

A MÖSSBAUER INVESTIGATION OF SOME CHLORITES AND THEIR OXIDATION PRODUCTS

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ABSTRACT

Three trioctahedral chlorites (Fe-clinocllore, Mn-Mg-chamosite and Mg-chamosite) and their oxidation products were investigated by ^{57}Fe Mössbauer spectroscopy. The computed Mössbauer parameters of all three chlorites before oxidation indicate that at least 65% of the total iron is in the ferrous state and that the Fe^{2+} cations exist in two different octahedral environments characterized by quadrupole doublets $\Delta E_Q \approx 2.70$ and ≈ 2.46 mm/s, respectively, with isomer shift (*I.S.*) ≈ 1.10 mm/s. For Fe^{3+} , there is only one quadrupole doublet with $\Delta E_Q \approx 0.66$ mm/s and *I.S.* ≈ 0.39 mm/s, indicating that Fe^{3+} is also octahedrally co-ordinated. The principal quadrupole doublets of Fe^{2+} and Fe^{3+} are not split magnetically at helium temperatures even in the samples of iron-rich chlorite, *i.e.*, chamosite. In contrast, the parameters of all chlorites after oxidation indicate a single Fe^{2+} quadrupole doublet and two Fe^{3+} quadrupole doublets. The ΔE_Q value of residual Fe^{2+} in the oxidized Fe-clinocllore is smaller than those of the two samples of oxidized chamosite, suggesting that the Fe^{2+} co-ordination in the former is a distorted octahedron. This may be significant in relation to structural changes in the chlorites after oxidation: Fe-clinocllore alters to a regularly interstratified chlorite-vermiculite, whereas in both samples, chamosite alters to vermiculite.

Keywords: ferrous chlorites, Fe-clinocllore, Mn-Mg-chamosite, Mg-chamosite, oxidation, Mössbauer spectra, distorted octahedral co-ordination.

SOMMAIRE

Trois chlorites trioctaédriques (clinocllore-Fe, chamosite-Mn-Mg et chamosite-Mg) et leurs produits d'oxydation ont été étudiés par spectroscopie Mössbauer du ^{57}Fe . Les paramètres de Mössbauer

calculés pour ces trois chlorites à l'état sain montrent qu'au moins 65% du fer se trouve à l'état ferreux, et que le Fe^{2+} occupe deux environnements octaédriques différents, caractérisés par les doublets quadrupoles $\Delta E_Q \approx 2.70$ et ≈ 2.46 mm/s, respectivement, et un dédoublement isomère (*I.S.*) d'environ 1.10 mm/s. Pour le Fe^{3+} , il y a un seul doublet quadrupole, $\Delta E_Q \approx 0.66$ mm/s, *I.S.* ≈ 0.39 mm/s, ce qui montre que le Fe^{3+} aussi est coordonné octaédriquement. Les principaux doublets quadrupoles de Fe^{2+} et Fe^{3+} ne sont pas séparés magnétiquement aux températures de l'hélium, même dans le cas de la chlorite riche en fer, c'est-à-dire la chamosite. Par contre, une fois oxydées, toutes les chlorites montrent, par leurs paramètres, un seul doublet quadrupole pour Fe^{2+} et deux doublets pour le Fe^{3+} . La valeur ΔE_Q pour le Fe^{2+} résiduel est moindre dans le clinocllore-Fe oxydé que dans les deux échantillons de chamosite oxydés; ceci serait le résultat d'une difformité de l'octaèdre de coordination du Fe^{2+} dans le clinocllore-Fe. Cette observation pourrait expliquer le comportement structural des chlorites après oxydation; le clinocllore-Fe se transforme en chlorite-vermiculite régulièrement interstratifiée, tandis que la chamosite, dans les deux cas, passe à la vermiculite.

(Traduit par la Rédaction)

Mots-clés: chlorites à l'état ferreux, clinocllore-Fe, chamosite-Mn-Mg, chamosite-Mg, oxydation, spectre de Mössbauer, octaèdre difforme de coordination.

INTRODUCTION

Trioctahedral chlorites containing ferrous iron have been converted into a vermiculitic structure by oxidizing Fe^{2+} using bromine (Ross 1975, Ross & Kodama 1976). The extent of the vermiculitization appears to be related to the Fe^{2+}

content of original chlorites. A magnesium chamosite was altered to vermiculite (Ross 1975), whereas a ferrous clinochlore was transformed into a regularly interstratified chlorite-vermiculite structure (Ross & Kodama 1976).

