The structure of triclinic chloritoid and chloritoid polymorphism

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Abstract

The crystal structure of triclinic chloritoid from Chibougamau, Quebec, [$a = 9.46(1)$, $b = 5.50(1)$, $c = 9.15(1)$Å, $\alpha = 97.05(2)$, $\beta = 101.56(2)$, and $\gamma = 90.10(2)°$; $Z = 4$] was solved using symbolic addition methods, and refined in space group $C\bar{1}$ to $R = 0.080$ ($R_w = 0.060$). The triclinic structure is topologically very similar to that of its monoclinic polymorph. Substitution of Fe^{3+} for Al and Mg for Fe^{2+} occurs in the same two sites in the trioctahedral layer, M(1A) and M(1B) respectively, as in the monoclinic polymorph, and the observed average M–O bond distances for these sites (1.948 and 2.155Å) are in good agreement with those calculated using the refined occupancies of these sites. Other average bond distances in the structure are: M(2A)–O = 1.907, M(2B1)–O = 1.906, M(2B2)–O = 1.906 (octahedral sites occupied by aluminum), and T–O = 1.638Å (tetrahedral site occupied by silicon). Because the structures are so similar, interlayer hydrogen bonding is assumed to occur in the same way as it does in the monoclinic structure, although no hydrogen positions were determined for triclinic chloritoid. The monoclinic and triclinic structures cannot be strictly considered polytypes because there are significant differences between the observed monoclinic atomic coordinates and those calculated from the triclinic atomic coordinates.

Introduction

Two polymorphs of chloritoid, ideally $FeAl_2SiO_5(OH)_2$, are known to occur, one triclinic and the other monoclinic. The monoclinic chloritoid crystal structure has been solved (Harrison and Brindley, 1957) and refined (Hanscom, 1975).

Halferdahl (1961) published an X-ray powder pattern for triclinic chloritoid, and showed that the unit cells of the two chloritoid polymorphs appear to be related so that twinning on a unit-cell scale of the triclinic chloritoid structure can result in a monoclinic structure. Thus, the polymorphism of chloritoid gives all appearances of polytypism with the contents of two unit cells of triclinic chloritoid stacking in the direction of the c axis to give the monoclinic structure.

Close association of monoclinic and triclinic chloritoid is frequently described in the literature, and specimens of chloritoid giving X-ray powder patterns characteristic of both structure types have been reported (Halferdahl, 1961).

This paper describes the triclinic chloritoid crystal structure, and the relationship between the two chloritoid structure types.

Occurrence

Several specimens of chloritoid from the Siderite Hill showing, Chibougamau, Quebec, were provided by Dr. L. B. Halferdahl. This locality is a shear zone in a meta-anorthosite near Towle Lake, and about two miles east-southeast of the Chibougamau townsite. The chloritoid occurs as 1 to 2 mm grains in an extremely fine-grained groundmass of sericite and chlorite with minor quartz and carbonate. The geology of the Chibougamau Lake area and the Siderite Hill showing is described in detail by Allard (1960).

Chloritoid from this locality has been analyzed (Halferdahl, 1961, p. 61, #101), and the optical properties have been determined (Halferdahl, 1961, p. 88, Table 20, #12). The observed density is 3.58(2) g cm^{-3}. The crystal used for data collection is a triangular basal cleavage fragment with a computed crystal volume of 1.59×10^{-3} mm^3.

Unit cell and space group

Like monoclinic chloritoid, the triclinic structure possesses strong pseudo-hexagonal symmetry. For

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this reason, there are three similar, C-centered, triclinic unit cells. The cell parameters of these three cells are given by Halferdahl (1961, p. 68, Table 10). A C-centered cell was chosen, rather than the reduced cell, for ease of comparison with the monoclinic structure. The cell parameters of the data crystal—$a = 9.46(1)$, $b = 5.50(1)$, $c = 9.15(1)$Å, $\alpha = 97.05(2)$, $\beta = 101.56(2)$, and $\gamma = 90.10(2)°$—were obtained during crystal alignment on the diffractometer, and standard deviations were estimated from the variance of repeated determinations.

