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MAGNETIC INTERACTION AT LOW TEMPERATURE IN CHLORITE AND ITS PRODUCTS OF OXIDATION: A MÖSSBAUER INVESTIGATION

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ABSTRACT

Three trioctahedral chlorites (Fe-clinochlore, Mn-Mg-chamosite and Mg-chamosite) and their products of oxidation, an interstratified chlorite–vermiculite for the clinochlore and vermiculite for chamosite, have been studied by ^{57}Fe Mössbauer spectroscopy at temperatures down to 1.3 K. Magnetic order is established inhomogeneously in a range of temperatures below 7 K. The Fe^{2+} magnetic-hyperfine field is larger in chlorite than in vermiculite, and the range of Néel temperatures is lower in vermiculite. The results suggest that iron atoms are not uniformly distributed in octahedral sites of the hydroxide sheet and 2:1 layer. A magnetic-hyperfine-field distribution at Fe^{2+} in chlorite, and at Fe^{2+} and Fe^{3+} in oxidized chlorite, indicates varying local environments around the iron nuclei. Comparison of the Mössbauer spectra of chlorite and its products of oxidation, together with X-ray and chemical analyses, shows that even at 1.3 K there are magnetic and nonmagnetic domains in the hydroxide sheet and 2:1 layer of chlorite. The absence of long-range magnetic order in Mn–Mg-chamosite at 1.6 K, inferred from neutron-diffraction data (Ballet *et al.* 1985a), is reinterpreted in terms of short correlation-lengths for magnetic order.

Keywords: chlorite, interstratified, vermiculite, Mössbauer spectra, low-temperature magnetic interaction.

SOMMAIRE

Trois chlorites trioctaédriques (clinochlore-Fe, chamosite-Mn–Mg et chamosite-Mg) et leurs produits d'oxydation, chlorite-vermiculite pour clinochlore et vermiculite pour chamosite, ont été étudiées par spectroscopie Mössbauer ^{57}Fe à basses températures (jusqu'à 1.3 K). L'ordre magnétique s'établit de façon hétérogène au-dessous de 7 K. Le champ magnétique hyperfin Fe^{2+} est plus grand dans la chlorite que dans la vermiculite, et le domaine de température de Néel est plus bas dans la vermiculite. Les résultats font penser que le Fe n'est pas distribué de façon uniforme dans les sites octaédriques des feuillets "hydroxyde" et "silicate". La distribution du champ magnétique aux sites Fe^{2+} dans la chlorite, et aux sites Fe^{2+} et Fe^{3+} dans la chlorite oxydée, révèle l'environnement variable des atomes de fer. La comparaison des spectres Mössbauer de la chlorite et de la chlorite oxydée, ainsi que les résultats des analyses (chimique et par rayons X), montre que, même à 1.3 K, il se trouve des domaines magnétiques et nonmagnétiques dans les feuillets "hydroxide" et "silicate". On réinterprète l'absence d'ordre magnétique à longue distance dans la chamosite-Mn–Mg à 1.6 K, déduite des données de la diffraction neutronique (Ballet *et al.* 1985a), par la petitesse des distances de correlation pour l'ordre magnétique.

Mots-clés: chlorite, interstratifiée. vermiculite, spectre Mössbauer, interaction magnétique de basse température.

INTRODUCTION

Chlorite-group minerals are 2:1:1 sheet silicates in which a single sheet of cations octahedrally co-ordinated by hydroxyl groups is sandwiched between two 2:1 silicate layers. The 2:1 silicate layer is built up of two tetrahedral Si (Al)–O_4 sheets with their vertices pointing inward; between them, cations such as Mg, Fe, Al, *etc.*, are octahedrally co-ordinated with four oxygen atoms at the vertices and two incorporated hydroxyl groups. These two hydroxyl groups may be in a *cis* or *trans* position in the octahedron (Fig. 1; Bailey 1980).

Specimens of trioctahedral chlorite containing Fe^{2+} ions have been converted into a vermiculite structure, in which the hydroxide sheet is replaced by intercalated water molecules, by oxidizing Fe^{2+} using bromine (Ross 1975, Ross & Kodama 1976). The extent of vermiculitization appears to be related to the Fe^{2+} content of the original chlorite. A magnesium chamosite was changed to vermiculite (Ross 1975), whereas a clinochlore was transformed into a regularly interstratified chlorite–vermiculite structure (Ross & Kodama 1976).

Several papers have been published on Mössbauer spectra of chlorite-group minerals at room temperature (Weaver *et al.* 1967, Taylor *et al.* 1968, Ericsson *et al.* 1977, Blaauw *et al.* 1979, 1980, Hayashi *et al.* 1972, Borgaard *et al.* 1982, Goodman & Bair 1979). However, analysis of room-temperature spec-