It is known that Mössbauer spectroscopy provides useful information concerning oxidation state ($\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio), electronic configuration, co-ordination number, magnetic state and crystal symmetry of Fe atoms in solids (Bancroft 1973). Several papers have been published on Mössbauer spectra of chlorites, although the interpretations are rather conflicting (Weaver *et al.* 1967, Taylor *et al.* 1968, Ericsson *et al.* 1977). Hayashi *et al.* (1972) reported changes in Mössbauer spectra and parameters with increasing dehydroxylation by progressive heat-treatments and found that the amount of Fe^{3+} increases with the treatments. More recently, Goodman & Bain (1979) examined samples of trioctahedral chlorite having a wide range of composition and concluded that no components can be speci-

cally assigned to the interlayer hydroxide sheets, although any Fe^{2+} occurring there must have parameters similar to Fe^{2+} in the octahedral sheet of silicate layer. They also investigated the oxidation behavior of Fe^{2+} during the conversion to vermiculite by dehydroxylation followed by the acid treatment of Ross & Kodama (1974).

The present investigation was undertaken to gain information concerning the oxidation behavior of Fe^{2+} in Fe-clinocllore and Mg-chamosite in relation to their vermiculization during chemical oxidation.

EXPERIMENTAL

The specimens and relevant chemical data used in this study are listed in Table 1. X-ray-diffraction data were obtained by means of a 114.6-mm-diameter Debye-Scherrer camera and a Philips diffractometer using Fe-filtered Co radiation. The untreated specimens, all trioctahedral chlorite with the IIb polytype structure,

TABLE 1. CHEMICAL COMPOSITION OF CHLORITES

	Fe-Clinocllore	Mn-Mg-Chamosite	Mg-Chamosite
SiO_2	33.55%	25.89%	30.66%
Al_2O_3	22.62	19.85	22.69
Fe_2O_3	2.51	12.61	14.58*
FeO	15.74	30.57	25.48*
MnO	-	6.31	1.09
MgO	25.58	4.77	5.50
Numbers of ions on the basis of $\text{O}_{10}(\text{OH})_8$			
Si	2.91	2.61	2.89
Al ^{IV}	1.09	1.39	1.11
Al ^{VI}	1.23	0.96	1.41
Fe^{3+}	0.16	0.95	1.04*
Fe^{2+}	1.14	2.57	2.01*
Mn	-	0.54	0.09
Mg	3.31	0.72	0.77
Σ_{OCT}	5.84	5.74	5.32
$\text{Fe}^{2+}/\text{Fe}^{3+}$	7.13	2.71	1.93*

All chemical analyses were taken from literature, then corrected for impurity (iron oxides) based on Mössbauer and normalized to 100% after subtracting $\text{H}_2\text{O}(+)$ and $\text{H}_2\text{O}(-)$ contents.

1. Middletown Valley, Maryland, U.S.A. (Ross & Kodama 1976). Sample was originally called brunsvigite and contained 0.87% hematite.
2. Ichinokoshi, Toyama, Japan (Sudo 1943). Sample was originally called thuringite and contained 2.55% hematite.
3. Donna Ana County, New Mexico, U.S.A. (Ross 1975). Sample was originally called diabantite.

*Allocation was made based on Mössbauer data using total iron content as Fe_2O_3 from chemical data.

are described as Fe-clinocllore, Mn-Mg-chamosite and Mg-chamosite, according to a nomenclature scheme recently recommended by Bailey *et al.* (1979). For those specimens, the number of Al atoms per four tetrahedral sites was calculated from an average value of d_{001} using the relationship (Bailey 1975) $d_{001} = 14.648(\text{\AA}) - 0.378 \text{ }^{26}\text{Al}$ (Table 2). The asymmetrical distribution of octahedral heavy metal atoms was evaluated from the basal intensity ratio, I_{003}/I_{005} , following the method of Petruk (1964).

