Structure and crystal chemistry of clintonite

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ABSTRACT

Crystal-structure refinements were made of two green clintonite-*1M* crystals from the Chichibu mine, Japan (R = 2.1%), and Ertsberg, Irian Jaya (New Guinea) (R = 2.1%), and of a brown specimen from Edenville, New York (R = 3.9%). The refinements were made in space group $C2/m$. The octahedral *trans* M(1) site is larger than the *cis* M(2) sites in all specimens because of the preferential ordering of Fe^{2+} plus Mg relative to Al in M(1) for the green specimens and of Mg relative to Al in the brown specimen. Fe^{2+} is disordered in the brown specimen, which may be a consequence of the disordered substitution of F for OH (0.45 atoms per formula unit) and local Fe-F avoidance. The result for the Chichibu mine specimen is opposite to that of an earlier, less accurate refinement of a crystal from the same locality, and it can be concluded that all ordered mica structures refined to date with monoclinic or trigonal symmetry have the same octahedral ordering pattern with M(1) larger than M(2). The presence of β angles greater than ideal, owing to larger M(1) sites and consequent overshifts ($> -a/3$) of the tetrahedral sheets within the 2:1 layer, indicates the same ordering pattern in clintonite-*1M* crystals from seven other localities. Only *Md* random stacking was found in eight clintonite samples from four other localities. For these samples, β is nearly ideal. No $2M_1$ or $3T$ polytypes were found. There is no correlation of regularity of stacking with any compositional parameter.

The tetrahedra are flattened as a consequence of their large Al contents (plus Fe^{3+} in the two green specimens), and the large lateral misfit of tetrahedral and octahedral sheets is relieved by tetrahedral rotations of 22.75° to 23.4°. The smallest rotation occurs in the brown Edenville specimen as a result of less tetrahedral substitution and misfit. Less tetrahedral rotation and less H^+-Ca repulsion allow the interlayer Ca to sink deeper into the larger ditrigonal opening, thereby reducing the c repeat distance and cell volume appreciably. Plots of cell parameters versus elemental components for 18 samples are linear, with the major exception of the brown samples from Edenville and nearby localities in Orange County, New York. The brown color of the five clintonites from Orange County, New York, correlates with octahedral Ti (0.01 to 0.03 atoms pfu), but a brown color also can result from secondary oxidation.

INTRODUCTION

The name *clintonite* has priority for the trioctahedral brittle mica of ideal composition $Ca(Mg_2Al)(SiAl_3)O_{10}(OH)_2$ and supersedes variety names based on differences in color and optical orientation, such as *xanthophyllite, seybertite, holmesite, brandisite,* and *valuevite* (Forman et al., 1967). Clintonite is the only common rock-forming trioctahedral Ca mica and forms as a result of thermal metamorphism of Ca- and Al-rich, Si-poor rocks. Clintonite is unique in its large tetrahedral Al content, which requires violation of the aluminum avoidance principle of Loewenstein (1954). Although the tetrahedral Si: Al ratio is ideally 1:3, natural specimens are known to range from about 1.1:2.9 to 1.4:2.6. Olesch (1975) synthesized clintonite with tetrahedral Si:Al ratios from 0.6: 3.4 to 1.4:2.6 and reported that the layer-stacking sequences became more regular as tetrahedral and octahedral Al increased. Tetrahedral sheets with these compo-

sitions have high net negative charges (-2.6 to -3.4) that require substantial substitutions of trivalent cations into the octahedral sheet to reduce the overall layer charge to -2.0 per formula unit. Natural clintonites have only minor substitutions of elements outside the Ca-Mg-Al-Si cation system. The primary substituent is Fe, with maximum reported values of 2.56% FeO and 3.24% Fe_2O_3 (Olesch, 1975). Annersten and Olesch (1978) found a maximum Fe_2O_3 content of 5.58% in synthetic clintonite. The only common polytype is *1M*. The $2M_1$ form is rare (Akhundov et al., 1961; Ohta et al., 1978), and no verified *3T* form has been reported. Specimens with *Md* stacking disorder are common.

Farmer and Velde (1973) reported infrared spectra for two clintonites that indicated disorder of the tetrahedral Si and Al cations. The absence of a positive optical second harmonic signal for three clintonites studied by Guggenheim et al. (1983) indicated the ideal space group of

TABLE 1.   Samples studied and compositions

Locality	Source	Dominant polytype	Color	Microprobe analyses			
				CaO	SiO$_2$	Al$_2$O$_3$	MgO
1. Chichibu mine, Japan	USNM 105455	1M	green	13.53	15.41	45.11	20.21
2. Ertsberg, Irian Jaya	U.W. 1782/5	1M	green	13.25	15.76	44.02	19.96
3. Edenville, Orange County, New York	USNM 47758	1M	brown	12.89	18.88	40.86	20.87
4. Alaska	USNM 94594	1M	green	13.04	17.46	42.31	20.31
5. Prince of Wales Island, Alaska	USNM 152797	1M	green	12.71	17.37	41.02	20.29
6. Trentino, Italy	USNM R4489-1	1M	green	12.87	17.00	42.69	19.70
7. Amity, Orange County, New York	USNM C3701	Md	brown	12.90	18.78	40.00	20.56
8. Amity, Orange County, New York	USNM C3702	Md	brown	12.92	19.01	41.17	20.38
9. Crestmore, California	USNM 151682	Md	green	12.81	18.09	39.91	20.56
10. Crestmore, California	USNM 95682	Md	green	13.27	16.33	42.88	20.24
11. Ural Mountains, USSR	USNM 144924	Md	green	13.42	16.35	43.06	20.34
12. Zlatoust, Ural Mountains, USSR	USNM 96223-2	Md	green	13.36	15.84	44.05	20.38
13. Zlatoust, Ural Mountains, USSR	USNM 79034	Md	green	13.52	16.01	43.67	20.17
14. Warwick, Orange County, New York	Harvard 87020	1M, Md	brown	12.91	19.33	40.37	20.70
15. Warwick, Orange County, New York	Harvard 57441	Md, 1M	brown	12.84	17.77	42.57	18.92
16. Copper Bluff, Sulzer, Alaska	Harvard 91421	1M	green	12.87	16.55	43.27	19.50
17. Crestmore quarry, California	Harvard 108087	1M, Md	green	12.89	18.31	39.40	20.75
18. Monzoni, Tyrol, Italy	Harvard 87021	1M	green to brown	12.77	16.86	42.60	19.79

* Assuming 11 oxygens and all Fe as octahedral Fe^{2+}.

$C2/m$ to be probably correct. This symmetry requires (Si, Al) disorder because it permits only one independent tetrahedron. A neutron refinement of clintonite-$1M$ from Adamello, Italy, in $C2/m$ symmetry by Joswig et al. (1986) gave a low residual R value of 2.0%, and no ordering of tetrahedral cations was found on attempting further refinement of the structure in subgroups $C2$ and Cm. Mössbauer analysis indicated substitution of 0.11 atoms of Fe^{3+} in the tetrahedral site for the Adamello clintonite.

The main crystallographic interest in clintonite concerns the ordering pattern of its octahedral Mg, Al, and Fe cations. The normal ordering pattern in monoclinic or trigonal micas (Bailey, 1984) is to have the *trans* M(1) site larger than the two *cis* M(2) sites, either through the presence of a larger cation or a vacancy (effective ionic radius of about 0.82 Å, Weiss et al., 1985) in M(1). Guggenheim and Eggleton (1987) have pointed out that this pattern is to be expected because a small M(1) site surrounded by six larger M(2) sites would be inherently unstable owing to the long shared edges that would result. The only exception to this pattern has been the structural refinement of a clintonite-$1M$ (labeled xanthophyllite) from the Chichibu mine, Saitama Prefecture, Japan, by Takéuchi and Sadanaga (1959, 1966). These authors used 384 film-collected X-ray reflections to refine the structure to $R = 10.4\%$. Their atomic coordinates yield mean octahedral bond lengths (as recalculated by the present writers) of M(1)–O,OH = 2.019 Å and M(2)–O,OH = 2.050 Å. These values were interpreted to indicate site occupancies of M(1) = $Al_{0.72}Mg_{0.18}\square_{0.10}$ and M(2) = $Mg_{1.0}$. The more accurate neutron-diffraction study of the Adamello clintonite by Joswig et al. (1986), on the other hand, gave the normal ordering pattern with mean M(1)–O,OH = 2.046 Å and mean M(2)–O,OH = 2.020 Å. These values were interpreted to indicate site occupancies of M(1) = $Mg_{0.73}Al_{0.22}Fe^{2+}_{0.05}$ and M(2) = $Mg_{0.77}Al_{0.23}Ti_{0.003}$ so that the

larger size of M(1) is due entirely to its Fe^{2+} content in this specimen.

