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CATION DISTRIBUTION, MÖSSBAUER SPECTRA, AND MAGNETIC PROPERTIES OF FERRIPYROPHYLLITE

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Abstract—A sample of ferripyrophyllite, a mineral with ideal composition $Fe_2Si_4O_{10}(OH)_2$, was analyzed by Mössbauer spectroscopy, magnetization and magnetic susceptibility measurements. The iron is entirely ferric, and the main feature of the Mössbauer spectrum at room temperature is a single absorption line with isomer shift $\delta = 0.36(1)$ mm/sec due to iron in M2 sites. The line is broadened by a slight quadrupole splitting $\Delta = 0.18(1)$ mm/sec, the smallest yet reported for a sheet silicate. Weaker features corresponding to quadrupole doublets with relative intensities of 7% and 8% having $\delta = 0.43(1)$ mm/sec; $\Delta = 1.22(2)$ mm/sec and $\delta = 0.14(1)$ mm/sec; $\Delta = 0.59(2)$ mm/sec are assigned to ferric iron in nonequivalent octahedral and tetrahedral sites, respectively, giving the following formula, based on published chemical analysis:

$$Ca_{0.05}(Fe^{3+}{}_{1.87}Mg_{0.11}Al_{0.09})^{VI}(Si_{3.80}Fe^{3+}{}_{0.16}Al_{0.04})^{IV}O_{10}(OH)_2,$$

where Ca is in interlayer sites. Ferripyrophyllite orders antiferromagnetically at 18(2)°K. The Mössbauer spectrum at 4.2°K consists of a single, resolved magnetic pattern with hyperfine field $B_{hf} = 51.8$ T. The relatively high Néel temperature compared with other dioctahedral ferric phyllosilicates provides further evidence that Fe^{3+} cations tend to be ordered on M2 sites within the octahedral sheet.

Key Words—*Cations, Ferripyrophyllite, Iron, Magnetic properties, Mössbauer spectra, Pyrophyllite.*

INTRODUCTION

Chukhrov *et al.* (1979a, 1979b) identified a ferric analogue of pyrophyllite in a precipitate formed from low-temperature hydrothermal solutions at Strassenschacht in the German Democratic Republic. From X-ray and electron powder diffraction data, they reported a monoclinic unit cell with $a = 5.26$ Å, $b = 9.10$ Å, $c = 19.1$ Å, and $\beta = 95.5°$ for this material. They indicated that the 2:1 layers are staggered so that silicon hexagons of adjacent layers do not overlap, as in the 2M polytype of pyrophyllite. Although most of the sample did not expand with water, a small proportion (~5%) of a smectite phase that consisted of expanding layers which dehydrated to the ferripyrophyllite structure was reported. The following structural formula was obtained from chemical analysis by assigning Si, Al, and Fe^{3+} to tetrahedral sites in that order, in accordance with the standard procedure:

$$Ca_{0.05}(Fe^{3+}{}_{1.96}Mg_{0.11})^{VI}(Si_{3.80}Al_{0.13}Fe^{3+}{}_{0.07})^{IV}O_{10}(OH)_2,$$

where Ca is in interlayer sites. As the ferric form of pyrophyllite, the prototype dioctahedral layer silicate, the Strassenschacht material approaches an ideal structure composed of uncharged ferric 2:1 layers.

The aims of the present work were to specify the cation distribution by means of the Mössbauer spectra and magnetic properties of the mineral and to assess conflicting interpretations in the literature of the spectra of ferric 2:1 layer minerals in light of data on this newly available end-member species. Several critical reviews of Fe^{57} Mössbauer spectroscopy as a technique for clay mineral research have appeared recently (Coey, 1980; Goodman, 1980; Heller-Kallai and Rozenson, 1981), and Coey (1984) discussed the problems associated with attributing Mössbauer subspectra of silicates to iron in specific crystallographic sites. The magnetic properties of silicates (Coey *et al.*, 1982) may also be expected to be quite sensitive to the iron cation distribution. We show here how both sorts of measurements, when taken together, can be used to resolve the cation distribution of iron in such materials.