Mössbauer spectra were recorded on a constant acceleration Mössbauer spectrometer with a ^{57}Co source in a Rh matrix. Velocities were calibrated against Fe foil. A helium dewar was used to allow spectra to be recorded at temperatures down to 4.2 K. For the analysis of spectra, each spectrum was computer-fitted using a least-squares iterative procedure with a pre-selected number of narrow absorption lines of Lorentzian shape, together with a parabolic background. Isomer shifts (*I.S.*) are reported in mm/s with respect to the isomer shift of ^{57}Fe in metallic iron. The determination of $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios was based on the relative proportion of areas under the absorption peaks due to Fe^{2+} and Fe^{3+} . This assumes that in these materials, the Mössbauer fraction *f* is equal for Fe^{2+} and Fe^{3+} and is independent of the crystallographic site.

RESULTS AND DISCUSSION

X-ray and chemical data

The degree of asymmetry is defined in the following formula: (number of heavy atoms in the octahedral sheet of silicate layer) - (number of heavy atoms in the interlayer hydroxide sheet) (Petruk 1964). The values obtained for the untreated chlorites all have a positive sign (Table 2), indicating that the heavy atoms are more concentrated in the octahedral sheet of the silicate layer than the interlayer hydroxide sheet.

Results of chemical analyses (Table 1) show that a majority of octahedral heavy atoms in the chlorites are Fe atoms. Based on the degree of asymmetry, the total octahedral heavy atoms can then be allocated to the corresponding positions in silicate layer and hydroxide sheet (Tables 1, 2). Thus, 87% of total Fe atoms in the Fe-clinocllore are in octahedral sites of the silicate layer, whereas 68% or less (due to the presence of Mn) of those in the Mg-chamosite and the Mn-Mg-chamosite occupy octahedral sites of the silicate layer.

After reaction with saturated bromine water on a steambath for 4 weeks to oxidize the ferrous iron, about 80% of Mg-chamosite and at least 60% of Mn-Mg-chamosite were converted to a vermiculite structure. Under similar conditions but for a prolonged treatment of 4 months, Fe-clinocllore was transformed into the regularly interstratified chlorite-vermiculite structure, with 23% of the original remaining unchanged.

Mössbauer data

Spectra of the chlorites before and after oxidation are shown in Figures 1 to 3 and the computed parameters are listed in Table 3. The spectra in Figure 1 are characterized by a major doublet with broad line-widths and a minor dip in absorption between the two lines of the doublet. These features are similar to those reported for chlorite by other investigators (Taylor *et al.* 1968, Hayashi *et al.* 1972, Ericsson *et al.* 1977, Goodman & Bain 1979). In the Fe-clinocllore and Mn-Mg-chamosite specimens, a small amount of hematite is indicated as an impurity; this was not detected by X-ray diffraction methods. The computed parameters (Table 3) indicate that for all three specimens, at least 65% of total iron is in the ferrous state and that the Fe^{2+} exists in two different octahedral environments characterized by ΔE_a in the range 2.69–2.71 mm/s and ΔE_a in the range 2.45–2.47

TABLE 2. POPULATIONS OF TETRAHEDRAL AL AND OCTAHEDRAL HEAVY ELEMENTS OF CHLORITES AS DETERMINED BY X-RAY-DIFFRACTION METHOD

	d_{001} (Å)	Al ^{IV}	Degree of Asymmetry	Total Octahedral Heavy Elements (A)	Heavy Element Population in Octahedral Coordination		B/A(%)
					Octahedral Sheet of Silicate Layer (B)	Interlayer Hydroxide Sheet	
Fe-clinocllore	14.17 ₄	1.25	+ 0.95	1.30	1.13	0.17	87
Mn-Mg-Chamosite	14.15 ₅	1.30	+ 1.15	4.06	2.60	1.46	64
Mg-Chamosite	14.19 ₄	1.20	+ 1.15	3.14	2.14	1.00	68