This paper reports a study of the crystal chemistry of a suite of 18 clintonite specimens and includes a redetermination of the structure of the Chichibu mine specimen plus refinements of a brown clintonite from Edenville, New York, and a newly reported green clintonite from Irian Jaya (New Guinea). The goals of the study were to determine (1) whether the reported reverse octahedral ordering pattern in the Chichibu mine specimen was correct or an artifact due to incomplete refinement, (2) the relative sizes of M(1) and M(2) in other specimens by structural refinement and by a method using accurate cell dimensions, (3) whether octahedral ordering is only due to the Fe^{2+} distribution, (4) the prevalence of tetrahedral Fe^{3+}, (5) whether stacking regularity is related to Al content, (6) the relationship of composition to unit-cell parameters, and (7) the possible presence of polytypes other than $1M$.

SPECIMENS STUDIED

The 18 clintonite specimens used in this study are listed in Table 1. The clintonite from Irian Jaya (sample 2) has not been previously described. It was obtained from a pit in the Solo skarn 1.6 km (1 mi) from Ertsberg, Irian Jaya (New Guinea), by George Katchan, formerly of the University of Sydney. Associated minerals in the pit and nearby drill holes are calcite, dolomite, anhydrite, monticellite, forsterite, vesuvianite, and aluminian lizardite. Complete locality descriptions were not available for all specimens. Because of similar appearance, chemistry, cell dimensions, and diffraction patterns (see below), it is likely that sample 11 (Ural Mountains) is from the same locality as samples 12 and 13, (Zlatoust, Ural Mountains). The brown clintonites 3, 7, 8, 14, and 15 from Orange County, New York, are labeled as collected from

TABLE 1—*Continued*

Microprobe analyses				Structural formulas*									
FeO	MnO	TiO$_2$	F	Ca	Mg	Al	Fe	Ti	Σ oct	Si	Al	OH	F
1.25	0.01	0.00	0.00	1.00	2.11	0.82	0.07	0.00	3.00	1.08	2.92	2.00	0.00
2.95	0.04	0.02	0.00	1.00	2.08	0.74	0.18	0.00	3.00	1.10	2.90	2.00	0.00
1.92	0.04	0.22	2.03	0.97	2.18	0.70	0.11	0.01	3.00	1.32	2.68	1.55	0.45
2.48	0.00	0.06	0.66	0.98	2.13	0.74	0.15	0.00	3.02	1.23	2.77	1.85	0.15
3.91	0.05	0.08	0.00	0.97	2.15	0.68	0.23	0.00	3.06	1.24	2.76	2.00	0.00
2.81	0.00	0.00	0.00	0.98	2.08	0.78	0.17	0.00	3.03	1.21	2.79	2.00	0.00
1.86	0.00	0.54	2.01	0.97	2.15	0.70	0.11	0.03	2.99	1.32	2.68	1.55	0.45
1.93	0.00	0.61	1.92	0.97	2.12	0.71	0.11	0.03	2.97	1.33	2.67	1.58	0.42
3.72	0.04	0.05	0.00	0.98	2.19	0.64	0.22	0.00	3.05	1.29	2.71	2.00	0.00
2.49	0.03	0.05	0.00	1.00	2.12	0.73	0.15	0.00	3.00	1.16	2.84	1.98	0.02
2.33	0.00	0.07	0.00	1.00	2.12	0.74	0.14	0.00	3.00	1.16	2.84	2.00	0.00
2.23	0.02	0.07	0.00	1.00	2.11	0.76	0.13	0.00	3.00	1.12	2.88	2.00	0.00
2.03	0.00	0.06	0.00	1.00	2.12	0.76	0.12	0.00	3.00	1.13	2.87	1.97	0.00
1.46	0.00	0.11	1.98	0.97	2.17	0.71	0.09	0.01	2.98	1.36	2.64	1.56	0.44
3.08	0.00	0.15	1.45	0.97	2.00	0.80	0.18	0.01	2.99	1.26	2.74	1.67	0.33
2.83	0.00	0.00	0.00	0.98	2.07	0.80	0.17	0.00	3.04	1.18	2.82	2.00	0.00
3.65	0.00	0.00	0.00	0.99	2.21	0.63	0.22	0.00	3.06	1.31	2.69	2.00	0.00
2.24	0.00	0.00	0.42	0.98	2.11	0.78	0.13	0.00	3.02	1.20	2.80	1.91	0.09

Edenville, Amity, and Warwick, three towns located in a triangle about four miles apart at the northern end of the Franklin marble belt. Amity, New York, is the type locality for clintonite. The compositions and cell dimensions of the five samples are different, however, and the localities should be considered different. The regularity of layer stacking of sample 3 from Edenville is markedly better than for the other four samples and was selected for structural refinement. The regularity of layer stacking is better for sample 17 relative to samples 9 and 10, all from Crestmore, California, but in this case the chemistry and cell dimensions of samples 9 and 17 are nearly identical, but significantly different from sample 10. The chemistry and cell dimensions of sample 4 (Alaska) are sufficiently different from those of samples 5 (Prince of Wales, Alaska) and 16 (Copper Bluff, Alaska) to suggest it is not from either of the latter localities. The 18 samples thus represent 15 clintonites of different chemistry from 10 localities.

EXPERIMENTAL DETAILS

Quantitative chemical analyses were obtained for all samples using the ARL-SEMQ electron microprobe at the University of Wisconsin–Madison (Table 1). Samples were analyzed by wavelength-dispersive analysis using an accelerating potential of 15 kV, a sample current of 15 mA, and a slightly defocused (10 μm) beam. F was analyzed at 10 kV. No volatilization of F was observed for four times the counting time. Natural crystalline standards were used for all elements except F, for which synthetic fluorphlogopite was used. Matrix corrections were made using a modified Bence-Albee (1968) scheme or a ZAF correction program (EMPADR VII). Six to sixteen spots were analyzed on each of at least two grains for specimens 1 to 13. For specimens 14 to 18, the microprobe data are analyses of the one flake used to determine unit-cell dimensions. The accuracy of reported analyses is ±3% of the amount present for major elements and ±5–10% of the amount present for elements with <1 wt% abundance.

Mössbauer spectra were obtained for the two green specimens (samples 1 and 2) for which X-ray structural refinements were made. Each spectrum of ^{57}Fe was taken at room temperature using conventional techniques, 20-mCi ^{57}Co in a Pd matrix source, and constant acceleration with symmetric triangular wave form. Absorber density for the Irian Jaya clintonite was about 3 mg Fe/cm^2, but much less sample was available for the Chichibu specimen and its absorber density was only about 0.5 mg Fe/cm^2. The run times were 2 d for the former sample and 10 d for the latter. The spectra were folded and then fitted by least-squares assuming Lorentzian profiles.

Single-crystal X-ray precession photographs were taken of at least five crystals from all samples to determine crystal perfection and the polytypes present. Debye-Scherrer patterns also were taken of all samples. The best crystals found were used to determine accurate cell dimensions on a Nicolet P2$_1$ automated single-crystal diffractometer. Fourteen strong $k = 3n$ reflections in the 2θ range 67°–95° were centered using the resolved MoKα_1 wavelength. Unit-cell dimensions and volume (Table 2) were refined by least-squares fit of the centered positions.