The intensity data were subjected to the zero-moment test (Howells et al., 1950), and show a centric distribution. The centrosymmetric space group $C\bar{1}$ was chosen for refinement. The calculated density is 3.56 ($Z = 4$), in good agreement with the observed density.

Experimental procedure

Intensities were determined with a Picker FACS-1 diffractometer, niobium-filtered MoKα radiation, and $\theta/2\theta$ scans with fixed background counts at the extremes of the scan. The data collection was carried out over a hemisphere of reciprocal space (l positive), but was limited to reflections in the range 8 to 47° 2θ because the data crystal has a large mosaic spread that affects intensity determination at high 2θ. Reflections with $h + k$ odd were excluded from the data collection, and a total of 780 intensities were determined.

Lorentz and polarization corrections were applied during data reduction. The standard deviation of the integrated intensity was calculated using counting statistics (see Burnham et al., 1971, for details of the procedure). 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 with numerical integration techniques (Burnham, 1966). The transmission factors ranged between 0.74 and 0.65. Equivalent F's were averaged, and 690 unique structure factors resulted.

Structure solution and refinement

Because the unit cell parameters of triclinic chloritoid are very similar to those of monoclinic chloritoid with $c_T \cong c_M/2$, Halferdahl (1961) theorized that the monoclinic structure resulted from twinning of the triclinic structure on a unit cell scale. Using the atomic coordinates for monoclinic chloritoid determined by Harrison and Brindley (1957), and assuming this sort of relationship between the two struc-

tures, he calculated positional parameters for the triclinic structure. Least-squares refinement was initiated with these positional parameters; however, convergence was reached with a rather large R, and further attempts at refinement were not fruitful.

Symbolic addition was used to solve the structure [FAME and MAGIC (Dewar, 1970)]. The statistical distribution of E's verifies the choice of the centrosymmetric space group:

$\langle E^2 \rangle = 1.0$	$\|E\| > 1.0$ 28.1%
$\langle E \rangle = 0.804$	$\|E\| > 2.0$ 4.9%
$\langle E^2 - 1 \rangle = 0.994$	$\|E\| > 3.0$ 0.3%

The application of symbolic addition was straightforward, and four sign combinations with reasonable figures of merit resulted. The third sign combination proved to be correct, and the structure determined in this way is very similar to that of monoclinic chloritoid.

Refinement of this structure was carried out with RFINE (written by L. W. Finger, Geophysical Laboratory), and scattering curves for Fe^{2+}, Fe^{3+}, Al^{3+}, Mg^{2+}, Si^{4+}, and O^- (Cromer and Mann, 1968) were used. 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 $R_w^2 = \sum w (|F_o| - |F_c|)^2/\sum w \ |F_o|^2$. Initial site occupancies were assumed to be those of the Fe^{2+} end-member [i.e. M(1A) = Al and M(1B) = Fe^{2+}]. Isotropic thermal parameters determined for the monoclinic structure (Hanscom, 1975) were used in the initial stage of refinement that had $R = 0.316$ ($R_w = 0.248$). After two additional cycles of refinement, the temperature factor of M(1A) was negative, and that of M(1B) was too large ($B = 1.22$). Since the major substituents in this chloritoid are Fe^{3+} and Mg with minor Mn, Fe^{3+} is assumed to substitute for Al in M(1A) and Mg for Fe^{2+} in M(1B). The small amount of Mn present was assumed to have scattering behavior similar to Fe^{2+}, and was treated as such. The occupancies of M(1A) and M(1B) were fixed so that the chemical composition of the refinement model was approximately the same as calculated from the chemical analysis, and refinement was resumed. After four more cycles of refinement, R was 0.095 ($R_w = 0.080$). The thermal parameters of M(1A) (0.26Å^2) and M(1B) (0.90Å^2) were more well-behaved. The iron occupancy of the M(1A) and M(1B) sites was then allowed to vary, but total iron in the structure was constrained to agree with the analysis (Finger, 1969). A difference syn-

thesis was computed that showed little else but evidence of anisotropic thermal motion for some atoms. Attempts at anisotropic refinement were futile, however, because of the small number of data.

