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Neutron-diffraction and Mössbauer spectroscopic study of clintonite (xanthophyllite)

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ABSTRACT

A clintonite-1M from Lago della Vacca, Adamello (Italian Alps), was investigated by single-crystal neutron diffraction and by Mössbauer spectroscopy. Cell dimensions are $a = 5.2037(9)$, $b = 9.0126(5)$, $c = 9.8145(9)$ Å, $\beta = 100.26(1)°$, space group $C2/m$. The chemical composition is $(Ca_{1.00}Na_{0.007})(Mg_{2.29}Al_{0.70}Fe^{2+}_{0.05}Ti_{0.006})(Si_{1.20}Al_{2.69}Fe^{3+}_{0.11})O_{10}(OH)_2$. The refinement with 558 unique reflections converged to $R = 0.020$ and $R_w = 0.020$. No cation ordering was detected in the tetrahedral sheet, whereas partial cation ordering was observed in the octahedral sheet: M(1)–O, 2.046(1) Å; M(2)–O, 2.020(1) Å. The O–H dipole is perpendicular to (001), with an O–H distance of 0.943(2) Å. The analysis of the Mössbauer spectrum of ^{57}Fe and the refinement of the neutron-scattering length of the T site revealed an incorporation of Fe^{3+} in the tetrahedral site in competition with an excess of Al^{3+}.

INTRODUCTION

The (Si,Al) distribution in brittle micas has been studied by Farmer and Velde (1973) by infrared spectroscopy. They proposed substantial tetrahedral ordering for margarite, which contains equal amounts of Si and Al, but a random distribution for clintonite with an Al to Si ratio larger than 2. X-ray (Guggenheim and Bailey, 1975, 1978) and neutron-diffraction studies (Joswig et al., 1983) confirmed the almost complete (Si, Al) ordering for margarite. Loewenstein's aluminum avoidance rule (Loewenstein, 1954) is therefore followed in margarite; in clintonite, however, the chemical composition requires a violation of this rule.

The neutron-diffraction study locates the O–H dipole precisely and elucidates cation ordering in the octahedral and tetrahedral sheet. However, as neutrons do not distinguish between Fe^{3+} and Fe^{2+}, an additional Mössbauer experiment was carried out on material from the same source as the neutron study. A previous Mössbauer study by Annersten and Olesch (1978) on several natural and synthetic clintonites gave some evidence on the distribution of these cations.

EXPERIMENTAL PROCEDURE

Neutron diffraction

About 80 clintonite crystals from different localities were examined by X-ray precession photographs in order to find a crystal with a regular stacking sequence. Only a few specimens from Lago della Vacca, Adamello (Italian Alps), showed periodicity along **c***. A crystal of 1.2 × 1.1 × 0.1 mm was selected, which, even in overexposed (0*kl*)-precession photographs, showed no diffuse streaks parallel **c*** for reflections with $k \neq 3n$, ensuring a complete stacking ordering of this clintonite-1M. The chemistry as determined from electron-microprobe analysis is given in Table 1. The lattice constants were obtained from X-ray four-circle diffractometer data with high-order reflections using Mo$K\alpha$ radiation: $a = 5.2037(9)$, $b = 9.0126(5)$, $c = 9.8145(9)$ Å, $\beta = 100.26(1)°$. The neutron-diffraction experiment was performed on the four-circle diffractometer D 8 at the HFR (high-flux reactor) of the Institute Laue-Langevin (ILL), Grenoble. About 850 reflections up to $\sin \theta/\lambda = 0.69$ were collected in an $\omega/x\theta$ scan with a wavelength $\lambda = 1.2618$ Å from a Cu(200) plane monochromator. The intensities of the 0*k*0 reflections were severely affected by extinction, which was as high as 40% for 060. These reflections were therefore measured by psi-scans to determine the position of minimal extinction. Symmetry averaging yielded 637 independent reflections. A total of 558 reflections with $|F_o|^2 > 2\sigma_c$ were used for the CRYLSQ link of the X-RAY SYSTEM (Stewart et al., 1975). A weighting scheme of the form $w(F_o) = [\sigma_c^2 + 0.1 \times 10^{-3} F_o^2]^{-1}$ was employed. The refinement in space group $C2/m$ was carried out on positional parameters of all atoms, the neutron-scattering lengths of the cations and the H, and an isotropic extinction factor to produce 65 varied parameters. A final agreement factor of $R = 0.020$ and $R_w = 0.020$ was achieved. Final parameters are given in Table 2.

