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Mössbauer spectra of minnesotaite and ferroan talc

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ABSTRACT

Mössbauer spectra of five samples of minnesotaite and one of ferroan talc have been recorded at 296 K and 4.2 K. A single ferrous doublet with isomer shift $\delta = 1.13$ mm/s relative to αFe and quadrupole splitting $\Delta = 2.74$ mm/s is observed in all minnesotaite samples at room temperature. The ferroan talc has a smaller quadrupole splitting, $\Delta = 2.55$ mm/s. All minnesotaite samples order antiferromagnetically, with Néel points in the range 25–37 K, but ferroan talc does not order magnetically down to 4.2 K. Two distinct ferrous populations in minnesotaite are inferred from the resolved magnetically split spectra at 4.2 K. The minority sites may be those coordinated by the excess OH in the minnesotaite structure. The *P*-cell and *C*-cell variants have distinctly different hyperfine fields (10.4 and 14.9 T for the two sites in the *P* cell but 8.9 and 14.4 T in the *C* cell), although their Néel points are similar.

INTRODUCTION

Minnesotaite was originally considered by Gruner (1944) to be an Fe analogue of talc having ideal formula $\{Fe_3^{2+}\}[Si_4]O_{10}(OH)_2$, where { } and [ ] denote the octahedral and tetrahedral sites, respectively. More recently, X-ray and electron diffraction studies (Guggenheim and Bailey, 1982; Guggenheim and Eggleton, 1986) showed that the structure is considerably more complex. The structure differs from that of talc by its periodic modulation along *a* as a result of inverted tetrahedra that form chains along *b* in the interlayer region. These chains cross link adjacent 2:1 layers and tetrahedral strips. Three major structural varieties exist; two possess unit cells forming primitive (*P*) or end-centered (*C*) Bravais lattices. A third form shows extensive streaking in the diffraction pattern, indicating disorder in the displacements and widths of the strips. Intergrowths of the three forms as well as less common forms that have greater variations in strip widths have been reported by Guggenheim and Eggleton (1987) and Ahn and Buseck (1989).

Although the ideal formula of the *P* form of minnesotaite is $(Fe,Mg)_{30}Si_{40}O_{96}(OH)_{28}$ and that of the *C* form is $(Fe,Mg)_{27}Si_{36}O_{86}(OH)_{26}$, the analyses may be recast to give a formula analogous to talc, with a tetrahedral : octahedral cation ratio of 4:3. Furthermore, it is noted that when the structural modulation is ignored, minnesotaite has a subcell that closely approximates the unit cell of talc (Guggenheim and Eggleton, 1986). Evans and Guggenheim (1988) reviewed published analyses of minnesotaite, ferroan talc, and talc and found a lack of compositions having the octahedral Fe fraction in the range 0.45–0.60, perhaps indicating the chemical limits of the structures.

Both minnesotaite and talc have a continuous octahedral sheet (Fe in minnesotaite, Fe,Mg in ferroan talc) but differ in the nature of the tetrahedral sheets. It is therefore of interest to determine whether the different structures produce distinctive Mössbauer spectra. Minnesotaite is one of the few sheet silicates that exhibit long-range magnetic order (Ballet al., 1985a, 1985b; Coey, 1987, 1988). A disordered *P*-cell sample investigated by Coey et al. (1990) showed planar antiferromagnetic order below about 30 K with moments in the *ab* planes, but both the interlayer magnetic order and the long-range ferromagnetic correlations in the octahedral sheets can be destroyed by applying a magnetic field. Mössbauer spectra of the same sample in the magnetically ordered state show a characteristic ferrous hyperfine pattern (Coey, 1984; Townsend et al., 1985), which was earlier fitted with a single Fe^{2+} magnetic component. Here we analyze Mössbauer spectra of five samples of minnesotaite and one of ferroan talc in order to define the range of hyperfine parameters for these minerals and to attempt to correlate variations in the spectra with structural and magnetic properties.