The origin was translated to (1/4,1/4,0) to permit ease of comparison with the monoclinic structure, and the final cycle of refinement gave $R = 0.096$ ($R_w = 0.084$) for all reflections, and $R = 0.080$ ($R_w = 0.060$) for unrejected reflections. In addition to 68 'unobserved' structure factors, 36 F's were rejected when it appeared that they were adversely affected by the rather large mosaic spread of the data crystal.

Correlations were all less than 0.45 in magnitude except in one case. The occupancy of M(1A) was correlated with the isotropic temperature factor (0.72).

The final atomic coordinates are given in Table 1, and values of F_o and F_c in Table 2.[2] Bond distances and angles were computed using BADTEA (written by L. W. Finger, Geophysical Laboratory), and are given in Table 3.

Discussion

The structure of triclinic chloritoid is very similar to the monoclinic structure. The M(2B) site that occupies the general equipoint in monoclinic chloritoid is located on two special positions in the triclinic structure; however, the number of Layer 2 atoms is the same and their spatial distribution is very similar in both structures.

The M(2A) and M(2B) sites are believed to be fully occupied by Al, and the average M–O bond distances and thermal parameters support this conclusion.

The distribution of cations in Layer 1 sites is less straightforward. Changes that occurred in the early stages of refinement of the thermal parameters of M(1A) and M(1B) indicated that the occupancy of M(1B) (Fe^{2+}) represented excessive scattering power, and that of M(1A) (Al^{3+}) not enough. Since the predominant substituents are Fe^{3+} and Mg^{2+} and minor Mn^{2+}, it was assumed that Fe^{3+} substitutes for Al in M(1A) and Mg^{2+} substitutes for Fe^{2+} in M(1B). The iron (plus Mn) content of the least-squares model was constrained to agree with the chemical analysis, and the results are given in Table 1. The analysis shows a deficiency of R^{2+} species that can be partially accomodated by permitting excess Fe^{3+} to occupy the

Table 1. Positional parameters and site occupancies of triclinic chloritoid*

Atom	Occupancy	x	y	z	B (Å)
M(1A)	0.160(15) Fe^{3+} 0.840 Al^{3+}	1/4	1/4	0	1.08(14)
M(2A)	Al^{3+}	0	1/2	1/2	0.59(10)
M(1B)	0.885 Fe^{2+} 0.075 Mg^{2+}	0.0837(2)	0.7470(4)	0.0018(3)	0.74(5)
M(2B1)	Al^{3+}	1/4	1/4	1/2	0.67(10)
M(2B2)	Al^{3+}	1/4	3/4	1/2	0.72(7)
T	Si^{4+}	0.4620(4)	0.4643(7)	0.3135(5)	0.72(7)
O(1A)	O^-	0.1093(9)	0.4142(16)	0.1062(10)	1.17(18)
O(1B)	O^-	0.2655(10)	0.9615(15)	0.1027(10)	1.15(19)
O(1C)	O^-	0.4204(10)	0.4217(15)	0.1264(11)	1.19(19)
O(2A)	O^-	0.3942(9)	0.2316(14)	0.3759(10)	0.73(16)
O(2B)	O^-	0.3939(9)	0.7186(14)	0.3750(10)	0.76(17)
O(2C)	O^-	0.1351(9)	0.9753(14)	0.3737(10)	0.73(17)
O(2D)	O^-	0.1486(9)	0.4811(14)	0.4013(10)	0.84(17)

Least-Squares Refinement:
$(Fe^{2+}_{1.77} Mg^{2+}_{0.15}) Al_{3.84} Fe^{3+}_{0.16} Si_2 O_{10} (OH)_4$

Analysis:
$(Fe^{2+}_{1.79} Mg^{2+}_{0.10} Mn^{2+}_{0.03}) Al_{3.93} Fe^{3+}_{0.11} Si_{2.03} O_{10} (OH)_{3.82}$

*Estimated standard errors (in parentheses) refer to the last digit given.

