

## Refinement of the Crystal Structure of Monoclinic Chloritoid

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Chloritoid from Weaver Hill, Vermont, is monoclinic, space group  $C2/c$  with  $Z=8$ . The cell parameters are:  $a=9.4818$  (5),  $b=5.4842$  (4),  $c=18.1824$  (10) Å, and  $\beta=101.738$  (2)°. The chemical composition determined by electron microprobe analysis is  $(\text{Fe}_{1.67}^{2+}\text{Mg}_{0.26}\text{Mn}_{0.06}^{2+})\text{Al}_{3.88}\text{Fe}_{0.08}^{3+}\text{Si}_{2.05}\text{O}_{11.99}$ . Refinement was carried out using intensities determined with standard  $\theta/2\theta$  scans and Mo  $K\alpha$  X-radiation on a Picker computer-controlled four-circle diffractometer. 3047 structure factors from one quadrant of reciprocal space were used in the refinement. The final  $R$  was 0.041 ( $R_w=0.033$ ) for all structure factors, and 0.034 ( $R_w=0.033$ ) for the unrejected structure factors. The chloritoid structure consists of two octahedral layers connected by isolated silicon tetrahedra. Substitution of Mg for  $\text{Fe}^{2+}$ , and  $\text{Fe}^{3+}$  for Al occurs in the trioctahedral layer with mean M–O bond distances of 2.163 and 1.935 Å for these sites respectively. Both sites in the aluminum octahedral layer have mean M–O bond distances of 1.896 Å, and no substitution occurs in these sites. The mean tetrahedral bond distance is 1.643 Å. Both hydrogen atoms in the structure were located in a difference synthesis computed during the final stage of refinement. The hydroxyls in one octahedral layer form hydrogen bonds with oxygens in the adjacent octahedral layer. The hydrogen-bonded O...O distances are 2.666 (2) and 2.814 (2) Å.

### Introduction

Chloritoid crystallizes in at least two polymorphic modifications, one triclinic and the other monoclinic. Because the cell parameters of the monoclinic polymorph are approximately equal to those of the triclinic polymorph with  $c$  doubled, the monoclinic polymorph was believed to be a polytypic modification of the triclinic structure. A study of both structures was initiated to determine how they are related, and, if possible, what dictates their relative stabilities. A paper dealing with the triclinic structure is in preparation.

The chemical composition of chloritoid can be represented ideally by  $\text{Fe}_2\text{Al}_4\text{Si}_2\text{O}_{10}(\text{OH})_4$ ; however, partial substitution of Mn and Mg for ferrous iron, and ferric iron for aluminum takes place (Halferdahl, 1961). The composition limits of this mineral are not fully defined, partly because chloritoid commonly contains a great deal of included material that makes conventional wet chemical analysis very difficult. Chloritoid formed during regional metamorphism of pelitic sediments is typically near the ferrous iron end-member in composition, and contains some Mg and minor Mn.

The first refinement of the monoclinic structure was carried out by visual estimates of film data (Brindley & Harrison, 1952; Harrison & Brindley, 1957). It showed that the structure was not related to the mica structure as was previously assumed, but contained isolated silicon tetrahedra between two types of octahedral layers. A preliminary cation distribution was suggested based on  $h0l$  and  $0kl$  Fourier projection peak

heights. The present study verifies this proposed structure, and the refined cation occupancies are in general agreement with those that were originally suggested.

### Experimental procedure

A quartz-sericite schist containing porphyroblasts of chloritoid 1 to 5 mm in diameter was collected by the author from an outcrop of the Pinney Hollow formation on the west side of Weaver Hill, near Tyson, Vermont.

An electron-microprobe analysis of this chloritoid was carried out at the Geophysical Laboratory, Washington D.C. The chloritoid is homogeneous with little difference in composition between grains (Finger, 1972). The results were averaged (a total of 12 spots on three grains) and recalculated on the basis of eight cations. The ratio of ferric iron to total iron was assumed to be the same as that of a chloritoid from a nearby locality that was analysed by wet chemical methods (Hanscom, 1973). The recalculated formula is:



The optical properties and density are:  $\alpha=1.720$  (5),  $\beta=1.725$  (5),  $\gamma=1.732$  (5) (Na light at 22°C);  $2V=60^\circ$  (+),  $\rho_o=3.56$  (1) g cm<sup>-3</sup> (Berman balance).