The best $1M$ crystals from the Chichibu mine, Irian Jaya, and Edenville localities were also studied by Weissenberg films for crystal perfection, and one was selected from each sample for structural refinement. Crystals from the first two localities were light green in color and that from Edenville was light brown; all three crystals were transparent. There was no streaking of $k \neq 3n$ reflections for the selected crystals, and all exhibited sharp optical extinction. The crystal from the Chichibu mine measures 0.30 × 0.25 × 0.02 mm, that from Irian Jaya 0.40 × 0.20 × 0.03 mm, and that from Edenville 0.50 × 0.37 × 0.03 mm. Intensity data were measured in all eight octants of the limiting sphere to $2\theta = 60°$ on a Nicolet P2$_1$ automated single-crystal diffractometer with graphite-monochromated MoKα radiation. The data were collected in the θ:2θ variable-scan-rate mode. One standard reflection was checked after every 50 reflections in order to monitor electronic and crystal stability. No instability was noted. Reflections were considered observed if $I > 2\sigma(I)$. Integrated intensity I was calculated from $I = [S - (B_1 + B_2)/B_r]T_r$, where S is the scan count, B_1 and B_2 the backgrounds, B_r the ratio of background time to scan time, and T_r the 2θ scan rate

TABLE 2.   Cell dimensions

Sample	a (Å)	b (Å)	c (Å)	β_{obs} (°)	β_{ideal} (°)	Volume (Å³)
1	5.197(1)	9.002(2)	9.812(2)	100.32(2)	100.17	451.6(2)
2	5.199(2)	9.005(3)	9.812(3)	100.30(2)	100.17	452.0(2)
3	5.200(1)	9.005(2)	9.779(2)	100.30(2)	100.21	450.5(2)
4	5.201(1)	9.010(2)	9.814(2)	100.30(1)	100.17	452.5(1)
5	5.204(1)	9.014(2)	9.816(2)	100.26(2)	100.18	453.1(2)
6	5.199(2)	9.005(2)	9.800(3)	100.26(2)	100.19	451.5(2)
7*	5.199(1)	9.006(2)	9.779(2)	100.23(2)	100.21	450.6(2)
8*	5.198(1)	9.006(3)	9.778(3)	100.22(2)	100.21	450.5(2)
9*	5.203(1)	9.015(2)	9.815(2)	100.18(2)	100.18	453.1(2)
10*	5.200(1)	9.007(2)	9.813(2)	100.20(2)	100.17	452.3(2)
11*	5.198(1)	9.008(3)	9.814(3)	100.18(2)	100.17	452.3(2)
12*	5.200(2)	9.004(3)	9.812(3)	100.17(3)	100.17	452.2(2)
13*	5.199(1)	9.007(2)	9.813(2)	100.15(2)	100.17	452.3(2)
14	5.200(2)	9.006(3)	9.778(3)	100.28(3)	100.21	450.6(3)
15*	5.197(2)	9.003(3)	9.776(3)	100.20(3)	100.21	450.2(3)
16	5.200(2)	9.006(3)	9.814(3)	100.29(3)	100.17	452.4(3)
17	5.204(2)	9.014(3)	9.816(3)	100.25(3)	100.18	453.1(3)
18	5.199(2)	9.005(3)	9.802(3)	100.27(3)	100.18	451.5(3)

* Md stacking present.

in °/min. Values of $\sigma(I)$ were calculated from standard counting statistics. Intensities were corrected for Lorentz and polarization factors. Absorption corrections were made by the semiempirical psi-scan technique of North et al. (1968).

POLYTYPES OBSERVED

The $1M$ polytype is ubiquitous for the regularly stacked crystals, and no $2M_1$ or $3T$ polytypes were observed. Many crystals show some measure of randomness of stacking as well, as indicated by light to heavy streaks connecting the sharp $k \neq 3n$ spots on precession photographs. Bi-

refringence and sharpness of extinction on the (001) cleavage correlate well with the regularity of stacking. The birefringence decreases markedly with decreasing regularity of stacking. Md crystals are either essentially uniaxial or are mosaics composed of tiny birefringent centers. Decreasing birefringence in turn correlates well with decreasing crystallographic β angle.

Many $1M$ crystals are twinned by $\pm 120°$ rotations about the normal to the (001) cleavage. Such twinning causes extra spots on precession photographs that indicate an apparent three-layer periodicity, but that can be recognized as due to twinning either by irregular spacings or by marked intensity differences between spots along $02l$ and $11l$ row lines (as indexed on the $1M$ cell). A true $3T$ polytype has regular spacings and a reasonably uniform distribution of intensity over spots along these row lines. Some crystals from Amity, New York, simulate the $3T$ polytype closely in that volumes of the three twin components are about equal. Most crystals from Amity are disordered, wholly or partially.

STRUCTURAL REFINEMENTS

The data sets, after averaging over 2700 reflections to those equivalent by monoclinic symmetry, consisted of 607 independent nonzero reflections for the Chichibu specimen (no. 1), 604 for the Irian Jaya specimen (no. 2), and 673 for the Edenville specimen (no. 3). Scattering factors from Cromer and Mann (1968) appropriate for the compositions, 50% ionization, and cation disorder were used at the start and modified to fit the ordering pattern as refinement progressed. Unit weights were used

TABLE 3.   Atomic coordinates and thermal parameters

Atom	x	y	z	$\beta(1,1)$	$\beta(2,2)$	$\beta(3,3)$	$\beta(1,2)$	$\beta(1,3)$	$\beta(2,3)$
					Chichibu mine				
T	0.5705(1)	0.1670(1)	0.2101(1)	0.0055(2)	0.0017(1)	0.0014(1)	−0.0000(1)	0.0005(1)	−0.0000(1)
M1	0.0000	0.5000	0.5000	0.0042(5)	0.0013(1)	0.0016(1)	0.0000	0.0004(2)	0.0000
M2	0.5000	0.3292(1)	0.5000	0.0042(3)	0.0014(1)	0.0015(1)	0.0000	0.0004(1)	0.0000
Ca	0.5000	0.5000	0.0000	0.0069(3)	0.0021(1)	0.0014(1)	0.0000	0.0004(1)	0.0000
O1	0.4265(5)	0.0000	0.1523(3)	0.0089(8)	0.0029(3)	0.0021(2)	0.0000	−0.0000(3)	0.0000
O2	0.8627(3)	0.1878(2)	0.1512(2)	0.0089(6)	0.0032(2)	0.0021(2)	−0.0007(3)	0.0011(2)	−0.0004(2)
O3	0.6316(5)	0.1689(2)	0.3889(2)	0.0102(6)	0.0028(2)	0.0018(1)	−0.0001(3)	0.0006(2)	0.0000(1)
OH	0.6277(5)	0.5000	0.3990(3)	0.0093(8)	0.0047(3)	0.0013(2)	0.0000	0.0001(3)	0.0000
H⁺	0.095	0.000	0.313						
					Irian Jaya				
T	0.5703(1)	0.1670(1)	0.2100(1)	0.0051(2)	0.0019(1)	0.0011(1)	−0.0000(1)	0.0005(1)	0.000(1)
M1	0.0000	0.5000	0.5000	0.0034(5)	0.0014(2)	0.0013(2)	0.0000	0.0004(2)	0.0000
M2	0.5000	0.3292(1)	0.5000	0.0035(3)	0.0013(1)	0.0011(1)	0.0000	0.0005(1)	0.0000
Ca	0.5000	0.5000	0.0000	0.0075(4)	0.0026(1)	0.0012(1)	0.0000	0.0005(2)	0.0000
O1	0.4260(5)	0.0000	0.1528(3)	0.0094(9)	0.0032(3)	0.0019(2)	0.0000	0.0001(4)	0.0000
O2	0.8631(3)	0.1876(2)	0.1513(2)	0.0091(6)	0.0037(2)	0.0020(2)	−0.0008(3)	0.0010(2)	−0.0004(2)
O3	0.6311(3)	0.1685(2)	0.3887(2)	0.0094(6)	0.0030(2)	0.0016(2)	0.0000(3)	0.0006(2)	−0.0004(2)
OH	0.6281(5)	0.5000	0.3981(3)	0.0088(9)	0.0047(3)	0.0009(2)	0.0000	0.0002(4)	0.0000
H⁺	0.088	0.000	0.303						
					Edenville				
T	0.5703(2)	0.1669(1)	0.2096(1)	0.0044(3)	0.0014(1)	0.0015(1)	0.0000(1)	0.0007(1)	0.0000(1)
M1	0.0000	0.5000	0.5000	0.0034(6)	0.0008(2)	0.0018(2)	0.0000	0.0008(2)	0.0000
M2	0.5000	0.3302(1)	0.5000	0.0039(4)	0.0012(1)	0.0018(1)	0.0000	0.0007(2)	0.0000
Ca	0.5000	0.5000	0.0000	0.0077(4)	0.0024(1)	0.0026(1)	0.0000	0.0010(2)	0.0000
O1	0.4295(6)	0.0000	0.1508(3)	0.0115(11)	0.0030(3)	0.0023(3)	0.0000	0.0003(5)	0.0000
O2	0.8609(4)	0.1895(3)	0.1500(2)	0.0101(7)	0.0035(3)	0.0024(2)	−0.0009(3)	0.0016(3)	−0.0004(2)
O3	0.6306(4)	0.1681(2)	0.3877(2)	0.0080(7)	0.0022(2)	0.0018(2)	−0.0000(3)	0.0007(3)	−0.0000(2)
OH	0.6291(6)	0.5000	0.3977(3)	0.0083(10)	0.0033(3)	0.0014(3)	0.0000	0.0003(4)	0.0000
H⁺	0.1065	0.0000	0.3100						