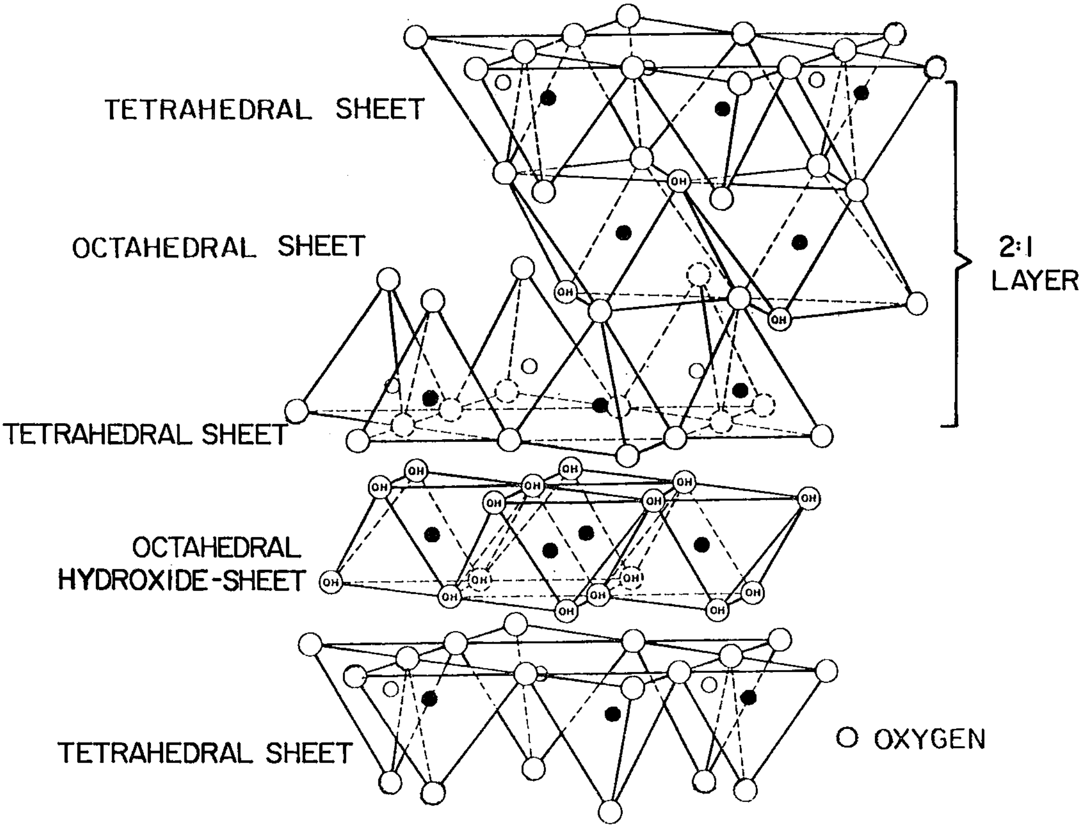

FIG. 1. The chlorite structure.

tra can be ambiguous, and the interpretations can be conflicting. In this work, by recording spectra at very low temperature, and hence high resolution, we have tested some of the hypotheses made.

There have been few studies of chlorite at low temperature, although, in principle, studies of magnetic properties of iron-rich silicates can lead to detailed information on magnetic and structural properties (Coey *et al.* 1981, Ballet & Coey 1982, Regnard 1976, Borg & Borg 1974, Moukarika *et al.* 1983). In a preliminary study, Kodama *et al.* (1982) examined the Mössbauer spectra of iron-clinochlore, Mn–Mg-chamosite and Mg-chamosite before and after oxidation. They noted that Fe^{2+} ions in distorted sites appear to be preferentially oxidized, but they were not able to make a meaningful interpretation of their low-temperature results because the spectra were recorded only at temperatures down to 8 K and those of oxidized chlorites, down to 4 K. As shown in this work, chlorite orders in a range of temperatures below 7 K.

We report the Mössbauer spectra at 1.3 K of three specimens of chlorite and their oxidation products. These spectra are the most detailed reported to date. Computer fits are given to all of these spectra. From their analysis an attempt is made to understand further the mechanism of vermiculitization and interstratification in chlorite-group minerals.

Ballet *et al.* (1985a), in work carried out concurrently with this study, have examined the magnetic, Mössbauer and neutron-diffraction properties of several types of chlorite. Their Mössbauer data for Mn–Mg-chamosite at low temperature are similar to those reported here. Their conclusions that Fe^{2+} ions are indistinguishable in *cis* and *trans* octahedral sites of the 2:1 layer and in octahedral sites of the hydroxide sheet are in agreement with the conclusions reached in this work. Their results concerning magnetic susceptibility suggest predominant ferromagnetic coupling for Fe^{2+} ions in the 2:1 layer and hydroxide sheets, with alternate octahedral planes coupled antiferromagnetically. Such magnetic structures have been observed previously in sheet silicates (Coey *et al.* 1981, Ballet & Coey 1982, Ballet *et al.* 1985b). Because Ballet *et al.* (1985a) observed no long-range magnetic order from neutron diffrac-

TABLE 1. POPULATIONS OF TETRAHEDRAL Al AND OCTAHEDRAL HEAVY ELEMENT OF CHLORITES AS DETERMINED BY X-RAY DIFFRACTION METHOD

					Heavy Element Population in Octahedral Co-ordination		
	d_{001}(Å)	^{IV}Al	Degree of Asymmetry	Total Octahedral Heavy Elements (A)	Octahedral Sheet of Silicate Layer-3 sites (B)	Interlayer Hydroxide Sheet-3 sites (C)	B/A(%)
Fe-Clinochlore	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

tion at 1.6 K in Mn–Mg-chamosite (nor in biotite), they invoked a vortex magnetic ground-state. They hypothesized that this state is induced by competition between antiferromagnetic coupling of Fe^{3+} pairs through 90° Fe^{3+}–O–Fe^{3+} bond angles in the 2:1 layer and hydroxide sheet, and ferromagnetic coupling of Fe^{2+}. In their model, the spin directions would be expected to spiral randomly. An alternative model is advanced in the present work.

EXPERIMENTAL METHOD AND RESULTS

The specimens and relevant chemical and X-ray data used in this study have been described previously (Kodama *et al.* 1982). The chlorites, iron-clinochlore, Mn–Mg-chamosite and Mg-chamosite, are trioctahedral, with the IIb polytype structure. The asymmetric distribution of octahedrally co-ordinated heavy-metal atoms between the 2:1 layer and hydroxide sheet of the chlorites was evaluated from the basal intensity ratio I_{003}/I_{005} following the method of Petruk (1964). The latter method is, however, subject to errors in estimating accurate intensities for the (003) and (005) reflections. A new method using intensities of (00ℓ) neutron-diffraction reflections, where ℓ is odd, is likely to be a useful alternative (Ballet *et al.* 1985a).