EXPERIMENTAL METHODS

A 10-mg sample of the Strassenschacht ferripyrophyllite was prepared as a Mössbauer absorber, mixed with finely ground sugar to avoid preferential orientation, and spread between two beryllium discs with an area of 2 cm². Spectra were collected at 290°K using a conventional constant acceleration spectrometer (Halder MS250), and a source of Co^{57} in rhodium. All data were computer fitted using the least squares program of J. Teillet and F. Varret (Laboratoire de Spec-

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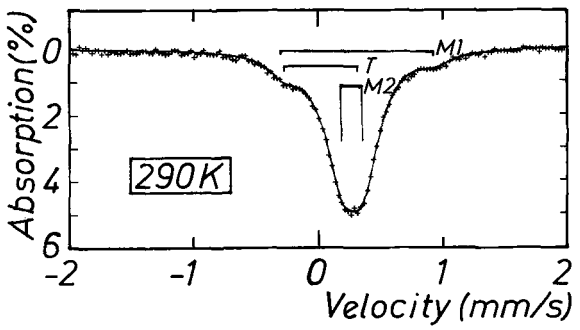


Figure 1. Room temperature Mössbauer spectrum of ferripyrophyllite. The fit of the data as the sum of three quadrupole doublets associated with iron in M1, M2, and tetrahedral sites is shown.

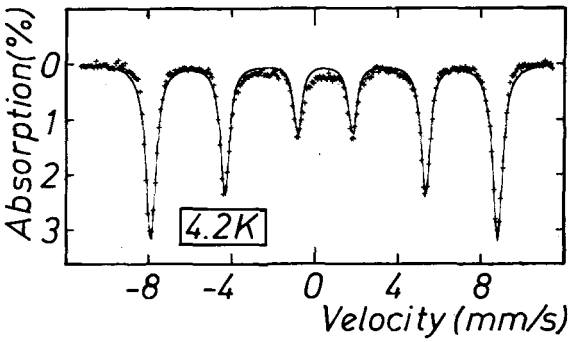


Figure 2. Mössbauer spectrum of ferripyrophyllite at 4.2°K. The fit of the data to a single magnetic hyperfine pattern is shown.

troscopie Mössbauer, Université du Maine, F-72017 LeMans, France, personal communication). Isomer shifts are quoted here relative to a metallic iron absorber. Measurements of magnetization as a function of applied field at fixed temperature, from 4°K to 80°K, were made with a vibrating sample magnetometer, operating with a 5 T superconducting solenoid. An 18.5-mg sample was used.

RESULTS

The room-temperature Mössbauer spectrum of a randomly oriented powder sample is shown in Figure 1. The main feature of the data is an intense, broadened absorption line at 0.25 mm/sec; however, two additional weak features of unequal intensity exist at −0.2 and 0.9 mm/sec. Three elements are therefore required in the fit. There is no sign whatever of Mössbauer lines or features indicative of the presence of ferrous iron; thus, $Fe^{2+}/Fe_{total} < 0.02$.

Decomposition of the spectrum into three ferric quadrupole doublets, as shown in Figure 1, gives an excellent fit ($\chi^2 = 202$ for 238 degrees of freedom) and yields sets of parameters which are compatible with those found in a range of other ferric dioctahedral 2:1 layer silicates (Coey, 1980; Heller-Kallai and Rozenson, 1981) (Table 1). Unlike many other decompositions of the Mössbauer spectra of 2:1 layer silicates, that shown in Figure 1 is almost unambiguous, because the spectral features are well resolved. The principal uncertainty concerns the association of the two weak, overlapping, low-velocity lines with their high-velocity partners, but even if the assignment were reversed, the changes in isomer shift (δ) and quadrupole splitting (Δ) are insignificant, being less than 0.03 mm/sec.

Table 1. Mössbauer parameters for the fit of the ferripyrophyllite spectrum at 290°K.

Site	M2, *cis*	M1, *trans*[1]	Tetrahedral
Isomer shift, δ (mm/sec)[2]	0.36 (1)	0.43 (4)	0.14 (4)
Quadrupole splitting, Δ (mm/sec)	0.18 (1)	1.22 (8)	0.59 (8)
Line width, Γ (mm/sec)	0.32 (2)	0.30 (4)	0.35 (4)
Relative intensity (%)	85 (2)	7 (3)	8 (3)

[1] Attribution of this doublet is discussed in the text.
[2] Relative to an absorber of metallic iron.