M(1B) site. Even then the M(1B) site is not fully occupied, so the total occupancy of M(1B) in the refinement was fixed at 0.96. The least-squares model contains an excess of Mg^{2+} in M(1B), and this fact is reflected in the value of the thermal parameter of M(1B), which is smaller than expected. This problem arises from the way in which Fe^{2+} (plus Mn) and Fe^{3+} are constrained during refinement, and it is difficult to avoid if occupancies are to be varied.

Other arrangements of these cations are possible, but none explain both the bond distances and the behavior of the thermal parameters. The average bond distances [1.948 and 2.155Å respectively for M(1A) and M(1B)] for these sites are in good agreement with those calculated (1.95 and 2.18Å) from site occupancies and the ionic radii given by Shannon and Prewitt (1969) and Prewitt and Shannon (1970).

The average T–O bond distance for the structure agrees very well with what is expected for orthosilicates (Birle et al., 1968). This site is probably fully occupied by Si.

The monoclinic and triclinic chloritoid structures are topologically very similar. They both consist of alternating octahedral sheets joined by isolated SiO_4 tetrahedra. Interlayer hydrogen bonding occurs in the monoclinic structure (Hanscom, 1975), and al-

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[2] To obtain a copy of Table 2, order Document AM-80-134 from the Business Office, Mineralogical Society of America, 2000 Florida Avenue, NW, Washington, D.C. 20009. Please remit $1.00 in advance for the microfiche.

Table 3. Bond distances and angles for triclinic chloritoid†

C	1	2	Distances (Å)			Angle (°)
			C-1	C-2	1-2	1-C-2
M(1A)	O(1A)[1]	O(1C)[1]	1.959(9)§	1.951(8)§	2.911(13)§	96.2(4)§
	O(1A)[1]	O(1C)[4]			2.611(12)§*	83.8(4)§
	O(1A)[1]	O(1B)[2]		1.932(9)§	2.898(14)§	96.2(4)§
	O(1A)[1]	O(1B)[3]			2.598(13)§*	83.8(4)§
	O(1B)[2]	O(1C)[1]			2.885(13)§	96.0(4)§
	O(1B)[3]	O(1C)[1]			2.599(13)§*	84.0(4)§
			mean M(1A)-O = 1.948			
M(2A)	O(2A)[5]	O(2D)[1]	1.954(9)§	1.814(9)§	2.759(12)§	94.1(4)§
	O(2A)[5]	O(2D)[7]			2.570(13)§*	85.9(4)§
	O(2A)[5]	O(2B)[5]			2.821(13)§	92.5(4)§
	O(2A)[5]	O(2B)[6]			2.702(12)§	87.5(4)§
	O(2B)[5]	O(2D)[7]	1.952(8)§		2.565(12)§*	85.8(4)§
	O(2B)[5]	O(2D)[1]			2.760(12)§	94.2(4)§
			mean M(2A)-O = 1.907			
M(1B)	O(1A)[1]	O(1B)[3]	2.159(10)	2.132(10)	2.598(13)*	74.5(4)
	O(1A)[1]	O(1B)[1]		2.071(8)	3.357(13)	105.0(4)
	O(1A)[1]	O(1A)[8]		2.038(9)	2.792(18)*	83.3(4)
	O(1A)[1]	O(1C)[9]		2.248(10)	3.323(14)	97.9(4)
	O(1B)[1]	O(1B)[3]			2.781(17)*	82.8(4)
	O(1B)[1]	O(1C)[9]			3.324(14)	100.5(3)
	O(1A)[8]	O(1C)[9]			2.611(12)*	74.9(4)
	O(1A)[8]	O(1B)[3]			3.257(14)	102.7(4)
	O(1C)[3]	O(1C)[9]	2.281(10)		3.201(20)*	89.9(4)
	O(1C)[3]	O(1A)[8]			3.287(14)	99.0(4)
	O(1C)[3]	O(1B)[1]			2.599(13)*	73.2(3)
	O(1C)[3]	O(1B)[3]			3.325(14)	97.7(4)
			mean M(1B)-O = 2.155			

