

THE CRYSTAL STRUCTURE AND SITE-CHEMISTRY OF A ZINCIAN TIRODITE BY LEAST-SQUARES REFINEMENT OF X-RAY AND MÖSSBAUER DATA

F. C. HAWTHORNE* AND H. D. GRUNDY

Department of Geology, McMaster University, Hamilton, Ontario, Canada

ABSTRACT

The crystal structure of a zincian tirodite, $\text{Na}_{0.21}\text{Ca}_{0.28}\text{Mg}_{3.70}\text{Mn}_{1.60}\text{Zn}_{0.75}\text{Fe}^{2+}_{0.42}\text{Fe}^{3+}_{0.07}\text{Al}_{0.09}\text{Si}_{7.87}\text{O}_{22}(\text{OH})_2$; a 9.606(1), b 18.126(1), c 5.317(1) Å, β 102.63(1)°, $C2/m$; has been refined by full-matrix least-squares methods to an R -index of 3.7% using 1383 observed intensities measured with $\text{MoK}\alpha$ radiation on a 4-circle diffractometer. Fe^{2+} and Fe^{3+} site-populations were assigned from peak intensity ratios obtained by least-squares refinement of Mössbauer spectra recorded at 273°K and 77°K, and the distribution of Mg, Mn and Zn over the three non-equivalent octahedral sites was refined using bulk chemical constraints from the mineral analysis.

The results of previous infrared studies of Mn-cumingtonites are confirmed. Mn is strongly ordered into the $M(4)$ site whereas Fe^{2+} is ordered into $M(4)$ and $M(2)$. Zn shows octahedral site-preference of $M(1) > M(3) \gg M(2) > M(4)$ and Mn shows the site preference $M(3) > M(1) > M(2)$. Zincian tirodite is isotypic with other C-centred cumingtonites previously studied.

SOMMAIRE

La structure cristalline d'une tyrodite zincifère, $\text{Na}_{0.21}\text{Ca}_{0.28}\text{Mg}_{3.70}\text{Mn}_{1.60}\text{Zn}_{0.75}\text{Fe}^{2+}_{0.42}\text{Fe}^{3+}_{0.07}\text{Al}_{0.09}\text{Si}_{7.87}\text{O}_{22}(\text{OH})_2$, a 9.606(1), b 18.126(1), c 5.317(1) Å, β 102.62(1)°, $C2/m$, a été affinée, par la méthode des moindres carrés à matrice entière, jusqu'à un résidu de 3.7% sur 1383 intensités observées en rayonnement $\text{MoK}\alpha$ au moyen d'un diffractomètre à 4 cercles. Les sites de Fe^{2+} et Fe^{3+} ont été choisis à partir des proportions de l'intensité des pics obtenus par l'affinement par moindres carrés des spectres de Mössbauer enregistrés à 273° et 77°K. La distribution de Mg, Mn et Zn dans les trois sites octaédriques non-équivalents a été affinée à partir des contraintes imposées par l'analyse chimique du minéral.

Les résultats des études précédentes à l'infrarouge des cumingtonites-Mn sont confirmés. Mn est fortement ordonné dans le site $M(4)$, tandis que Fe^{2+} est ordonné dans $M(4)$ et $M(2)$. La préférence de Zn pour les sites octaédriques est dans l'ordre: $M(1) > M(3) \gg M(2) > M(4)$. Pour Mn, cet ordre est: $M(3) > M(1) > M(2)$. La tyrodite zincifère est isostructurale avec d'autres cumingtonites centrées en C précédemment étudiées.

(Traduit par la Rédaction)

INTRODUCTION

The characterization of intracrystalline cation ordering in minerals has received considerable attention from mineralogists and crystallographers in the past decade, due to its potential use as a geothermometer. Of the many experimental techniques that may be used to derive site-populations, the three most common techniques are X-ray diffraction (Whittaker 1949; Zussman 1955), Mössbauer spectroscopy (Bancroft *et al.* 1967b, 1968; Bancroft 1970) and infrared spectroscopy (Burns & Strens 1966; Burns & Prentice 1968). However, the precise characterization of site-occupancies is often limited by the applicability of the experimental method used. For example, Fe and Mn cannot be directly distinguished by X-ray diffraction due to the similarity of their scattering factors; in most silicates, Mössbauer spectroscopy may only be used to derive site-populations of iron; infrared spectra may be too complex to resolve (Bancroft & Burns 1969) and oxidation can occur during sample preparation. These problems can be substantially reduced by choosing a combination of experimental techniques pertinent to the specific problems encountered during an experimental study. Bancroft *et al.* (1966, 1967a) and Bancroft & Burns (1969) have shown the utility of this approach in deriving site-populations by combined Mössbauer and infrared studies. During the present study of the crystal structure of a zincian tirodite, the problems involved in deriving site-occupancies were extreme; however, a combination of Mössbauer spectroscopy and X-ray diffraction site-population refinement techniques substantially reduced the number of assumptions necessary to derive complete site-populations and demonstrates the utility of combined experimental methods in the resolution of site-chemistry in complex minerals.

