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ANALYSIS OF IRON IN LAYER SILICATES BY MOSSBAUER SPECTROSCOPY

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Abstract—Analysis of Mossbauer effect in layer silicates provides a spectroscopic method for determining valences and coordination of iron. In this study Mossbauer spectra were obtained for amesite, cronstedtite, nontronite, two glauconites, biotite, lepidomelane, chlorite, minnesotaite, vermiculite, stilpnomelane, and chloritoid.

Trivalent iron was detected in tetrahedral coordination. Abundant trivalent iron in octahedral coordination apparently causes quadrupole splitting values of divalent iron in the same mineral to decrease. This phenomenon was noted in cronstedtite and glauconite. In cases where divalent iron predominates in the mineral, the quadrupole splitting is larger. It is generally accepted that ferrous iron is largely in octahedral coordination. This suggests that the octahedral sites may be more distorted when ferric iron is present in the octahedral sheet. In biotite, quadrupole splitting of divalent iron is decreased when trivalent iron is present in tetrahedral sheets. This suggests that there is also more distortion in the octahedral sheet because of iron in tetrahedral positions.

INTRODUCTION

FERROUS and ferric iron are known to exist in many layer silicate minerals. The exact lattice position of the iron ions, however, is difficult to determine. The Mossbauer effect provides an excellent spectroscopic method for studying iron cation positions in layer silicate minerals. The isomer shift, obtained from the Mossbauer spectrum, indicates the valence state of iron in the mineral. The magnitude of the quadrupole splitting reflects the local surroundings of the iron ions.

The exact position of iron ions can be determined in the two-sheet phyllosilicates which have limited cation sites available. The structural position of iron in the more complex layer silicate minerals can be ascertained by comparison of isomer shift and quadrupole splitting values to those from iron in known octahedral and tetrahedral coordination.

Iron-57, which is the iron isotope used in Mossbauer spectroscopy, occurs as 2·17 per cent of iron in nature and, as a result, natural minerals provide excellent absorbers. The mineral samples are not destroyed by this method.

THE MOSSBAUER EFFECT

The Mossbauer effect refers to the process of recoil-free emission and resonant absorption of nuclear gamma rays in solids (Mossbauer, 1958; Wertheim, 1964). The useful parameters, which are determined from the Mossbauer spectrum, are the isomer shift and the electric quadrupole splitting. The isomer shift arises from the electrostatic interaction between the nucleus and the *s*-electron density of the overlapping electron cloud. The electric quadrupole splitting results from the interaction between the nuclear quadrupole moment and the electric field gradient at the nucleus.

LAYER SILICATE STRUCTURES AND POSSIBLE IRON SITES

The phyllosilicates have two different structural arrangements. The two-sheet structure, composed of one sheet of silica tetrahedrons and one sheet of octahedrons (Grim, 1953), contains one tetrahedral and one octahedral site. The octahedral site, 0_c, consists of four hydroxyls and two adjacent oxygens at the apexes. The minerals amesite and cronstedtite, which were used in this investigation, exhibit the two-sheet trioctahedral structure (Steinfink and Brunton, 1956; Steadman and Youell, 1957).

The three-sheet structure, which consists of an octahedral sheet sandwiched between two silica tetrahedral sheets (Grim, 1953), contains one tetrahedral cation site and two different octahedral sites. Two hydroxyls and four oxygens form the

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apexes of the octahedron. The 0_a site has hydroxyls on opposed apexes and the 0_b site has the hydroxyls on adjacent tips (Pollak *et al.*, 1962). Biotite, lepidomelane, minnesotaite, vermiculite, chlorite, nontronite, and glauconite have the three-sheet structure. Chlorite has an additional cation site, 0_h, situated in the brucite-like sheet which is sandwiched between the two talc-like layers (Grim, 1953).

Stilpnomelane will also contain 0_a and 0_b sites according to the structure as presented by Gruner (1937 and 1944). The structure depicted by Eggleton and Bailey (1966) would contain 0_c and 0_P octahedral sites. The 0_P site consists of four hydroxyls and opposed oxygens on the apexes of the octahedron.

The chloritoid structure (harrison and Brindley, 1957) also exhibits 0_c and 0_P sites in the brucite-like sheet. An 0_0 site, with oxygens on the apexes of the octahedron, exists in the corundum-type sheet.

EXPERIMENTAL DATA

Mossbauer spectrometer

A Nuclear Science and Engineering Corporation Model B Mossbauer Spectrometer was used in this study. The source was Co_{57} in stainless steel.

Samples and sample mounting

Samples, or absorbers, were mounted in two ways:

1.Cleavage flakes were mounted directly to obtain spectra parallel to the "*c*" crystallographic axis.

2.Predetermined weights of powdered mineral were hardened for 24 hr in "Duco" cement.

The samples used, their localities, and sources of samples are listed in Table 1.