Magnetic hyperfine splitting appears in the liquid helium temperature range. Figure 2 shows the spectrum at 4.2°K, a single magnetic sextet with rather broad lines. Their full width at half maximum is $\Gamma \simeq 0.5$ mm/sec. The details of three component subspectra were not resolved, so the data were fitted to a single sextet with different linewidths for inner, middle, and outer doublets. This procedure yielded reliable average parameters despite a poor value of χ^2, 1460 for 243 degrees of freedom. The isomer shift at 4.2°K is $\delta = 0.48(4)$ mm/sec, the quadrupole shift is $\epsilon = -0.04(4)$ mm/sec, and the hyperfine field is $B_{hf} = 51.8(5)$ T.

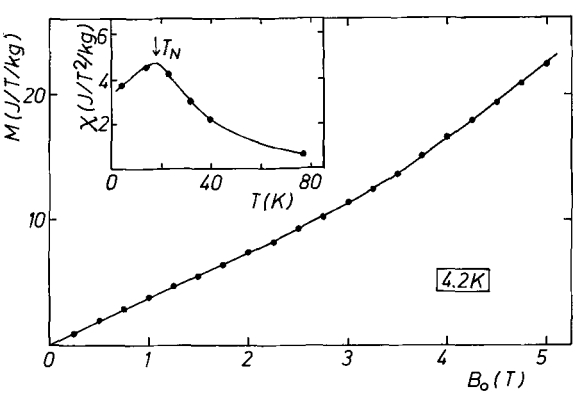


Figure 3. Magnetization curve of ferripyrophyllite at 4.2°K. The insert shows the temperature dependence of the initial susceptibility.

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Evidence for magnetic ordering at low temperatures is also apparent in the magnetization and susceptibility data shown in Figure 3. The susceptibility measured in a field of 0.1 T passes through a maximum at T_N = 18(2)°K, which is identified as the Néel temperature where the mineral orders antiferromagnetically. The magnetization curve at 4.2°K also indicates fairly strong antiferromagnetic interactions. Only a small proportion (17%) of the saturation magnetization expected from collinear alignment of the iron moments (133.6 J/T/kg) is achieved in a field of 5 T. In the absence of antiferromagnetic interactions, this proportion would be 90%, as given by the Brillouin function for S = 5/2 (Smart, 1966).

DISCUSSION

Mössbauer spectra

The intense, unresolved doublet (Figure 1) with δ = 0.36 mm/sec, comprising 85% of the total absorption area, is due to Fe^{3+} in octahedral sites with little departure from cubic symmetry. Its quadrupole splitting Δ = 0.18 mm/sec is the smallest yet reported for ferric iron in any sheet silicate. Ferric quadrupole splitting depends mainly on the electric field gradient created by the first neighboring shells of ions: it follows that local environments of all sites contributing to the doublet are alike because its linewidth, Γ = 0.32 mm/sec, is close to the instrumental resolution Γ_0 = 0.26 mm/sec. A similar feature with a somewhat larger quadrupole splitting, which decreases, however, with increasing iron content, exists in the spectra of other 2:1 layer silicates, including illites (Coey, 1980; Heller-Kallai and Rozenson, 1981), glauconites (Rozenson and Heller-Kallai, 1978; Govaert *et al.,* 1979; Kotlicki *et al.,* 1981), and nontronites (Goodman *et al.,* 1976), where it has been attributed to iron in M2 sites (*cis* hydroxyls). In ferripyrophyllite also it must be associated with M2 iron for the following reasons: recoilless fractions at different sites in silicates normally differ by less than 10%; thus the intense doublet represents 85 ± 2% of the total iron or 1.74 Fe atoms per formula unit. The feature cannot therefore be attributed solely to iron in M1 sites. As it is quite implausible that iron in M1 sites in a dioctahedral mineral will have precisely the same local environment as iron in M2 sites, the intense doublet must be associated with iron in M2 sites alone. A survey of the literature on dioctahedral 2:1 layer minerals (Coey, 1980; Heller-Kallai and Rozenson, 1981) indicates that the M2 quadrupole splitting increases in the order ferripyrophyllite < nontronite < glauconite < montmorillonite ≤ illite < muscovite. The sequence is, broadly, that of decreasing *b* parameter and decreasing iron occupancy in the octahedral layer. The sequence corresponds in some sense to increasing distortion of the M2 site, and Heller-Kallai and Rozenson (1981) found that the overriding factor determining Δ for Fe^{3+} in M2 and M1 sites is the distortion of the octahedral bond angles.