EXPERIMENTAL RESULTS

Details of the six Fe-rich samples examined are given in Table 1. The cell type (*P* or *C*) was determined by selected area electron diffraction using a transmission electron microscope (TEM). The Bluebell minnesotaite (MC1) showed *hk*0 patterns with maxima within diffuse streaking along **a***, indicating structural organization ap-

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TABLE 1. Sample data

	Minnesotaite*	Minnesotaite	Minnesotaite**	Minnesotaite†	Minnesotaite‡	Talc§
Sample	1 BM 131	2 Brit. Mus. 1975,420	3	4 DC-21	5 MC1	6
Locality	Sagamore pit, Cuyuna district, Minnesota	near Empire mine, Marquette Range, Marquette Co., Michigan	Auburn mine, Minnesota	near Ardua Lake, Quebec	Bluebell mine, Riondel, British Columbia	Sterling mine, Antwerp, N.Y.
Structure type	*C*	unknown	*P*	*P*	disordered *P*	*1Tc*—disordered
T_N (K)	37(2)	33(2)	31(1)		28(2)	—
Composition						
SiO_2	51.79		52.26	53.85	51.47	54.5
Al_2O_3	1.46		0.36	0.15	1.57	0.2
Fe_2O_3	0.61		31.45‖	30.53‖	3.23	4.7
FeO	35.65				30.50	12.6
MnO	0.78		0.02	0.53	1.83	
MgO	3.21		8.40	9.68	5.10	17.2
Na_2O	0.06		b.d.	0.15		
K_2O	0.44		0.36	0.17		
H_2O^+	5.03				5.88	4.5
H_2O^+	0.03				0.16	0.5

Note: The abbreviation b.d. = below detection.

* See Blake (1965) and Guggenheim and Eggleton (1986).

**Analysis represents an average from Guggenheim and Eggleton (1986).

† See Lesher (1978) and Guggenheim and Eggleton (1986).

‡ Analysis from Perrault and Hébert (1968); see also Guggenheim and Eggleton (1986). This sample shows severe disorder along *X**, but maxima within streaks approximate a *P* cell.

§ Analysis from Robinson and Chamberlain (1984). The sample shows complete disorder along *Z**.

‖ Fe_{tot} as FeO.

proaching the *P* cell but with considerable strip-width disorder. Talc, in contrast to minnesotaite, does not show disorder along **a*** but may show stacking disorder along **c*** due to 2:1 layer displacements. The Sterling talc is fully disordered. The Empire mine minnesotaite was not examined by TEM or microprobe.

Mössbauer spectra were obtained using a constant acceleration spectrometer with a source of ^{57}Co in a Rh matrix. Experimental data were fitted using a nonlinear least-squares program that adjusts the parameters appearing in the hyperfine Hamiltonians for Fe^{2+} and Fe^{3+}. The Hamiltonian for the nuclear excited state for Fe^{2+} is not diagonal for a general orientation of the electric field gradient relative to the direction of the magnetic hyperfine field, so the ferrous magnetic patterns normally comprise eight lines. Isomer shifts are quoted relative to αFe. Samples were dispersed in icing sugar to avoid preferred orientation.

The magnetic ordering temperature was taken as the point of inflection in thermomagnetic scans in an applied field of 50 mT (Fig. 1). This definition of the magnetic ordering temperature was established by neutron diffraction and thermomagnetic analysis of sample 5 (Ballet et al., 1985a). No sign of magnetic order was observed in the ferroan talc.

Figure 2 shows typical room-temperature spectra, the main component of which is the ferrous doublet; there is also a small amount of Fe^{3+} present (5–20% of the Fe_{tot} in the silicate). Spectra of associated Fe oxides are detected in some cases—magnetite for the Ardua Lake minnesotaite (65% of Fe_{tot}) and hematite for the ferrous talc (less than 5% of Fe_{tot}). The least-squares fitted parameters are shown in Table 2, with parameters for magnesium talc included for comparison. Ferrous line widths (full-width at half maximum) are approximately 0.4 mm/s, as is usual for clay minerals. As in chlorite (Coey, 1984), there is no evidence of two separate doublets in the minnesotaite spectra that could be attributed to Fe on M1 and M2 sites, nor is the goodness-of-fit parameter χ^2 significantly reduced when two components are allowed. The parameters for *P*- and *C*-cell minnesotaite are indistinguishable from each other [$\delta = 1.13(1)$ mm/s, $\Delta = 2.74(2)$