because experience in this laboratory has shown them to be superior to sigma weights for the intensity distributions found in layer-silicate minerals. Starting from the atomic coordinates of Takéuchi and Sadanaga (1966) in space group $C2/m$ for the Irian Jaya specimen and from the refined coordinates of that crystal for refinement of the Chichibu and Edenville specimens, repeated cycles of least-squares fit were run with a modified ORFLS program (Busing et al., 1962). Refinement of scale factor, atomic positions, isotropic temperature factors, and then anisotropic temperature factors progressed to residuals of $R = 2.2\%$ for specimens 1 and 2 and to $R = 4.0\%$ for specimen 3. Difference electron density (DED) maps were flat at all atomic positions at this stage, and extra maxima indicated the positions of the H^+ protons associated with the OH groups. Further refinement, incorporating but not varying the H^+ positions, reduced R to 2.1% for specimens 1 and 2 and to 3.9% for specimen 3. Table 3 gives the resultant atomic positions and thermal parameters. Table 4 lists F_o and F_c values.[1]

For the Edenville specimen, the order-disorder of the substitution of 0.45 atoms per formula unit (pfu) of F for OH was also investigated. Space groups $C2/m$ and $C2$ do not permit ordering of F and OH within a single $5 \times 9 \times 10$ Å unit cell. Any such ordering adopted would require creation of a supercell or lowering of the symmetry to Cm, Pm, $P2$, or triclinic space groups. No evidence of a supercell or violations of C-centering were found from the film data; the data are monoclinic and not triclinic. Ordering is possible in Cm symmetry, but DED maps constructed for that symmetry do not show any differences in the densities or positions of the independent F and OH atoms. It is concluded that the substitution is random.

DISCUSSION OF STRUCTURAL FEATURES

Tetrahedral Fe^{3+} substitution and (Si,Al) disorder

Refinement in ideal space group $C2/m$ gave final R values from 2.1% to 3.9% for the three clintonite-$1M$ specimens. The possibility of obtaining lower values by refinement in subgroup symmetry can be discounted on the basis of the refinements by Joswig et al. (1986). The tetrahedral cations, therefore, are disordered.

Mössbauer spectra of the two green samples (nos. 1 and 2) are nearly identical to one another and to the spectrum for the Adamello clintonite published by Joswig et al. (1986). The spectra can be best interpreted as consisting of two quadrupole doublets, one for octahedral Fe^{2+} and one for tetrahedral Fe^{3+}. The doublet with the smaller isomer shift and quadrupole splitting was assigned to tetrahedral Fe^{3+}. The parameters (Table 5) are in good agreement with those of Annersten and Olesch (1978) and Joswig et al. (1986), except that the isomer shift and quadrupole splitting for tetrahedral Fe^{3+} in the Chichibu

TABLE 5. Mössbauer parameters for clintonite

	Fe^{3+}		Fe^{2+}	
	Chichibu mine	Irian Jaya	Chichibu mine	Irian Jaya
IS* (mm/s)	0.173	0.234	1.109	1.084
QS* (mm/s)	0.473	0.646	2.371	2.327
Rel. peak area	0.268	0.302	2.232	0.198
χ^2	1.07	1.54		

* IS = Isomer shift relative to α-Fe. QS = Quadrupole splitting.

mine sample are smaller than previously reported for clintonite—although still within the range for tetrahedral Fe^{3+} in trioctahedral micas (Dyar, 1987). This discrepancy may be caused by the poor quality of the Chichibu spectra resulting from the small amount of sample available and its low Fe content.

The relative amounts of Fe^{2+} and Fe^{3+} present were assigned by assuming the occupancies to be proportional to the ratios of the areas of the Mössbauer doublets (Table 5), namely 53.6% and 60.4% Fe^{3+} for the specimens from the Chichibu mine and Irian Jaya, respectively. This gives tetrahedral compositions of $Si_{1.083}Al_{2.878}Fe^{3+}_{0.039}$ for clintonite from the Chichibu mine and $Si_{1.107}Al_{2.788}Fe^{3+}_{0.105}$ for the clintonite from Irian Jaya. The observed mean T–O bond lengths are identical (1.728 Å) for the two specimens (Table 6). The values calculated for the compositions above using the effective ionic radii of Shannon (1976) are also identical (1.722 Å). The slightly smaller Fe^{3+} content of the clintonite from the Chichibu mine is compensated by a slightly larger ^{IV}Al content.

The small amounts of Fe^{3+} (0.04 to 0.11 atoms pfu) present in tetrahedral coordination in the two green clintonites nos. 1 and 2 are comparable to the 0.11 atoms pfu tetrahedral Fe^{3+} in clintonite from Adamello refined by Joswig et al. (1986). Thus, the three green clintonite specimens for which detailed structures are available have small amounts of tetrahedral Fe^{3+}. Annersten and Olesch (1978) cited Mössbauer data indicating tetrahedral Fe^{3+} present also in clintonites from Achamatovsk, USSR, and Crestmore, California.

Using Mössbauer analysis, Annersten and Olesch (1978) found no Fe^{3+} to be present in brown clintonite from Amity, New York, and we have assumed this to be true also for brown clintonite from the nearby Edenville locality in accord with the presence of graphite in the hand sample. The tetrahedral composition by microprobe analysis of the Edenville crystal is $Si_{1.324}Al_{2.676}$. The mean T–O bond lengths of 1.722 Å (observed) and 1.712 Å (calculated) are shorter than those of the green clintonites above because of a smaller content of tetrahedral Al and the absence of any tetrahedral Fe^{3+}. Tetrahedral Fe^{3+}, therefore, appears to be a common but not universal constituent of clintonite.

Octahedral ordering

In all three specimens the *trans* M(1) octahedral site is larger than the *cis* M(2) site, with mean M–O,OH values

TABLE 6. Interatomic distances (Å) and angles (°)

Chichibu mine

T-O1	1.792(1)	O1-O2	2.829(3)	O1-T-O2	109.8(1)
-O2	1.729(2)	O1-O2'	2.830(2)	O1-T-O2'	109.9(1)
-O2'	1.728(2)	O1-O3	2.820(3)	O1-T-O3	109.4(1)
-O3	1.726(2)	O2-O2'	2.830(2)	O2-T-O3	109.0(1)
Mean	1.728	O2-O3	2.813(2)	O2'-T-O3	108.8(1)
		O2'-O3	2.809(2)	O2-T-O2'	109.9(1)
		Mean	2.822	Mean	109.5

M1-O3	2.058(2) ×4	M2-O3	2.001(2) ×2	
-OH	2.010(3) ×2	-O3	2.026(2) ×2	
Mean	2.042	-OH	2.006(2) ×2	
		Mean	2.011	

Unshared lateral edges

O3-O3	3.041(4) ×2	O3-O3	2.981(2) ×2
O3-OH	3.045(3) ×4	O3-OH	2.982(2) ×2
Mean	3.044	O3-OH	2.979(3) ×2
		Mean	2.981

