

THE CRYSTAL STRUCTURE AND CATION DISTRIBUTION OF A GRUNERITE

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ABSTRACT

Three-dimensional, counter-measured, X-ray diffraction data have been used in the refinement of the anisotropic atomic parameters and cation distribution of a grunerite from the Wabush iron formation, Labrador, Canada. The occupancies of the cation sites were determined by assuming the chemical composition of $(\text{Fe}_{6.2}\text{Mg}_{0.8})\text{Si}_8\text{O}_{22}(\text{OH})_{1.5}\text{F}_{0.5}$ and constraining the occupancies so that each of the four independent sites was full of Fe + Mg and the overall chemistry matched the formula. The resulting occupancies for Mg are as follows: $M(1)$, 0.152 ± 0.008 ; $M(2)$, 0.227 ± 0.007 ; $M(3)$, 0.112 ± 0.012 ; and $M(4)$, 0.015 ± 0.008 . These occupancies are in agreement with the previous determinations for this mineral.

The refinement of the crystal structure of a grunerite was undertaken to investigate the ordering of Fe and Mg in an amphibole containing very little Mg. The technique of least-squares was used to assign the average chemical composition of each site. This mineral series has been studied by Ghose and Hellner (1959) and Ghose (1961), who determined the ordering by adjusting the site composition and the resulting scattering factor in order to make the isotropic temperature factors the same for each of the four sites occupied by Fe and Mg. This procedure is unsatisfactory because the temperature factor for one of the octahedral sites, $M(4)$, is found to be larger than the others, as shown by Papike and Clark (1968) and Fischer (1966). In an attempt to overcome this difficulty, Fischer (1966) used the structure factors of Ghose (1961) and refined that structure using a least-squares method. The Fe and Mg contents of a site were determined independently, however, a procedure that caused a strong coupling between the occupancies and the temperature factors. Initially in this study the occupancies were varied, with the use of least-squares techniques which required each site to be fully occupied but placed no restrictions on the bulk chemistry. Better results were obtained by constraining the site chemistry to agree with the chemical analysis.

UNIT CELL AND SPACE GROUP

The grunerite used in the present investigation is sample No. 1 of Klein (1964) from the Wabush iron formation, Labrador, Canada. The analysis showed this sample to be very close to the ideal cummingtonite-grunerite composition. For this refinement the chemical formula was simplified from $\text{Fe}_{6.14}\text{Mn}_{0.05}\text{Mg}_{0.77}\text{Ca}_{0.06}\text{Si}_8\text{O}_{22.1}(\text{OH})_{1.39}\text{F}_{0.51}$ to $\text{Fe}_{6.2}\text{Mg}_{0.8}\text{Si}_8\text{O}_{22}(\text{OH})_{1.5}\text{F}_{0.5}$.

Single crystals of this material display diffraction symmetry $2/mC-/-$, which is consistent with the space groups $C2$, Cm , and $C2/m$. There is no evidence for the absence of a center of symmetry, and in conjunction with all previous work, space group $C2/m$ was used throughout this refinement.

The unit-cell parameters for the crystal used in the intensity collection were determined at 23°C with a back-reflection Weissenberg camera with zero-level photographs about the b and c axes ($\text{FeK}\alpha_1$, $\lambda = 1.93597 \text{ \AA}$; $\text{FeK}\alpha_2$,

$\lambda = 1.93991 \text{ \AA}$). The unit-cell constants were refined with the lattice-constant refinement program of Burnham (1962). The observed data, corrected for absorption, film shrinkage, camera radius, and eccentricity errors, are $a = 9.5642 \pm 0.0007 \text{ \AA}$, $b = 18.393 \pm 0.002 \text{ \AA}$, $c = 5.3388 \pm 0.0003 \text{ \AA}$, $\beta = 101.892^\circ \pm 0.003^\circ$, $V = 919.0 \pm 0.2 \text{ \AA}^3$. One cell contains two formula units and has a calculated or X-ray density of 3.535 g/cm^3 . The unit-cell constants are in agreement with those of Klein (1964), which were determined on a powder sample from the same material.