The second doublet, with δ = 0.43 mm/sec and Δ = 1.22 mm/sec, is also associated with octahedral iron, judging from the value of its isomer shift. Two possible interpretations are (1) M1 iron, or (2) octahedral iron in the vicinity of a charge defect. The former assignment is the one that has generally been favored for the ferric quadrupole doublet with the larger splitting in 2:1 layer minerals, but the latter has been considered as an alternative, specifically for nontronite and celadonite (Goodman, 1978; Bookin *et al.,* 1978; Dainyak, 1980; Besson *et al.,* 1983). Furthermore, evidence exists from other silicates, omphacites and hornblendes, for example, that the charges of the nearest cation neighbors can influence the quadrupole splitting (Coey, 1984). Charge defects that might possibly be responsible for the second doublet are a trivalent tetrahedral cation neighbor, a divalent octahedral cation neighbor, or defects in the shell of anion neighbors. From the formula reported by Chukhrov *et al.* (1979a), and quoted in the introduction, the probability of a trivalent ion appearing in a tetrahedral site is 0.20/4 = 0.05. Each octahedral site has four tetrahedral sites as neighbors, so the random probability of having at least one trivalent tetrahedral neighbor is given by the binomial distribution as

$$1 - \frac{N!}{Z!(N - Z)!}(1 - x)^{(N-Z)}x^Z,$$

where N = 4, Z = 0, and x = 0.05, i.e., 19%.

The probability of a divalent ion appearing in an octahedral site is 0.055, so the random probability of an octahedral ion having at least one octahedral neighbor may be calculated similarly. This probability is 16% if N = 3, or for octahedral cation order on M2 sites, and even larger if both M1 and M2 sites are partially occupied. The observed intensity of the second doublet is only 8% of the octahedral ferric absorption, much too small to be explained by either a random distribution of trivalent tetrahedral or divalent octahedral neighbors. The possibility of a change in the anion shell is not so easily dismissed. Many minerals exhibit a similar doublet on dehydroxylation (Heller-Kallai and Rozenson, 1981), although the line width is generally ~0.6 mm/sec, twice what was observed for ferripyrophyllite. Dainyak (1980) attributed a similar quadrupole splitting for Fe^{3+}-bearing trioctahedral smectites to deprotonization of the hydroxyls of the *cis* octahedra. Furthermore, Kotlicki *et al.* (1981) discovered a correlation in glauconites between the intensity of the second doublet and the proportion of expanding layers. Although ferripyrophyllite fits into this correlation, because both the intensity of the second doublet and the proportion of expanding layers are small, the significance of finding this is questionable

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Table 2. Comparison of the Mössbauer parameters of ferripyrophyllite with representative values for other ferric diotahedral 2:1 layer minerals.

	M2			M1			T		
	δ	Δ	I	δ	Δ	I	δ	Δ	I
Ferripyrophyllite	0.36	0.18	85	0.43	1.22	7	0.14	0.59	8
Nontronite[1]	0.36	0.30	60	0.36	0.62	25	0.16	0.54	15
Glauconite[1]	0.36	0.40	70	0.35	0.95	30	—	—	—
Montmorillonite[1]	0.34	0.53	70	0.39	1.14	30	—	—	—
Illite[1]	0.34	0.62	85	0.38	1.21	15	—	—	—
Muscovite[1]	0.38	0.68	80	0.43	1.19	10	0.22	0.70	10

δ = isomer shift relative to iron, in mm/sec; Δ = quadrupole splitting, in mm/sec; I = relative intensity, in %.
[1] Data from compilations of Coey (1980) and Heller-Kallai and Rozenson (1981).

because the expanding layers in the present sample constitute a separate smectite phase. It is quite possible, however, that the sites responsible for the second doublet are not distributed at random, but are located in the hydroferripyrophyllite (smectite) phase whose swelling layers are intercalated by Ca (Chukhrov *et al.*, 1979a).

The third doublet can be attributed to iron on tetrahedral sites, on the basis of its isomer shift (see Annesten *et al.*, 1971). It follows that aluminum has no overriding preference for tetrahedral sites unoccupied by silicon; 80% of them are actually occupied by Fe^{3+}. Thus, the formula of Chukhrov *et al.* (1979a) should be modified to read:

$$Ca_{0.05}(Fe^{3+}{}_{1.87}Mg_{0.11}Al_{0.09})^{VI}$$
$$(Si_{3.80}Fe^{3+}{}_{0.16}Al_{0.04})^{IV}O_{10}(OH)_2$$

Finally, Mössbauer parameters of ferripyrophyllite are compared with those found for other dioctahedral 2:1 layer minerals in Table 2, where any ferrous iron has been ignored and the second doublet conventionally assigned to M1 sites.