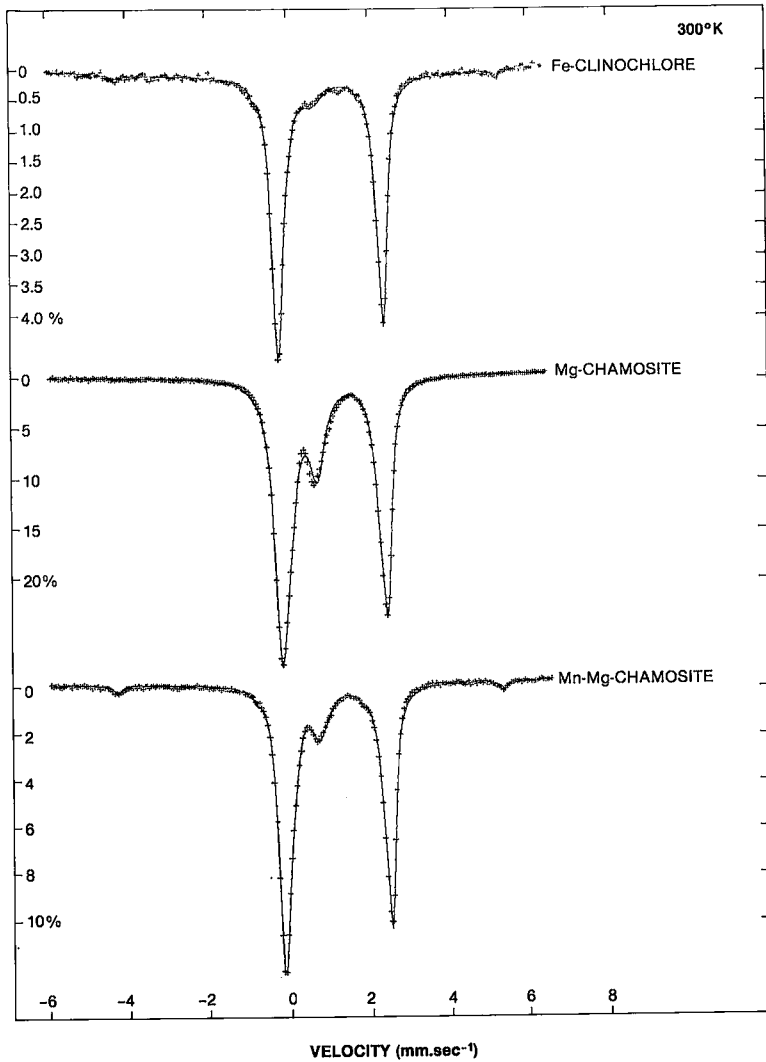


FIG. 1. Mössbauer spectra of the three samples of chlorite before oxidation (300 K).

mm/s, respectively, with $I.S. \approx 1.10$ mm/s. ΔE_Q increases with decreasing temperature, as is expected for Fe^{2+} where low-symmetry crystal-field splittings are $\lesssim 1000$ cm^{-1} . For Fe^{3+} , there is only one quadrupole doublet with ΔE_Q in the range 0.65–0.67 mm/s and $I.S.$ in the range 0.38–0.40 mm/s. Therefore, Fe^{3+} in the three specimens is also octahedrally co-ordinated, although Goodman & Bain (1979) found tetrahedrally co-ordinated Fe^{3+} in some chlorite samples. As pointed out by Goodman & Bain (1979), these Fe^{2+} and Fe^{3+} components resemble those reported for biotite, in which

they assigned to Fe^{2+} and Fe^{3+} in octahedral co-ordination with 2 OH and 4 O in either a *cis* (M_2 site) or *trans* (M_1 site) arrangement (Goodman & Wilson 1973). In the case of chlorites, however, there is another octahedral position in the interlayer hydroxide sheet; this category of site differs from the former in being co-ordinated to 6 OH. Therefore, unlike in the case of biotite, no specific assignment can be made for the Fe^{2+} and Fe^{3+} components in chlorites.

The parameters of all specimens after chemical oxidation indicate a single Fe^{2+} quadrupole doublet and two Fe^{3+} quadrupole doublets, in