Shared diagonal edges

O3-O3	2.774(3) ×2	O3-O3	2.774(3)
O3-OH	2.697(2) ×4	O3-OH	2.697(2) ×2
Mean	2.723	O3-O3	2.727(3) ×2
		OH-OH	2.575(5)
		Mean	2.699

Ca-O1	2.441(2) ×2	Ca-O1	3.565 ×2
-O2	2.439(2) ×4	-O2	3.557 ×4
Mean	2.440	Mean	3.560

H$^+$-OH 0.83   ∠Ca-H$^+$-OH 177.6

Edenville

T-O1	1.725(2)	O1-O2	2.820(4)	O1-T-O2	109.6(1)
-O2	1.726(2)	O1-O2'	2.818(3)	O1-T-O2'	109.6(1)
-O2'	1.723(2)	O1-O3	2.808(4)	O1-T-O3	109.5(1)
-O3	1.714(2)	O2-O2'	2.819(2)	O2-T-O3	109.3(1)
Mean	1.722	O2-O3	2.806(3)	O2'-T-O3	109.2(1)
		O2'-O3	2.802(3)	O2-T-O2'	109.6(1)
		Mean	2.812	Mean	109.5

M1-O3	2.055(2) ×4	M2-O3	2.017(2) ×2	
-OH	2.008(3) ×2	-O3	2.035(2) ×2	
Mean	2.039	-OH	2.007(2) ×2	
		Mean	2.019	

Irian Jaya

T-O1	1.729(2)	O1-O2	2.834(3)	O1-T-O2	110.0(1)
-O2	1.731(2)	O1-O2'	2.832(2)	O1-T-O2'	110.1(1)
-O2'	1.728(2)	O1-O3	2.813(3)	O1-T-O3	109.1(1)
-O3	1.725(2)	O2-O2'	2.832(2)	O2-T-O3	109.0(1)
Mean	1.728	O2-O3	2.813(2)	O2'-T-O3	108.8(1)
		O2'-O3	2.808(2)	O2-T-O2'	109.9(1)
		Mean	2.822	Mean	109.5

		M2-O3	2.004(2) ×2
M1-O3	2.056(2) ×4	-O3	2.030(2) ×2
-OH	2.012(3) ×2	-OH	2.012(2) ×2
Mean	2.041	Mean	2.015

Unshared lateral edges

		O3-O3	2.985(2) ×2
O3-O3	3.035(4) ×2	O3-OH	2.987(2) ×2
O3-OH	3.039(3) ×4	O3-OH	2.984(3) ×2
Mean	3.038	Mean	2.985

Shared diagonal edges

		O3-O3	2.774(3)
		O3-OH	2.704(2) ×2
O3-O3	2.774(3) ×2	O3-O3	2.736(3) ×2
O3-OH	2.704(3) ×4	OH-OH	2.593(5)
Mean	2.727	Mean	2.708

Ca-O1	2.442(3) ×2	Ca-O1	3.571(3) ×2
-O2	2.438(2) ×4	-O2	3.561(2) ×4
Mean	2.439	Mean	3.564

H$^+$-OH 0.92   ∠Ca-H$^+$-OH 176.0

Unshared lateral edges

O3-O3	3.027(4) ×2	O3-O3	2.990(2) ×2
O3-OH	3.032(3) ×4	O3-OH	2.988(2) ×2
Mean	3.030	O3-OH	2.991(3) ×2
		Mean	2.990

Shared diagonal edges

O3-O3	2.781(4) ×2	O3-O3	2.781(4)
O3-OH	2.706(3) ×4	O3-OH	2.706(3) ×2
Mean	2.731	O3-O3	2.751(4) ×2
		OH-OH	2.602(6)
		Mean	2.716

Ca-O1	2.446(3) ×2	Ca-O1	3.541(3) ×2
-O2	2.443(2) ×4	-O2	3.536(2) ×4
Mean	2.444	Mean	3.539

H$^+$-OH 0.84   ∠Ca-H$^+$-OH 177.3

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of 2.042 vs. 2.011 Å for the Chichibu mine clintonite, 2.041 vs. 2.015 Å for the Irian Jaya clintonite, and 2.039 vs. 2.019 Å for the Edenville clintonite. The anion-anion distances also reflect these sizes: 2.883 vs. 2.840 Å, 2.883 vs. 2.847 Å, and 2.881 vs.. 2.853 Å, respectively. In all three cases, this is the normal ordering pattern for octahedral cations in micas, and it must be assumed that the reverse ordering pattern reported previously by Takéuchi and Sadanaga (1959, 1966) for clintonite from the Chichibu mine is a result caused by less accurate film data and incomplete refinement.

The octahedral compositions derived on the basis of the observed bond lengths, DED maps, and adjustments of scattering factors during refinement are M(1) =

TABLE 7. Observed and calculated octahedral bond lengths (Å)

	Chichibu mine		Irian Jaya		Edenville	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
M(1)	2.042	2.047	2.041	2.045	2.039	2.055
M(2)	2.011	2.017	2.015	2.020	2.019	2.036

$Mg_{0.80}Al_{0.17}Fe^{2+}_{0.03}$ and M(2) = $Mg_{0.65}Al_{0.35}$ for clintonite from the Chichibu mine, M(1) = $Mg_{0.75}Al_{0.18}Fe^{2+}_{0.07}$ and M(2) = $Mg_{0.67}Al_{0.33}$ for the Irian Jaya clintonite, and M(1) = $Mg_{0.80}Al_{0.16}Fe^{2+}_{0.04}$ and M(2) = $Mg_{0.68}Al_{0.27}Fe^{2+}_{0.04}$ for the Edenville clintonite. The calculated M-O,OH bond lengths for these compositions, using the ionic radii derived for octahedral cations in micas by Weiss et al. (1985) but corrected for F content, are slightly larger than the observed bond lengths (Table 7). The deviations can be explained by at most only one standard deviation of the errors in the microprobe analyses for MgO and Al_2O_3 that were used to limit these compositions.

For the two green specimens, the larger size of M(1) is due to the presence of additional Fe^{2+} and Mg cations in the octahedron. Although the Fe^{2+} content is small (0.03 to 0.07 atoms pfu), it is concentrated entirely in M(1). For the clintonite from Adamello refined by Joswig et al. (1986), the larger size of M(1) is entirely due to its Fe^{2+} content. The best fit of observed and calculated octahedral bond lengths and electron densities for the clintonites from Chichibu and Irian Jaya, however, requires an additional small ordering of Mg into M(1) and Al into

TABLE 8. Other structural data

		Chichibu mine	Irian Jaya	Edenville
Tetrahedral sheet thickness (Å)		2.323	2.318	2.317
Octahedral sheet thickness (Å)		2.079	2.087	2.097
Interlayer separation (Å)		2.927	2.931	2.891
Δz basal oxygens (Å)		0.011	0.015	0.008
Intralayer shift		$-0.337a$	$-0.337a$	$-0.336a$
Layer offset		$-0.001a$	$-0.001a$	$0.000a$
Rotation angle α (°)		23.3	23.4	22.75
Tetrahedral τ (°)		109.1	109.0	109.3
Octahedral ψ (°)	M(1)	59.4	59.25	59.1
	M(2)	58.9	58.8	58.7
Octahedral counterrotation (°)	M(1)	0	0	0
	M(2)	1.4	1.2	0.91
Internal-angle deviations*	M(1)	5.56	5.51	5.38
	M(2)	5.49	5.33	5.22
External-angle deviations**	M(1)	4.10	3.90	3.79
	M(2)	3.72	3.60	3.58

* RMS deviations of the 15 internal octahedral angles.
** RMS deviations of the 36 external octahedral angles.

M(2). This tendency is even greater in the clintonite from Edenville, in which electron densities and scattering-factor adjustments show that the Fe^{2+} is distributed at random over the M(1) and M(2) octahedral sites. The size differential is thus caused by preferential ordering of Mg into M(1) and Al into M(2), although the amount of ordering is small. The disorder of octahedral Fe^{2+} in this specimen may be due to the disordered substitution of 0.45 atoms of F for OH and consequent local Fe-F avoidance, and it is likely that complete ordering of Fe^{2+} into M(1) occurs in all F-poor clintonites. Table 1 shows a consistent but small amount of Fe (1.25% to 3.80% reported as entirely FeO) in all clintonites, with F contents near 2.0% for the clintonites from Orange County, New York, and 0.42% and 0.66% for clintonites nos. 18 and 4, respectively, but essentially nil for all others.