Magnetic properties

The magnetic susceptibility of an antiferromagnet at its ordering temperature T_N is given, in molecular field theory (Smart, 1966), as $\chi = C/(T_N - \theta)$. The Curie constant C calculated for the present sample is 209 J·K/(T^2·kg) and $\chi(T_N) = 4.9(3)$ J/(T^2·kg). Thus, the parameter θ, which measures the strength of the average exchange interaction, is −22(4)°K. Table 3 draws a comparison of T_N, θ, and the magnetization, expressed as a fraction of saturation at 4.2°K in 2 T, for ferripyrophyllite, nontronite, and glauconite. In glauconite, the presence of Fe^{2+} permits $Fe^{2+} \rightarrow Fe^{3+}$ virtual electron transfer, which gives a ferromagnetic exchange coupling in addition to the normal Fe^{3+}–O–Fe^{3+} antiferromagnetic superexchange. The positive θ value has been previously ascribed to this interaction (Ballet and Coey, 1982). Comparison with nontronite is more instructive inasmuch as neither ferripyrophyllite nor nontronite contains ferrous iron. The strength of the antiferromagnetic interactions indicated by the negative θ value is similar in the two minerals, yet a discrepancy of a factor of 6 exists in their magnetic ordering temperatures. Because the proportion of tetrahedral iron is similar in nontronite (Besson *et al.*, 1983) and ferripyrophyllite, an explanation for the difference in magnetic properties must be sought in the octahedral cation distribution.

Figure 4, which shows the extremes of dioctahedral order on M2 sites and random population of ⅔ of all M1 and M2 sites, suggests how the cation distribution can influence antiferromagnetic ordering. It is possible to satisfy all the superexchange interactions simultaneously with the distribution of Figure 4a, arranging for the spins of neighboring cations to be antiparallel. The honeycomb lattice is said to be unfrustrated, because it involves only even-membered rings, and in molecular field theory, $T_N = -\theta$. Such descriptions fit ferripyrophyllite. On the other hand, if there is no M2 site preference (as shown in Figure 4b), triangles and other odd-membered rings of occupied sites will form where it is impossible to find a spin configuration with the spins of all neighboring atom pairs aligned anti-

Table 3. Magnetic properties of dioctahedral 2:1 layer silicates.

	Paramagnetic Curie temperature (θ) (°K)	Magnetic ordering temperature (T_N)[1] (°K)	M/M_s[2]	Reference
Ferripyrophyllite	−22	18	0.06	This work
Nontronite	−20	(~3)	0.10	Bonnin (1981)
Glauconite	10	(~4)	0.45	Ballet and Coey (1982)

[1] Values for nontronite and glauconite are taken to be the temperatures where half of the Mössbauer absorption is in a magnetically split hyperfine pattern. No evidence has been found for any long-range antiferromagnetic order in nontronite below this temperature.
[2] Ratio of the magnetization, in 2 T at 4.2°K, to the calculated colinear saturation value.

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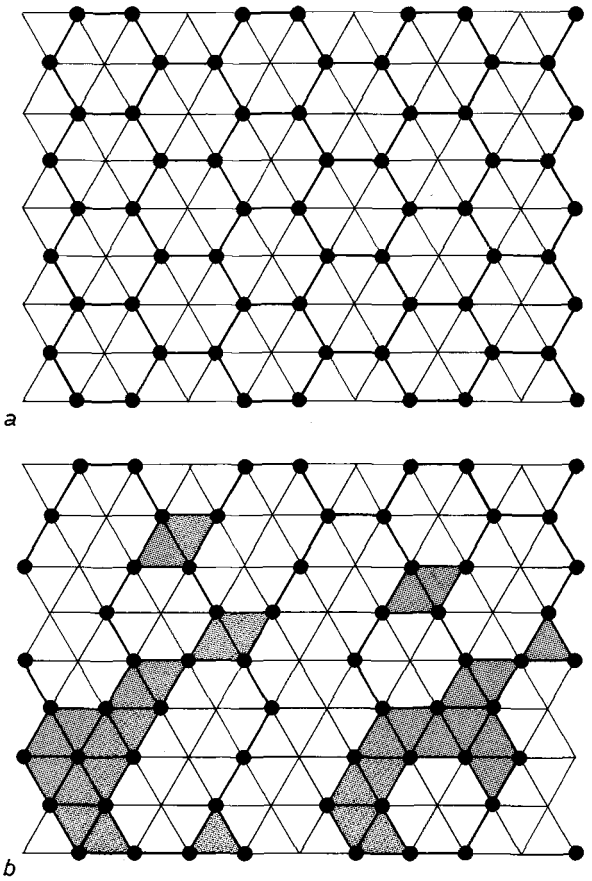