Table 3. (continued)

C	1	2	Distances (Å)			Angle (°)
			C-1	C-2	1-2	1-C-2
M(2B1)	O(2A)[10]	O(2D)[1]	1.938(9)§	1.814(9)§	2.570(13)§*	86.4(4)§
	O(2A)[10]	O(2C)[6]		1.965(8)§	2.821(12)§	92.6(4)§
	O(2A)[10]	O(2C)[2]			2.697(12)§	87.4(4)§
	O(2A)[10]	O(2D)[10]			2.736(12)§	93.6(4)§
	O(2C)[2]	O(2D)[1]			2.763(13)§	93.9(4)§
	O(2C)[2]	O(2D)[10]			2.582(12)§*	86.1(4)§
			mean M(2B1)-O = 1.906			
M(2B2)	O(2B)[1]	O(2D)[1]	1.941(9)§	1.801(8)§	2.728(13)§	93.5(4)§
	O(2B)[1]	O(2C)[6]		1.976(9)§	2.711(13)§	87.6(4)§
	O(2B)[1]	O(2D)[6]			2.565(12)§*	86.5(4)§
	O(2B)[1]	O(2C)[1]			2.827(12)§	92.4(4)§
	O(2D)[1]	O(2C)[1]			2.761(13)§	93.9(4)§
	O(2D)[1]	O(2C)[6]			2.582(12)§*	86.2(4)§
			mean M(2B2)-O = 1.906			
T	O(2A)[1]	O(1C)[1]	1.643(9)	1.664(10)	2.678(14)	108.2(4)
	O(2A)[1]	O(2B)[1]		1.626(9)	2.679(13)	110.1(5)
	O(2A)[1]	O(2C)[11]		1.619(9)	2.646(12)	108.5(5)
	O(1C)[1]	O(2C)[11]			2.707(12)	111.1(5)
	O(1C)[1]	O(2B)[1]			2.687(12)	109.5(5)
	O(2C)[11]	O(2B)[1]			2.649(12)	109.4(4)
			mean T-O = 1.638			

†Estimated standard errors (in parentheses) refer to the last digit given.

* Shared edges.

§ Two identical, symmetry-related elements, only one given.

Superscripts give the symmetry transformation below that was used to obtain the coordinates of the given atom from the atomic coordinates in the asymmetric unit (Table 1).

1.	x,	y,	z	7.	$\bar{x}$,	$1-y$, $1-z$
2.	x,	$y-1$,	z	8.	$\bar{x}$,	$1-y$, $\bar{z}$
3.	$1/2-x$,	$3/2-y$,	$\bar{z}$	9.	$x-1/2$,	$y+1/2$, z
4.	$1/2-x$,	$1/2-y$,	$\bar{z}$	10.	$1/2-x$,	$1/2-y$, $1-z$
5.	$x-1/2$,	$1-y$,	z	11.	$1/2+x$,	$y-1/2$, z
6.	$1/2-x$,	$3/2-y$,	$1-z$			

though the data for the triclinic structure are not of sufficient quality to be used to locate hydrogen in a difference synthesis, their sites and bond geometries are probably very nearly the same because the structures are so similar.