Other structural features

Some other structural features of the three clintonites are summarized in Table 8. As in all brittle micas, the high layer charges plus the divalent interlayer cation bring the layers close together (d_{001} = 9.62 to 9.65 Å). The interlayer separations of 2.89 to 2.93 Å suggest that the basal oxygens of adjacent layers are nearly in contact. The corrugation of these surfaces due to out-of-plane tilting is small (0.00 to 0.01 Å).

One unique feature of the three structures is the flattening of the tetrahedra indicated by the τ values of 109.0° to 109.3° relative to 109.47° for an ideal tetrahedron. We have calculated τ = 109.25° for the Adamello clintonite of Joswig et al. (1986). In all other disordered micas that have been well refined, the tetrahedra are elongate with τ values in the range 110° to 114°. Although the individual T–O bonds are all quite similar in clintonite, the bond to the apical oxygen is slightly shorter than those to the basal oxygens (Table 6). Takéuchi (1975) pointed out that tetrahedral distortions are examined best by comparison of tetrahedral edge lengths. In clintonite, the flattening is expressed by the basal edges being 0.02 Å longer than the pyramidal edges (Table 6). The flattening presumably is

a consequence of the high Al content and correspondingly high net negative charge of the tetrahedra. This is consistent with the least flattening (τ = 109.3°) being observed for the Edenville clintonite, which has the lowest ^{IV}Al content. Both the apical and basal oxygens are underbonded, which should provide a flattening tendency. Brown and Bailey (1963) noted that T–O_{basal} bonds tend to increase in length at a faster rate than T–O_{apical} bonds as tetrahedral Al content increases, and Takéuchi (1975) provided additional data to show that there is consequently a trend for basal tetrahedral edges to increase relative to pyramidal edges.

The trends above are for layer silicates with tetrahedral cation disorder, and they may or may not be evident in the individual τ, T–O, and O–O values for Al-rich and Si-rich tetrahedra linked to one another in the structure of an ordered species. We have examined data for the structures of 14 layer silicates in the literature with reported ordering of tetrahedral Si and Al and for which the difference in mean T–O bond lengths is greater than 0.03 Å and greater than 2.5 standard deviations of the errors involved. Three criteria were examined: Al-rich tetrahedra should have (1) the T–O_{apical} bond shorter than the mean T–O_{basal} bond, (2) basal edges greater than pyramidal edges, and (3) τ values smaller than for the linked Si-rich tetrahedra. Six structures were found to satisfy all three criteria, an additional two to satisfy two criteria, and the remaining six to satisfy one criterion.

The high tetrahedral Al content of clintonite creates a large lateral misfit between the tetrahedral and octahedral sheets, which is relieved by tetrahedral rotations (α) of 23.3°, 23.4°, and 22.75° in the three specimens of this study. These values represent misfits of 7.8% to 8.2%, relative to the b_{ideal} value in the equation cos α = b_{obs}/b_{ideal}, and these large rotations are exceeded in phyllosilicates only by the 23.5° value reported for franklinfurnaceite by Peacor et al. (1988). The brown clintonite from Edenville has an interlayer separation between basal oxygen planes that is 0.04 Å smaller than for the two green specimens (Table 8). This is a consequence of a smaller

amount of tetrahedral substitution and a smaller lateral misfit between sheets in the Edenville specimen relative to the two green clintonites. The smaller resultant tetrahedral rotation angle of 22.75° for this specimen allows the interlayer Ca to sink 0.02 Å deeper into the larger ditrigonal opening on both sides and thereby reduce the c repeat distance and cell volume appreciably. In addition to the larger ditrigonal opening, there is less repulsion involving Ca and H^+ as there is appreciable substitution of F for OH. This effect is noticeable on the cell dimensions of all five brown clintonites from Orange County, New York (Table 2).

The ψ values in Table 8 are all greater than the ideal value of 54.73° for an ideal octahedron. Both octahedra are flattened, therefore, with the larger M(1) flattened more than M(2). The RMS deviations (Table 8) of the 15 internal A–M–A angles (A = anion) and the 36 external A–A–A angles from their ideal values also indicate that M(1) is more distorted than M(2).

The OH group is overbonded as a consequence of the net positive charge on the octahedral sheet. It has moved along the mirror plane closer to the smaller and more highly charged M(2) cations, away from the larger and less highly charged M(1), so that it does not project exactly onto the interlayer Ca. The protons are located 0.83, 0.92, and 0.84 Å from the centers of their oxygen hosts in the specimens from the Chichibu mine, Irian Jaya, and Edenville, respectively, and are inclined 1.3°, 2.6°, and 2.7° from vertical and away from the interlayer Ca.

The orientations of the anisotropic thermal ellipsoids relative to the crystallographic axes are listed in Table 9 (see footnote 1). The RMS displacements of the ellipsoids are very similar in all specimens, as are the orientations if one takes into account the fact that those of all of the cations are either prolate or nearly spherical. The basal oxygen atoms are vibrating essentially perpendicular to the bonds joining them to their two tetrahedral cation neighbors.

USE OF CRYSTALLOGRAPHIC β ANGLE AS AN INDICATOR OF OCTAHEDRAL CATION ORDERING

Bailey (1975, 1984) noted that micas with sizes of M(1) > M(2) have β angles slightly larger than the ideal value [ideal $\beta = \arccos(-a/3c)$] observed when M(1) = M(2) in size. This is caused by an intralayer overshift (> $-a/3$) of the upper tetrahedral sheet within a 2:1 layer relative to the lower tetrahedral sheet in micas with M(1) > M(2) in size. Because apical oxygens of these opposing tetrahedral sheets are linked to diagonal edges of the *trans* M(1) octahedron, increasing the lengths of these diagonal edges by cation partitioning increases the effective intralayer shift relative to its ideal value of $-a/3$ and thereby increases the β angle. The overshift has the greatest effect on the observed β angle in *1M* micas where the intralayer shift direction is parallel to the resultant X axis. A smaller effect is observed in *2M* micas where the shift directions are oriented at 120° in adjacent layers and partly cancel

along the resultant X axis. The magnitudes of the deviations in β are 1.5° to 2° for dioctahedral *1M* micas but only 0.6° to 0.8° for dioctahedral $2M_1$ micas, both having vacancies in M(1). For trioctahedral micas the magnitude of the effect tends to be smaller than in dioctahedral micas and is a function of the sizes of the cations ordered in M(1) and M(2). The observed β angles can be affected also by small offsets of adjacent 2:1 layers around the interlayer cation. Such offsets are caused by ionic interactions between opposing layer surfaces, and tend to be very small except in unusual cases. Comparison of observed and ideal β angles in most cases, therefore, can be used as a guide to the relative sizes of M(1) and M(2) and to the presence of normal [M(1) larger than M(2)] or reverse [M(2) smaller than M(1)] octahedral cation ordering.

Overshifts occur in the three refined structures of this study ($-0.336a$ to $-0.337a$ vs. the ideal $-0.333a$), which give $\beta_{obs} = 100.32°$ vs. $\beta_{ideal} = 100.169°$ for clintonite from the Chichibu mine, $\beta_{obs} = 100.30°$ vs. $\beta_{ideal} = 100.166°$ for the Irian Jaya clintonite, and $\beta_{obs} = 100.30°$ vs. $\beta_{ideal} = 100.21°$ for the Edenville specimen. The differences in β values are 7.5, 6.7, and 4.5 standard deviations, respectively, of the error in measuring β_{obs}. The layer offsets are only $0.000a$ to $0.001a$, so that β_{obs} gives a good measure of the overshifts and the relative sizes of M(1) and M(2) in these clintonites. For the clintonite from Adamello (Joswig et al., 1986), $\beta_{obs} = 100.26(1)°$ and $\beta_{ideal} = 100.18°$. Because the deviation of β_{obs} from β_{ideal} is small, it is required that care be taken in determining accurate cell dimensions and angles.

