

DISTRIBUTION OF FERROUS AND FERRIC IRON IN CLINTONITE AND THE MÖSSBAUER CHARACTERISTICS OF FERRIC IRON IN TETRAHEDRAL COORDINATION

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ABSTRACT

Iron-bearing clintonites have been studied by use of the Mössbauer effect. It is found that most of the ferric iron occupies the tetrahedral sites because of the relatively large size of the tetrahedral interstices in clintonites as compared to other silicates. This feature is also responsible for the unusually large isomer shifts (0.24-0.27) mm/s at room temperature, relative to metallic iron) observed for tetrahedrally coordinated ferric iron in these clintonites.

SOMMAIRE

Nous avons étudié des clintonites ferrifères à l'aide de l'effet Mössbauer. Le fer ferrique se trouve surtout dans les sites tétraédriques, conséquence de la taille relativement grande de ces tétraèdres comparés à ceux des autres silicates. La même cause explique également les déplacements isomériques élevés (0.24-0.27 mm/s, mesurés à température ambiante, par rapport au fer métallique) que l'on trouve pour le fer ferrique en coordination tétraédrique dans ces clintonites.

(Traduit par la Rédaction)

INTRODUCTION

The simplified structural formula of the trioctahedral brittle micas that belong to the clintonite group (*i.e.*, clintonite, xanthophyllite, brandisite) may be written $\text{Ca}(\text{Mg,Fe,Al})_3(\text{Al,Fe,Si})_4\text{O}_{10}(\text{OH})_2$. The crystal chemistry and phase relationship of the clintonites were investigated by Olesch (1975) and Olesch & Seifert (1976). There are two main crystal-chemical features that distinguish the clintonite minerals from the common micas: (1) the almost complete occupancy of Ca in the interlayer positions, and (2) the very low Si/Al ratio in the tetrahedral layer (ranging between 0.18 to 0.54 in synthetic and 0.38 to 0.53 in natural clintonites) compensating

for the incorporation of Ca in the place of K and Na in the more common micas. Calcium in the interlayer position reduces the *c* and *b* dimensions of the clintonite structure with respect to K and Na micas. Crystal structure refinements of clintonites have also shown that the high amount of Al in tetrahedral sites increases the mean (Si,Al)-O distances in this polyhedron to 1.730(14) Å (Takeuchi & Sadanaga 1966) compared to 1.649(9) Å observed in phlogopite (Hazen & Burnham 1973). As a further consequence of the low Si/Al ratio, the tetrahedra have to rotate around the trigonal axis that is perpendicular to (001). The rotation angle, α , is mainly dependent on the Al occupancy; it is approximately 22° in clintonite, compared to 7° observed for phlogopite.

In natural clintonite, iron is reported as ferrous or ferric oxide or both; it amounts to at most 2.3 wt. % metallic iron calculated from the oxides (*e.g.*, in clintonite from Crestmore, California, analyzed by Eakle 1916). In view of the distinct differences in crystal structure between the clintonite micas and the alkali-rich micas it may be expected that the ion distribution will be different from that usually found in the common trioctahedral alkali-rich micas. By use of the Mössbauer effect (*e.g.*, Bancroft 1973), the intracrystalline ion distribution was investigated in iron-bearing clintonite of natural and synthetic origin.

INVESTIGATED SAMPLES AND EXPERIMENTAL DETAILS

The reported chemical composition, our observed cell parameters and calculated rotation angles α (Hazen & Wones 1972) of the samples investigated are shown in Table 1. The minerals, mostly of single-crystal quality, were examined by binocular microscope and X-ray diffraction technique for contamination before further handling. In addition to the natural samples, iron-bearing clintonites were synthesized. A maximum content of 5.58 wt. % Fe_2O_3 could

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TABLE 1. COMPOSITION AND STRUCTURAL PARAMETERS OF THE CLINTONITES INVESTIGATED