Results of chemical analyses (Kodama *et al.* 1982) show that a majority of the octahedrally co-ordinated heavy atoms in the chlorite samples consist of Fe. Based on the degree of asymmetry, the total octahedrally co-ordinated heavy atoms can then be allocated to the corresponding positions in the 2:1 layer and hydroxide sheets (Table 1). Thus 87% of total Fe atoms in the Fe-clinochlore is in octahedral sites of the 2:1 layer, whereas 68% or less (due to the presence of Mn) of those in the Mg-chamosite and similarly 64% or less of those in the Mn–Mg-chamosite occupy octahedral sites of the 2:1 layer.

Oxidized chlorites

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-clinochlore was transformed into a regularly interstratified chlorite–vermiculite structure, with 23% of the original remaining unchanged. The sample residues after oxidation were treated twice by sodium dithionite to remove metal oxides (mainly Fe and Al). Quantitative analysis of loss of iron during vermiculitization was difficult, and only qualitative determinations were made (Ross 1975, Ross & Kodama 1976).

Vermiculite and interstratified chlorite–vermiculite have crystallographic unit-cells with characteristic $\vec{c}$ dimensions (14.4 and approximately 29 Å, respectively) and were identified from their X-ray patterns. These dimensions compare with a $\vec{c}$ of 14.0 Å in Mg-chamosite.

Mössbauer spectra

Mössbauer spectra were recorded on a constant-acceleration Mössbauer spectrometer with a ^{57}Co source in a Rh matrix. Velocities were calibrated using Fe foil. A helium dewar was used to allow spectra to be recorded down to 1.3 K. Each spectrum was computer-fitted using a least-squares iterative procedure (Ruebenbauer & Birchall 1979) by the superposition of a number of component spectra, each generated from a set of parameters: H, the internal magnetic field, θ and ϕ, the polar angles of H in the axes of the principal electric-field gradient, $1/2e^2qQ$, the magnitude of the principal component of the electric-field-gradient tensor, η, the quadrupole parameter, Γ, the line width, and I.S., the isomer shift. A dimensionless magnetic-hyperfine field-distribution parameter, F Dist (Ruebenbauer & Birchall 1979), was used to take into account small variations in the local magnetic hyperfine field at an Fe atom owing to lattice disorder. Computer diagonalization of the full Hamiltonian was necessary for Fe^{2+} because the quadrupole splitting and magnetic hyperfine splitting for this cation are of the same order.

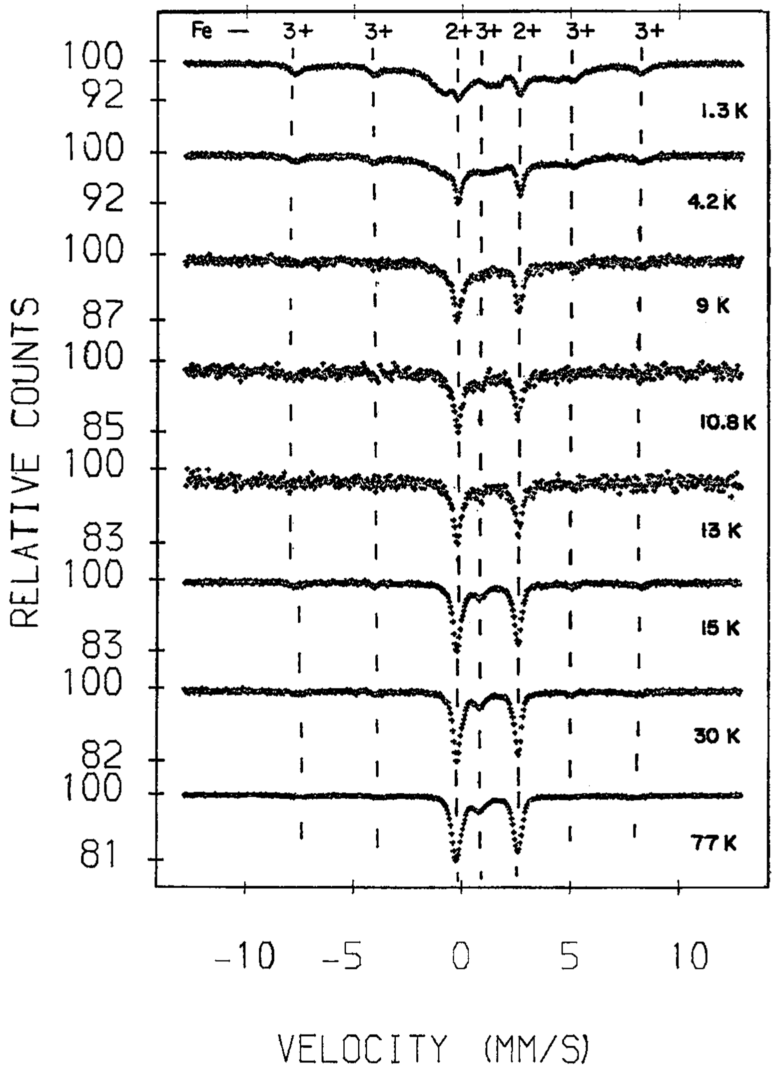

FIG. 2. Mössbauer spectra of Mg-chamosite mounted in icing sugar, at various temperatures.