The crystal used for intensity measurements is a rectangular cleavage flake with a computed crystal volume of  $5.62 \times 10^{-3}$  mm<sup>3</sup>.

Precision back-reflection Weissenberg photographs of this crystal were taken about three axes with Ni-filtered Cu  $K\alpha$  X-radiation. Measurements of 196 back reflections were used for least-squares refinement of the unit-cell parameters. Systematic-error terms were

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included in the refinement to correct the data for absorption, film shrinkage, and camera eccentricity (Burnham, 1962). The results of the refinement are:  $a=9.4818$  (5),  $b=5.4842$  (4),  $c=18.1824$  (10) Å;  $\beta=101.738$  (2)°;  $V=925.7$  (1) Å<sup>3</sup>.

Because systematic absences are of the type  $(h+k)$  odd for all  $hkl$ , and  $l$  odd for  $h0l$ , the diffraction symbol is  $2/mC-c$ , which is consistent with space groups  $Cc$  or  $C2/c$ . The intensity data have a hypercentric distribution when subjected to the zero-moment test (Howells, Phillips & Rogers, 1950), after excluding the  $0k0$  and  $h0l$  data. The  $h0l$  reflections of monoclinic chloritoid from Île de Groix, France, possess a centric distribution (Harrison & Brindley, 1957), so space group  $C2/c$  was chosen for refinement. Eight formula units per cell,  $Z=8$ , lead to  $\rho_c=3.57$  g cm<sup>-3</sup>, in good agreement with the observed density.

Intensities were determined with a Picker computer-controlled four-circle diffractometer, niobium-filtered Mo  $K\alpha$  X-radiation, and  $\theta/2\theta$  scans with fixed background counts at the extremes of the scan. The data collection was carried out in one quadrant of reciprocal space from  $8$  to  $82^\circ 2\theta$ . Miller indices were allowed to vary from  $-16$  to  $16$  ( $h$ ),  $0$  to  $10$  ( $k$ ), and  $0$  to  $32$  ( $l$ ). Systematic absences were excluded from the data collection, and 3969 intensities were measured.

The estimated standard deviation of an intensity was computed using counting statistics (for details see Burnham, Ohashi, Hafner & Virgo, 1971), and, when an integrated intensity was less than  $2\sigma_I$ , it was considered unobserved and assigned the value  $2\sigma_I/3$  (Hamilton, 1955).

The data were corrected for absorption by numerical integration techniques (Burnham, 1966), and  $\mu_t=36.89$  cm<sup>-1</sup>. The transmission factors ranged from  $0.4425$  to  $0.7240$ . Equivalent data were averaged after data reduction into a set of 3047 non-equivalent structure factors, including 440 unobserved  $F^s$ .

### Least-squares refinement

Computation of full-matrix least-squares refinement was accomplished using *RFINE* (written by L. W. Finger of the Carnegie Institute of Washington) adapted for an IBM 360/65. Scattering curves for neutral atoms were taken from Cromer & Mann (1968), and corrections for anomalous dispersion were used (*International Tables for X-ray Crystallography*, 1968). *RFINE* minimizes the function  $\sum w(|F_o| - |F_c|)^2$ , where  $w = \sigma_F^{-2}$ . The residual,  $R$ , and the weighted residual,  $R_w$ , were computed for all cycles of refinement using  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$  and  $R_w^2 = \sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2$ .