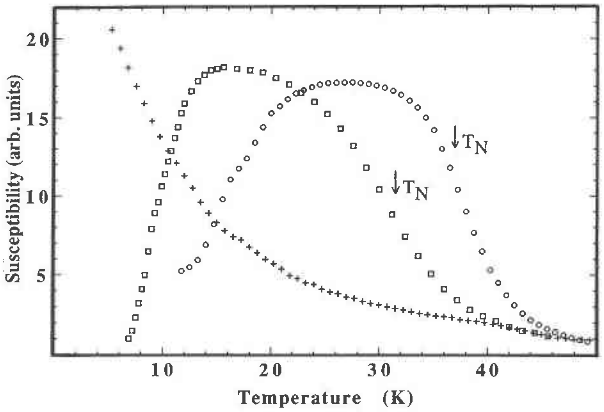

Fig. 1. Magnetic susceptibility on heating zero-field cooled samples in an applied field of 50 mT. Open squares = *P*-cell minnesotaite (Auburn mine); open circles = *C*-cell minnesotaite (Sagamore pit); crosses = ferroan talc (Sterling mine). The Néel temperatures of the minnesotaite samples are indicated by the arrows.

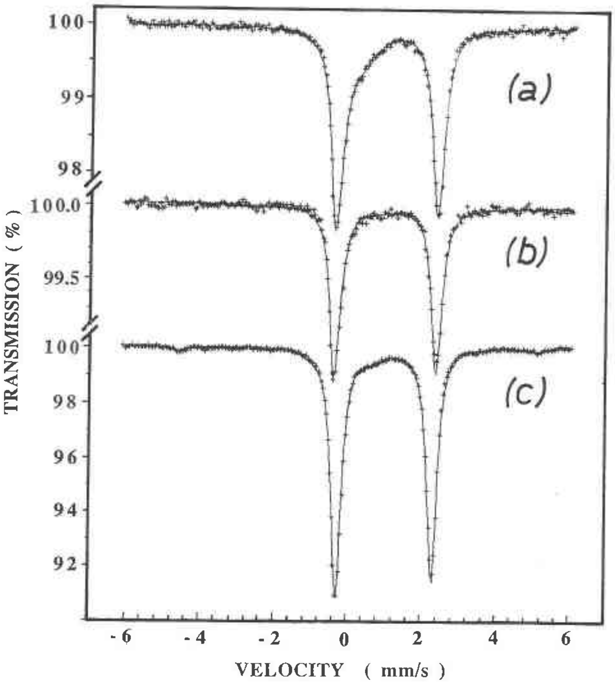

Fig. 2. Mössbauer spectra at 296 K for (a) *P*-cell minnesotaite (Auburn mine); (b) *C*-cell minnesotaite (Sagamore pit); (c) ferroan talc (Sterling mine). Solid line represents least-squares fit to the experimental points.

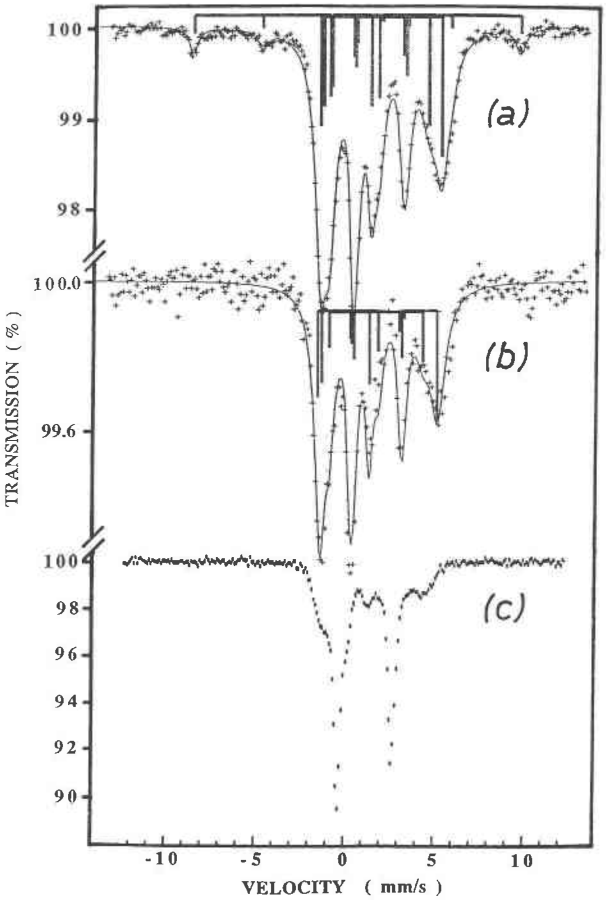

Fig. 3. Mössbauer spectra at 4.2 K for (a) *P*-cell minnesotaite (Auburn mine); (b) *C*-cell minnesotaite (Sagamore pit); (c) ferroan talc (Sterling mine). Solid lines represent least-squares fit to the experimental points.

mm/s for both], but the quadrupole splitting for ferroan talc is significantly different [$\delta = 1.12(1)$ mm/s, $\Delta = 2.53(4)$ mm/s].