INTENSITY DATA

The intensity data were collected on a crystal about $0.11 \times 0.17 \times 0.34 \text{ mm}$ in size, using a Supper-Pace equi-inclination diffractometer. The diffractometer was operated in the step-scan mode with $\text{MoK}\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$) and an Nb filter. The diffracted radiation was collected with a scintillation counter with the pulse-height analyzer set to pass the central 90 percent of the energy distribution. The data were recorded with a step increment of $0.04^\circ \phi$ and with a step counting time of 3 seconds. The scan ranges were determined with the formula of Finger and Burnham (1968). The step data were converted to intensities with an unpublished computer program by Burnham, which uses formulae modified from Cetlin and Abrahams (1963). These integrated intensities were converted to structure factors by correcting for the Lorentz, polarization, and absorption effects ($\mu_l = 55.5 \text{ cm}^{-1}$) with the general absorption correction program of Burnham (1966), using an eight-point Gaussian quadrature integration. In the data reduction process, the standard deviation of the integrated intensity was computed from counting statistics. Those reflections that had an integrated intensity less than twice this value were regarded as being less than the minimum observable, and the structure factors for such reflections were computed using the most probable intensity in the manner of Hamilton (1955).

REFINEMENT OF THE CRYSTAL STRUCTURE

The final atomic coordinates and temperature factors of Fischer (1966) were used as the starting values in this study. The scattering curves of Doyle and Turner (1968) and the anomalous scattering coefficients of Cromer (1965) were used, with all atoms assumed to be in the neutral state. In the first stage of refinement the scale factor and atomic coordinates were converged, but the temperature factors were fixed and the octahedral sites were assumed to be all Fe. Next, the octahedral occupancies were varied, again with the temperature factors fixed. The occupancy parameters were constrained so that each site was fully occupied, but the total chemistry was variable. In this case, the shifts in the occupancy parameters caused the composition to shift towards a higher magnesium value than

TABLE 2. FINAL ATOMIC POSITIONAL PARAMETERS, EQUIVALENT ISOTROPIC TEMPERATURE FACTORS AND SITE OCCUPANCIES FOR GRUNERITE

Atom	$x(\sigma)$	$y(\sigma)$	$z(\sigma)$	$B \text{ \AA}^2(\sigma)$	Occupancy, atoms per site
$M(1)$	0	0.08781(8)	0.5	0.51(3)	0.152 ± 0.008 Mg 0.848 ± 0.008 Fe
$M(2)$	0	0.17936(9)	0	0.51(4)	0.227 ± 0.007 Mg 0.773 ± 0.007 Fe
$M(3)$	0	0	0	0.56(5)	0.112 ± 0.012 Mg 0.888 ± 0.012 Fe
$M(4)$	0	0.25741(8)	0.5	0.92(4)	0.015 ± 0.008 Mg 0.985 ± 0.008 Fe
Si(1)	0.2867(2)	.0836(1)	.2707(3)	0.44(3)	1.0
Si(2)	.2993(2)	.1667(1)	.7780(4)	0.49(3)	1.0
O(1)	.1120(5)	.0882(2)	.2044(9)	0.67(8)	1.0
O(2)	.1253(4)	.1735(2)	.7142(8)	0.59(7)	1.0
O(3)-OH	.1147(7)	0	.7035(13)	1.09(12)	0.75 OH, 0.25 F
O(4)	.3839(5)	.2416(2)	.7689(8)	0.58(7)	1.0
O(5)	.3483(5)	.1275(2)	.0519(8)	0.77(7)	1.0
O(6)	.3478(4)	.1182(2)	.5530(8)	0.86(8)	1.0
O(7)	.3376(6)	0	.2700(13)	0.74(11)	1.0

indicated by the analysis. The curves of unit-cell volume *versus* composition found by Viswanathan and Ghose (1965) and Klein and Waldbaum (1967), however, show that the chemistry of the single crystal is very nearly the same as that of the powder studied by Klein (1964). Because the thermal model interacts with the occupancy parameters, the temperature factors and occupancies were refined in the next stage, but this refinement did not correct the difficulty.