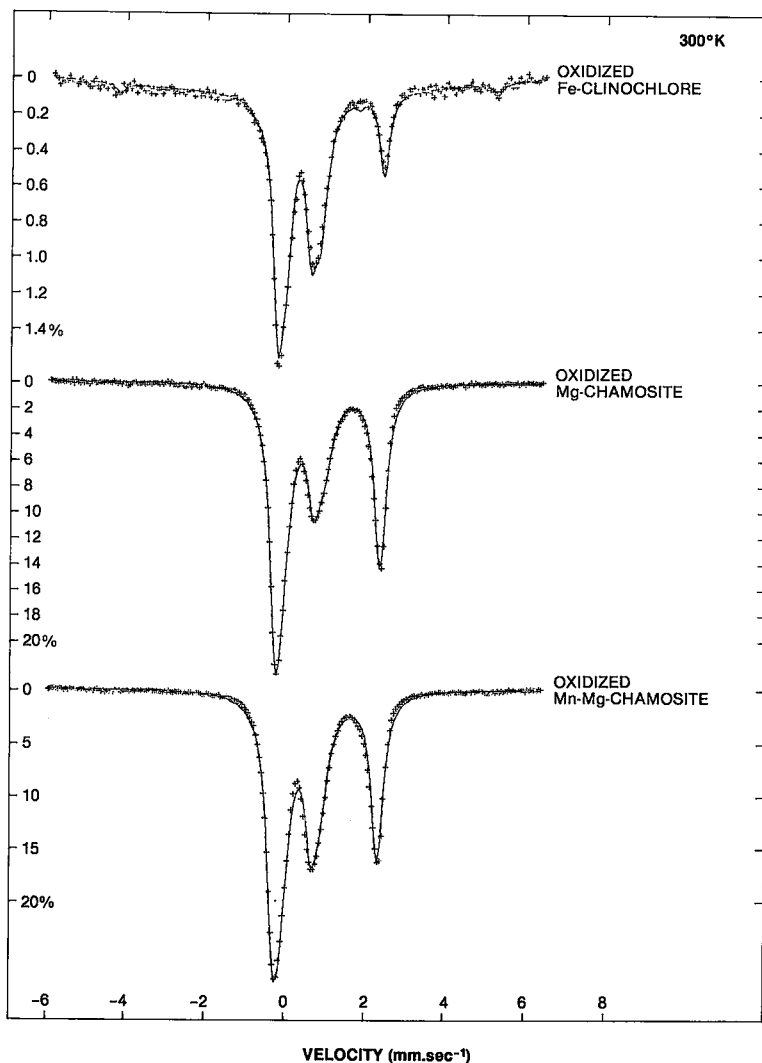


FIG. 2. Mössbauer spectra of the samples of chlorite after oxidation (300 K).

contrast to two Fe^{2+} components and single Fe^{3+} component before oxidation (Fig. 2, Table 3). Oxidized Fe-clinocllore has one Fe^{2+} quadrupole doublet with the smaller value of ΔE_Q , whereas oxidized Mn-Mg-chamosite and Mg-chamosite have a quadrupole doublet with the larger value of ΔE_Q . These estimated values are slightly smaller than the corresponding values for unoxidized specimens. As detected by X-ray, oxidized specimens contain 20 to 40% structurally unchanged chlorite. The results indicate a preferential oxidation of Fe^{2+} situated in a specific environment. For Fe^{3+} components,

values of ΔE_Q may be grouped into those ranging from 0.80 to 0.82 mm/s and from 0.88 to 1.04 mm/s, and the former may correspond to those in unoxidized material with ΔE_Q in the range 0.65–0.67 mm/s. Our Mössbauer spectra show that the principal Fe^{2+} and Fe^{3+} quadrupole doublets are not split magnetically at a low temperature. However, in the oxidized specimens at 4.2 K (Fig. 3), complex magnetic hyperfine components are superimposed on the unbroadened quadrupole doublets. This effect is much less marked in the unoxidized specimens at 8 K.