Refinement was initiated using the structure parameters of Harrison & Brindley (1957), and assuming the composition of the ferrous iron end-member [ $M(1B) = \text{Fe}$  and  $M(1A) = M(2A) = M(2B) = \text{Al}$ ]. After several cycles of refinement, the temperature factor of  $M(1A)$  became negative, and that of  $M(1B)$  was excessively large. Since the major substituents in this chloritoid are Mg, Fe<sup>3+</sup> and Mn, it was assumed that Fe<sup>3+</sup> substitutes for Al in  $M(1A)$ , and Mg<sup>2+</sup> substitutes for Fe<sup>2+</sup> in  $M(1B)$ . In addition the small amount of Mn present was treated as Fe<sup>2+</sup>, assuming their scattering behavior is similar. The occupancies of these sites were fixed to agree approximately with the microprobe analysis [ $0.9$  Al and  $0.1$  Fe<sup>3+</sup> in  $M(1A)$ , and  $0.85$  Fe<sup>2+</sup> (and Mn) and  $0.15$  Mg in  $M(1B)$ ]. The initial  $R$  was  $0.205$  ( $R_w=0.153$ ), and after two cycles of refinement, it was reduced to  $0.062$  ( $R_w=0.049$ ). At this point anisotropic thermal parameters were introduced, and during the next stage of refinement the occupancies of the two cation sites in the octahedral layer [ $M(1A)$  and  $M(1B)$ ] were allowed to vary, but the total iron in the structure was forced to equal total iron in the analysis using the method of Finger (1969). Features that appeared to be hydrogen atoms were located in a

Table 1. Atomic coordinates and thermal parameters

Thermal parameters are  $\times 10^{-5}$ . Least-squares standard errors in parentheses. The thermal parameters satisfy an expression of the form  $\exp\{-\sum_i \sum_j h_i h_j \beta_{ij}\}$ .

	$x$	$y$	$z$	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
M(1A)	$\frac{1}{2}$	$\frac{1}{2}$	0	91 (8)	270 (24)	30 (2)	-3 (12)	9 (4)	-13 (7)
M(2A)	0	0.40144 (19)	$\frac{1}{2}$	65 (8)	192 (23)	28 (2)	0	13 (4)	0
M(1B)	0.08357 (4)	0.74690 (8)	0.00105 (2)	107 (3)	377 (9)	62 (1)	-17 (5)	17 (1)	-9 (3)
M(2B)	0.24986 (9)	0.65260 (13)	0.24879 (5)	71 (5)	186 (16)	30 (2)	-18 (8)	7 (2)	-6 (4)
T	0.46321 (6)	0.40161 (12)	0.15626 (3)	56 (5)	171 (14)	16 (1)	-2 (8)	2 (2)	1 (4)
O(1A)	0.11529 (16)	0.39106 (32)	0.05330 (9)	139 (14)	448 (42)	38 (4)	2 (23)	12 (6)	-16 (12)
O(1B)	0.26504 (17)	0.94453 (29)	0.05039 (9)	175 (15)	378 (43)	36 (4)	0 (21)	10 (6)	4 (11)
O(1C)	0.42445 (16)	0.39556 (32)	0.06415 (9)	136 (14)	404 (40)	24 (4)	-23 (22)	5 (6)	-6 (12)
O(2A)	0.39376 (17)	0.15829 (28)	0.18846 (10)	60 (14)	229 (39)	35 (4)	-1 (18)	8 (6)	3 (10)
O(2B)	0.39457 (17)	0.64634 (27)	0.18757 (10)	73 (14)	191 (40)	34 (4)	3 (18)	9 (6)	-8 (10)
O(2C)	0.13835 (15)	0.90298 (30)	0.18719 (9)	57 (13)	273 (38)	39 (4)	0 (21)	3 (6)	-2 (11)
O(2D)	0.14838 (15)	0.40084 (29)	0.20243 (8)	55 (12)	166 (35)	25 (4)	1 (20)	1 (5)	3 (11)

Occupancy

M(1A)

0.080 (3) Fe<sup>3+</sup>

0.920 Al

M(1B)

0.865 Fe<sup>2+</sup>

0.135 Mg

Obtained from least-squares refinement

(Fe<sub>1.73</sub>Mg<sub>0.27</sub>)Al<sub>3.92</sub>Fe<sub>3.08</sub>Si<sub>2</sub>O<sub>10</sub>(OH).