Mössbauer spectra of the relatively iron-poor Fe-clinochlore and its oxidation product indicate only slight magnetic ordering, even at 1.3 K; the spectra are not greatly different from those reported previously at temperatures down to 4 K (Kodama *et al.* 1982). Mössbauer spectra at various temperatures of Mn–Mg-chamosite and Mg-chamosite and their oxidation products are shown in Figures 2–7. Computed parameters are given in Table 2. Fits of Fe^{2+} and Fe^{3+} magnetic and nonmagnetic components are indicated by stick-diagrams on each spectrum, as well as the overall theoretical line-fit.

The determination of Fe^{2+}/Fe^{3+} ratios and site occupancies (Table 2) is based on the relative proportion of areas under the appropriate absorption-peaks. 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.

Samples of the chlorite specimens and their oxidation products were mounted in grease to record the Mössbauer spectra. There are no great differences between the spectra at 1.3 K of Mg-chamosite mounted in grease or in icing sugar (Fig. 4). Some effects of preferential orientation or possibly relax-

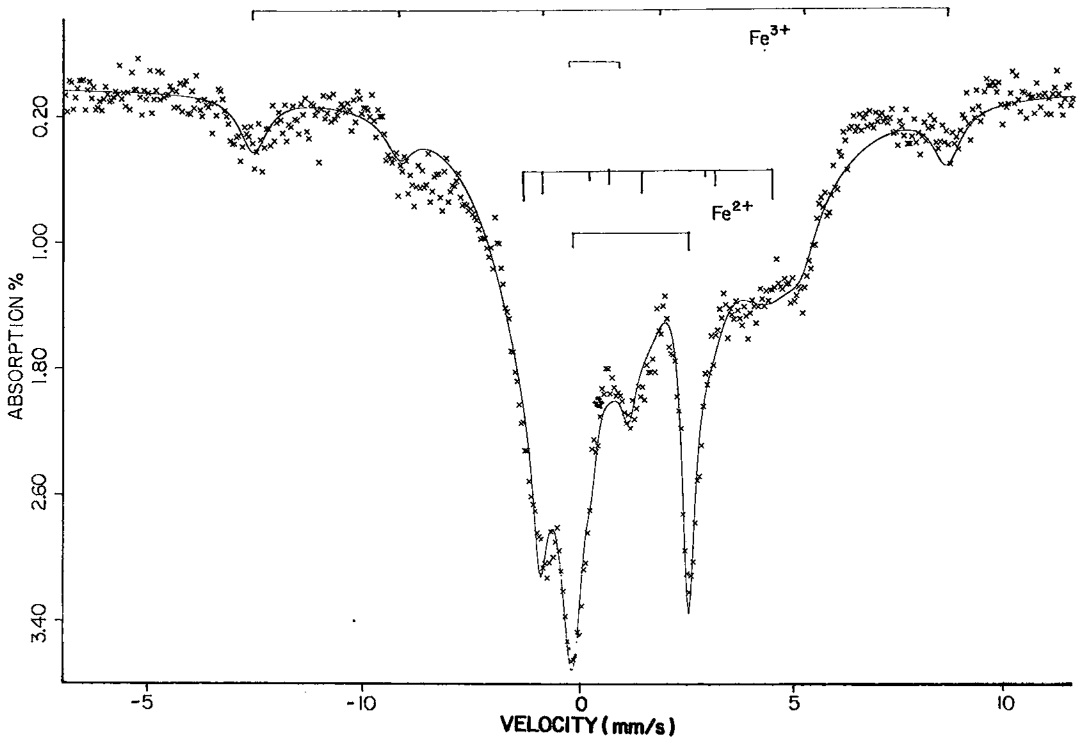

FIG. 3. Mössbauer spectrum of Mn–Mg-chamosite at 1.3 K.

ation do appear at low temperature in the oxidized chlorites. Here the magnetic Fe^{3+} sextet has been fitted with an intensity ratio of 3:2.8:1:1:2.8:3.

Although a detailed structural analysis is difficult, the major features of the spectra are clear from our study of their temperature dependence as discussed below. It is instructive to glance at Figure 2 before details of the fits are studied. Mössbauer spectra of Mg-chamosite at temperatures up to 77 K are shown here. The strong Fe^{2+} quadrupole doublet, with components at about +2.75 mm s^{-1} and -0.15 mm s^{-1}, is present down to the lowest temperature, 1.3 K, as indicated by the dashed lines of Figure 2. However, below 9 K its intensity is diminished, and a magnetic Fe^{2+} spectrum can be seen superimposed on this quadrupole doublet. A range of magnetic-ordering temperatures from just below 9 K to 0 K is indicated. (The oxidized chlorites appear to order in a slightly lower range of temperature.) The Fe^{3+} quadrupole component seen as a broad line at about 0.8 mm at higher temperatures vanishes abruptly below 9 K. We must assume that it arises from the chlorite, which becomes partially magnetized below 9 K, and the magnetic component then appears as a magnetic sextet superimposed on the more intense magnetic Fe^{3+} sextet at low temperature. The isomer shifts of Fe^{3+} in all the nonmagnetic hyperfine spectra, 0.49–0.63 mm s^{-1} (Table 2), show that Fe^{3+} ions are predominantly in octahedral sites. Earlier, some substitution of Fe^{3+} for tetrahedrally co-ordinated silicon had been proposed (Goodman & Bain 1979).

The four outside lines of the Fe^{3+} magnetic sextet indicated by dashed lines on Figure 2 are clearly still present at 77 K, although with diminished intensity. The value of the magnetic hyperfine splittings of this Fe^{3+} component at 1.3 K in Mg-chamosite and Mn–Mg-chamosite, 481 and 521 kOe, respectively, suggest the presence of a small-particle hematite impurity. This small-particle component is not detected by X-ray analysis.