For the ten clintonite specimens in Table 1 having regular or nearly regular *1M* stacking of layers, β_{obs} is larger than β_{ideal} (Table 2). Therefore, M(1) is larger than M(2) for each specimen, and the normal ordering pattern is present. This includes the three samples for which structural refinements were made. For eight other samples (marked by asterisks in Table 3), random *Md* stacking is dominant. In some of the *Md* crystals, $k \neq 3n$ spots are associated with the streaks, but the amount of such regular stacking must be small for the sample as a whole because Debye-Scherrer patterns of large volumes of powdered material did not show recognizable $k \neq 3n$ lines. The observed β angle is very close to β_{ideal} for all *Md* samples because the intralayer shifts are random along three directions at 120° to each other. If these three shift directions are present in equal numbers, the observed β angle may be described either as 90° or as exactly equal to β_{ideal} (neglecting layer offsets).

A corollary of the above relationship of the β angle to regular versus random stacking is that crystals with a mixture of regular and random stacking present, showing $k \neq 3n$ spots superimposed on streaks on single-crystal photographs, will have smaller β angles than would be the case if regular stacking were present throughout. This corollary was observed for specimens 4, 5, 6, 14, 15, and 17. For example, a crystal with regular stacking from

specimen 14 has a β angle of 100.31(3)°, one with a mixture of regular and random stacking has β = 100.21(3)°, and one with entirely random stacking from the same specimen has β = 100.16(3)°. The cell-dimension data in Table 3 are from the most regular crystals observed for each specimen. In a structural refinement, a reduced β angle due to partial random stacking would translate into a smaller M(1) size, not representative of the true size in those parts of the crystal with regular stacking. Takéuchi (1965) and Takéuchi and Sadanaga (1966) noted that the crystal from the Chichibu mine used for their refinement had diffuse streaks associated with the $k \neq 3n$ reflections. This would be a contributing, but probably not determining, factor in their finding of reduced β and M(1) sizes in their refinement.

CRYSTAL CHEMISTRY

Chemical compositions

Table 1 shows that natural clintonites have a remarkably consistent composition with little substitution outside the Ca-Mg-Al-Si cation system. For example, the CaO contents range from 12.81 wt% to 13.53 wt% for the 18 samples. K_2O + Na_2O + BaO + SrO totals of 0.03% and 0.01% were measured for specimens 1 and 2, respectively, and were not analyzed in other specimens. The MgO contents range from 18.92% to 20.87% (2.00 to 2.21 atoms pfu). The main octahedral substituent is Fe^{2+}. The FeO contents in Table 1 range from 1.25% to 3.91%, but in most cases this includes undifferentiated tetrahedral Fe^{3+} and octahedral Fe^{2+}. TiO_2 contents range from nil to 0.08% in green clintonites but 0.15% to 0.61% (0.01 to 0.03 atoms pfu) in the transparent brown crystals from Orange County, New York. The brown color in these specimens is likely due to the Ti, as concluded by Manning (1969) on the basis of optical absorption spectra. Ti cannot be the sole cause of brown color, however, because opaque brown crystals of sample 18 from Monzoni, Italy, do not contain Ti. In a few crystals of the latter sample, an original green coloration can be seen, with secondary oxidation along cracks and cleavages causing the brown color. The Cl content was below detection limits in all samples, but the F content can be as great as 2.03% (0.45 atoms pfu) in clintonites from the F-rich Franklin marble belt.

The tetrahedral compositions range from ($Si_{1.08}Al_{2.88}$-$Fe^{3+}_{0.04}$) for clintonite (no. 1) from the Chichibu mine, Japan, which most closely approaches the ideal $SiAl_3$ ratio, to ($Si_{1.36}Al_{2.64}$) for clintonite (no. 14) from Warwick, New York. The amount of tetrahedral Fe^{3+} is known only for specimens 1 and 2, for which Mössbauer data are available. These Si:Al limits compare favorably with those noted for other natural specimens, reported by Olesch (1975) as 1.1:2.9 to 1.4:2.6, but they do not approach the 0.6:3.4 limit for synthetic Si-poor clintonite. Because interlayer Ca is virtually constant at 0.97 to 1.0 atoms pfu, charge balance requires that a higher Si:Al ratio (de-creasing the net negative charge on the tetrahedral sheets) must be compensated by a corresponding decrease in net positive charge on the octahedral sheet. This is accomplished in the specimens of this study by a decrease in octahedral Al and possibly, depending on Fe^{2+}:Fe^{3+} ratios, by the presence of a very small number of octahedral vacancies.

Variation of cell parameters as a function of composition

With the major exception of the brown clintonites from Orange County, New York (Fig. 1), plots of cell parameters versus compositional components are nearly linear. The lateral dimensions a and b increase with increasing contents of the large Mg + Fe cations. However, there is a decrease in the lateral dimensions with increasing tetrahedral substitution for Si. This is because of a general increase in both octahedral and tetrahedral Al plus the greater tetrahedral rotation that is required to alleviate the increased lateral misfit of sheets. Some of the scatter in Figure 1 (left half) may be due to lack of differentiation of Fe^{2+} and Fe^{3+}, because octahedral Fe^{2+} and tetrahedral Fe^{3+} have opposite effects on the lateral dimensions.

The c repeat distance and unit-cell volume likewise increase with increasing Mg + Fe and decrease with increasing tetrahedral substitution for Si. It is on these plots that the brown clintonites from Orange County, New York, deviate most markedly from the other specimens and form a separate group of five samples lying on trend lines nearly parallel to those of the others. The structural analysis of sample 3 from Edenville showed that the smaller c repeat distance and cell volume are caused by a smaller amount of tetrahedral substitution (Fig. 1, right half, and Table 1) and consequent smaller amount of tetrahedral rotation. The interlayer Ca sinks deeper into the ditrigonal rings, both because of the larger size of the openings and the smaller amount of H^+-Ca repulsion (due to F substitution for OH). A similar but smaller structural effect can be expected for samples 6 and 18 based on their intermediate positions on the plots of Figure 1. Both of the latter samples come from the Tyrol region of northern Italy, but the labels are not sufficiently detailed for precise locations. They differ macroscopically in the marked secondary alteration of sample 18 and chemically by the presence of F in 18. The Adamello clintonite refined by Joswig et al. (1986) comes from the same general region, but is structurally and compositionally different from 6 and 18 (Fig. 1).