difference synthesis near O(1A) and O(1B), so isotropic hydrogens ( $B=2.0$ ) were introduced in the refinement at this point. After several cycles, the hydroxyl O-H distances became impossibly small, and the hydrogen

temperature factors became quite large. The hydrogen atoms were removed, and after two more cycles of refinement, the final  $R$  was 0.041 ( $R_w=0.033$ ) for all structure factors and 0.034 ( $R_w=0.033$ ) for the un-

Table 3. Bond distances and angles

2 × : two identical, symmetry-related elements, only one given. Estimated standard deviations are in parentheses. The standard deviation of cation-oxygen distances is 1 to  $2 \times 10^{-3}$ , and of oxygen-oxygen distances 2 to  $3 \times 10^{-3}$ . The superscript gives the symmetry transformation below that was used to generate the coordinates of the given atom from the atomic coordinates in the asymmetric unit (Table 1).

	1.	$x, y, z$	6.	$\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$	
	2.	$x, y-1, z$	7.	$x+\frac{1}{2}-1, y-\frac{1}{2}, z$	
	3.	$\frac{1}{2}-x, 1+\frac{1}{2}-y, \bar{z}$	8.	$\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$	
	4.	$\frac{1}{2}-x, \frac{1}{2}-y, \bar{z}$	9.	$\bar{x}, 1-y, \bar{z}$	
	5.	$\frac{1}{2}+x-1, \frac{1}{2}+y, z$	10.	$x+\frac{1}{2}, y-\frac{1}{2}, z$	

  