Figure 4. Cation distributions within the octahedral sheet: (a) iron occupies M2 sites only; (b) iron occupies ⅔ of M1 and M2 sites, at random. Antiferromagnetic nearest-neighbor interactions cannot be simultaneously satisfied in the shaded regions.

parallel. The result of this 'frustration' of the antiferromagnetic interactions is a random, noncollinear magnetic ground state whose energy is considerably higher than that of the antiferromagnetic honeycomb lattice. The magnetic ordering temperature is correspondingly lower.

A good example of the frustration effect was found in FeF_3, whose crystal structure contains only even membered Fe rings and has a Néel temperature of 363°K. The noncrystalline FeF_3 probably includes roughly equal numbers of odd- and even-membered rings (Coey and Murphy, 1982), and the magnetic ordering temperature, where the spins actually freeze in random directions, is reduced by an order of magnitude, to 29°K (Ferey *et al.*, 1980). Antiferromagnetic coupling of ferric iron in octahedral sites of a 2:1 layer involves superexchange with a near 90° Fe–F–Fe superexchange in FeF_3, but the principle of reduction of the ordering temperature, by topological frustration of the exchange interactions, is the same. Comparison of the θ and T_N values in Table 3 suggests a cation distribution similar to that shown in Figure 4a for ferripyrophyllite and to that shown in Figure 4b for nontronite (Bonnin, 1981). A recent magnetic neutron diffraction study in this laboratory of nontronite at 2°K found no sign of long-range antiferromagnetic order; thus, the transition of T_N should be regarded as a spin freezing transition rather than an antiferromagnetic Néel point.

In conclusion, the magnetic properties and Mössbauer spectra of ferripyrophyllite indicate that this mineral is an ordered dioctahedral mineral with the bulk of the octahedral iron (>90%) in M2 sites.

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REFERENCES

Annersten, H., Devanarayanan, S., Häggström, L., and Wäppling, R. (1971) Mössbauer study of synthetic ferriphlogopite: *Phys. Stat. Sol.* **64b,** K137–138.

Ballet, O. and Coey, J. M. D. (1982) Magnetic properties of sheet silicates; 2:1 layer minerals: *Phys. Chem. Minerals* **8,** 218–229.

Besson, G., Bookin, S., Dainyak, L. G., Rautureau, M., Tsipurski, S. I., Tchoubar, C., and Drits, V. A. (1983) Use of diffraction and Mössbauer methods for the structural and crystallochemical characterization of nontronites: *J. Appl. Cryst.* **16,** 374–380.

Bonnin, D. (1981) Propriétés magnétiques liées aux désordres bidimensionnels dans un silicate lamellaire ferique: la nontronite: Thèse d'Etat, Paris, 82 pp.

Bookin, A. S., Dainyak, L. G., and Drits, V. A. (1978) Interpretation of the Mössbauer spectra of layer silicates on the basis of structural modelling: *Phys. Chem. Minerals* **3,** 58–59.

Chukhrov, F. V., Zvyagin, B. B., Drits, V. A., Gorshkov, A. I., Ermilova, L. P., Goilo, E. A., and Rudnitskaya, E. S. (1979a). The ferric analogue of pyrophyllite and related phases: in *Proc. Int. Clay Conference, Oxford, 1978,* M. M. Mortland and V. C. Farmer, eds., Elsevier, Amsterdam, 55–64.

Chukhrov, F. V., Zvyagin, B. B., Drits, V. A., Gorshkov, A. I., Ermilova, L. P., Goilo, E. A., and Rudnitskaya, E. S. (1979b) Über ferripyrophyllit: *Chem. Erde* **38,** 324–330.

Coey, J. M. D. (1980) Clay minerals and their transformations studied with nuclear techniques: the contribution of Mössbauer spectroscopy: *Atomic Energy Review* **18,** 73–124.