A special sequence of refinement steps was designed to overcome the problems of this site refinement. They consisted of converging the model with fixed occupancies followed by a cycle of least-squares with variable occupancies and fixed temperature factors. Then the occupancies were normalized to the correct chemistry, and the process was repeated. After this operation was applied several times, the temperature factors were converted to be anisotropic and the process was continued. When the changes in the temperature factors were insignificant, the final occupancies were checked with a difference Fourier synthesis, which showed the residual electron density in the vicinity of the atomic locations to be on the order of $1/\text{\AA}^3$. The final occupancies are in good agreement with the values

obtained from infrared studies by Burns and Strens (1966), combined with the Mössbauer spectra of Bancroft, Burns, and Maddock (1967).

Dr. C. T. Prewitt, of E. I. du Pont de Nemours and Company (personal communication), suggested overcoming the difficulties in refinement by constraining the total chemistry to agree with the chemical analysis. Although this seems to be a logical requirement, it was not necessary in previous occupancy refinements, such as those of omphacite (Clark and Papike, 1968) and glaucophane (Papike and Clark, 1968), and was not expected to be required here. After the least-squares program RFINE was modified to constrain the site chemistry, the structure converged in two cycles to the values for the occupancies found by the procedure outlined above. However, the final estimated errors were smaller by about a factor of 3. The method used to constrain the chemistry is described by Finger (1969).

The final discrepancy factors for this crystal were 0.039 for the 1216 reflections used in the refinement and 0.058 for all 1505 data. The least-squares process minimized $[\sum \omega(|F_o| - |F_c|)^2 / \sum \omega |F_o|^2]^{1/2}$. This function was 0.034 for the reflections

TABLE 3. ANISOTROPIC TEMPERATURE FACTOR COEFFICIENTS FOR GRUNERITE^a

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
$M(1)$	0.0012(2)	0.00055(5)	0.0036(5)	0	0.0008(2)	0
$M(2)$.0012(2)	.00048(5)	.0045(5)	0	.0008(2)	0
$M(3)$.0014(2)	.00050(7)	.0045(8)	0	.0003(3)	0
$M(4)$.0019(2)	.00096(5)	.0080(5)	0	.0017(2)	0
Si(1)	.0009(2)	.00041(5)	.0040(6)	-0.00003(8)	.0002(3)	-0.0000(2)
Si(2)	.0010(2)	.00038(5)	.0054(6)	-0.00019(8)	.0003(3)	-.0000(1)
O(1)	.0013(5)	.0006(1)	.0065(18)	-0.0000(2)	.0007(8)	.0003(4)
O(2)	.0009(4)	.0006(1)	.0068(16)	-0.0001(2)	.0011(7)	-.0003(4)
O(3)	.0042(8)	.0007(2)	.0092(25)	0	.0023(12)	0
O(4)	.0020(5)	.0004(1)	.0041(15)	-0.0001(2)	-.0002(7)	.0002(4)
O(5)	.0008(4)	.0008(1)	.0090(16)	-0.0003(2)	.0009(7)	.0015(4)
O(6)	.0009(4)	.0012(2)	.0055(15)	0.0004(2)	-.0001(7)	-.0009(4)
O(7)	.0019(7)	.0000(2)	.0146(25)	0	.0021(11)	0

^a Standard deviations, σ , given in parentheses.