				Distances (Å)			Angle (°)	
C	1	2	C-1	C-2	1-2	1-C-2		
M(1A)	O(1A <sup>1</sup> )	O(1B <sup>2</sup> )	1.916 2 ×	1.901 2 ×	2.837 2 ×	95.99 (7) 2 ×		
	O(1A <sup>1</sup> )	O(1B <sup>3</sup> )			2.555 2 × *	84.01 (7) 2 ×		
	O(1B <sup>2</sup> )	O(1C <sup>1</sup> )		1.987 2 ×	2.883 2 ×	95.70 (7) 2 ×		
	O(1B <sup>2</sup> )	O(1C <sup>4</sup> )			2.610 2 × *	84.30 (7) 2 ×		
	O(1A <sup>1</sup> )	O(1C <sup>1</sup> )			2.898 2 ×	95.84 (6) 2 ×		
	O(1A <sup>1</sup> )	O(1C <sup>4</sup> )			2.617 2 × *	84.16 (6) 2 ×		
	Mean M(1A)-O=1.935							
	M(2A)	O(2D <sup>1</sup> )	O(2A <sup>5</sup> )	1.795 2 ×	1.947 2 ×	2.763 2 ×	95.10 (8) 2 ×	
		O(2D <sup>1</sup> )	O(2B <sup>7</sup> )		1.945 2 ×	2.747 2 ×	94.45 (8) 2 ×	
		O(2D <sup>1</sup> )	O(2B <sup>8</sup> )			2.539 2 × *	85.40 (7) 2 ×	
O(2D <sup>1</sup> )		O(2A <sup>6</sup> )			2.532 2 × *	85.05 (7) 2 ×		
O(2A <sup>5</sup> )		O(2B <sup>7</sup> )			2.808 2 ×	92.33 (6) 2 ×		
O(2B <sup>7</sup> )		O(2B <sup>8</sup> )			2.703	88.02 (10)		
O(2A <sup>5</sup> )		O(2A <sup>6</sup> )			2.689	87.37 (10)		
Mean M(2A)-O=1.896								
M(1B)	O(1A <sup>1</sup> )	O(1B <sup>3</sup> )	2.165	2.141	2.556*	72.78 (6)		
	O(1A <sup>1</sup> )	O(1A <sup>9</sup> )		2.083	2.871*	84.97 (6)		
	O(1A <sup>1</sup> )	O(1C <sup>5</sup> )			3.334	98.75 (6)		
	O(1A <sup>1</sup> )	O(1B <sup>1</sup> )		2.077	3.356	104.60 (6)		
	O(1C <sup>3</sup> )	O(1B <sup>3</sup> )	2.285		3.355	98.55 (6)		
	O(1C <sup>3</sup> )	O(1A <sup>9</sup> )			3.293	97.70 (6)		
	O(1C <sup>5</sup> )	O(1C <sup>3</sup> )	2.228		3.189*	89.92 (6)		
	O(1C <sup>3</sup> )	O(1B <sup>1</sup> )			2.610*	73.34 (6)		
	O(1B <sup>3</sup> )	O(1A <sup>9</sup> )			3.324	103.71 (7)		
	O(1A <sup>9</sup> )	O(1C <sup>5</sup> )			2.617*	74.63 (6)		
	O(1C <sup>5</sup> )	O(1B <sup>1</sup> )			3.300	100.08 (6)		
	O(1B <sup>3</sup> )	O(1B <sup>1</sup> )			2.789*	82.78 (7)		
	Mean M(1B)-O=2.163							
	M(2B)	O(2A <sup>6</sup> )	O(2C <sup>8</sup> )	1.947		2.793	91.23 (7)	
O(2A <sup>6</sup> )		O(2D <sup>6</sup> )		1.795	2.736	93.90 (8)		
O(2A <sup>6</sup> )		O(2C <sup>1</sup> )			2.699	87.88 (7)		
O(2A <sup>6</sup> )		O(2D <sup>1</sup> )		1.792	2.532*	85.14 (7)		
O(2B <sup>1</sup> )		O(2C <sup>8</sup> )	1.935		2.712	88.18 (7)		
O(2B <sup>1</sup> )		O(2D <sup>6</sup> )			2.539*	85.69 (7)		
O(2B <sup>1</sup> )		O(2C <sup>1</sup> )			2.806	92.71 (7)		
O(2B <sup>1</sup> )		O(2D <sup>1</sup> )			2.755	95.25 (8)		
O(2C <sup>8</sup> )		O(2D <sup>6</sup> )	1.962		2.744	93.72 (8)		
O(2D <sup>6</sup> )		O(2C <sup>1</sup> )			2.543*	85.62 (7)		
O(2C <sup>1</sup> )		O(2D <sup>1</sup> )	1.943		2.767	95.52 (8)		
O(2D <sup>1</sup> )		O(2C <sup>8</sup> )			2.543*	85.13 (7)		
Mean M(2B)-O=1.896								
T	O(1C <sup>1</sup> )	O(2B <sup>1</sup> )	1.640	1.643	2.695	110.36 (9)		
	O(1C <sup>1</sup> )	O(2A <sup>1</sup> )		1.647	2.675	108.89 (9)		
	O(1C <sup>1</sup> )	O(2C <sup>10</sup> )		1.641	2.697	110.54 (8)		
	O(2C <sup>10</sup> )	O(2A <sup>1</sup> )			2.683	109.36 (8)		
	O(2C <sup>10</sup> )	O(2B <sup>1</sup> )			2.670	108.78 (8)		
	O(2A <sup>1</sup> )	O(2B <sup>1</sup> )			2.677	108.86 (8)		
Mean T-O=1.643								

\* shared edges.

rejected structure factors. Final atomic coordinates and thermal parameters are given in Table 1, and observed and calculated structure factors in Table 2.\*

Large correlations (greater than 0.7) were observed during refinement only when the occupancy of the Fe–Mg site [M(1B)] and the scale factor were allowed to vary independently. By forcing total iron in the structure to agree with the microprobe analysis, the problem of large correlations with the scale factor was avoided. The most significant correlations in the refinement occurred between the occupancy and thermal parameters of M(1A), and were only 0.37 to 0.34 in magnitude.

Bond distances and angles, and thermal ellipsoid data (Tables 3 and 4\*) were computed with *BADTEA* (written by L. W. Finger of the Carnegie Institute of Washington). There is no specific preferred orientation of the thermal ellipsoids with respect to bonds. The thermal motion is not markedly anisotropic, and there are no obvious thermal effects related to cation substitution. The axis of maximum r.m.s. displacement (*Z*) is generally oriented nearly parallel to *c*. Only in certain cases involving bonding normal to the octahedral layers [Si, O(1C), O(1A) and O(1B)] is this approximate orientation not observed.