Table 1. Locality and source of minerals

Mineral	Locality	Source
Amesite	Saranovskoye Chromite Deposit, Northern Urals, USSR	Smithsonian Institution Cat. No. 103312
Biotite$_1$	Marquette Iron Range, Marquette, Michigan	L. L. Babcock
Biotite$_2$	Black Hills, South Dakota	Mineralogy Collection, Mich. Tech. Univ.
Biotite$_3$	Marquette Iron Range, Marquette, Michigan	L. L. Babcock
Chlorite$_1$	Michipicoten Iron Range, Ontario, Canada	R. A. Turpin
Chlorite$_2$	Keweenawan Lava Series, Keweenaw County, Michigan	R. J. Weege
Chloritoid	Champion Mine, Champion, Michigan	L. L. Babcock
Cronstedtite	Kisbanya, Rumania	Smithsonian Institution Cat. No. R7807
Glauconite$_1$	Auburn Mine, Mesabi Iron Range, Minnesota	S. W. Bailey University of Wisconsin
Glauconite$_2$	Cambrian sandstone, Wisconsin	S. W. Bailey University of Wisconsin
Lepidomelane	Hastings County, Ontario, Canada	J. A. Mandarino Royal Ontario Museum
Minnesotaite	Cuyuna Iron Range, Minnesota	Mineralogy Collection, Mich. Tech. Univ.
Nontronite	Spokane, Washington	Ward's Natural Science, Est., H-33a
Stilpnomelane	Cuyuna Iron Range, Minnesota	Mineralogy Collection, Mich. Tech. Univ.
Vermiculite$_1$	Location unknown	Mineralogy Collection Mich. Tech. Univ.
Vermiculite$_2$	Libby, Montana	Professor K. Spiroff Mich. Tech. Univ.

RESULTS

Determination of iron site

In each of the layer silicate minerals iron has at least two cation sites available. By detailed analy-

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sis of the quadrupole splittings and isomer shifts, obtained from the Mossbauer spectra, the location of the iron in the structure can be determined. Different minerals with similar cation sites aid in the determination.

The Mossbauer spectrum of amesite (Fig. 1a) shows that ferric iron is present (isomer shift) in two different sites (quadrupole splitting producing two double lines). Since only tetrahedral and 0_c sites are available in amesite, ferric iron must enter both of these sites. The doublet showing the widest quadrupole splitting should correspond to ferric iron in tetrahedral coordination, the other to ferric iron in octahedral coordination (Ingalls, 1964).

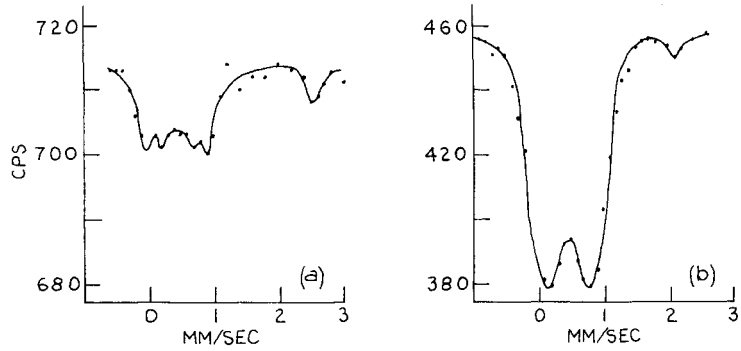


Fig. 1. Mossbauer spectra of (a) amesite and (b) cronstedtite.

The Mossbauer spectrum for nontronite shows a single peak, actually an unresolved doublet, corresponding to ferric iron in a single site (Fig. 2a). Iron in nontronite usually occurs in the octahedral layer (Grim, 1953). Therefore, the unresolved doublet must correspond to ferric iron in either the 0_a site or the 0_b site, or both. The isomer shift and quadrupole splitting of ferric iron in nontronite is comparable to that produced by the two inside peaks in amesite (Tables 2 and 3). Empirically, the two outside peaks in amesite, showing the widest quadrupole splitting, must be produced by ferric iron in a tetrahedral site.

Similar cation sites in different layer silicate minerals should produce similar isomer shifts and quadrupole splittings. In this way the site determination of ferric iron is possible.

Determination of the position of divalent iron in layer silicates is more difficult. Peaks indicating divalent iron occur in the neighborhood of 0·0 mm/sec and 2·5 mm/sec. The low velocity ferrous iron peak masks some ferric iron peaks completely and others partially. Divalent iron is usually thought to be situated in the octahedral sheet (Grim, 1953). It has been suggested (Pollak *et al.*,

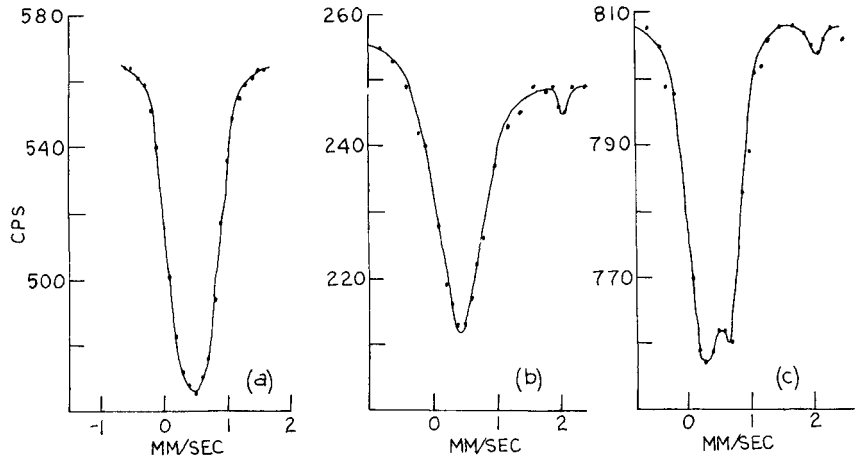


Fig. 2. Mossbauer spectra of (a) nontronite, (b) glauconite$_1$, and (c) glauconite$_2$.