TABLE 4. SELECTED INTERATOMIC DISTANCES IN GRUNERITE

Atoms	Distance (Å)	Atoms	Distance (Å)
Si(1)-O(1)	1.637(4)	Si(1)-Si(2)	3.090(3)
Si(1)-O(5)	1.627(5)	Si(1)-Si(2')	3.066(3)
Si(1)-O(6)	1.630(4)	Si(1)-Si(1')	3.075(4)
Si(1)-O(7)	1.613(2)	<i>M</i> (1)-O(1) (2×)	2.082(5)
Average Si(1)-O	1.627	<i>M</i> (1)-O(2) (2×)	2.160(4)
Si(2)-O(2)	1.633(4)	<i>M</i> (1)-OH (2×)	2.122(4)
Si(2)-O(4)	1.604(4)	Average <i>M</i> (1)-O	2.121
Si(2)-O(5')	1.611(5)	<i>M</i> (2)-O(1) (2×)	2.161(5)
Si(2)-O(6)	1.638(5)	<i>M</i> (2)-O(2) (2×)	2.128(4)
Average Si(2)-O	1.622	<i>M</i> (2)-O(4) (2×)	2.075(4)
		Average <i>M</i> (2)-O	2.121
Si(1) tetrahedron		<i>M</i> (3)-O (1) (4×)	2.118(5)
O(1)-O(5)	2.656(6)	<i>M</i> (3)-OH (2×)	2.103(6)
O(1)-O(6)	2.669(6)	Average <i>M</i> (3)-O	2.113
O(1)-O(7)	2.664(6)	<i>M</i> (4)-O(2) (2×)	2.135(5)
O(5)-O(6)	2.682(6)	<i>M</i> (4)-O(4) (2×)	1.988(4)
O(5)-O(7)	2.629(5)	<i>M</i> (4)-O(6) (2×)	2.757(5)
O(6)-O(7)	2.638(6)	Average <i>M</i> (4)-O	2.293
Average O-O	2.656	<i>M</i> (4)-O(5) (2×)	3.298(5)
Si(2) tetrahedron			
O(2)-O(4)	2.733(6)		
O(2)-O(5')	2.633(6)		
O(2)-O(6)	2.657(6)		
O(4)-O(5')	2.649(6)		
O(4)-O(6)	2.536(6)		
O(5')-O(6)	2.668(6)		
Average O-O	2.646		

used in the refinement and 0.040 for all data. The final standard deviation of an observation of unit weight is 6.49. The final calculated and observed structure factors are presented in Table

TABLE 5. BOND ANGLES OF THE SILICA TETRAHEDRA IN GRUNERITE^a

Atoms	Angle	Atoms	Angle
O(1)-Si(1)-O(5)	108.9(2)°	O(2)-Si(2)-O(4)	115.2(2)°
O(1)-Si(1)-O(6)	109.6(2)°	O(2)-Si(2)-O(5')	108.5(2)°
O(1)-Si(1)-O(7)	110.1(3)°	O(2)-Si(2)-O(6)	108.7(2)°
O(5)-Si(1)-O(6)	110.9(2)°	O(4)-Si(2)-O(5')	110.9(2)°
O(5)-Si(1)-O(7)	108.5(3)°	O(4)-Si(2)-O(6)	103.0(2)°
O(6)-Si(1)-O(7)	108.9(3)°	O(5')-Si(2)-O(6)	110.4(2)°
Si(1)-O(5)-Si(2')	142.4(3)°	Si(1)-O(7)-Si(1')	144.8(4)°
Si(1)-O(6)-Si(2)	142.1(3)°	O(5)-O(6)-O(5')	172.7(3)°

^a Standard deviations, σ , given in parentheses.

¹,¹ in which the reflections that were below the minimum observable intensity are marked with an asterisk.

DISCUSSION OF THE STRUCTURE

The final atomic coordinates, equivalent isotropic temperature factors of Hamilton (1959), and site occupancies are presented in Table 2. The standard deviation of the occupancy of *M*(4), calculated by using the standard formula for propagation of errors and neglecting any error in the chemical analysis, is a measure of the internal error only. The final values of the anisotropic temperature factor

¹ Table 1 may be ordered as NAPS Document 00451 from ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 West 34th St., New York, N.Y. 10001; remitting in advance \$1.00 for microfiche or \$3.00 for photocopies, payable to ASIS-NAPS.