In the fits for chlorite and oxidized chlorites, all parameters were allowed to float but not necessarily at the same time. In the final fit, line widths were constrained, as were values of η, θ, ϕ. In all fits, there is a weak broad absorption accounting for 3–4% of total Fe in the region of -0.8 mm, not indicated on the stick diagrams. This can only arise from magnetic Fe^{2+} and has been assigned accordingly in Table 2. It could originate from a small concentration of a second magnetic Fe^{2+} site or it could, in part, be due to preferential orientation of crystals

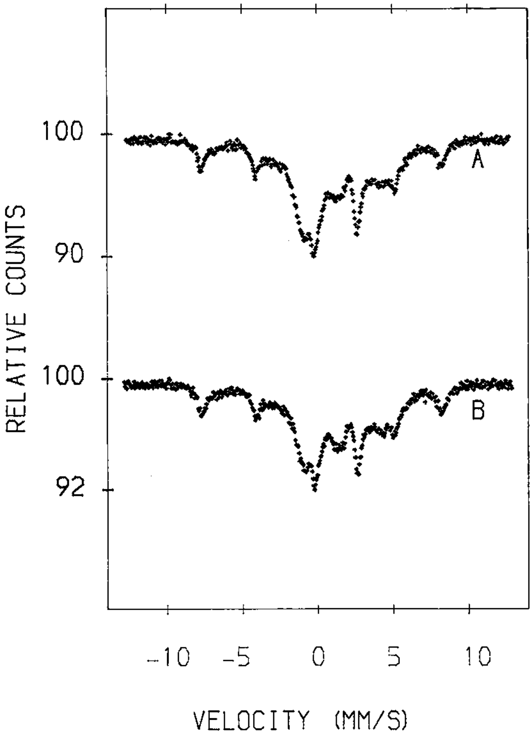

FIG. 4. Mössbauer spectrum at 1.3 K of Mg-chamosite (A) mounted in grease and (B) mounted in icing sugar.

in the powder, where the two lowest-velocity lines of Fe^{2+} would increase slightly in intensity.

DISCUSSION

The Fe^{2+} magnetic spectra of Mn–Mg-chamosite and Mg-chamosite at 1.3 K are somewhat similar to the spectrum at 4 K of biotite, a 2:1 layer silicate (Ballet & Coey 1982). This may not be so surprising because the octahedral sites in the 2:1 layer of Mn–Mg-chamosite and Mg-chamosite contain 64% and 68%, respectively, of the total Fe content.

It has been proposed, based on the analysis of room-temperature spectra, that Fe^{2+} ions are restricted to the 2:1 layer in chlorite (Borgaard *et al.* 1982, Blaauw *et al.* 1980). The present results (Tables 1, 2) show that this cannot be so. Indeed, Ross & Kodama (1976) showed that the extent of vermiculitization of chlorite depends on the concentration of Fe^{2+} in the hydroxide sheet.

In the octahedral sites of the hydroxide sheet and 2:1 layers of chlorite, an iron atom is at the centre of a hexagon of next-nearest-neighbor cations. For magnetic order, continuous paths of iron atoms are required in the sheets. This means that, for a trioctahedral sheet, the population of iron atoms per site must exceed 1/3. In Table 1, columns B and C indicate the population of heavy elements in the three octahedral sites of the 2:1 layer and hydroxide sheets, respectively. These results, together with those of

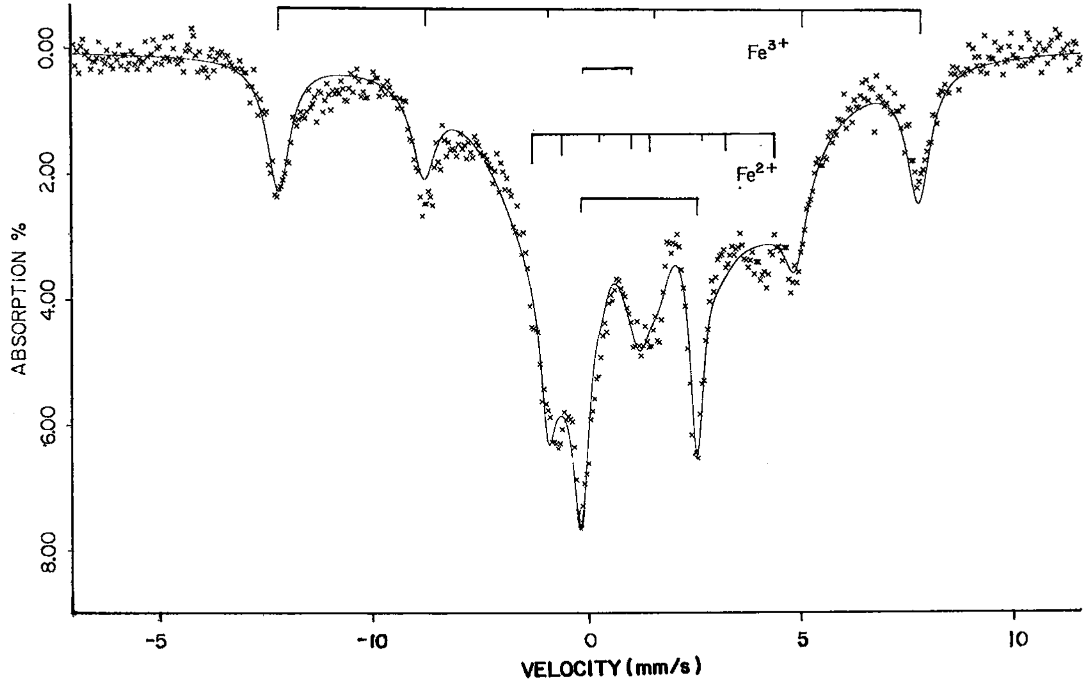

FIG. 5. Mössbauer spectrum of Mg-chamosite at 1.3 K.