Triclinic chloritoids are frequently disordered and poorly crystalline. Diffuse scattering parallel to c^* from triclinic chloritoid is generally more pronounced than from monoclinic chloritoid, indicating a greater degree of stacking disorder. Note that the thermal parameters for all Layer 1 sites [except M(1B)] are significantly larger than those in the remainder of the structure. Layer 1 is a trioctahedral layer that, if idealized, has rotational symmetry normal to the sheet. The larger thermal parameters for Layer 1 sites may reflect rotational disorder of this sheet in the structure.

Polymorphism

Halferdahl (1961) suggested that the monoclinic chloritoid structure resulted from twinning of the triclinic on a unit-cell scale. To test this hypothesis, the triclinic chloritoid atomic coordinates were transformed to the monoclinic cell using:

$$\begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & -0.195 \\ 0 & 0 & 1/2 \end{vmatrix}$$

This transformation was derived from the relation between the unit-cell parameters of the two polymorphs given by:

$$c_T + 0.195\, b_T \simeq 1/2\, c_M$$

The transformed triclinic atomic coordinates are compared to the monoclinic atomic coordinates in Table 4. Although the two sets of positional parameters are very similar, the differences appear to be real, and with that in mind the two structures cannot be considered polytypes. However, the data for the triclinic structure are not as well refined as those for the monoclinic structure.

One possible mechanism for twinning of the tri-

Table 4. Comparison of transformed triclinic atomic coordinates and monoclinic atomic coordinates*

Atom	x	y	z
M(1A)	1/4 (1/4)	1/4 (1/4)	0 (0)
M(2A)	0 (0)	0.4025 (0.4014)	1/4 (1/4)
M(1B)	0.0837 (0.0836)	0.7466 (0.7469)	0.0009 (0.0011)
M(2B1)-M(2B2) (M(2B))	1/4 (0.2499)	0.6525 (0.6526)	1/4 (0.2488)
T	0.4620 (0.4632)	0.4032 (0.4016)	0.1568 (0.1563)
O(1A)	0.1093 (0.1153)	0.3935 (0.3911)	0.0531 (0.0533)
O(1B)	0.2655 (0.2650)	0.9415 (0.9445)	0.0514 (0.0504)
O(1C)	0.4204 (0.4245)	0.3971 (0.3956)	0.0632 (0.0642)
O(2A)	0.3942 (0.3938)	0.1583 (0.1583)	0.1880 (0.1885)
O(2B)	0.3939 (0.3946)	0.6455 (0.6463)	0.1875 (0.1876)
O(2C)	0.1351 (0.1384)	0.9024 (0.9030)	0.1869 (0.1872)
O(2D)	0.1486 (0.1484)	0.4028 (0.4008)	0.2007 (0.2024)

Average difference = 0.0008
Maximum difference = 0.0060

*Monoclinic atomic coordinates (Hanscom, 1975) in parentheses.

clinic structure on a unit-cell scale is rotation of one unit cell relative to another. If two triclinic chloritoid unit cells are stacked on top of one another so that their a and b axes are parallel and their c axes are collinear, and then the upper unit cell is rotated clockwise 60°, the resulting unit cell is very similar to dimensions to that of monoclinic chloritoid. The degree to which this can take place in the chloritoid structure depends on the pseudosymmetry present and the invariance of the structure to 60° rotation about the normal to (001).

Identification

X-ray powder patterns for a triclinic and monoclinic chloritoid were calculated using POWDER (Smith, 1963). The results are in excellent agreement with the powder patterns reported by Halferdahl, and the distinguishing lines given by him (Halferdahl, 1961, p. 82, Table 17) are useful in identifying the structure type.

Stability

The range of stability of the two chloritoid structures is not known. The results of several studies of

the distribution of chloritoid structure types in metamorphic terranes are not entirely conclusive (Plas et al., 1958; Capdevila, 1968; Chen, 1963). It is generally accepted that the triclinic polymorph is more stable in lower-grade metamorphic rocks, and disappears with increasing grade. Capdevila (1968) has shown that pressure may delay the disappearance of the triclinic polymorph at higher grades. My determination of the triclinic unit cell is not of sufficient quality to be of use in determining if a ΔV term favors one form over the other.