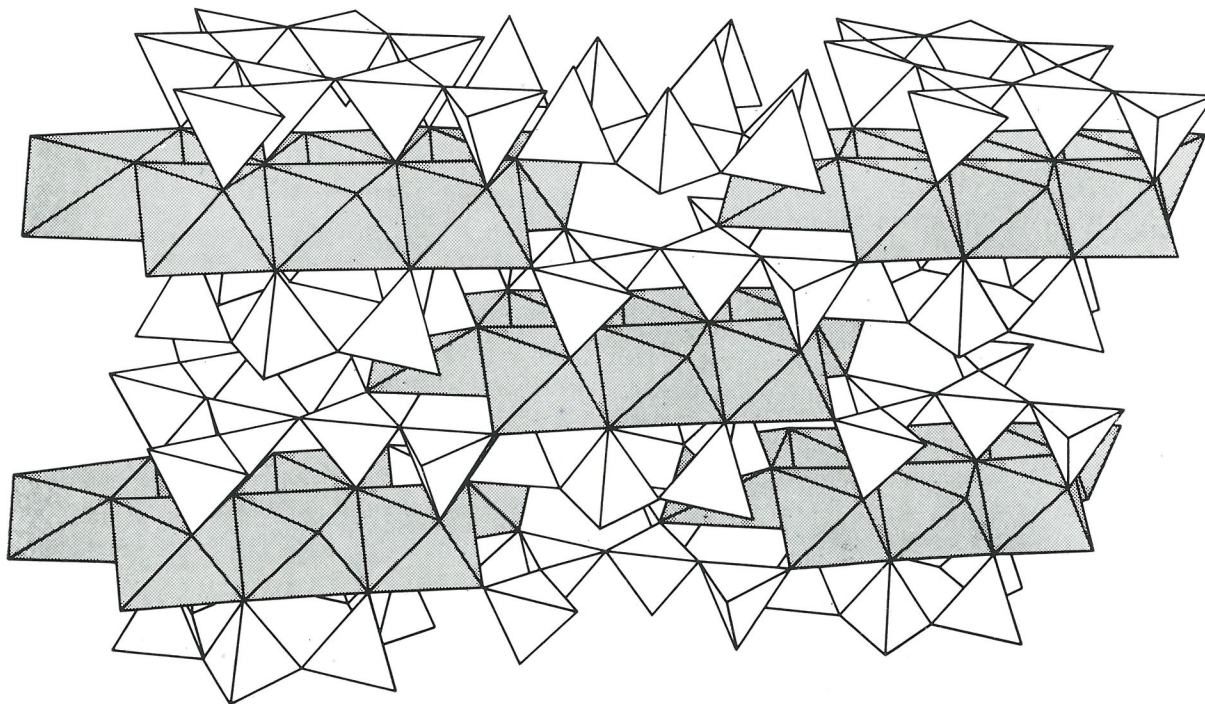


FIG. 1. The grunerite structure in perspective view.