Figure 3 shows typical spectra at 4.2 K for three samples. The spectra for *P*- and *C*-cell minnesotaite exhibit clear ferrous magnetic hyperfine structure, with a ferric hyperfine pattern appearing also for the *P*-cell samples. The ferroan talc, which showed no sign of magnetic order in the susceptibility measurements, exhibits a mixed spectrum that may reflect a broad range of magnetic relaxation times centered around 5×10^{-9} s (Rao et al., 1979).

TABLE 2. Hyperfine parameters at 296 K

Sample	1	3	4	5	6
δ (mm/s)	1.13(2)	1.13(2)	1.13(2)	1.13(2)	1.12(2)
Δ (mm/s)	2.74(2)	2.74(2)	2.75(2)	2.72(2)	2.53(2)
A (%)	100	82	34	85	83
δ (mm/s)		0.32(2)		0.41(2)	0.27(2)
Δ (mm/s)		0.47(2)		0.78(2)	0.79(2)
A (%)		18		15	9
δ (mm/s)			0.25(2)		0.30(2)
Δ (mm/s)			0.02(1)		−0.20(2)
B_{hf} (T)			49.5(2)		51.7(3)
A (%)			20		8
δ (mm/s)			0.64(2)		
Δ (mm/s)			0.02(1)		
B_{hf} (T)			46.1(3)		
A (%)			46		
χ^2	1.1	1.3	1.4	1.2	1.5

Note: The symbols are defined as follows: δ = isomer shift relative to αFe; Δ = quadrupole splitting or quadrupole shift; B_{hf} = magnetic hyperfine field; A = relative absorption area; χ^2 = per degree of freedom in the fit.

The magnetically ordered spectra of all the minnesotaite samples require a minimum of two ferrous subspectra for an adequate fit that reproduces, for example, the asymmetry in the line at ~5 mm/s. The χ^2 parameter is reduced by approximately 30% on passing from a fit with one eight-line ferrous pattern to one with two eight-line patterns. Fitted parameters are included in Table 3. Both ferrous subspectra have similar isomer shifts $\delta \approx 1.28(2)$ mm/s, a negative quadrupole splitting of $\Delta \approx -3.0$ mm/s, and an asymmetry parameter $\eta \approx 0$. The negative symmetric quadrupole interaction is familiar from other trioctahedral silicates such as greenalite and biotite (Coey, 1988), where it is associated with the hard **c**-axis magnetic anisotropy resulting from the orbital singlet ground state of Fe^{2+} (Varret 1976). Furthermore the angle θ between the **c** axis and the direction of the magnetic hyperfine field is 90°, as expected for easy-plane anisotropy. The two subspectra have distinctly different hyperfine

Table 3. Hyperfine parameters at 4.2 K

Sample	1	2	3	5
δ (mm/s)	1.26(2)	1.27	1.30(2)	1.28(2)
Δ (mm/s)	−2.96(2)	−3.01	−3.03(2)	−3.06(2)
B_{hf} (T)	14.4(2)	15.1.	14.9(2)	14.8(2)
η	0	0	0	0
θ (°)	90	90	90	90
A (%)	72	39	53	50
δ (mm/s)	1.28(2)	1.28(2)	1.30(2)	1.30(2)
Δ (mm/s)	−2.94(2)	−2.96(2)	−2.95(2)	−2.94(2)
B_{hf} (T)	8.9(2)	10.6(2)	10.4(2)	10.3(2)
η	0	0	0	0
θ (°)	90	90	90	90
A (%)	28	53	42	40
δ (mm/s)		0.49(2)	0.46(2)	0.55(2)
Δ (mm/s)		−0.15(2)	−0.02(2)	0.03(2)
B_{hf} (T)		51.0(2)	52.5(2)	45.5(2)
A (%)		8	5	10
χ^2	1.0	1.6	1.8	1.9