Coey, J. M. D., Moukarika, A., and Ballet, O. (1982) Magnetic order in silicate minerals: *J. Appl. Phys.* **53,** 8320–8325.

Coey, J. M. D. and Murphy, P. J. K. (1982) An octahedral random network: *J. Noncryst. Solids* **50,** 125–129.

Coey, J. M. D. (1984) Silicate minerals: in *Mössbauer Spectroscopy Applied to Inorganic Chemistry,* G. J. Long, ed., Plenum Press, New York (in press).

Dainyak, L. G. (1980) Interpretation of ngr spectra of some Fe^{3+}-bearing layer silicates on the basis of structural modelling: Candidates Thesis, Kazan State University, 125 pp. (in Russian).

https://doi.org/10.1346/CCMN.1984.0320307 Published online by Cambridge University Press

Ferey, G., Varret, F., and Coey, J. M. D. (1979) Amorphous FeF_3: a non-crystalline magnet with antiferromagnetic interactions: *J. Phys. C.* **12,** L531–L537.

Goodman, B. A., Russell, J. D., Fraser, A. R., and Woodhams, F. W. D. (1976) A Mössbauer and i.r. spectroscopic study of the structure of nontronite: *Clays & Clay Minerals* **24,** 53–59.

Goodman, B. A. (1978) The Mössbauer spectra of nontronites: consideration of an alternative assignment: *Clays & Clay Minerals* **26,** 176–177.

Goodman, B. A. (1980) Mössbauer spectroscopy: in *Advanced Chemical Methods for Soil and Clay Minerals Research,* J. W. Stucki and N. W. L. Banwart, eds., Reidel, Dordrecht, The Netherlands, 1–92.

Govaert, A., de Grave, E., Quartier, H., Chambraere, D., and Robbrecht, G. (1979) Mössbauer analysis of glauconites from different Belgian localities: *J. Physique* **40,** 442–444.

Heller-Kallai, L. and Rozenson, I. (1981) The use of Mössbauer spectroscopy of iron in clay mineralogy: *Phys. Chem. Minerals* **7,** 223–238.

Kotlicki, A., Szczyrba, J., and Wiewiora, A. (1981) Mössbauer study of glauconites from Poland: *Clay Miner.* **16,** 221–230.

Rozenson, I. and Heller-Kallai, L. (1978) Mössbauer spectra of glauconites reexamined: *Clays & Clay Minerals* **26,** 173–175.

Smart, J. S. (1966) *Effective Field Theories of Magnetism:* Saunders, Philadelphia, p. 58.

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Резюме—Образец феррипирофиллита, минерала с идеальной формулой $(Fe_2)(Si_4)O_{10}(OH)_2$, исследован с помощью Мессбауэровской спектроскопии, измерений намагничивания и магнитной восприимчивости. Все железо полностью является окисным, и главной чертой Мессбауэровских спектров при комнатной температуре является одиночная линия поглощения с изомерным сдвигом $\delta = 0{,}36(1)$ мм/с, относящаяся к железу в позиции M2. Линия расширена слабым квадрупольным расщеплением $\Delta = 0{,}18(1)$ мм/с, наименьшим из до сих пор известных для слоистых силикатов. Более слабые особенности, выражаемые квадрупольными дублетами с относительными интенсивностями в 7 и 8%, имеющие $\delta = 0{,}43(1)$ мм/с, $\Delta = 1{,}22(2)$ мм/с; и $\delta = 0{,}14(1)$ мм/с, $\Delta = 0{,}59(2)$ мм/с отнесены к окисному железу в неэквивалентных октаэдрических и тетраэдрических позициях соответственно, что на основании опубликованных данных химического анализа дает следующую формулу $Ca_{0,05}(Fe^{3+}{}_{1,87}Mg_{0,11}Al_{0,09})^{VI}(Si_{3,80}Fe^{3+}{}_{0,16}Al_{0,04})^{IV}O_{10}(OH)_2$. Феррипирофиллит характеризуется антиферромагнитным упорядочением при 18(2)°K. Мессбауэровский спектр при 4,2°K состоит из одиночного секстета с разрешением сверхтонкой картины магнитного поля $B_{hf} = 51{,}8$°T. Сравнительно высокая температура Нееля (в отличие от таковой у других филосиликатов окисного железа) служит дополнительным свидетельством тенденции к упорядоченному распределению катионов Fe^{3+} по октаэдрическим позициям M2.