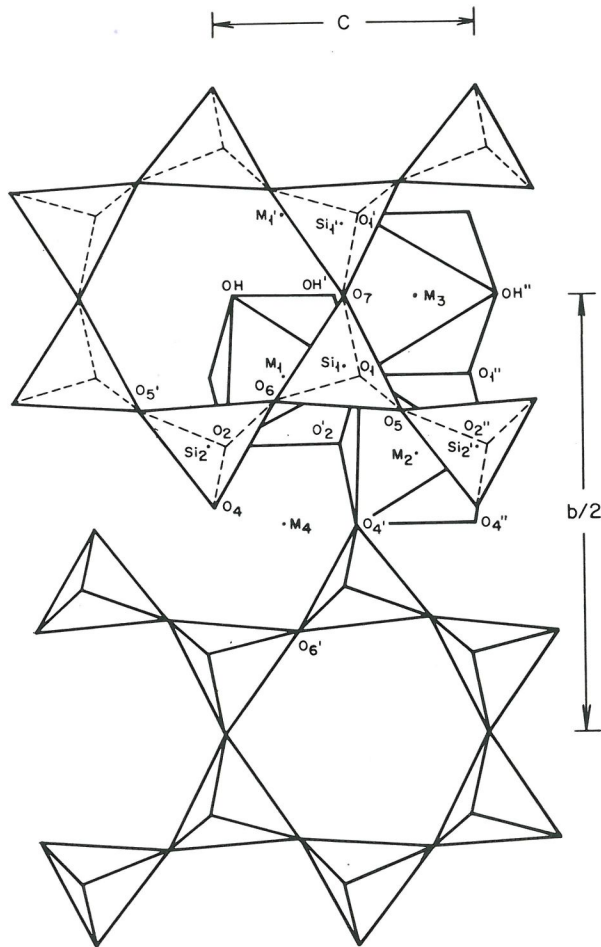


FIG. 2. A partial projection of the grunerite structure on (100) showing the atoms involved in important bonds.

coefficients are presented in Table 3 with the anisotropic temperature factors computed from the formula

$$T = \exp \left(- \sum_i \sum_j h_i h_j \beta_{ij} \right).$$

Selected interatomic distances and associated errors are presented in Table 4, and the angles in the silicate double chains are listed in Table 5. All errors were computed with the use of the full-matrix, propagation-of-error formula and were calculated with the author's program BADTEA.

The crystal structure of grunerite, described by Ghose and Hellner (1959), is very similar to that of other clin amphiboles, *e.g.* cummingtonite (Ghose, 1961; Fischer, 1966), tremolite (Warren, 1930; Zussman, 1959), crocidolite (Whittaker, 1949), actinolite (Zussman, 1955), riebeckite (Colville and Gibbs, 1964), and glaucophane (Papike and Clark, 1968). The essential features of the structure are strips of Fe-Mg ions in octahedral coordination with oxygen and hydroxyl, extending parallel to the *c* axis and linked together with double chains of SiO_4 tetrahedra.

A perspective view of the structure, prepared with the computer program ORTEP, is shown in Figure 1. Figure 2 shows a partial projection of the structure on (100) and is useful in interpreting Tables 4 and 5.

The tetrahedral chain has two crystallographically independent silicon positions, Si(1) and Si(2). The former links with its mirrored symmetry equivalent and shares a