	1	2	3	4	5
SiO ₂ (wt.%)	17.11	17.15	19.45	16.74	15.52
Al ₂ O ₃	41.71	42.21	38.70	42.70	39.39
Fe ₂ O ₃	0.80	1.39	-	2.85	5.58
FeO	0.94	0.63	1.46	0.41	-
MnO	0.03	tr.	0.01	-	-
MgO	21.03	20.93	22.95	20.03	20.83
CaO	13.17	13.14	13.05	13.09	14.49
Na ₂ O	0.89	-	0.07	-	-
K ₂ O	0.12	-	-	-	-
H ₂ O	4.03	4.77	n.d.	4.49	4.19
Total	99.83	100.22	95.11	100.31	100.00
Fe ²⁺ / Fe ²⁺ +Fe ³⁺	0.54	0.31	-	0.13	-
<i>a</i> Å	5.204(1)	5.200(1)	5.200(1)	5.204(1)	5.206(1)
<i>b</i> Å	9.015(2)	9.008(2)	9.011(2)	9.014(2)	9.016(2)
<i>c</i> Å	9.810(2)	9.810(2)	9.777(2)	9.817(2)	9.808(4)
<i>β</i> °	100.19 (2)	100.19 (2)	100.20 (1)	100.17 (1)	100.21 (2)
<i>V</i> Å ³	452.98(17)	452.29(17)	450.89(14)	453.21(12)	453.06(21)
<i>α</i> °	22.4 (2)	22.5 (2)	21.6 (2)	22.4 (2)	22.7 (2)

1. Dark green clintonite associated with fassaite, grossularite, spinel, perovskite; contact of dolomitic limestone with tonalite, Lago della Vacca, Adamello (Sanero 1940).
2. Light green clintonite associated with grossularite, calcite, clinchlore, magnetite; Nikolaje Maximilianowsk, Achmatowsk, Urals (Koch 1935).
3. Brown clintonite associated with pargasite, chondrodite, calcite, spinel, graphite; Amity, New York; anal. D. Ackerman (microprobe analysis, total Fe as FeO and includes 0.05 Cr₂O₃, 0.37 TiO₂).
4. Green clintonite associated with calcite, monticellite; contact of marble with monzonitic dykes, Crestmore, California (Eakle 1916).
5. Synthetic clintonite, this report.

be incorporated in clintonite at $800 \pm 5^\circ\text{C}$, 2.0 ± 0.1 kbar, 89 hours run duration. High oxygen fugacity was maintained during the run by adding platinum (IV) oxide to the charge. To avoid serious contamination of the sample by platinum the charge was separated from the platinum dioxide by a neck in the gold tubes. At the end of the run the platinum dioxide was not found to be completely reduced. The clintonite solid solution coexists with $\alpha\text{-Fe}_3\text{O}_4$ in the run products; this phase can be easily separated from clintonite in the Mössbauer spectrum. Lattice constants were obtained through least-squares refinements using the program of Burnham (1962) and at least 26 *hkl* reflections from the diffractometer charts.

Mössbauer spectra of the powder samples were obtained at room temperature by means of an ELSCINT spectrometer using ⁵⁷Co in Rh as a source. The counts were accumulated in a 1024 MCA and the reported Mössbauer parameters are average values obtained from computer-fitting left and right sides of the spectra separately (512 channels each). Velocity calibration of the spectrometer was made against a metallic iron foil. Absorbers were made by mixing the finely powdered clintonite with transoptic powder. In order to avoid any preferred orientation of the

mica grains, the mixture was carefully poured into a sample holder of molybdenum, fitted with mylar windows. Absorbers thus prepared contained approximately 2–4 mg Fe/cm².

In the computer fit of spectra of ferrous+ ferric iron-bearing clintonites, line width and intensity of the strong overlapping low-velocity peaks were constrained equally in each doublet. Releasing the constraints resulted in unrealistic values. Chi-square values for the fits (13 variables, 512 channels) ranged between 483 and 630.

RESULTS

Results of the Mössbauer investigation are shown in Figure 1 and the observed Mössbauer parameters are summarized in Table 2. Iron is dominantly in the ferric state except in the clintonite from Amity, N.Y. (Fig. 1). The misfit indicated by the arrow may be interpreted as due to the small amounts of ferric iron present in this specimen; the coexistence of clintonite and graphite (Table 1) indicates a very low oxygen fugacity. Manning (1969) did not observe bands in his optical absorption of a sample from the same locality, which could be attributed to ferric iron. This sample is also distinguished by its low *c* lattice constant and different color (Table 1).

Ferrous iron

The ferrous-iron Mössbauer parameters indicate that this species occupies the octahedral positions of *M1* and *M2* (*cis* and *trans* configuration, respectively) in agreement with earlier investigations on trioctahedral biotites (Goodman & Wilson 1973; Annersten 1974; Bancroft & Brown 1975). The low ferrous-iron content in some of the samples made resolution of two ferrous-iron doublets unsuccessful. The ferrous iron distribution seems to be somewhat more ordered in *M2*, in contrast to the random distribution in biotite observed by Annersten (1974) and Bancroft & Brown (1975). However, the mean bond lengths at *M1* and *M2* differ by considerably more than in biotite; ionic size considerations would predict an easier entry of the larger ferrous iron ion into *M2* (2.072 (14)Å) than in the smaller *M1* site (2.016(14)Å), as observed by Takeuchi & Sadanaga (1966).