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Table 2. Mossbauer parameters for two-sheet trioctahedral minerals

Mineral	Oxidation state	Peak position mm/sec		Isomer shift	Quadrupole splitting	Site
Amesite	Fe^{++}	0·00	2·55	1·28	2·55	0_c
	Fe^{+++}	0·00	0·90	0·45	0·90	Tetra
	Fe^{+++}	0·20	0·70	0·45	0·50	0_c
Cronstedtite	Fe^{++}	0·40	2·10	1·25	1·70	0_c
	Fe^{+++}	0·00	0·90	0·45	0·90	Tetra
	Fe^{+++}	0·15	0·75	0·45	0·60	0_c

Table 3. Mossbauer parameters for three-sheet dioctahedral minerals

Mineral	Oxidation state	Peak position mm/sec		Isomer shift	Quadrupole splitting	Site
Nontronite	Fe^{+++}	0·30	0·70	0·50	0·40	0_a, 0_b
$Glauconite_1$	Fe^{++}	0·40	2·05	1·23	1·65	0_a, 0_b
	Fe^{+++}	0·30	0·70	0·50	0·40	0_a, 0_b
	Fe^{+++}					Tetra
$Glauconite_2$	Fe^{++}	0·40	2·10	1·25	1·70	0_a, 0_b
	Fe^{+++}	0·30	0·70	0·50	0·40	0_a, 0_b
	Fe^{+++}					Tetra

1962; Herzenberg and Toms, 1966) that ferrous iron occurs in both 0_a and 0_b sites in the octahedral sheet and that the resulting Mossbauer spectrum consists of two superimposed lines in each peak. Lepidomelane, biotite, chlorite, and minnesotaite (Figs. 3 and 4) show strong absorption lines most probably corresponding to ferrous iron in octahedral sites.

0_c and 0_P sites, in chloritoid and possibly stilpnomelane, which contain ferrous iron show similar isomer shifts and quadrupole splittings as those produced by ferrous iron in 0_a and 0_b sites (Fig. 5).

In summary, it is not possible from data obtained in this investigation to state that ferrous iron is in either octahedral or tetrahedral coordination. However, the writers agree with most investigators that most ferrous iron is found in octahedral coordination. Furthermore, there is no evidence from this investigation to indicate that possible sub-sites within layers can be discriminated. According to the theory developed in the previous section, ferric iron can be detected in either octahedral or tetrahedral coordination.

The possibility of iron in 0_h and 0_o sites will be discussed under chlorite and chloritoid respectively.

Two-sheet trioctahedral minerals

Mossbauer spectra were obtained for the two-sheet minerals containing iron. Amesite has the general chemical formula

$$(Mg_4Al_2)(Si_2Al_2)0_{10}(0H)_8$$

and cronstedtite can be represented by the formula

$$(Fe_2^{+2}Fe_2^{+3})(Si_2Fe_2^{+3})0_{10}(0H)_8$$

The spectrum for amesite suggests two doublets (Fig. 1a), which probably correspond to ferric iron in both octahedral and tetrahedral coordination, since only these two positions are a available in amesite. Thus, the Mossbauer spectrum for amesite provides a basis for determining the position of ferric iron in three-sheet di- and trioctahedral minerals.

The absorption peaks for amesite are not intense suggesting that only minor amounts of ferric iron have replaced magnesium or aluminum in the octahedral layer and aluminum in the tetrahedral layer. The spectrum also indicates ferrous iron in amesite, which is probably contained in the octahedral, 0_c, site. Ferrous iron is most commonly located in octahedral coordination in layer silicate minerals (Grim, 1953).

According to the formula for cronstedtite, ferric iron is present in both the octahedral and tetrahedral sheets. Intense absorption peaks for ferric iron are present from iron in the 0_c sites (Fig 1b). The peaks show pronounced broadening near the background count which may be an indication of less intense absorption peaks for tetrahedral iron. The peaks from iron in the tetrahedral site are

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masked by the more intense peaks from ferric iron in the 0_c site. This is in agreement with the interpretation by Weaver *et al.*(1967). Their results indicated that tetrahedral ferric iron produced a larger quadrupole splitting value than that of octahedral ferric iron. Ferrous iron is also indicated, probably in the 0_c site.

The Mossbauer parameters for amesite and cronstedtite are shown in Table 2.

Three-sheet dioctahedral minerals

Mossbauer spectra were obtained for nontronite,

$(Mg, Ca)_{0\cdot7}(Mg,Fe^{+3},Al)_{6\cdot0}(Al,Si)_{8\cdot0}0_{20}(0H)_4 \cdot 8H_20,$

and glauconite,

$(K,Na,Ca)_{1\cdot2-2\cdot0}(Fe^{+3},Al,Fe^{+2},Mg)_{4\cdot0}(Si_{7-7\cdot6} \times Al_{1-0\cdot4})0_{20}(0H)_4.nH_20.$