TABLE 6. MAGNITUDES AND ORIENTATION OF PRINCIPAL AXES OF THERMAL ELLIPSOIDS IN GRUNERITES

Atom, axis	rms displacement $\text{\AA}(\sigma)$	Angle, in degrees, with respect to		
		+ <i>a</i> (σ)	+ <i>b</i> (σ)	+ <i>c</i> (σ)
<i>M</i> (1), 1	0.063(6)	133(15)	90	31(15)
2	.078(5)	137(15)	90	121(15)
3	.097(4)	90	0	90
<i>M</i> (2), 1	.069(5)	157(18)	90	55(18)
2	.081(5)	113(18)	90	145(18)
3	.091(5)	90	0	90
<i>M</i> (3), 1	.075(7)	49(32)	90	52(32)
2	.084(7)	41(32)	90	142(32)
3	.092(7)	90	0	90
<i>M</i> (4), 1	.081(5)	155(6)	90	54(6)
2	.109(4)	115(6)	90	144(6)
3	.128(4)	90	0	90
Si(1), 1	.063(6)	24(19)	85(13)	78(19)
2	.077(5)	66(20)	91(37)	168(20)
3	.084(5)	86(19)	175(14)	89(37)
Si(2), 1	.059(7)	31(9)	61(10)	92(9)
2	.084(5)	105(20)	49(29)	129(38)
3	.089(5)	116(14)	56(31)	39(38)
O(1), 1	.075(14)	172(29)	97(25)	77(37)
2	.090(13)	95(41)	62(32)	148(33)
3	.108(12)	96(18)	29(31)	61(31)
O(2), 1	.058(17)	170(14)	98(18)	73(17)
2	.091(13)	88(22)	132(38)	137(36)
3	.105(12)	80(14)	137(38)	52(36)
O(3)-OH, 1	.105(16)	117(21)	90	15(21)
2	.107(17)	90	180	90
3	.138(13)	27(21)	90	75(21)
O(4), 1	.069(15)	79(36)	113(61)	32(24)
2	.079(14)	119(26)	147(49)	98(58)
3	.104(11)	148(21)	67(22)	59(16)
O(5), 1	.031(32)	149(13)	116(9)	65(10)
2	.086(13)	118(14)	60(10)	128(10)
3	.144(9)	102(6)	42(7)	49(7)
O(6), 1	.056(18)	16(12)	102(11)	91(28)
2	.080(13)	84(29)	108(9)	161(7)
3	.152(9)	105(6)	158(6)	71(7)
O(7), 1	.012(117)	90	0	90
2	.087(18)	5(12)	90	106(12)
3	.142(12)	85(12)	90	16(12)

corner with two of the Si(2) tetrahedra. This configuration is very similar to the tetrahedra in a mica, and this coordination polyhedron is fairly regular. Si(2) shares two corners with other tetrahedra, however, and has the configuration of a pyroxene tetrahedron (Papike and Clark, 1968). In addition, two of the oxygens coordinated with Si(2), namely O(4) and O(6), are also involved in the coordination polyhedron of M(4). The covalent bonding between M(4) and O(6) reduces the strength of the O(6)-Si(2) bond, forcing an increase in the strengths of the O(4) and O(5) bonds to Si(2). These distances are therefore shortened, and the tetrahedron is distorted. The effect of participation of O(6) in the M(4) polyhedron may be seen in the O(4)-O(6) distance, which is a "shared" edge.

The nature of the partial ordering of the octahedral cations is in general agreement with the previous determination in grunerite (Ghose and Hellner, 1959) and cummingtonite (Ghose, 1961; Fischer, 1966). The M(4) site is greatly enriched in iron relative to the bulk composition, M(1) and M(3) are slightly depleted in iron, and M(2) is strongly enriched in magnesium. Ghose (1965) suggested that strongly polarizing cations like Fe²⁺ will be found in M(4) because of the highly covalent nature of the bonding. On the other hand, covalent bonding in the interior sites would tend to buckle the strip, and therefore the interior sites are relatively deficient in iron, with M(2) even more depleted to allow the octahedral layer to fit the tetrahedral dimensions along the chains.

The root-mean-square (rms) amplitudes of the principal axes of the thermal ellipsoids and the angles between these axes and the direct cell axes are presented in Table 6.

These quantities and their associated errors were computed with the full-matrix, error-of-propagation formula and with program BADTEA. In this structure, all ellipsoids are triaxial, and the atoms on the mirror planes or the two-fold axes are constrained to have one principal axis parallel to the *b* axis. All other ellipsoids have a completely general orientation. The geometry agrees qualitatively with the structural position of the atom. Each of the octahedral cations has the largest principal axis parallel to *b* or toward an edge shared with other octahedra. The silicon atoms have ellipsoids that tend toward oblate spheroids, with the unique axis pointed toward the apical oxygens O(1) and O(2). In turn, these oxygens have their short axis toward the silicons. The O(3) or hydroxyl position tends toward a prolate spheroid and has its long axis parallel to the O(3)-O(3) edge shared between the M(1) octahedra. The ellipsoid for O(7) is very nearly nonpositive definite since the rms amplitude of axis 1 is 0.012 ± 0.117 Å. This axis points approximately toward the two coordinating Si(1) atoms and should be the short axis, but this extreme shortness was not predictable.

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