Samples 5, 9, and 17 have tetrahedral substitutions similar to those of the five brown clintonites from Orange County, New York (Fig. 1, right half), and have large octahedral Mg contents (Fig. 1, left half, and Table 1) so that tetrahedral rotations even smaller than those of the Orange County clintonites might be predicted. The positions of these three samples on the upper regression lines of the figures, instead of the lower lines, appear anomalous. The compositions differ from those of the
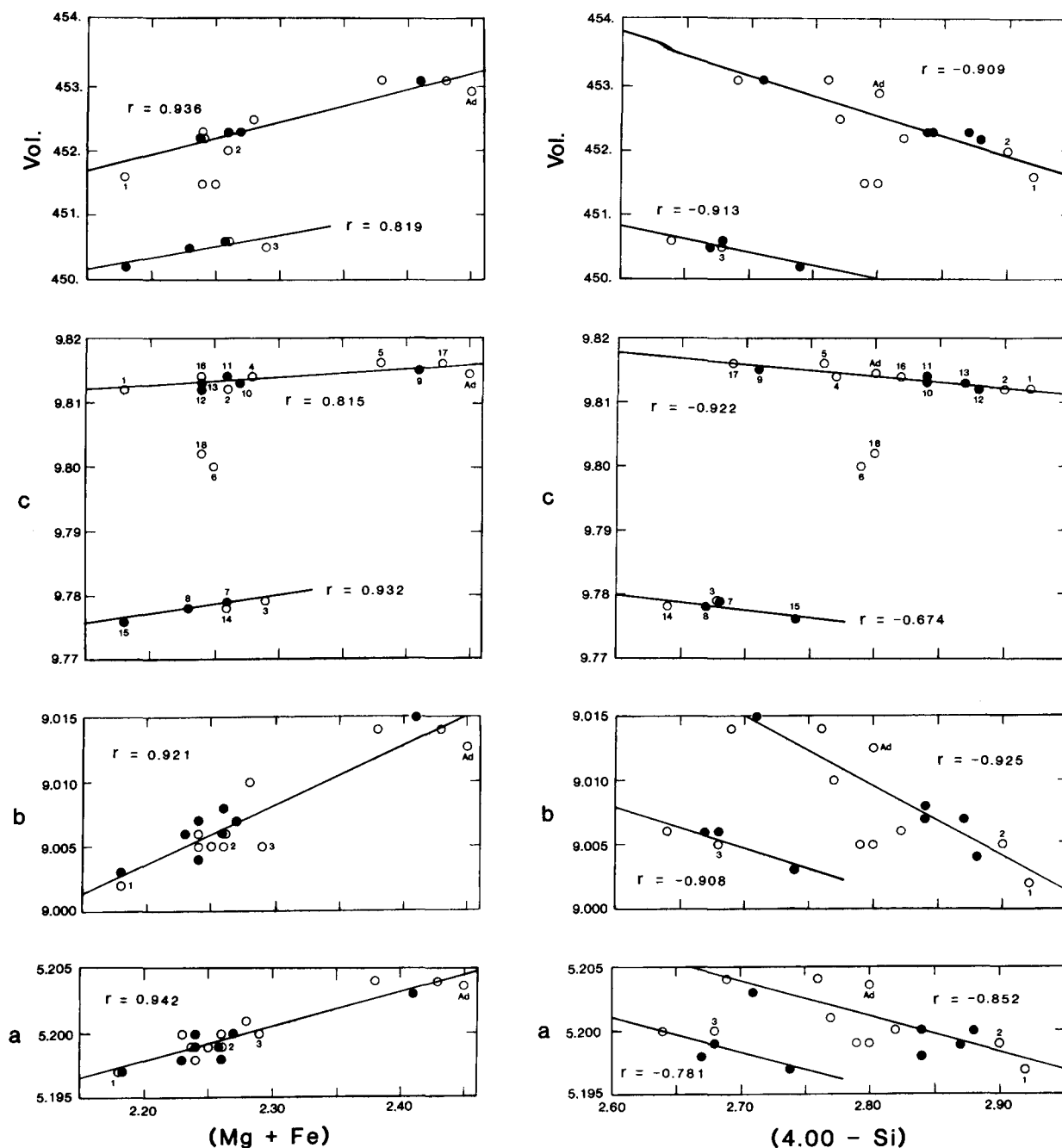
Fig. 1. (Left) Plots of cell parameters (Å) vs. number of Mg + Fe atoms per formula unit. Fe includes undifferentiated Fe^{2+} and Fe^{3+}. *Md* stacking samples shown as solid circles, *1M* stacking as open circles. Coincident points have been slightly displaced horizontally. Samples are the 18 clintonites of the present study plus that from Adamello, Italy, refined by Joswig et al. (1986). Lines through points calculated by least-squares fit. Samples 6 and 18 were included only in the regressions vs. *a* and *b*. (Right) Plots of cell parameters (Å) vs. [4.00 − Si] in atoms per formula unit. Notation same as at left. Samples 6 and 18 were not used in any of the regressions.

Orange County clintonites, however, in two important respects. Their total Fe contents are the largest measured in this study, and they contain no F (Table 1). The most plausible explanation for their positions on the regression plots is a large tetrahedral Fe^{3+} content that would increase tetrahedral rotation and, combined with Ca-H^+ repulsion, lead to the observed large *c* repeat distances. No confirmatory chemical or Mössbauer data are available

for sample 5 from Prince of Wales Island, Alaska. Samples 9 and 17 are from Crestmore, California, however, and Annersten and Olesch (1978) reported 2.85% tetrahedral Fe_2O_3 and 0.14% octahedral FeO from Mössbauer data for a sample from the same locality. This supports the proposed explanation.

Samples with a dominant *Md* stacking are shown as solid circles in Figure 1. It is evident that the regularity of stacking is not dependent on either of the compositional parameters plotted. Although Olesch (1975) reported that the stacking sequences in synthetic clintonites became more regular as tetrahedral and octahedral Al increased, other plots (not shown) involving these latter parameters do not show any correlation. Microprobe analyses of one *1M* and one *Md* flake from the same sample (no. 14) indicate that all elements other than Si and Al are the same, but octahedral Al and tetrahedral Al are 0.02 and 0.03 atoms, respectively, larger in the disordered stacking variant. This difference is small and is in the opposite direction to that noted by Olesch. The natural clintonites in this study, however, do not extend to as large Al contents as in the synthetic specimens.

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REFERENCES CITED

Akhundov, Y.A., Mamedov, K.S., and Belov, N.V. (1961) The crystal structure of brandisite. Doklady Akademii Nauk SSSR, 137, 167–170 (translation, Doklady of the Academy of Sciences of the USSR, Earth Sciences Sections, 137, 438–440, 1962).

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

Bailey, S.W. (1975) Cation ordering and pseudosymmetry in layer silicates. American Mineralogist, 60, 175–187.

——— (1984) Crystal chemistry of the true micas. Mineralogical Society of America Reviews in Mineralogy, 13, 13–60.

Bence, A.E., and Albee, A.L. (1968) Empirical correction factors for the electron microanalysis of silicates and oxides. Journal of Geology, 76, 382–403.

Brown, B.E., and Bailey, S.W. (1963) Chlorite polytypism. II. Crystal structure of a one-layer Cr-chlorite. American Mineralogist, 48, 42–61.

Busing, W.R., Martin, K.O., and Levy, H.A. (1962) ORFLS, a FORTRAN crystallographic least-squares refinement program. U.S. National Technical Information Service, ORNL-TM-305.

Cromer, D.T., and Mann, J.B. (1968) X-ray scattering factors computed from numerical Hartree-Fock wave functions. Acta Crystallographica, A24, 321–324.

Dyar, M.D. (1987) A review of Mössbauer data on trioctahedral micas: Evidence for tetrahedral Fe^{3+} and cation ordering. American Mineralogist, 72, 102–112.

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

Forman, S.A., Kodama, H., and Maxwell, J.A. (1967) The trioctahedral brittle micas. American Mineralogist, 52, 1122–1128.

Guggenheim, S., and Eggleton, R.A. (1987) Modulated 2:1 layer silicates: Review, systematics, and predictions. American Mineralogist, 72, 724–738.

Guggenheim, S., Schulze, W.A., Harris, G.A., and Lin, J.-C. (1983) Noncentric layer silicates: An optical second harmonic generation, chemical, and X-ray study. Clays and Clay Minerals, 31, 251–260.

Joswig, W., Amthauer, G., and Takéuchi, Y. (1986) Neutron-diffraction and Mössbauer spectroscopic study of clintonite (xanthophyllite). American Mineralogist, 71, 1194–1197.

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

Manning, P.G. (1969) On the origin of colour and pleochroism of astrophyllite and brown clintonite. Canadian Mineralogist, 9, 663–677.

North, A.C.T., Phillips, D.C., and Mathews, F.S. (1968) A semi-empirical method of absorption correction. Acta Crystallographica, A24, 351–359.

Ohta, T., Takéuchi, Y., and Takeda, H. (1978) Structural study of brittle micas (II). Statistical mode of stacking sequences in a valuevite crystal as deduced by computer simulation. Mineralogical Journal (Japan), 9, 1–15.

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

Peacor, D.R., Rouse, R.C., and Bailey, S.W. (1988) The crystal structure of franklinfurnaceite: A tri-dioctahedral zincosilicate intermediate between chlorite and mica. American Mineralogist, 73, in press.

Shannon, R.D. (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Crystallographica, A32, 751–767.

Takéuchi, Y. (1965) Structure of brittle micas. Clays and Clay Minerals, 13, 1–25.

——— (1975) The distortion of Si(Al)-tetrahedra in sheet silicates. In K. Henmi, Ed., Contributions to clay mineralogy, Toshio Sudo volume, p. 1–6. Pergamon Press, New York.

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.

Weiss, Z., Rieder, M., Chmielová, M., and Krajícek, J. (1985) Geometry of the octahedral coordination in micas: A review of refined structures. American Mineralogist, 70, 747–757.