In order to test for a possible tetrahedral and/or octahedral M(1), M(2) and M(3) ordering, refinements in subgroups $C2$ and Cm (only for tetrahedral ordering) were carried out. No convergence for the parameters, especially of the scattering lengths of the tetrahedral and octahedral cations, was obtained. The space group $C2/m$ is therefore the correct space group for clintonite-1M.

Mössbauer spectroscopy

Two Mössbauer spectra were taken with the absorber at room and liquid N temperature, respectively, using conventional tech-

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Table 1. Electron-microprobe analysis of clintonite

		(wt%)	Calculation for 22 positive charges		
SiO_2		17.05	Si	1.20	4.00 (IV)
Al_2O_3		40.90	Al	2.69	
Fe_2O_3	(total Fe)	2.90	Fe^{3+*}	0.11	
FeO			Fe^{2+*}	0.05	3.046 (VI)
			Al	0.70	
TiO_2		0.11	Ti	0.006	
MgO		21.90	Mg	2.29	
MnO		0.03			
CaO		13.13	Ca	1.00	1.007 (XII)
Na_2O		0.05	Na	0.007	
K_2O		n.d.			
Total		96.24			

* By Mössbauer spectroscopy.

niques: 20 mCi $^{57}Co/Pd$ source, constant acceleration with symmetric triangular velocity wave form, 5-mg Fe/cm^2 absorber density, refrigerator cryostat. The two simultaneously recorded spectra (512 channels each) were folded and then fitted by least-squares method assuming Lorentzian lines. The angle between the incident gamma-ray and the absorber was kept at 54.7° in order to avoid texture effects (Ericsson and Wäppling, 1976).

RESULTS

The structure thus refined is similar to the one reported by Takéuchi and Sadanaga (1959, 1966) using X-ray film data. The results, however, provide more details on the clintonite structure type. Also the investigations of natural and synthetic clintonite by Olesch (1975) show that only the 1M polytype is realized for the brittle mica clintonite. The structure is characterized, as in phlogopite (Joswig, 1972), by nearly ideal trigonal symmetry within the sheets. Characteristic structural features are listed in Table 3 and the bond lengths and angles in Table 4. Similar to phlogopite (Joswig, 1972) and the talc-like sheet in penninite (Joswig et al., 1980), the O–H dipole in clintonite is perpendicular to (001), the O–H bond length being 0.943(2) Å. The thermal vibration of the H atom describes an oblate ellipsoid with the short axis parallel **c***.

The Mössbauer spectrum of ^{57}Fe in the clintonite taken at room temperature is shown in Figure 1. The Mössbauer parameters evaluated from both spectra are listed in Table 5. The spectrum in Figure 1 exhibits three lines with decreasing peak heights at higher velocities. The liquid N spectrum looks quite similar. Best-fit values of both spectra could be obtained assuming two quadrupole doublets. The doublet with the larger area, the smaller quadrupole splitting, and smaller isomer shift is assigned to Fe^{3+}; the doublet with the smaller area, the larger quadrupole splitting, and larger isomer shift to Fe^{2+}. Assuming similar recoil-free fractions of Fe^{2+} and Fe^{3+} at 77 K, about one-third of the iron is Fe^{2+}. Attempts to fit three doublets (2 Fe^{2+}, 1 Fe^{3+} or 2 Fe^{3+}, 1 Fe^{2+}) or four doublets (2 Fe^{2+}, 2 Fe^{3+}) could only be achieved by constraining the line width of all the doublets to be equal. However, such a fitting procedure is not justified because of the different next-nearest-neighbor environment of Fe^{2+} and Fe^{3+} at the different lattice sites of this natural clintonite, resulting in a different distribution of electric-field gradients at the different positions, respectively. In addition, the goodness of fit parameter chi squared increased compared to the two doublet fit.

Table 3. Characteristic features of the structure

Rotation angle of the tetrahedra (α_{tet})	23.1°
Sheet thickness	
Tetrahedral	2.322 Å
Octahedral	2.103 Å
Interlayer	2.911 Å
Basal oxygen ΔZ_{aver} "corrugation"	0.013 Å

DISCUSSION

The results presented above are a base for the discussion of an ordering pattern for the octahedral sheet. The neutron diffraction gave clear evidence that the (*trans*) octahedron M(1) is larger than the two equivalent (*cis*) octahedra M(2). The average distances are M(1)–O, 2.046(1) Å and M(2)–O, 2.020(1) Å. This clintonite is therefore no exception of the general rule: M(1) ≥ M(2) given by Bailey (1984). The scattering-lengths refinement gave $b_{M(1)} = 5.17(4)$, $b_{M(2)} = 4.97(3)$ for the two sites, an indication for a preference of Fe^{2+} for M(1) that is in agreement with the larger site.