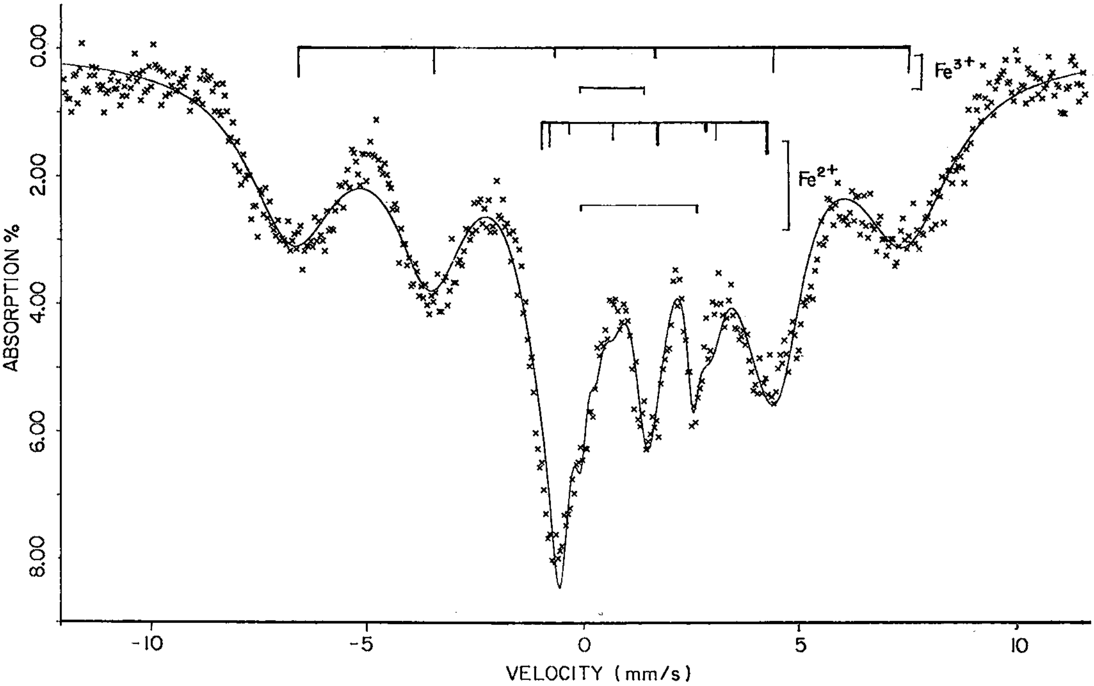

FIG. 6. Mössbauer spectrum of oxidized Mn–Mg-chamosite at 1.3 K.

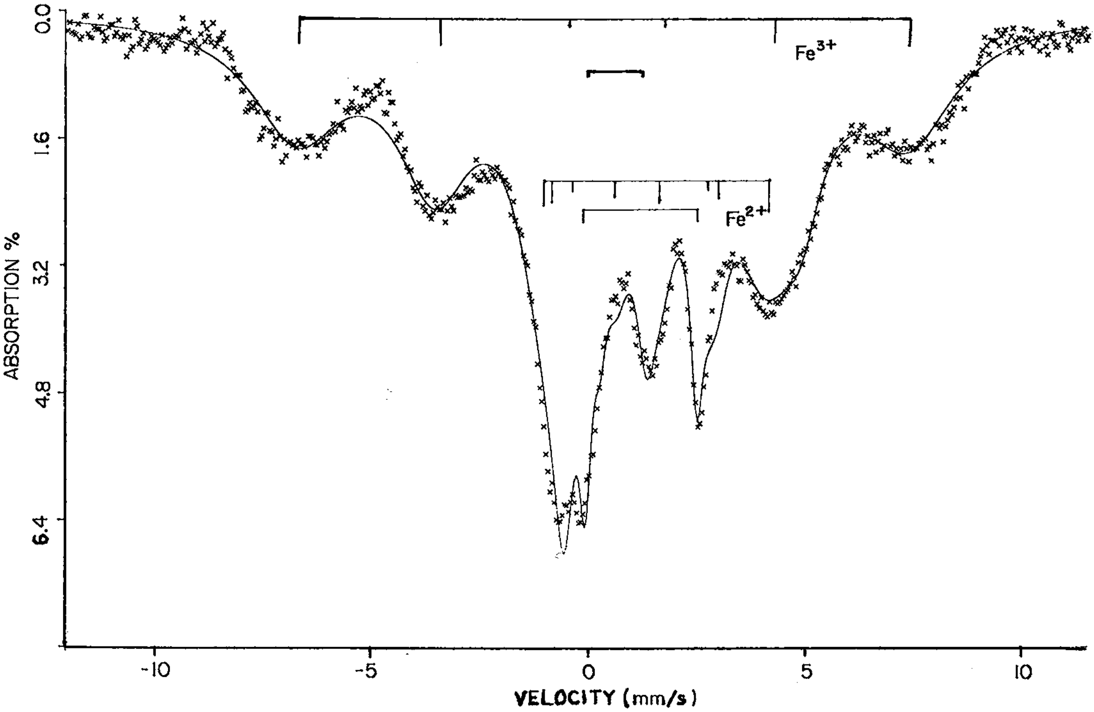

FIG. 7. Mössbauer spectrum of oxidized Mg-chamosite at 1.3 K.

