined parameters for a muscovite (Fe^{2+} I.S. = 1.37, Q.S. = 2.98; Fe^{3+} I.S. = 0.66, Q.S. = 0.72). The muscovite parameters are in excellent agreement with the present results; the reported Fe^{3+} splittings for nontronite and glauconite are somewhat higher.

DISCUSSION

Because of the relative constancy of the isomer shifts, our discussion will be confined to the observed trends in quadrupole splittings. The splitting for Fe^{2+} is due primarily to localized distortion of the electron cloud at the iron site. Due to the spherical symmetry of the d^5 configuration, a noncubic charge distortion external to the ion is necessary for quadrupole splitting of the Fe^{3+} line. For Fe^{2+} Ingalls has discussed the effect of the crystal field on the quadrupole splitting (Ingalls, 1964) and his interpretation has been used in discussion of results on other silicates (Bancroft, Maddock and Burns, 1967). With perfect octahedral symmetry about Fe^{2+} , no splitting would be observed. Application of an axial field increases the splitting up to a maximum value of 3.7 mm/sec (Ingalls, 1964), but spin-orbit effects, structural contributions, and high temperatures all tend to reduce the splitting observed. For a given axial field, application of a rhombic distortion will also reduce the observed splitting.

The constancy of Q.S. among a mica group indicates the relative unimportance of a number of factors on the electric field gradient. The tri-octahedral micas span a range of iron content from 4.7 to 20.3 percent. Wide variations occur in content of Al, Mg, and other elements (see Table 1). The structure has been expanded, replacing K^+ with Ca^{2+} or

Mg²⁺, and collapsed again. None of these factors affect Q.S. either for Fe²⁺ or Fe³⁺. A similar result was found for the muscovites. However, the Fe²⁺ Q.S. has an average of 2.9 for the muscovites and 2.5 for the trioctahedrals. The value of 2.9 is about the same as the largest values reported for six-coordinate Fe²⁺ in the silicates (Bancroft, Maddock and Burns, 1967). The large Fe²⁺ Q.S. for the muscovites is associated with a Fe³⁺ Q.S. smaller than that for the trioctahedrals. If the Fe³⁺ Q.S. is assumed due to the external geometry, that contribution is smaller for the muscovites. As expected theoretically, a smaller structural contribution gives rise to a larger Fe²⁺ Q.S.

Both the glauconite and nontronite fall into another category with the smallest Fe³⁺ Q.S. Generally, both glauconite and nontronite have higher Si to Al ratio in the tetrahedral layer and, consequently, less layer charge than ordinary micas (Warshaw and Roy, 1961). The nontronite was an expanded material with an exchange capacity of 0.84 meq/gm, but the glauconite had a broad basal mica spacing and a layer charge (2.2 meq/gm) not much less than that of the muscovites (2.3–2.4 meq/gm). The similar half-width of all the samples seems to rule out more than one iron site, such as tetrahedral and octahedral iron (Weaver, Wampler and Pecuil, 1967), contributing to the low splitting in nontronite. High iron content by itself did not affect Q.S. for the trioctahedral case. Although the structural reason is unclear, the iron environment appears less distorted for nontronite and glauconite than for the other samples studied.

The interpretation of the quadrupole splittings of the micas needs more study to insure that the regularities observed are indeed general. However, our results provide strong evidence that the splittings are primarily caused by structural variations in the plane of the layers, and that distortion and expansion between layers have little, if any, effect. Thus, vermiculite Mössbauer parameters are apparently determined by the parent mica. The variation among micas is significant enough to distinguish among several groups. Changes in oxidation state of the iron can be easily followed, and a quantitative determination of both ferrous and ferric iron can be made.

ACKNOWLEDGMENTS

We thank Dr. R. A. Leonard for much of the chemical characterization of the samples and J. E. Bercau for assistance in the early stages of this work.

REFERENCES

- BANCROFT, G. M., R. G. BURNS, AND A. G. MADDOCK (1967) Determination of cation distribution in the cumingtonite-grunerite series. *Amer. Mineral.*, **52**, 1009–1026.
- , A. G. MADDOCK, AND R. G. BURNS (1967) Applications of the Mössbauer effect to silicate mineralogy—I. Iron silicates of known crystal structure. *Geochim. Cosmochim. Acta*, **31**, 2219–2246.

- HAFEMEISTER, D. W., AND E. B. SHERA (1966) Calculation of Mössbauer absorption areas for thick absorbers. *Nucl. Inst. Meth.*, **41**, 133-134.
- HERZENBERG, C. L., AND D. TOMS (1966) Mössbauer absorption measurements in iron-containing minerals. *J. Geophys. Res.*, **71**, 2661-2677.
- HOFMAN, U., E. FLUCK, AND P. KUHN (1967) Mössbauer spectrum of the iron in glauconite. *Angew. Chem. Int. Ed.*, **6**, 561-562.
- INGALLS, R. (1964) Electric-field gradient tensor in ferrous compounds. *Phys. Rev.*, **133**, A784-A795.
- MALDEN, P. J., AND R. E. MEADS (1967) Substitution by iron in kaolinite. *Nature*, **215**, 844-846.
- MÖSSBAUER, R. L. (1958) Kernresonanzfluoreszenz von gammastrahlung in Ir^{191} . *Z. Physik*, **151**, 124-143.
- MUIR, A. H., JR., K. J. ANDO, AND H. M. COOGAN (1966) *Mössbauer Effect Data Index 1958-1965*. Interscience, New York.
- POLLAK, H., M. DE COSTER, AND S. AMELINCKX (1962) Mössbauer effect in biotite. *Phys. Stat. Sol.*, **2**, 1653-1659.
- NEWMAN, A. C. D., AND G. BROWN (1966) Chemical changes during the alteration of micas. *Clay Minerals Bull.*, **6**, 297-310.
- REED, M. G., AND A. D. SCOTT (1962) Kinetics of potassium release from biotite and muscovite in sodium tetraphenylboron solutions. *Soil Sci. Soc. Amer. Proc.*, **26**, 437-440.
- REICHEN, L. E., AND J. J. FAHEY (1962) An improved method for the determination of FeO in rocks and minerals including garnet. *U. S. Geol. Surv. Bull.*, **1144-B**.
- SHAPIRO, L., AND W. W. BRANNOCK (1956) Rapid analysis of silicate rocks. *U. S. Geol. Surv. Bull.* **1036-C**, p. 19-56.
- WARSHAW, C. M., AND R. ROY (1961) Classification and a scheme for the identification of layer silicates. *Geol. Soc. Amer. Bull.*, **72**, 1455-1492.
- WEAVER, C. E., J. M. WAMPLER, AND T. E. PECUIL (1967) Mössbauer analysis of iron in clay minerals. *Science*, **156**, 504-508.
- WERTHEIM, G. K. (1964) *Mössbauer Effect: Principles and Applications*. Academic Press, New York.

Manuscript received, July 4, 1968; accepted for publication, September 21, 1968.