Note: The symbols are defined as follows: δ = isomer shift relative to αFe; Δ = quadrupole splitting or quadrupole shift; B_{hf} = magnetic hyperfine field; A = relative absorption area; η = asymmetry parameter; θ = angle between the principal component of the electric field gradient and B_{hf}; χ^2 = per degree of freedom in the fit.

fields: 14.9 and 10.4 T for *P*-cell minnesotaite and 14.4 and 8.9 T for *C*-cell minnesotaite. The smaller hyperfine field for the *C*-cell structure is an intrinsic effect, unrelated to ordering temperature, since it may be seen from Table 1 that T_N is higher in the *C*-cell material. The Fe^{3+} in *P*-cell minnesotaite gives a separate magnetic hyperfine pattern, with a hyperfine field that is quite sample dependent, ranging from 45.5 to 52.5 T (see Table 2).

DISCUSSION

A great deal has been written about the interpretation of the paramagnetic Mössbauer spectra of 2:1 layer silicates in terms of Fe site preferences (*cis* vs. *trans;* proximity of trivalent cations on tetrahedral sites; octahedral site environment). Some reviews are given by Heller-Kallai and Rozenson (1981), Coey (1984), and Dyar (1987). However, there is little to be learned from Mössbauer spectra if the paramagnetic doublets from Fe in different sites overlap and are not at least partially resolved. In minnesotaite and chlorite (Ballet et al., 1985b), the Fe is present in such large amounts that it must occupy different sites, yet the ferrous absorption is well fitted by a single quadrupole doublet with somewhat broadened lines. Different site populations may nevertheless be resolved at low temperatures if the Mössbauer spectrum of minnesotaite is magnetically split.

It is apparent from the 4.2-K data that there are at least two distinct types of Fe sites, which have different hyperfine fields but are similar in other respects. The Fe-site populations are roughly 3:1 in the *C*-cell and 3:2 in the *P*-cell samples, with the larger amount of Fe in the site with the greater hyperfine field. Minnesotaite has no net layer charge, and there is little substitution of trivalent cations for Si, so one possibility might be to associate M2 Fe with the larger hyperfine field (~15 T) and M1 Fe with the smaller (~10 T), where M1 and M2 refer to octahedral sites with *cis* and *trans* configurations of the two OH groups in the minnesotaite subcell. However, the average ferrous hyperfine field in biotite, which has both M1 and M2 ferrous occupancy, is 15 T (Coey, 1988). The partial tetrahedral inversions in minnesotaite are likely to create greater perturbations in the hyperfine field because they increase the number of OH groups in the octahedron. The excess OH is related to substitution of OH for tetrahedral apical O where the tetrahedra are inverted. Furthermore, these OH groups are not linked to further Si atoms. In view of the similarity in quadrupole interaction, the orbital contribution to the ferrous hyperfine field should be similar at the two sites, so the main difference should be in the contact term. It is known from the Fe^{3+} hyperfine fields in ferric oxides and hydroxides that substitution of OH^- for O^{2-} reduces the contact field; hence, we suggest that the Fe with the smaller hyperfine field is in sites that are coordinated by excess OH, whereas the Fe with the greater hyperfine field is located in the unperturbed segments of the 2:1 layers. A quantitative explanation of the differences between these fields in *P*- and *C*-cell minnesotaite, in terms of the contact, orbital, and dipolar contributions, is not feasible without much more detailed structural information.

In contrast to the ferrous absorption, the ferric hyperfine field at 4.2 K in *P*-cell minnesotaite appears to be quite sample dependent, being greatest in the samples with the greatest structural order.

CONCLUSIONS

1. Minnesotaite shows a characteristic ferrous doublet at room temperature, with $\delta = 1.13(1)$ mm/s and $\Delta = 2.74(2)$ mm/s, that is insensitive to the cell type.
2. Ferroan talc has a different quadrupole splitting, $\Delta = 2.55(2)$ mm/s, and can therefore be distinguished from minnesotaite on this basis.
3. The subspectra of two Fe site populations are resolved in magnetically split spectra taken in the liquid He temperature range but not in the paramagnetic spectra at room temperature. The minority sites may be those coordinated by the excess OH in the minnesotaite structure.
4. The hyperfine fields at 4.2 K for *C*-cell minnesotaite are distinctly lower than for *P*-cell minnesotaite. Relative site occupancies also differ, with a smaller minority site population in *C*-cell minnesotaite.

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