TABLE 2. COMPUTED MÖSSBAUER PARAMETERS FOR CHLORITES AND THEIR OXIDIZED PRODUCTS AT 1.3 K

	$\frac{1}{2}e^2qQ$ mm/s	HkOe	η	θ	ϕ	I.S.$^+$	Γ* mm/s	FDist	Counts/ch	χ^2	%
Mn-Mg-chamosite Fe^{2+}	-3.0	127	0.38	90°	0°	1.38	0.4	0.45	1.2x10^6	1.7	60
$(Fe_2O_3)\gtrsim$ 70%-Fe^{3+}	+0.3	521	0	90°	0°	.475	0.7	0			22
Fe^{2+}	2.83	-	-	-	-	1.23	0.4	-			11
Fe^{3+}	1.36	-	-	-	-	0.49	0.4	-			7
Mg-chamosite Fe^{2+}	-2.58	122	0.33	90°	0°	1.37	0.4	0.48	3x10^5	1.96	66
$(Fe_2O_3)\gtrsim$ 70%-Fe^{3+}	+0.53	481	0	90°	0°	0.485	0.7	0			22
Fe^{2+}	2.83				0°	1.27	0.4	-			8
Fe^{3+}	1.4	-	-	-	-	0.63	0.4	-			4
Oxidized Mn-Mg-chamosite Fe^{2+}	-2.9	100	0.4	90°	0°	1.38	0.4	0.39	1.5x10^5	1.9	42
Fe^{3+}	+0.3	442	0	90°	0°	0.44	0.4	0.12			47
Fe^{2+}	2.9	-	-	-	-	1.3	0.4	-			7
Fe^{3+}	1.5	-	-	-	-	0.5	0.4	-			4
Oxidized Mg-chamosite Fe^{2+}	-2.9	101	0.33	90°	0°	1.38	0.4	0.39	8x10^5	3.3	46
Fe^{3+}	+0.3	451	0	90°	0°	0.46	0.4	0.12			54
Fe^{2+}	2.85	-	-	-	-	1.3	0.4	-			8
Fe^{3+}	1.3	-	-	-	-	0.6	0.4	-			2

*Γ linewidth, FDist dimensionless magnetic-hyperfine field-distribution factor (Ruebenbauer & Birchall 1979), + I.S. mm/s with respect to Fe.

chemical analysis, indicate that apart from the hydroxide sheet of Fe-clinochlore, there is always sufficient iron per site (more than 1/3) for magnetization and, if these Fe atoms were uniformly distributed in the hydroxide sheet and 2:1 layer, complete magnetic order would be anticipated at a sufficiently low temperature.

The Mössbauer spectra of Fe-clinochlore, Mn-Mg-chamosite and Mg-chamosite indicate that magnetic order in all three chlorites occurs in a range of temperatures below 7 K. Even at 1.3 K there is a considerable fraction of Fe atoms, on the order of 10–20% for the two varieties of chamosite, and much more for the relatively iron-poor clinochlore, either in the paramagnetic state or in internal magnetic fields of very low magnitude. This indicates that the Fe atoms are not distributed uniformly in the octahedral sites of the hydroxide sheet and 2:1 layer and implies the presence of magnetic and nonmagnetic domains at this temperature.

The Fe^{2+} magnetic-hyperfine spectra on Mn–Mg-chamosite and Mg-chamosite are characterized by small hyperfine fields with a large distribution (Table 2). This again indicates that the Fe^{2+} ions in the 2:1 layer and hydroxide sheet see varying local environments owing to random next-nearest-neighbor substitution of Mg^{2+}, Mn^{2+}, Al^{3+} or vacancies, *etc.* This broadening of the Fe^{2+} magnetic-hyperfine spectrum precludes any discrimination by Mössbauer spectroscopy between Fe^{2+} ions of octahedral *cis* or *trans* sites in 2:1 layers or in hydroxide sheets.

The Fe^{3+} magnetic-hyperfine spectra in oxidized chlorite are broad and asymmetric. The broad lines indicate a varying local field at Fe^{3+} consistent with that observed at Fe^{2+} before oxidation. Relaxation effects may also be present in Fe^{3+}. The asymmetry may result from correlations between distributions in hyperfine parameters.

The disorder among iron atoms is consistent with the absence of a sharp Néel temperature. Long-range antiferromagnetic order requires either an interaction by weak magnetic exchange, or dipolar interaction between 2:1 layers, or an anisotropic field in the octahedral plane. This is necessary because long-range magnetic order in an isotropic or planar anisotropic Heisenberg system is unstable to thermal excitations (Mermin & Wagner 1966). Exchange coupling between Fe atoms along the *c* axis would be remarkable in that it would involve a chain of intervening oxygen and silicon atoms in chlorite plus intercalated molecules of water in vermiculite. Regnault (1982) proposed that the magnetization of planar $BaCo_2(PO_4)_2$ is stabilized by superexchange in a similarly long chain of diamagnetic atoms.

Recently, Ballet *et al.* (1985a) have shown from neutron diffraction of Mn–Mg-chamosite and of biotite that only short-range magnetic order exists at 1.6 K. They interpreted the absence of long-range magnetic order in terms of a vortex ground-state in the 2:1 layer brought about by antiferromagnetic coupling of Fe^{3+} pairs, through 90° Fe^{3+}–O–Fe^{3+} bond angles in the silicate plane, competing with ferromagnetic coupling of Fe^{2+} pairs. However, whereas empirical rules do predict antiferromagnetic coupling of 90° Fe^{3+} pairs (Goodenough 1963), experimental results, in Fe_2O_3, for example, show ferromagnetism (Samuelsen & Shirare 1970).

Whereas we accept that certain localized vortices may possibly exist, we do not believe that this is the prime reason for the absence of long-range magnetic order. Disorder among Fe^{2+}, Al^{3+}, Fe^{3+}, Mn^{2+}, Mg^{2+} ions and the presence of vacancies in the 2:1 layer which, as discussed above, lead to a range of Néel temperatures and imply the presence of magnetic and nonmagnetic domains at 1.3 K, indicate short correlation-lengths for magnetization in the 2:1 layer and hydroxide sheet, and along the direction of the $\vec{c}$ axis. The shortest correlation-length is likely to be along the $\vec{c}$ axis.