Ferric iron

Where present, ferric iron was found to occur in at least two types of sites, *i.e.*, tetrahedrally as well as octahedrally coordinated. We have assigned the doublet with the smaller isomer shift to ferric iron at the tetrahedral position and the

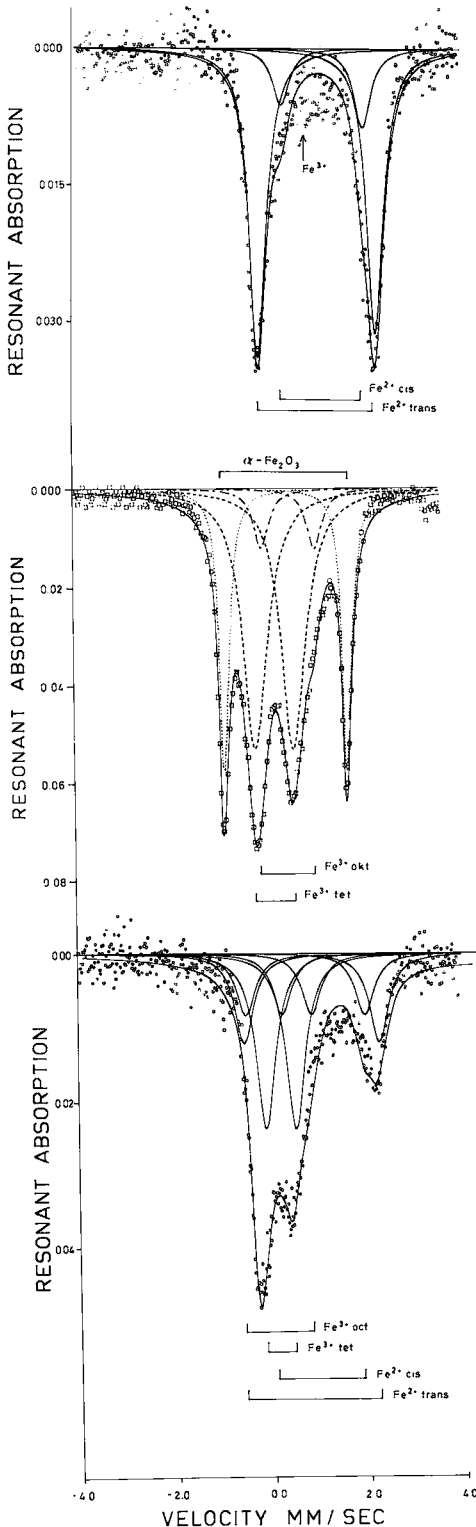


TABLE 2. OBSERVED MÖSSBAUER PARAMETERS IN CLINTONITE*

Sample		1.	2.	3.	4.	5.
Fe ²⁺ M1 cis	ΔE_Q mm/s	1.72	nd	1.85	nd	no
	I.S. mm/s	1.04	nd	1.15	nd	no
	Area %	6.2	nd	23.7	nd	no
Fe ²⁺ M2 trans	ΔE_Q mm/s	2.48	2.11	2.46	2.39	no
	I.S. mm/s	1.08	1.09	1.13	1.08	no
	Area %	28.7	26.4	76.5	23.6	no
Fe ³⁺ oct	ΔE_Q mm/s	1.05	1.20	no	no	1.08
	I.S. mm/s	0.52	0.52	no	no	0.49
	Area %	11.2	19.0	no	no	13.1
Fe ³⁺ tet	ΔE_Q mm/s	0.62	0.68	no	0.65	0.80
	I.S. mm/s	0.27	0.24	no	0.26	0.24
	Area %	53.3	54.7	no	76.4	86.9
FWHM	mm/s	0.52	0.46	0.36	0.47	0.57
Counts/channel $\times 10^6$		0.25	0.21	0.25	0.19	1.6
χ^2		483	587	761	630	612

* I.S. relative to metallic iron; determined at room temperature. Estimated error in E_0 and I.S. ± 0.02 mm/s. FWHM: full width half height. No: not observed, nd: not determined.