### Discussion

The chloritoid crystal structure consists of two types of octahedral sheets that parallel (001), the predominant cleavage. Layer 1 is a trioctahedral sheet that contains two sites of substitution in the structure, M(1A) and M(1B). Layer 2 is an aluminum octahedral sheet in which each octahedron shares four edges with adjacent octahedra, and three out of every four octahedral sites are occupied. These sheets are connected by isolated tetrahedra that are attached to both surfaces of the aluminum sheets over the vacant octahedral positions. The apices of the tetrahedra are oxygens in the adjacent trioctahedral sheets. The remainder of the anions in the trioctahedral sheets are hydroxyl groups, and interlayer hydrogen bonding takes place between these hydroxyls and some of the oxygens in layer 2.

Both cation sites in the aluminum octahedral sheet are believed to be fully occupied by aluminum. The thermal parameters and average cation–oxygen bond distances for these sites [M(2A) and M(2B)] support this conclusion.

The occupancies of the two octahedral sites in layer 1, the trioctahedral layer, are somewhat more problematic however. Changes in the thermal parameters during the initial stages of refinement using the ferrous

iron end-member composition clearly show that more scattering power is necessary in M(1A) and less in M(1B). For this reason it was assumed that Fe<sup>3+</sup> substitutes for Al in M(1A), and Mg substitutes for Fe<sup>2+</sup> in M(1B). Subsequent refinement based on these assumptions yields reasonable average cation–oxygen bond distances and thermal parameters. Calculated bond distances, derived from the ionic radii of Shannon & Prewitt (1969, 1970) and the occupancies given in Table 1, are 1.93 [M(1A)–O] and 2.17 Å [M(1B)–O], in good agreement with the observed bond distances.

Chemical analyses of chloritoid frequently do not conform to the idealized formula  $R^{2+}R_2^{3+}SiO_5(OH)_2$ , but often show either an excess or deficiency of cations in the R<sup>2+</sup> and/or R<sup>3+</sup> sites. The recalculated microprobe analysis of this chloritoid has a deficiency of R<sup>3+</sup> species. However, in order to simplify the occupancy refinement, fully occupied cation sites were assumed. Some of the discrepancies between the microprobe analysis and the occupancy refinement are the result of this assumption.

Other substitution schemes are possible; however they are not supported by both the observed bond distances and the changes in thermal parameters that took place during refinement of the structure. Additional data for compositions nearer the Mn and Mg chloritoid end-members ought to answer some of the questions that remain about the occupancies of these sites.

The tetrahedral site has an average T–O distance of 1.643 Å. This is larger than average tetrahedral Si–O distances in comparable orthosilicate structures (Novak & Gibbs, 1971; Birle, Gibbs, Moore & Smith, 1968). The long average T–O bond distance and small thermal parameter (0.21 Å<sup>2</sup>) suggest that small amounts of a larger cation substitute here for Si, perhaps Al. However, a substitution of this sort conflicts with the microprobe analysis that shows a deficiency of R<sup>3+</sup> cations and an excess of Si.

### Hydrogen bonding

Hydrogen atoms are considered to be closely associated with the oxygens in the trioctahedral sheet that are not bonded to silicon (Harrison & Brindley, 1957). The interlayer distance in monoclinic chloritoid is conducive to the formation of hydrogen bonds between these hydroxyl groups and oxygens in adjacent layers.

Estimated bond valences (Donnay & Allmann, 1970) for monoclinic chloritoid were calculated, and the valence sum of bonds to each anion shows that O(1A) and O(1B) are the most likely sites for hydroxyl groups. Maxima of about 0.6 e Å<sup>-3</sup> in magnitude near these sites in a difference synthesis were believed to result from hydrogen atoms. Since it was not possible to refine the hydrogen positional parameters, they were determined from the difference synthesis that was computed during the final stage of least-squares refinement

\* Tables 2 and 4 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30743 (20 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

and are given in Table 5 along with some of the interlayer bond distances and angles.