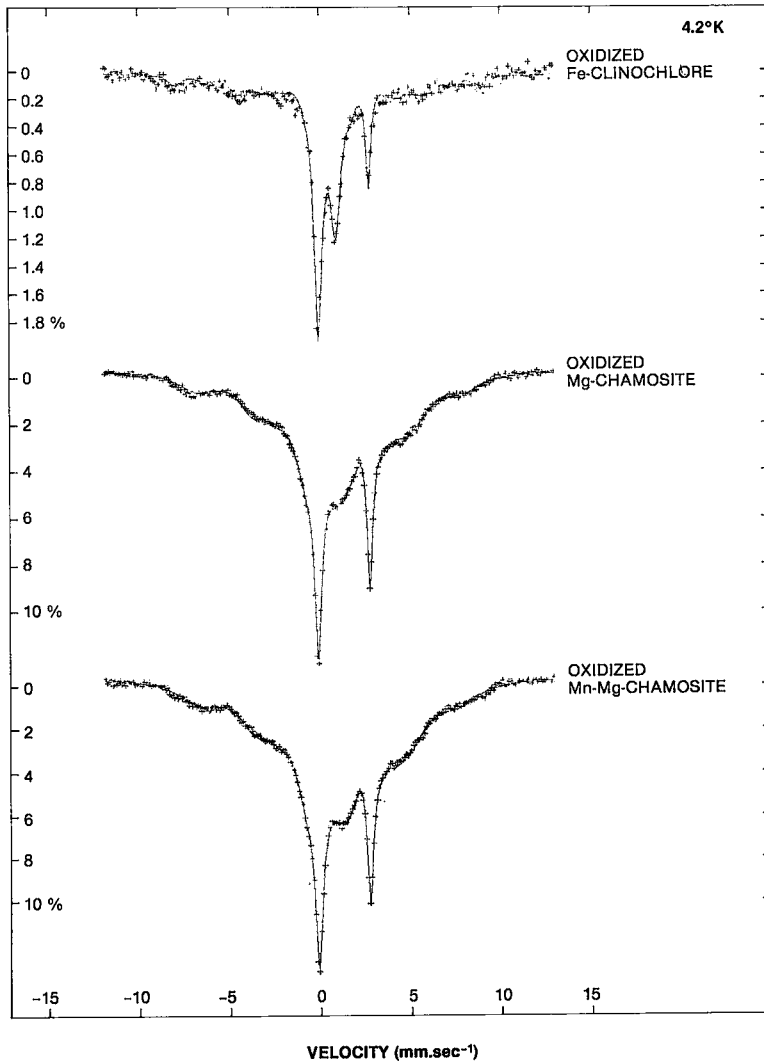


FIG. 3. Mössbauer spectra of the three samples of chlorite after oxidation (4.2 K).

If the spectra of Figure 3 were due to spin relaxation in the majority of iron atoms in the octahedral sheet of the silicate layer, the central quadrupole-doublet components would be broadened concomitantly with the appearance of magnetic hyperfine components in the wings. Relaxation effects would likely broaden the Fe^{3+} doublets first because the ground state is orbitally nondegenerate. In contrast, our experimental results show that the Fe^{3+} and Fe^{2+} lines remain clearly distinguished and unbroadened.

The results indicate that the majority of iron atoms in the octahedral sites in both unoxidized

and oxidized specimens are not coupled magnetically at a low temperature. The origin of the superimposed magnetic hyperfine components is not clear. They appear to be broadened, suggesting supermagnetism arising from magnetic clusters. These clusters could be small particles ($\sim 200 \text{ \AA}$) of goethite or hematite impurities formed in the oxidation process. For relaxation processes arising from the superparamagnetism of small particles, the magnitude of the magnetic hyperfine splitting depends on the grain-size distribution, which is not known. Hence, any attempt to assign the component lines would

TABLE 3. COMPUTED MÖSSBAUER PARAMETERS FOR CHLORITES AND THEIR OXIDIZED PRODUCTS

	Fe ²⁺						Fe ³⁺						Fe ²⁺ /Fe ³⁺ In Chlorites	Fe ³⁺			As Impurity Assignment
	ΔE_Q	I.S.	%	ΔE_Q	I.S.	%	ΔE_Q	I.S.	%	ΔE_Q	I.S.	%		H KDe	I.S.	%	
Fe-Chloritoid (300 K)	2.69	1.13	58	2.46	1.11	22	0.65	0.38	15				5.33	510	0.50	5	Hematite
Fe-Chloritoid Oxidized (300 K)				2.42	1.24	21	0.82	0.22	37	1.04	0.36	35	0.29	508	0.46	7	Hematite
Fe-Chloritoid oxidized (4 K)				2.83	1.29	20				0.94	0.41	56	0.36	527 415 327	0.49 0.60 0.80	8 7 9	+ + +
Mn-Mg-Chamosite (300 K)	2.70	1.12	44	2.45	1.10	27	0.67	0.39	23				3.09	510	0.46	6	Hematite
Mn-Mg-Chamosite Oxidized (300 K)	2.62	1.10	41				0.80	0.33	18	0.88	0.49	40	0.72				
Mn-Mg-Chamosite Oxidized (4 K)	2.84	1.29	19							1.44	0.54	34	0.56	437 251	0.37 1.37	25 22	+ +
Mg-Chamosite (300 K)	2.71	1.13	35	2.47	1.10	31	0.67	0.40	34				1.94				
Mg-Chamosite Oxidized (300 K)	2.62	1.11	49				0.82	0.33	22	0.96	0.51	29	0.96				
Mg-Chamosite Oxidized (4 K)	2.86	1.29	21							1.30	0.50	34	0.62	451 238	0.46 1.37	20 25	+ +

*The magnetic hyperfine spectra are typically those shown by spin-relaxation effects, and most likely result from super paramagnetic amorphous fine-grained iron oxides.

be difficult. Magnetic hyperfine components, probably resulting from the hematite impurity, are indicated in Table 3. A possible alternative interpretation is that iron atoms substitute non-uniformly for aluminum in the octahedral sheet of the silicate layer, forming isolated magnetic clusters.