pattern with the larger shift to octahedrally coordinated ferric iron (Table 2), in general agreement with the observations made in iron-magnesium silicates (summarized values in Annersten & Hålenius 1976). The observed intensities of the respective patterns indicate that a dominant part of the ferric iron occupies the tetrahedral position. Quadrupole splittings of the tetrahedral pattern are larger than found in ferriphlogopite (0.50 mm/s, Annersten *et al.* 1971), which agrees with the observed larger distortion of the tetrahedral site in clintonite than in phlogopite. Isomer shift of the same pattern is also characteristically larger than usually observed at the Si site in silicates. We attribute this feature to the exceptionally large interatomic distances found in the tetrahedral polyhedra in clintonite, as further discussed below.

Fitting only one ferric-iron doublet in the ferric-iron spectra resulted in an unfitted shoulder on the high-velocity side of the dominant doublet. The added doublet is assigned to ferric iron in octahedral sites. Although closely overlapping, the Mössbauer parameters obtained are in good agreement with the same species in tri-

FIG. 1. Mössbauer spectra of clintonite measured at room temperature. Upper spectrum: Sample from Amity, N. Y. Arrow indicates trace amounts of ferric iron. Middle spectrum: Synthetic sample (no. 5). Notice the inner lines from ferrimagnetic α -Fe₂O₃. Lower spectrum: Sample from Lago della Vacca.

octahedral alkali-rich micas (Annersten 1974; Bancroft & Brown 1975). The resolution of this pattern does not allow us to separate the octahedral ferric iron into *M1* or *M2* but the values are close to those reported for Fe^{3+} in *M2* in biotite (Annersten 1974; Bancroft & Brown 1975).

DISTRIBUTION OF FERROUS AND FERRIC IRON IN CLINTONITE

From the reported chemical analyses and the observed area ratios in Mössbauer spectra, the cation distribution in clintonite can be calculated. It is assumed that similar recoil-free fractions for ^{57}Fe in the different types of sites makes the iron occupancies directly proportional to the ratio of areas (Hogarth *et al.* 1970). The result is shown in Table 3. It is evident from comparison with Table 1 that our observed ferrous/ferric iron ratio is larger than earlier reported values, emphasizing the often-recognized difficulties in determining these ratios in silicates by wet chemical analysis.

The strong preference for the tetrahedral site of ferric iron over Al is in marked contrast to the crystal-chemical behavior of ferric iron in Fe-Mg silicates in Al-rich systems. This feature can be attributed to the unusually large tetrahedral sites in clintonites compared to those in other silicates. Thus the larger Fe^{3+} ion (0.65\AA) will more easily fit in this site than the smaller Al^{3+} ion (0.57\AA). In fact, the observed mean tetrahedral bond length in clintonite ($1.730(14)\text{\AA}$) is characteristically larger than the mean $\text{Fe}^{3+}\text{-O}$ bond lengths in ferriphlogopite (1.68\AA ; Steinfink 1962) and melanite garnet (1.683\AA ; Amthauer *et al.* 1977).

MÖSSBAUER ISOMER SHIFTS AS AN INDICATOR OF FERRIC IRON SUBSTITUTION IN TETRAHEDRAL SITES

As mentioned above the large isomer shift observed for the tetrahedrally coordinated ferric

iron is attributed to the large bond lengths at the tetrahedral site in clintonite, resulting from the high Al/Si ratio in this mineral. The ^{57}Fe isomer shift is sensitive to the electron density around the nucleus (Bancroft 1973) and thus is also dependent on the bond lengths between the ligands and the iron nucleus in the lattice. Increasing the bond lengths yields a lower electron density, resulting in an increased isomer shift value for ^{57}Fe . This fact is further supported by Figure 2 where previously presented Mössbauer isomer shifts (relative to metallic iron) for tetrahedrally coordinated ferric iron in silicates are plotted against the observed mean interatomic distances in $\text{Si}(\text{Al})\text{-O}$ tetrahedra, obtained from X-ray diffraction data. We are of course aware of the