Table 5. *Hydrogen coordinates and bond distances and angles*

	x	y	z
H(1A)	0.145	0.390	0.105
H(1B)	0.285	0.950	0.090

  

i	j	k	Distances (Å)			Angle
			i-j	j-k	i-k	(°)
O(1A)-H(1A)···O(2D)	0.925	1.766	2.666 (2)	163.51		
O(1B)-H(1B)···O(2A)	0.707	2.196	2.814 (2)	146.77		
···O(2C)		2.474	2.983 (2)	130.55		
···O(2B)		2.500	3.026 (2)	132.92		

Only one oxygen [O(2D)] is close enough to H(1A) to permit interlayer hydrogen bonding. The O(1A)-O(2D) distance (2.666 Å) is within the range of observed hydrogen-bonded O-O separations, and it appears that a hydrogen bond occurs here. The hydrogen bond distance [H(1A)···O(2D)] of 1.766 Å is further evidence of a hydrogen bond. In projection on (001), the other hydrogen, H(1B), falls near the center of a triangle of oxygens [O(2A), O(2B) and O(2C)] in the adjacent octahedral layer. All three of these O-O distances are near the upper limit of commonly accepted hydrogen-bonded O-O separation. If hydrogen bonding occurs here at all, it is probably weak. In this case the hydrogen-bond distances themselves are inconclusive because the hydroxyl O-H distance (0.707 Å) is extremely short. Although average X-ray determined O-H distances are commonly shorter than those determined by means of neutron diffraction (0.8 vs. 1.0 Å, Hamilton & Ibers, 1968), a hydroxyl O-H distance of 0.7 Å is probably too short to be used to compute definitive hydrogen-bond distances.

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## References

- BIRLE, J. D., GIBBS, G. V., MOORE, P. B. & SMITH, J. V. (1968). *Amer. Min.* **53**, 807-824.
- BRINDLEY, G. W. & HARRISON, F. W. (1952). *Acta Cryst.* **5**, 698-699.
- BURNHAM, C. W. (1962). *Carnegie Inst. Wash. Yb.* **61**, 132-135.
- BURNHAM, C. W. (1966). *Amer. Min.* **51**, 159-167.
- BURNHAM, C. W., OHASHI, Y., HAFNER, S. S. & VIRGO, D. (1971). *Amer. Min.* **56**, 850-876.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst. A* **24**, 321-324.
- DONNAY, G. & ALLMANN, R. (1970). *Amer. Min.* **55**, 1003-1015.
- FINGER, L. W. (1969). *Carnegie Inst. Wash. Yb.* **67**, 216-217.
- FINGER, L. W. (1972). Private communication.
- HALFERDAHL, L. B. (1961). *J. Petrol.* **2**, 49-135.
- HAMILTON, W. C. (1955). *Acta Cryst.* **8**, 185-186.
- HAMILTON, W. C. & IBERS, J. A. (1968). *Hydrogen Bonding in Solids*. New York: Benjamin.
- HANSCOM, R. H. (1973). *The Crystal Chemistry and Polymorphism of Chloritoid*. Ph.D. Thesis, Harvard Univ.
- HARRISON, F. W. & BRINDLEY, G. W. (1957). *Acta Cryst.* **10**, 77-82.
- HOWELLS, E. R., PHILLIPS, D. C. & ROGERS, D. (1950). *Acta Cryst.* **3**, 210-214.
- International Tables for X-ray Crystallography* (1968). Vol. III, 2nd ed., p. 215. Birmingham: Kynoch Press.
- NOVAK, G. A. & GIBBS, G. V. (1971). *Amer. Min.* **56**, 791-825.
- SHANNON, R. D. & PREWITT, C. T. (1969). *Acta Cryst.* **B25**, 925-946.
- SHANNON, R. D. & PREWITT, C. T. (1970). *Acta Cryst.* **B26**, 1046-1048.