The isomer shift of the Fe^{2+} doublet in the Mössbauer spectra shows that Fe^{2+} is located at the octahedral sites, although this value is within the lower range usually measured for Fe^{2+} at octahedrally coordinated sites in silicates. As already mentioned, it was not possible to fit two Fe^{2+} doublets for M(1) and M(2). The most probable explanation for this failure is the low Fe^{2+} content of this sample.

The cation-ordering pattern in the octahedral sheet is

Table 2. Neutron-scattering lengths, atomic coordinates, and anisotropic thermal parameters ($U_{ij} \times 10^{-2}$) of clintonite

Atom	b (10^{-15} m)	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ca	4.61(4)	0.50	0.50	0.00	1.00(7)	0.77(7)	0.70(7)	0.00	0.23(5)	0.00
M(1)	5.17(4)	0.00	0.50	0.50	0.34(5)	0.37(5)	0.72(6)	0.00	0.12(4)	0.00
M(2)	4.97(3)	0.50	0.32982(9)	0.50	0.48(4)	0.47(4)	0.73(4)	0.00	0.14(3)	0.00
T	3.82(2)	0.57049(14)	0.16705(8)	0.20976(7)	0.61(4)	0.47(4)	0.61(4)	−0.04(2)	0.12(3)	0.01(3)
O(1)	5.803	0.42771(16)	0.00	0.15161(9)	1.22(4)	1.07(4)	1.05(4)	0.00	0.05(3)	0.00
O(2)	5.803	0.86158(11)	0.18853(6)	0.15029(6)	1.13(2)	1.17(3)	1.09(3)	−0.12(2)	0.31(2)	−0.10(2)
O(3)	5.803	0.63088(10)	0.16856(6)	0.38782(6)	1.08(3)	0.93(3)	0.85(2)	−0.01(2)	0.16(2)	0.05(2)
O(4)	5.803	0.62827(14)	0.50	0.39774(8)	1.04(3)	1.35(4)	0.68(4)	0.00	0.13(3)	0.00
H	−3.60(4)	0.5966(4)	0.50	0.3001(2)	5.16(13)	6.07(15)	0.99(9)	0.00	0.25(8)	0.00

Table 4. Interatomic distances (Å) and bond angles (°) of clintonite

Tetrahedron

		Edge lengths		Bond angles
T–O(1)	1.730(1)	O(3)–O(1)	2.815(1)	109.40(5)
T–O(2)	1.729	O(3)–O(2)	2.812	109.25
T–O(2)	1.729	O(3)–O(2)	2.810	109.10
T–O(3)	1.720	O(2)–O(1)	2.828	109.68
		O(2)–O(2)	2.828	109.74
		O(1)–O(2)	2.828	109.66
Mean	1.727		2.820	109.47

Octahedra

	M(1)			M(2)	
M(1)–O(3)	2.062(1)	×4	M(2)–O(3)	2.014(1)	×2
M(1)–O(4)	2.014	×2	M(2)–O(3)	2.037	×2
			M(2)–O(4)	2.011	×2
Mean	2.046			2.020	

Shared edges

O(4)–O(4)	2.601(1)
O(3)–O(3)	2.751
O(3)–O(3)	2.788
O(3)–O(4)	2.715
Mean	2.713

Unshared edges

	M(1)			M(2)	
O(3)–O(4)	3.041(1)	×4	O(3)–O(3)	2.987(1)	×2
O(3)–O(3)	3.038	×2	O(3)–O(4)	2.989	×2
			O(3)–O(4)	2.988	×2
Mean	3.040			2.988	

Ca polyhedron

	Inner		Outer	
Ca–O(1)	2.447(1)	×2	3.558(1)	×2
Ca–O(2)	2.441	×4	3.551	×4
Mean	2.443		3.553	

OH dipole

O(4)–H	0.943(2)	OH ∧ (001)	89.7°(1)