These polymorphs may be anomalous in terms of volume and entropy changes, and symmetry (or pseudosymmetry) elements normal to the twin plane may favor small or negative values of free energy change for the twin boundary (Strens, 1967). In this case, Strens postulates that gradations may occur in a mineral from multi-layer structures, to multi-layer structures containing stacking faults, to single-layer structures with frequent twin planes, to single-layer structures. This may explain the number of 'mixed' chloritoids that have been reported by Halferdahl (1961) and others.

References

Allard, G. (1960) South half of McKenzie Township: Part II. South half of the southeast quarter. Quebec Department of Mines Geological Report 95.

Birle, J. D., G. V. Gibbs, P. B. Moore and J. V. Smith (1968) Crystal structures of natural olivines. Am. Mineral, 53, 807–824.

Burnham, C. W. (1966) Computation of absorption corrections and the significance of end effect. Am. Mineral, 51, 159–167.

———, Y. Ohashi, S. S. Hafner and D. Virgo (1971) Cation distribution and atomic thermal vibrations in an iron-rich orthopyroxene. Am. Mineral., 56, 850–876.

Capdevila, R. (1968) La symétrie du chloritoïde dans les micaschistes de Galice Nord-orientale (Nordouest de l'Espagne). Bull. Soc. fr. Minéral. Cristallogr., 91, 508–510.

Chen, Pei-yuan (1963) Mineralogy and petrology of the chloritoid rock from Shakatangchi and Laohsichi area, Hualien, Taiwan. Acta Geol. Taiwanica, 10, 11–27.

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

Dewar, R. B. K. (1970) A system of direct methods programs. In F. R. Ahmed, Ed., Crystallographic Computing, p. 63–65. Munksgaard, Copenhagen.

Finger, L. W. (1969) Determination of cation distributions by least-squares refinement of single crystal data. Carnegie Inst. Washington Year Book, 67, 216–217.

Halferdahl, L. B. (1961) Chloritoid: its composition, X-ray and optical properties, stability and occurrence. *J. Petrol., 2,* 49–135.

Hamilton, W. C. (1955) On the treatment of unobserved reflexions in the least-squares adjustment of crystal structures. *Acta Crystallogr., 8,* 185–186.

Hanscom, R. H. (1975) Refinement of the crystal structure of monoclinic chloritoid. *Acta Crystallogr., B31,* 780–784.

Harrison, F. W. and G. W. Brindley (1957) The crystal structure of chloritoid. *Acta Crystallogr., 10,* 77–82.

Howells, E. R., D. C. Phillips and D. Rogers (1950) The probability distribution of X-ray intensities. II. Experimental investigation and the X-ray detection of centres of symmetry. *Acta Crystallogr., 3,* 210–214.

Plas, L. van der, T. Hugi, M. H. Mladeck and E. Niggli (1958)

Chloritoid vom Hennensädel Südlich Vals (Nördliche Adula-decke). *Schweiz. Mineral. Petrogr. Mitt., 38,* 237–46.

Prewitt, C. T. and R. D. Shannon (1970) Revised values of effective ionic radii. *Acta Crystallogr., B26,* 1046–1048.

Shannon, R. D. and C. T. Prewitt (1969) Effective ionic radii in oxides and fluorides. *Acta Crystallogr., B25,* 925–946.

Smith, D. K. (1963) *A FORTRAN program for calculating X-ray powder diffraction patterns.* Lawrence Radiation Laboratory, University of California, Livermore, California, UCRL 7196.

Strens, R. G. J. (1967) Symmetry–entropy–volume relationships in polymorphism. *Mineral. Mag., 36,* 565–577.