There appears to be no information on the minimum size of domain required to support Mössbauer magnetic-hyperfine splitting in a magnetic domain of Fe^{2+} ions. Evidently, however, this minimum size is considerably smaller than the correlation length required for coherent magnetic scattering in neutron diffraction. Thus we believe that the absence of long-range magnetic order observed in chlorite (and in biotite) by Ballet *et al.* (1985a) is not due primarily to a vortex magnetic ground-state in the silicate plane induced by antiferromagnetic Fe^{3+} pairs, but results rather from spin-correlation lengths sufficiently long to support magnetic-hyperfine splitting but too short to give coherent magnetic scattering in neutron diffraction.

Mössbauer spectra in an external field of biotite (Townsend & Longworth 1985) and glauconite (Longworth *et al.* 1985) provide compelling support for this argument. A vortex state in an external magnetic field of 40 kOe should show smeared-out Fe^{3+} hyperfine lines because of the random spin-directions, unless the vortex state were broken up in external field. The Mössbauer spectrum of biotite in an external field shows that Fe^{3+} hyperfine lines remain sharp but move in to give a smaller magnetic-hyperfine splitting, indicating ferromagnetic coupling of Fe^{3+} ions (Townsend & Longworth 1985), although Fe^{3+} ions in biotite may not necessarily be completely in nearest-neighbor pairs. In glauconite, containing predominantly Fe^{3+} ions, Mössbauer spectra in an external field show that the coupling of Fe^{3+} ions is again ferromagnetic (Longworth *et al.* 1985).

Ballet & Coey (1982) proposed that ferromagnetism in glauconite results from ferromagnetic, nearest-neighbor Fe^{2+}–Fe^{3+} coupling and that Fe^{3+}–Fe^{3+} nearest-neighbor coupling is always antiferromagnetic in the silicate sheet. This model and the vortex model require that Fe^{3+} and Fe^{2+} ions are randomly distributed in the 2:1 layer. On the other hand, if, as is quite possible, Fe^{3+} ions were contained in domains in the 2:1 layer, the results of Townsend & Longworth (1985) and Longworth *et al.* (1985) would necessarily show that nearest-neighbor Fe^{3+} ions must be coupled ferromagnetically in biotite and glauconite. The question of whether or not domains of Fe^{3+} ions exist in mixed-valence sheet silicates is of great interest to clay mineralogists.

In principle, further experiments on magnetic properties of sheet silicates could yield valuable information on this point. Unfortunately, our Mössbauer spectrum of Mg-chamosite at 1.3 K in an external magnetic field of 40 kOe throws no further light on the problem because of the impurity Fe^{3+} magnetic-hyperfine lines present.

The question of which Fe^{2+} ions, in the 2:1 layer or hydroxide sheet, may be oxidized preferentially is related to the above. Kodama *et al.* (1982) suggested that Fe^{2+} ions in more distorted sites, having smaller quadrupole splittings, were more likely to be oxidized. They speculated that decrease of the ionic radius in going from Fe^{2+} to Fe^{3+} would relax the strain at that particular site. However, other factors such as degree of covalency and crystal-field-stabilization energy should also be important; Rozenson & Heller-Kallai (1977) showed that the degree of covalency determined the distribution of Fe^{3+} ions between *cis* and *trans* sites in a number of smectite samples.

There are also indications that certain ions may prefer particular planes. It is known that substitution of trivalent ions for Mg^{2+} in the hydroxide sheet is charge-compensated by replacement of Si^{4+} by Al^{3+} in the sheet of tetrahedra of the silicate layer (Bailey 1980). Formation of an interstratified chlorite–vermiculite suggests variation in Fe^{2+} content of alternate hydroxide sheets in chlorite.The foregoing leads to the speculation that the nature of the local site may not determine the probability of oxidation. In vermiculite, as oxidation product, there may possibly be 2:1 layers containing predominantly Fe^{3+} interleaved with 2:1 layers accommodating mainly Fe^{2+}.

The value of the Fe^{2+} magnetic-hyperfine field in chlorite (127 kOe) is greater than that in vermiculite (100 kOe) at 1.3 K (Table 2). This probably results from the lower range of Néel temperatures in vermiculite. The latter could indicate a decrease in the magnetic interaction between 2:1 layers in vermiculite, where the partly magnetic hydroxide sheet is replaced by a layer of intercalated water molecules. Alternatively, there may be a decrease in average magnetic exchange interaction due to partial loss of iron in the 2:1 layer during the vermiculitization process.

CONCLUSIONS

A range of magnetic-ordering temperatures occurs below 7 K in chlorite, and its products of oxidation similar to vermiculite, indicating disorder of Fe^{2+}, Mn^{2+}, Mg^{2+}, Al^{3+} and vacancies in octahedral sites. There is a distribution in Fe^{2+} magnetic-hyperfine field in the spectra of chlorites and in Fe^{2+} and Fe^{3+} hyperfine fields in vermiculite. The Fe^{2+} magnetic-hyperfine field in vermiculite is smaller than in chlorite, and there are indications that the range of Néel temperatures is lower in vermiculite. The distribution of Fe^{2+} and Fe^{3+} cations between octahedral *cis* and *trans* sites of the 2:1 layer and octahedral sites of the hydroxide sheet cannot be determined from Mössbauer spectra, even at 1.3 K. Short-range magnetic order observed in neutron diffraction of Mn–Mg-chamosite at 1.6 K by Ballet *et al.* (1985a) is attributed here to correlation lengths sufficiently long to support Mössbauer magnetic-hyperfine splitting but too short to allow coherent magnetic scattering in neutron diffraction.

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