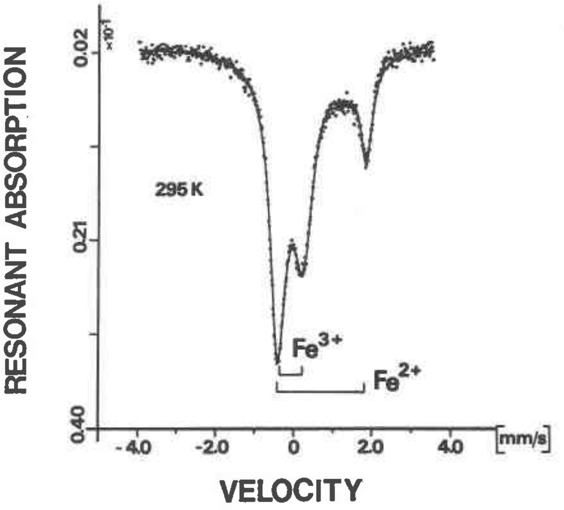

Fig. 1. Mössbauer spectrum of ^{57}Fe in clintonite taken at 295 K and fitted by two quadrupole doublets.

rather ambiguous because three different cations are involved. A comparison with well-refined trioctahedral micas—phlogopite (Joswig, 1972) and biotite-3T (Joswig et al., in prep.)—suggests a preferential occupation of the larger cation Fe^{2+} in M(1). We therefore propose the following site occupation based on the neutron-diffraction results: M(1) = $Mg_{0.73}Al_{0.22}Fe^{2+}_{0.05}$; M(2) = $Mg_{0.77}Al_{0.23}Ti_{0.003}$. It may be concluded that the partial ordering is due to the Fe^{2+}, whereas Mg and Al are randomly distributed over M(1) and M(2).

Table 5. Mössbauer parameters of ^{57}Fe in clintonite

	Fe^{3+}	Fe^{2+}	Fe^{3+}	Fe^{2+}
	77 K		295 K	
IS* (mm/s)	0.32	1.19	0.28	1.06
ΔE_Q** (mm/s)	0.73	2.60	0.66	2.34
Γ† (mm/s)	0.34	0.23	0.33	0.23
A‡ (%)	68.1	31.9	70.5	29.5
χ^2	0.51		1.05	

* Isomer shift relative to α-Fe at 295 K (±0.01 mm/s).
** Quadrupole splitting (±0.01 mm/s).
† Half width (±0.01 mm/s).
‡ Referred to the total resonant absorbtion area = 100% (±1.0%).

The refined neutron-scattering length of the tetrahedral site is $b_T = 3.82(2)$, which is significantly larger than the value $b_T = 3.66$ calculated from the composition $T = Si_{1.20}Al_{2.80}$ with $b_{Al} = 3.449$ and $b_{Si} = 4.149$. This value is, however, matched by the presence of Fe ($b_{Fe} = 9.54$) in the tetrahedral site. (All neutron-scattering lengths are given in units of 10^{-15} m; Koester, 1977).

In the Mössbauer spectra the observed isomer shifts indicate that Fe^{3+} is at the tetrahedral site even though the shifts are at the upper limit of tetrahedral Fe^{3+} isomer shifts in silicates. For comparison, in a garnet with the composition $Ca_3Fe_2Ti_{1.42}Si_{1.58}O_{12}$, the octahedral isomer shift of Fe^{3+} is 0.40 mm/s at 295 K and 0.51 mm/s at 77 K and the tetrahedral isomer shift of Fe^{3+} is 0.20 mm/s at 295 K and 0.30 mm/s at 77 K (Amthauer et al., 1976). A more complicated example is the mineral sapphirine, where Fe^{3+} is found to occupy preferentially the tetrahedral sites with isomer shifts of 0.29 and 0.30 mm/s at 295 K and 0.34 and 0.37 mm/s at 77 K (Steffen et al., 1984). These values are even higher than those observed in clintonite and are referred to the large tetrahedral cation–anion distances in sapphirine. A similar explanation may be valid for the high value of the isomer shift of tetrahedral Fe^{3+} in the clintonite, where the averaged tetrahedral cation–anion distance is rather high.

Therefore, it is concluded that Fe^{3+} occupies preferentially the tetrahedrally coordinated Al sites in clintonite. Annersten and Olesch (1978) reported an additional ferric doublet with a distinctly smaller area, which they assigned to octahedral Fe^{3+}. In our spectrum this fit could not be reproduced without applying unjustified constraints. Because of the unresolved spectra, it cannot be completely excluded that a small amount of Fe^{3+} (≤10%) may also occupy octahedral sites.