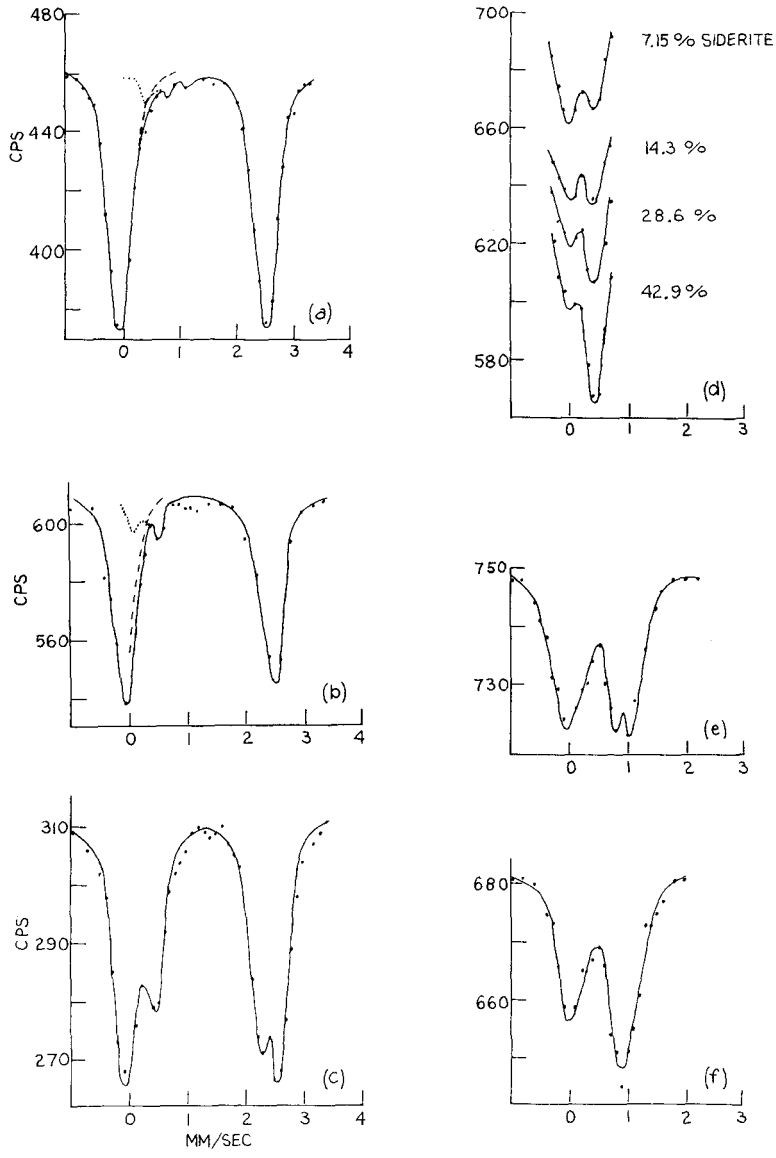


Fig. 3. Mossbauer spectra of (a) lepidomelane, (b) biotite$_1$, (c) biotite$_2$, and (d) biotite$_3$.

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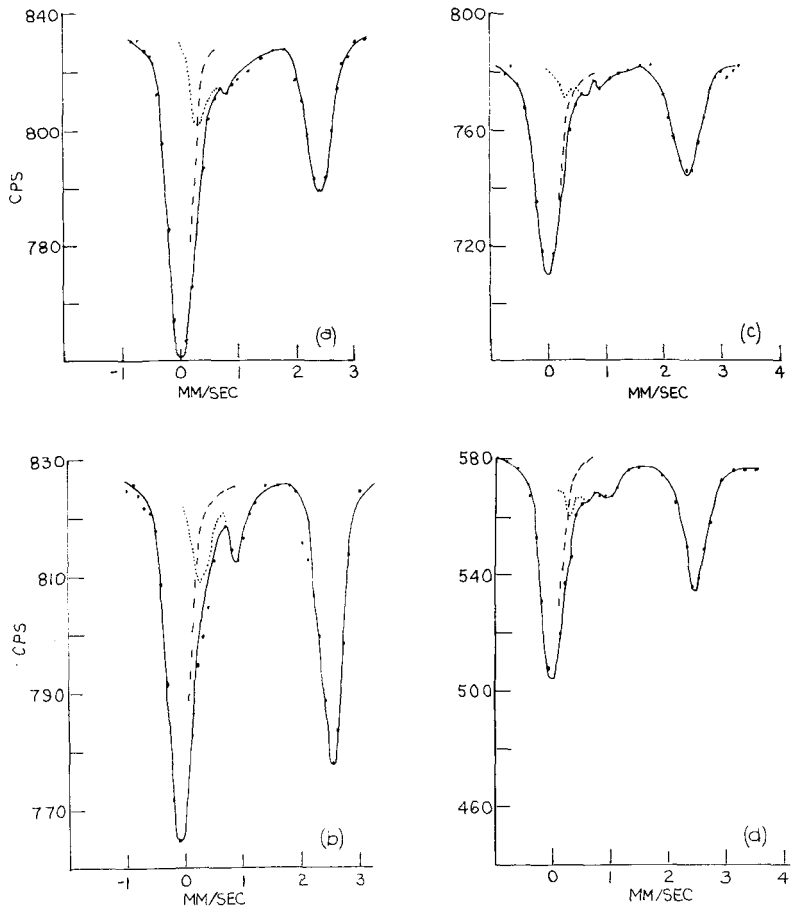


Fig. 4. Mossbauer spectra of (a) chlorite$_1$, (b) chlorite$_2$, (c) minnesotaite, (d) biotite-siderite mixtures, (e) vermiculite$_1$, and (f) vermiculite$_2$.

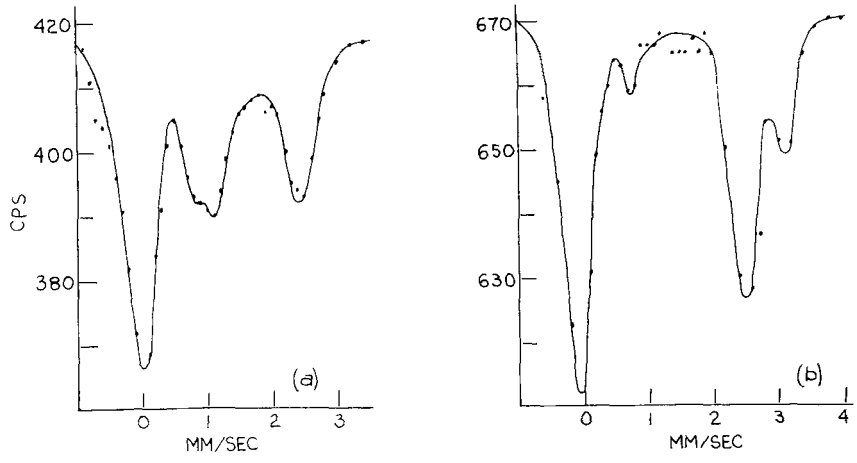


Fig. 5. Mossbauer spectra of (a) stilpnomelane and (b) chloritoid.