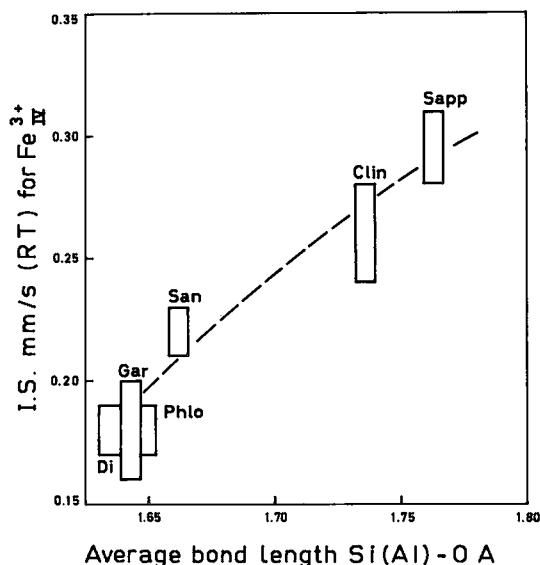


FIG. 2. Measured isomer shifts at 298 K for ferric iron in tetrahedral sites of different size. Di: ferri-diopside (Hafner & Huckenholz 1971), Phlo: ferri-phlogopite (Annersten *et al.* 1971), San: iron microcline (Annersten 1976), Gar: andradite garnet (Amthauer *et al.* 1977), Clin: clintonite (this report) and Sapp: sapphirine (Bancroft *et al.* 1968).

TABLE 3. STRUCTURAL FORMULAE OF THE CLINTONITES INVESTIGATED

Sample	Structural formulae based on 12 oxygens	New $\text{Fe}^{2+}/\text{Fe}^{2+}+\text{Fe}^{3+}$
1	$(\text{Ca}_{1.00}\text{Na}_{0.12}\text{K}_{0.01})_1(\text{Mg}_{2.21}\text{Mn}_{0.01}\text{Fe}_{0.034}^{2+}\text{Fe}_{0.011}^{3+}\text{Al}_{0.73})_{\text{oct}}(\text{Fe}_{0.055}^{3+}\text{Al}_{2.73}\text{Si}_{1.21})_{\text{tet}}\text{O}_{10}(\text{OH})_{1.89}$	0.34
2	$(\text{Ca}_{0.99}\text{Mg}_{0.01})_1(\text{Mg}_{2.17}\text{Fe}_{0.026}^{2+}\text{Fe}_{0.020}^{3+}\text{Al}_{0.77})_{\text{oct}}(\text{Fe}_{0.060}^{3+}\text{Al}_{2.74}\text{Si}_{1.19})_{\text{tet}}\text{O}_{10}(\text{OH})_{2.22}$	0.25
3	$(\text{Ca}_{0.98}\text{Na}_{0.01})_1(\text{Mg}_{2.35}\text{Fe}_{0.09}^{2+}\text{Al}_{0.55})_{\text{oct}}(\text{Al}_{2.64}\text{Si}_{1.36})_{\text{tet}}\text{O}_{10}(\text{OH})_2$	1.00
4	$(\text{Ca}_{0.99})_1(\text{Mg}_{2.10}\text{Fe}_{0.04}^{2+}\text{Al}_{0.85})_{\text{oct}}(\text{Fe}_{0.13}^{3+}\text{Al}_{2.69}\text{Si}_{1.18})_{\text{tet}}\text{O}_{10}(\text{OH})_{2.11}$	0.23
5	$(\text{Ca}_{1.11})_1(\text{Mg}_{2.22}\text{Fe}_{0.04}^{3+}\text{Al}_{0.72})_{\text{oct}}(\text{Fe}_{0.29}^{3+}\text{Al}_{2.60}\text{Si}_{1.11})_{\text{tet}}\text{O}_{10}(\text{OH})_2$	0.00

fact that the Si(Al)-O distances do not represent the actual Fe^{3+} -O tetrahedra. However, lack of data may make a relative comparison relevant. Ionic size and electronic theory predict an increase in tetrahedron size when Fe^{3+} proxies for Si or Al (cf., the Fe^{3+} -O values given above). It is to be noted that the low values of the tetrahedral ferric iron isomer shifts (0.18-0.19 mm/s are represented in Figure 2 by diopside, orthopyroxene, garnet, ferriphlogopite and phases that contain very little or no Al at tetrahedral sites. Thus these values most probably represent substitution $\text{Si} \rightleftharpoons \text{Fe}^{3+}$. The observed larger value 0.22 mm/s in an ordered microcline (Annersten 1976) suggests that Fe^{3+} proxies for Al, not Si, in agreement with single-crystal measurements on alkali feldspar using NMR and ESR techniques (Smith 1974). It is, therefore, tempting to suggest that the Mössbauer isomer shift may be used as a tool in the future for the recognition of the ordering of ferric iron in tetrahedral positions in structures that show Si/Al ordering. Such ordering is not observed in clintonite.

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