In many silicates with Si^{4+} deficiency, Fe^{3+} enters the tetrahedral sites also in competition with Al^{3+}, for instance, in natural schorlomite garnets (Amthauer et al., 1977; Huggins et al., 1977). Similar to that case there is very often a distribution of Al^{3+} and Fe^{3+} over the tetrahedral and octahedral sites with a stronger tetrahedral site preference of Al^{3+}. On the other hand in minerals such as sapphirine, a strong tetrahedral site preference of Fe^{3+} is observed. This may occur if Fe^{3+} substitutes for tetrahedral Al^{3+} and not for tetrahedral Si^{4+}.

Based on the evidence from both techniques, neutron diffraction and Mössbauer spectroscopy, it can be concluded that in the clintonite of this study, the Fe^{2+} is incorporated into the octahedral site, whereas the Fe^{3+}, although in competition with an excess of Al^{3+}, is almost completely at the tetrahedral site: $T = Si_{1.20}Al_{2.69}Fe^{3+}_{0.11}$.

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REFERENCES

Amthauer, G., Annersten, H., and Hafner, S.S. (1976) The Mössbauer spectrum of ^{57}Fe in silicate garnets. Zeitschrift für Kristallographie, 143, 14–55.

——— (1977) The Mössbauer spectrum of ^{57}Fe in titanium-bearing andradites. Physics and Chemistry of Minerals, 1, 399–413.

Annersten, H., and Olesch, M. (1978) Distribution of ferrous and ferric iron in clintonite and the Mössbauer characteristic of ferric iron in tetrahedral coordination. Canadian Mineralogist, 16, 199–203.

Bailey, S.W. (1984) Review of cation ordering in micas. Clays and Clay Minerals, 32, 81–92.

Ericsson, T., and Wäppling, R. (1976) Texture effects in 3/2–1/2 Mössbauer spectra. Journal de Physique, 37, C6-719–723.

Farmer, V.C., and Velde, G. (1973) Effects of structural order and disorder on the infrared spectra of brittle micas. Mineralogical Magazine, 39, 282–288.

Guggenheim, S., and Bailey, S.W. (1975) Refinement of the margarite structure in subgroup symmetry. American Mineralogist, 60, 1023–1029.

——— (1978) Refinement of the margarite structure in subgroup symmetry: Correction, further refinement, and comments. American Mineralogist, 63, 186–187.

Huggins, F.E., Virgo, D., and Huckenholz, H.G. (1977) Titanium-containing silicate garnets. I. The distribution of Al, Fe^{3+}, and Ti^{4+} between octahedral and tetrahedral sites. American Mineralogist, 62, 475–490.

Joswig, W. (1972) Neutronenbeugungsmessungen an einem 1M-Phlogopit. Neues Jahrbuch für Mineralogie, Monatshefte, 1–11.

Joswig, W., Fuess, H., Rothbauer, R., Takéuchi, Y., and Mason, S.A. (1980) A neutron diffraction study of a one-layer triclinic chlorite (penninite). American Mineralogist, 65, 349–352.

Joswig, W., Takéuchi, Y., and Fuess, H. (1983) Neutron-diffraction study on the orientation of hydroxyl groups in margarite. Zeitschrift für Kristallographie, 165, 295–303.

Koester, L. (1977) Neutron scattering lengths and fundamental neutron interactions. In G. Höhler, Ed. Neutron physics, Springer Tracts in Modern Physics, 80, 1–55. Springer-Verlag, Berlin.

Loewenstein, W. (1954) The distribution of aluminium in the tetrahedra of silicates and aluminates. American Mineralogist, 39, 92–96.

Olesch, M. (1975) Synthesis and solid stability of trioctahedral brittle micas in the system $CaO\text{-}MgO\text{-}Al_2O_3\text{-}SiO_2\text{-}H_2O$. American Mineralogist, 60, 188–199.

Steffen, G., Seifert, F., and Amthauer, G. (1984) Ferric iron in sapphirine: A Mössbauer spectroscopic study. American Mineralogist, 69, 339–348.

Stewart, J.M., Krüger, G.J., Ammon, H.L., Dickinson, L., Hall, S.R. (1975) The XRAY system—Version of June 1972, updated Nov. 1975. TR-192, Computer Science Center, University of Maryland, College Park, Maryland.

Takéuchi, Y., and Sadanaga, R. (1959) The crystal structure of xanthophyllite. Acta Crystallographica, 12, 945–946.

——— (1966) Structural studies of brittle micas. (I). The structure of xanthophyllite refined. Mineralogical Journal (Japan), 4, 424–437.

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