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Chemical analysis and X-ray data (Grim, 1953) indicate that nearly all ferric iron in nontronite is contained in the octahedral layer. Although two octahedral sites, 0_a and 0_b, are available, there is little indication from the Mossbauer spectrum (Fig. 2a) as to which site the iron ion prefers. Weaver *et al.*(1967) suggest that lack of resolution of the doublet indicates the possibility that tetrahedral ferric iron is present also. Ferrous iron appears to be absent in nontronite.

Similarly, the Mossbauer spectrum for glauconite shows that ferric iron is present, probably in the octahedral layer. Glauconite$_1$ shows a single peak which probably represents an unresolved doublet (Fig. 2b). Glauconite$_2$ shows a narrow doublet resulting from ferric iron in the octahedral position (Fig. 2c). The exact octahedral site, 0_a or 0_b, for ferric iron in glauconite cannot be determined.

Ferrous iron is indicated in both glauconites by the peak at 2·1 mm/sec (Table 3). Ferrous iron in glauconite and constedtite shows narrower quadrupole splitting than that for ferrous iron in the three-sheet trioctahedral minerals (Table 4). Only the high velocity ferrous iron peak is observed from the spectra for the cronstedtite and glauconite samples. The corresponding divalent iron peak, which is masked by the more intense ferric iron peaks, is assumed to have shifted to 0·40 mm/sec. This places the isomer shift value at about 1·25 mm/sec, which agrees with the isomer shift value for ferric iron in the three-sheet trioctahedral minerals (Table 4). The narrower quadrupole splitting may be caused by the large amount of iron in the octahedral layer. Weaver *et al.* (1967) also observed that quadrupole splitting values were less when abundant ferric iron was present in the layer silicates. Amesite, which has a structure similar to cronstedtite, contains only a minor amount of ferric iron in the octahedral sheet and shows the normal quadrupole splitting of about 2·5 mm/sec for ferrous iron in the octahedral sheet (Fig. 1a).

Three-sheet trioctahedral minerals

Mossbauer spectra were obtained for biotite lepidomelane, chlorite minnesotaite, and vermiculite All of these minerals contain tetrahedral and octahedral, 0_a, and 0_b, cation sites. Chlorite has an additional cation site 0_h, because of the presence of the brucite-like sheet.

Both biotite and lepidomelane can be represented by the formula

$$K_2(Mg,Fe^{+2})_{6-4}(Fe^{+3},Al,Ti)_{0-2}(Si_{6-5},Al_{2-3})0_{20}(0H,F)_{4-2}$$

since lepidomelane is considered to be a biotite rich in iron ($Fe^{+2}+Fe^{+3}$) (Deer, Howie, and Zussman, vol. 3, 1962). It is generally accepted that ferrous iron in lepidomelane and biotite is situated in the octahedral sheet (Grim, 1953).

Table 4. Mossbauer parameters for three-sheet trioctahedral minerals

Mineral	Oxidation state	Peak positions mm/sec		Isomer shift	Quadrupole splitting	Site
Lepidomelane	Fe^{++}	0·00	2·40	1·20	2·40	$0_a, 0_b$
	Fe^{+++}	0·30	0·80	0·55	0·50	$0_a, 0_b$
Biotite$_1$	Fe^{++}	−0·05	2·55	1·25	2·60	$0_a, 0_b$
	Fe^{+++}	0·30	0·90	0·60	0·60	$0_a, 0_b$
Biotite$_2$	Fe^{++}	0·00	2·45	1·23	2·45	$0_a, 0_b$
	Fe^{+++}	0·35	0·65	0·50	0·30	$0_a, 0_b$
	Fe^{+++}	0·00	0·95	0·48	0·95	Tetra
Biotite$_3$	Fe^{++}	−0·05	2·45	1·20	2·50	$0_a, 0_b$
	Fe^{+++}	0·30	0·60	0·45	0·30	$0_a, 0_b$
	Fe^{+++}	0·00	0·95	0·48	0·95	Tetra
Chlorite$_1$	Fe^{++}	−0·05	2·55	1·25	2·60	$0_a, 0_b$
	Fe^{+++}	0·40	0·80	0·60	0·40	$0_a, 0_b$
	Fe^{+++}	0·00	1·10	0·55	1·10	Tetra
Chlorite$_2$	Fe^{++}	−0·05	2·50	1·23	2·55	$0_a, 0_b$
	Fe^{+++}	0·10	0·50	0·30	0·40	$0_a, 0_b$
Minnesotaite	Fe^{++}	−0·05	2·55	1·25	2·60	$0_a, 0_b$
	Fe^{++}	0·45	2·30	1·38	1·85	Siderite
Vermiculite$_1$	Fe^{+++}	0·00	1·00	0·50	1·00	Tetra
	Fe^{+++}	0·30	0·80	0·55	0·50	$0_a, 0_b$
Vermiculite$_2$	Fe^{+++}	0·00	1·00	0·50	1·00	Tetra
	Fe^{+++}	0·30	0·75	0·53	0·45	$0_a, 0_b$

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Strong absorption peaks for ferrous iron in these minerals (Fig. 3) most likely correspond to ferrous iron in octahedral coordination. Previous work by Pollak *et al.*(1962), Herzenberg and Toms (1966), and Weaver *et al.*(1967) supports this theory.