Resümee—Eine Probe von Ferripyrophyllit, einem Mineral mit der idealen Zusammensetzung $Fe_2Si_4O_{10}(OH)_2$, wurde mittels Mössbauer-Spektroskopie, Magnetisierungs- und magnetischen Suszeptibilitäts-Messungen untersucht. Das Eisen ist ausschließlich Fe^{3+}, und das Hauptcharakteristikum des Mössbauer-Spektrums bei Raumtemperatur ist eine einzige Absorptionslinie mit einer Isomerverschiebung $\delta = 0{,}36(1)$ mm/sec, die durch Eisen auf M2-Plätzen hervorgerufen wird. Die Linie wird durch eine leichte Quadrupol-Aufspaltung von $\Delta = 0{,}18(1)$ mm/sec verbreitet, die kleinste, die je für ein Schichtsilikat angegeben wurde. Schwächere Charakteristika, die Quadrupol-Dubletten mit relativen Intensitäten von 7% und 8% entsprechen, und die Werte von $\delta = 0{,}43(1)$ mm/sec, $\Delta = 1{,}22(2)$ mm/sec und $\delta = 0{,}14(1)$ mm/sec; $\Delta = 0{,}59(2)$ mm/sec haben, deuten auf Fe^{3+} auf nichtäquivalenten oktaedrischen bzw. tetraedrischen Plätzen hin, woraus sich die folgende, auf publizierten chemischen Daten basierende Formel ergibt:

$$Ca_{0,05}(Fe^{3+}{}_{1,87}Mg_{0,11}Al_{0,09})^{VI}(Si_{3,80}Fe^{3+}{}_{0,16}Al_{0,04})^{IV}O_{10}(OH)_2,$$

wobei das Ca auf Zwischenschichtplätzen sitzt.

Ferripyrophyllit zeigt bei 18(2)°K antiferromagnetische Ordnung. Das Mössbauer-Spektrum bei 4,2°K besteht aus einem einzigen aufgelösten magnetischen Signal mit einem Hyperfeinfeld $B_{hf} = 51{,}8$ T. Die im Vergleich mit anderen dioktaedrischen Ferri-Phyllosilikaten relativ hohe Néel Temperatur liefert einen weiteren Beweis, dairs Fe^{3+}-Kationen dazu neigen, auf den M2-Plätzen innerhalb der Oktaederschicht angeordnet zu sein. [U.W.]

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Résumé—Un échantillon de ferripyrophyllite, un minéral dont la composition idéale est $Fe_2Si_4O_{10}(OH)_2$, a été analysé par spectroscopie Mössbauer, et par mesures d'aimantation et de susceptibilité magnétique. La fer est entièrement ferrique, et à température ambiante, la caractéristique principale du spectre Mössbauer est une seule raie d'absorption avec déplacement isomerique $\delta = 0{,}36(1)$ mm/sec à cause de la présence de fer dans les sites M_2. La raie est élargie par une légère dedoublement quadropolaire $\Delta = 0{,}18(1)$ mm/sec, jusqu'à présent, la plus petite rapportée pour une silicate à feuilles. Des caractéristiques plus faibles correspondant à des doublets quadropolaires ayant des intensités relatives de 7% et de 8%, et ayant $\delta = 0{,}43(1)$ mm/sec; $\Delta = 1{,}22(2)$ mm/sec et $\delta = 0{,}14(1)$ mm/sec; $\Delta = 0{,}59(2)$ mm/sec sont assignées au fer ferrique dans les sites octaédraux et tetraédraux nonéquivalents, respectivement, donnant la formule suivante, basée sur une analyse chimique publiée:

$$Ca_{0,05}(Fe^{3+}{}_{1,87}Mg_{0,11}Al_{0,09})^{VI}(Si_{3,80}Fe^{3+}{}_{0,16}Al_{0,04})^{IV}O_{10}(OH)_2,$$

où Ca est dans des sites intercouches.

La ferripyrophyllite s'ordonne antiferromagnétiquement à 18(2)°K. Le spectre Mössbauer à 4.2°K consiste en un seul cliché magnétique résolu avec un champ hyperfin $B_{hf} = 51{,}8$ T. La température de Néel relativement élevée comparée à d'autres phyllosilicates ferriques octaédriques fournit d'avantage d'évidence que les cations Fe^{3+} ont tendance à s'ordonner sur les sites M_2 au sein du feuillet octaédrique. [D.J.]

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