Certain iron-rich clay minerals do order magnetically at 4.2 K (Coe 1980). Magnetic hyperfine spectra enable a much more diagnostic analysis of site symmetries and valence states of iron in clay minerals (Borg & Borg 1974). Since the magnetic exchange interactions in insulators couple only nearest-neighbor ions, there is a critical concentration of octahedral magnetic ions, e.g., Fe²⁺, Fe³⁺ or Mn²⁺, for the appearance of continuous magnetic paths through the sheet. These paths are required for the existence of magnetic long-range order. The percolation limit is approximately 1/3 or 33% in trioctahedral clay minerals (Coe 1980).

If we combine the chemical and X-ray results from Tables 1 and 2, we estimate the Fe²⁺ + Fe³⁺ concentration in the octahedral sheet of the silicate layer of the chamosite to be much higher than the percolation limit. Experiments have not yet been carried out on these materials to see if magnetic ordering does indeed occur at temperatures down to 1 K, but these experiments are planned in the near future.

A further impediment to establishing mag-

netic order is the two-dimensional nature of the silicate layer. Unless iron also is present in tetrahedral sites, coupling between layers is weak. Thus, cronstedtite shows a clearly developed magnetic hyperfine spectrum at 4.2 K, whereas nontronite, with little tetrahedral iron, and glauconite, with none, show at most some signs of magnetic relaxation in their 4.2 K spectra. Where the magnetic ion is Fe²⁺, however, the single-ion anisotropy helps stabilize magnetic order. Thus, greenalite and certain samples of iron-rich biotite can order magnetically at temperatures below 20 K (Coe 1980).

In the samples of chamosite, our Mössbauer spectra indicate no tetrahedral iron. Hence, although the major component is Fe²⁺ and the magnetic ion concentration is above the percolation limit, the absence of tetrahedral iron appears to impede three-dimensional long-range magnetic ordering. The appearance of hyperfine components in the oxidized, but not the unoxidized, chamosites may be because the components result from impurities formed in the oxidation process. Alternatively, if the hyperfine spectra were inherent to the silicate structure, their absence in the samples of unoxidized chamosite might result from the different three-dimensional nature of the chamosite structure. However, based on our present data, further speculation is unwarranted.

According to Ingalls (1964), the total quadru-

pole interaction is the algebraic sum of a dominant ionic term and the lattice term, and the two contributions are expected to have opposite signs. For a distorted octahedral co-ordination, the total quadrupole interaction from Fe^{2+} should have a larger lattice-term contribution. Consequently, an absolute value for the total quadrupole interaction is expected to be smaller than that from Fe^{2+} in an undistorted octahedron. If this is the case, Fe^{2+} ions in distorted octahedral co-ordination in the two samples of chamosite are all oxidized during the treatment with saturated bromine water, whereas, in Fe-clinocllore, Fe^{2+} ions in undistorted octahedral co-ordination are oxidized. The case for the two samples of chamosite may be explained by the hypothesis that structurally strained Fe^{2+} ions are relatively easily oxidized because reduction in ionic radius from 0.74 (Fe^{2+}) to 0.64 Å (Fe^{3+}) with oxidation should relax the structural stress. However, in the case of Fe-clinocllore, a regularly interstratified chlorite-vermiculite structure was formed after oxidation. The presence of Fe^{2+} ions in distorted octahedral co-ordination after oxidation is significant in relation to the formation of the interstratified structure. This suggests that in Fe-clinocllore after oxidation, Fe^{2+} and Fe^{3+} ions are distributed in a certain regular manner in part to minimize electrostatic energy in the regulated layer-charge distribution; in this case, structurally distorted sites are necessarily occupied by Fe^{2+} ions.

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