The Mossbauer spectra for lepidomelane and biotite$_2$ were obtained from cleavage flakes oriented so that the gamma rays struck the cleavage plane at right angles. This orientation produced more intense low velocity peaks (Fig. 3). Biotite$_1$ and biotite$_3$ were powder samples, but still revealed a slight orientation effect because of the single cleavage of biotite.

Pollak *et al.*(1962) suggest that the ferrous iron doublet in biotite consists of two superimposed doublets. They reason that the superimposed high velocity peaks are offset slightly, thereby reducing the intensity. Both Pollak *et al.*(1962) and Herzenberg and Toms (1966) have tried to match each of the ferrous iron doublet to specific octahedral sites, but the results have been largely inconclusive.

Chemical analyses were obtained for lepidometane, biotite$_2$, and biotite$_3$ and are as follows:

	Fe^{+2}	Fe^{+3}
lepidomelane	15·2	5·2
biotite$_2$	1·3	5·8
biotite$_3$	16·7	3·8

The Mossbauer spectra of these minerals do not reflect any correlation between coordination preference and iron content.

In all cases the strong ferrous iron absorption peak in the low velocity area partially masks ferric iron doublets. The ferric iron peak positions can be determined by resolving the experimental ferrous iron peak into its component parts. A symmetrical absorption curve is drawn for the low velocity ferrous iron peak using the left-hand portion of the curve as a guide. The left-hand portion of the curve should be little affected by the ferric iron absorption peaks since these peaks commonly occur at velocities of 0·0 mm/sec or greater (amesite, Table 1; nontronite, Table 2). The symmetrical, right-hand portion of the ferrous iron peak is shown by the dashed line in Figs. 3, 4a, and 4b. The difference between the dashed line and the experimental curve represents the absorption due to ferric iron and is shown by the dotted lines in Figs. 3, 4a, and 4b.

Ferric iron absorption peaks for lepidomelane (Fig. 4a) and biotite$_1$ (Fig. 3b) show that trivalent iron is situated in the octahedral sheet. The gentle slope of the high velocity side of the 0·80 mm/sec peak in lepidomelane (Fig. 3a) suggests that a minor amount of ferric iron may be present in the tetrahedral position.

Two ferric iron doublets are present in biotite$_2$ and biotite$_3$. The doublet denoted by narrow quadrupole splitting (Table 4) represents trivalent iron in the octahedral site. The second ferric iron doublet in these biotites indicates ferric iron in the tetrahedral position. In both cases the peak positions are at 0·00 mm/sec and 0·95 mm/sec. The peak at 0·95 mm/sec is very distinct (Figs. 3c and 3d). The peak at 0·00 mm/sec coincides almost directly with the strong absorption peak for ferrous iron and cannot be detected by resolving the ferrous iron peak into its component parts. The quadrupole splitting which results from ferric iron in the octahedral sheet appears to be less when ferric iron occurs in the tetrahedral (Table 4).

Chlorite can be represented by the general formula

$$(Mg,Al,Fe^{+2})_{12}(Si,Al)_8O_{20}(OH)_{16}$$

The Mossbauer spectra for chlorite and chlorite$_2$ are similar to those obtained for the biotites. Strong ferrous iron absorption peaks indicate divalent iron in the octahedral position (Figs. 4a and 4b). The low velocity ferrous iron absorption peak can be resolved to determine the ferric iron peak positions. The Mossbauer spectrum for chlorite$_1$ (Fig. 4a) indicates two quadrupole doublets for trivalent iron. The doublet exhibiting narrow quadrupole splitting represents ferric iron in the octahedral position and the doublet showing the largest quadrupole splitting represents ferric iron in the tetrahedral position (Table 4). Ferric iron in chlorite$_2$ appears only in the octahedral layer.

A strong acid attack was conducted on 1·60 g of chlorite in order to remove the brucite-like layer. Ten ml of concentrated nitric acid were used on minus 170 mesh material. The Mossbauer spectrum showed little change although the chlorite became amorphous to X-rays. The ferric iron peaks, still very prominent, shifted 0·1 mm/sec toward the lower velocity side (Fig. 4a). If the acid attack was sufficient to remove the brucite-like sheet, it may be concluded that little or no ferric iron was present in the 0_h positions. Ferrous iron may be present in the brucite-like sheet, but the absorption peaks would probably coincide with the peaks produced by divalent iron in the 0_a and 0_b sites. Since peak positions for ferrous iron in 0_a, 0_b, 0_c, and 0_p sites are roughly coincidental, it is not inconsistent to reason that absorption peaks produced by ferrous iron in an 0_h site would be in the same range.

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Minnesotaite, $Mg_6Si_8O_{20}(OH)_4$ can be described structurally as an iron-rich talc (Deer, Howie and Zussman, vol. 3, 1962). The Mossbauer spectrum (Fig. 4c) indicates that minnesotaite contains ferrous iron in the octahedral position. The absorption peaks occur at −0·05 mm/sec and 2·55 mm/sec (Table 4). X-ray analysis of the minnesotaite sample shows that a minor amount of siderite is present. The doublet for ferrous iron represented by peaks at 0·45 mm/sec and 2·30 mm/sec corresponds to the divalent iron contained in the siderite (Weaver et al., 1967). As a check, Mossbauer spectra were obtained for the low velocity peaks of various mixtures of biotite and siderite (Fig. 4d). The low velocity minnesotaite-siderite peaks can be simulated with a sample of biotite containing about 7·15 per cent siderite. This test suggests an analytical application for determining mineral percentages in fine-grained, iron-bearing aggregates.

The Mossbauer spectra for vermiculite,

$$(Mg,Ca)_{0\cdot7}(Mg,Fe^{+3},Al)_{6\cdot0}(Al,Si)_{8\cdot0}O_{20}(OH)_4.8H_2O$$

indicate that only trivalent iron is present in the structure. The Mossbauer spectrum for vermiculite$_1$ (Fig. 4e) is similar to that for amesite (Fig. 1a). Absorption peaks at 0·00 mm/sec and 1·00 mm/sec indicate ferric iron in the tetrahedral position. The two inner peaks, which are partially masked by the tetrahedral iron peaks, represent trivalent iron in the octahedral sheet. There is no indication that ferric iron prefers to enter a particular octahedral site. It is reasonable to assume that ferric iron in either the O_a site or the O_b site would show similar isomer shifts and quadrupole splittings since this is the case for divalent iron in O_a and O_b sites. Also, divalent iron is more sensitive to its environment than is trivalent iron (Herzenberg and Toms, 1966).

Vermiculite$_2$ (Fig. 4f) exhibits a Mossbauer spectrum similar to that for vermiculite (Table 4) except that the doublet corresponding to octahedral ferric iron is almost completely masked by the tetrahedral ferric iron doublet. Vermiculite is the only three-sheet trioctahedral mineral tested in which trivalent iron predominates.

Related layer-type minerals

Two other layer type minerals were analysed to provide information on different octahedral sites.

Stilpnomelane can be represented by the general formula

$$(K,Na,Ca)_{0-1\cdot4}(Fe^{+3},Fe^{+2},MgAl,Mn)_{5\cdot9-8\cdot2}Si_8O_{20}(OH)_4-(0,0H,H\,0)_{3\cdot6-8\cdot5}$$

according to Gruner (1944) or, for a specific specimen, by

$$(Si_{3\cdot5}Al_{0\cdot5})(Fe^{+3}_{2\cdot1}Al^{+3}_{0\cdot13})(Fe^{+2}_{0\cdot03}Mg_{0\cdot63})O_{9\cdot5}(0H)_{4\cdot5}$$

according to Eggleton and Bailey (1966). The Mossbauer spectrum for stilpnomelane indicates divalent iron in octahedral coordination. If the structure presented by Eggleton and Bailey (1964) is correct the ferrous iron must be situated in O_c and O_p sites. The isomer shift and quadrupole splitting for divalent iron (Table 5) is similar to that for ferrous iron in the three-sheet structures (Table 4), where iron is located in O_a and O_b sites.

Two trivalent iron doublets are indicated by obvious peaks at 0·85 mm/sec and 1·10 mm/sec (Fig. 5a). The low velocity peaks are masked by the intense ferrous iron absorption peak at 0·00 mm/sec. The doublet consisting of peaks at 1·10 mm/sec and probably at 0·00 mm/sec (similar to vermiculite, Figs. 4e and 4f) can best be interpreted as trivalent iron in the tetrahedral position. The doublet composed of peaks at 0·85 mm/sec probably 0·25 mm/sec indicates ferric iron in O_c and/or O_p sites. Absorption peaks indicating interlayer iron (Gruner, 1944) are not detected although they may be masked by other more intense peaks.

W. F. Bradley (personal communication) suggests that some stilpnomelanes may be hydrobiotites, of fine grained habit, derived from high iron micas. The empirical formulae would be cited as gradations according to mixing proportions between biotite and vermiculite. The Mossbauer spectrum for stilpnomelane supports this view in the case of the Cuyuna Iron Range sample, since it resembles the combination of a biotite spectrum and a vermiculite spectrum.

Chloritoid can be represented chemically by the general formula

$$(Fe^{+2},MgMn)_2(Al,Fe^{+3})Al_3O_2(Si0_4)_2(0H)_4$$

Divalent iron in O_c and/or O_p sites in chloritoid (Fig. 5b) is represented by intense absorption peaks at −0·05 mm/sec and 2·55 mm/sec on the Mossbauer spectrum. These peaks are similar to those produced by ferrous iron in O_a and O_b sites. Divalent iron in octahedral coordination is indicated by the relatively intense peak at 3·10 mm/sec. The corresponding peak is also masked by the more intense ferrous iron peak at 0·00 mm/sec. The peaks cannot be resolved in this case since both right- and left-hand portions of the experimental curve appear to be distorted by hidden peaks. The best estimation of the position of the less intense ferrous iron peak in the low velocity

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area is about −0·35 mm/sec since the left-hand portion of the curve has a more gentle outward slope in this region. This doublet has an isomer shift of 1·38 mm/sec and a quadrupole splitting of 3·45 mm/sec (Table 5). Both values are larger than those of any previous minerals discussed. This must be due to divalent iron replacing aluminum in the corundum-type layer. A similar site, 0_o, is present in the olivine structure for which the quadrupole splitting value reported was larger than that for biotite (de Coster et al., 1963). The 0_o site is common only to chloritoid in the minerals tested during this research.

The small amount of ferric iron in chloritoid is represented by a doublet which has one small peak at 0·75 mm/sec.

creased (Table 4). This also suggests more distortion in the octahedral sheet because of iron in tetrahedral positions.

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Table 5. Mossbauer parameters for stilpnomelane and chloritoid

Mineral	Oxidation state	Peak positions mm/sec		Isomer shift	Quadrupole splitting	Site
Stilpnomelane	Fe^{++}	0·00	2·40	1·20	2·40	$0_c, 0_p$
	Fe^{+++}	0·00	1·10	0·55	1·10	Tetra
	Fe^{+++}	0·25	0·85	0·55	0·60	$0_c, 0_p$
Chloritoid	Fe^{++}	−0·05	2·50	1·23	2·55	$0_c, 0_p$
	Fe^{++}	−0·35	3·10	1·38	3·45	0_o
	Fe^{+++}	0·30	0·75	0·53	0·45	$0_c, 0_p$

CONCLUSIONS

Mossbauer analyses of iron-rich layer silicate minerals show that trivalent iron can be detected in tetrahedral and octahedral coordination. The exact octahedral environment cannot be determined for trivalent or divalent iron. Divalent iron is generally believed to be in octahedral coordination (Grim, 1953). Ferrous iron in 0_a, 0_b, 0_c, and 0_p sites produces peaks with similar isomer shifts and quadrupole splittings. No spectra were obtained where ferrous iron was believed to be in tetrahedral coordination.

Abundant trivalent iron in octahedral coordination in layer silicates appears to cause the quadrupole splitting value of divalent iron in the same mineral to decrease. This is exemplified by the minerals cronstedtite and glauconite (Tables 2 and 3). Where divalent iron predominates in the octahedral layer, the quadrupole splitting value is about 2·50 mm/sec (Table 4). This suggests that the octahedral sheet may be more distorted when ferric iron predominates in the octahedral sites (Bancroft, Maddock, and Burns, 1967).

In biotite, when trivalent iron is present in the tetrahedral sheet, the quadrupole splitting value for trivalent iron in octahedral coordination is de-

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Résumé—Une analyse de l'effet Mossbauer dans les silicates en couches donne une méthode spectroscopique pour déterminer les valences et la coordination du fer. Dans cette étude, des spectres Mossbauer ont été obtenus pour l'amésite, la cronstedtite, la nontronite, deux glauconites, la biotite, la lépidomelane, la chlorite, la minnésotaite, la vermiculite, la stilptomélane et la chloritoide.

Le fer trivalent a été détecté dans une coordination tétrahédrique. Une quantité importante de fer trivalent en coordination octahédrique cause une diminution des valeurs de fissuration quadripolaire du fer bivalent du même minéral. Ce phénomène fut noté pour la cronstedtite et la glauconite. Là où le fer bivalent prédomine dans le minéral, la fissuration quadripolaire est plus importante. Il est généralement accepté que le fer ferreux est largement en coordination octahédrique. Cela semble suggérer que les emplacements octahédriques peuvent être davantage déformés lorsqu'il se trouve du fer ferrique dans la feuille octahédrique. Dans la biotite, la fissuration quadripolaire du fer bivalent s'augmente lorsque le fer trivalent se trouve présent dans les feuilles tétrahédriques. Cela fait penser qu'il y a également plus de déformation dans la feuille tétrahédrique par suite du fer dans les emplacements tétrahédriques.

Kurzreferat—Die Analyse des Mossbauer Effektes in Schichtsilikaten liefert eine spektroskopische Methode für die Bestimmung der Valenzen und der Koordination des Eisens. In dieser Arbeit wurden Mossbauer Spektren erhalten für Amesit, Cronstedtit, Nontronit, zwei Glaukonite, Biotit, Lepidomelan, Chlorit, Minnesotait, Vermiculit, Stilpnomelan und Chloritiod.

Dreiwertiges Eisen wurde in tetraedrischer Koordination aufgefunden. Im Überschuss vorhandenes dreiwertiges Eisen scheint die Abnahme quadrupolarer Spaltwerte von zweiwertigem Eisen im gleichen Mineral hervorzurufen. Diese Erscheinung wurde im Cronstedtit sowie im Glaukonit beobachtet. Wenn das zweiwertige Eisen in dem Mineral überwiegt so ist die quadrupolare Spaltung grösser. Es wird allgemein angenommen, dass sich das Ferro-eisen weitgehend in octaedrischer Koordination befindet. Das deutet darauf hin, dass die octaedrischen Besetzungsstellen mehr verzerrt sein werden wenn sich Ferri-eisen in der octaedrischen schichte befindet. Im Biotit nimmt die quadrupolare Spaltung von zweiwertigem Eisen ab wenn dreiwertiges Eisen in tetraedrischen schichte anwesend ist. Das weist darauf hin, dass auch durch die Anwesenheit von Eisen in tetraedrischen Stellungen mehr Verzerrung in der octaedrischen schichte auftritt.

Резюме—Анализ эффекта Мосбауера в слоистых силикатах предоставляет спектроскопический метод определения валентностей и координации железа. В настоящем исследовании, спектры Мосбауера были получены для амезита, кронштедтита, нонтронита, двух глауконитов, биотита, лепидомелана, хлорита, миннезотаита, вермикулита, стилъпломелана и хлоритоида.

Трехвалентное железо было обнаружено в тетраэдрической координации. Обилие трехвалентного железа в октаэдрической координации вероятно вызывает понижение квадруполъных расщепляющих значений двухвалентного железа в том же минерале. Явление это наблюдалосъ в кронштедтите и глауконите. В случаях, когда двухвалентное железо преобладает в минерале, квадруполъное расщепление будет болъшим. Общепринято, что двухвалентное железо находится преимущество в октоэдрической координации. Это намекает на то, что октоэдрические места могут бытъ более искажены когда трехвалентное железо присутствует в октоэдрическом листе. В биотите, квадруполъное расщепление двухвалентного железа понижается, когда трехвалентное железо присутствует в тетраэдрических листах. Подсказывает это, что болъше искажений имеется также и в октоэдрическом листе, так как железо находится в тетраэдрических положениях.

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