Crystal-structure refinements of cumingtonite (Ghose 1961; Fischer 1966) and grunerite (Ghose & Hellner 1959) first showed that Fe^{2+} preferentially occupies the $M(4)$ site in ferromagnesian amphiboles. This was subsequently

*Present address: Department of Earth Sciences, University of Manitoba, Winnipeg, Manitoba, Canada.

confirmed by Mössbauer (Bancroft 1967; Bancroft *et al.* 1967a; Ghose & Hafner 1968; Hafner & Ghose 1971) and infrared spectroscopy (Strens 1966). Although the X-ray results of Ghose (1961) indicated some ordering on the octahedral [$M(1)$, $M(2)$ and $M(3)$] sites in cummingtonite, this was not detected by the spectroscopic studies. However, this has since been confirmed by combined Mössbauer and infrared studies (Bancroft *et al.* 1967a) and precise site-population refinement of single-crystal X-ray data (Finger 1967, 1969a). It has long been recognized that the presence of additional cations in a crystal can significantly affect the Mg-Fe^{2+} site-ordering pattern. This was shown to be the case in Mn cummingtonite (Bancroft *et al.* 1967a; Buckley & Wilkins 1971) where Mn^{2+} exhibits a much stronger preference than Fe^{2+} for the $M(4)$ site, thus altering the Fe^{2+} site-ordering pattern.

Crystal-structure refinements of $P2_1/m$ cummingtonite and C -centred Mn cummingtonite were reported by Papike *et al.* (1968, 1969). Prewitt *et al.* (1970) showed that $P2_1/m$ cummingtonite transforms to $C2/m$ cummingtonite upon heating, and crystal-structure refinements of high cummingtonite at various temperatures have been reported by Sueno *et al.* (1972a,b).

EXPERIMENTAL

The crystals used in this investigation are from Franklin, New Jersey and were kindly supplied by Dr. Jun Ito. Chemical analysis and physical properties are reported by Klein & Ito (1968), #90384; the structural formula is given in Table 1.

X-ray diffraction

Single-crystal precession photographs exhibited diffraction symmetry $2/mC/-$ consistent

with space groups $C2/m$, $C2$ and Cm . In line with previous work (Ghose 1961; Papike *et al.* 1969), the centric space group was adopted and found to be satisfactory. A euhedral cleavage fragment showing the $\{110\}$ form was selected for the intensity measurements. Unit cell dimensions were measured on a Syntex P1 4-circle automatic diffractometer and are presented in Table 1 together with the unit-cell contents and other data pertinent to data collection and processing. Details of the data collection methods and data reduction procedures are reported elsewhere (Hawthorne & Grundy 1976).

Mössbauer resonance spectra

Mössbauer spectra were recorded with an Austin Science Associates drive system used in conjunction with a Victoreen P1P400A multi-channel analyzer. The velocity wave form was of the asymmetric sawtooth type with the source velocity varying between ± 5.5 mm/sec. The source was ^{57}Co in a palladium matrix and the velocity scale calibration was made against the spectrum of iron foil. In order to reduce asymmetry effects due to sample orientation, samples were mixed and finely ground with sugar before mounting (R. G. Burns, pers. comm.). Absorber thickness corresponding to 1.6 mg of natural iron per cm^2 was used, as both the iron content and the amount of sample available were small. Off-resonance counts in excess of 2.5×10^6 were accumulated.

INTERPRETATION OF MÖSSBAUER SPECTRA

The experimental spectrum shows two quadrupole-split ferrous doublets; by analogy with the previous work on ferromagnesian amphiboles, the outer doublet was assigned to Fe^{2+} in $M(1)$, $M(2)$ and $M(3)$ and the inner doublet to Fe^{2+} in $M(4)$. The small half-width of the outer doublet indicates that either this overlap is nearly perfect or the octahedral Fe^{2+} is ordered into one site.

In addition to these two doublets, an inflection is present on the upper velocity side of the lower velocity component of the $M(4)$ ferrous doublet. The chemical analysis indicates the presence of Fe^{3+} in both octahedral and tetrahedral coordination, and this inflection can be assigned to the high-velocity component of an octahedrally coordinated Fe^{3+} doublet. Even allowing for the hidden $\text{Fe}^{3+}_{\text{VI}}$ component, the total lower velocity absorption is much greater than the total higher velocity absorption. The method of sample preparation precludes significant asymmetry effects due to preferred orientation. This suggests the presence of another ferric iron

TABLE 1. MISCELLANEOUS DATA

unit formula			
Si	7.87	a	9.606(1) Å
Al	0.09	b	18.126(1)
Tetrahedral Σ	7.94	c	5.317(1)
		β	102.63(1)°
		V	903.38 Å ³
Fe^{3+}	0.07	Sp. Gp.	$C2/m$
Fe	0.42	Z	2
Mn	1.60	D	3.24(2) g/cm ³
Zn	0.75	D _{obs}	3.25
Mg	3.70	μ calc	34.5 cm ⁻¹
Ca	0.26	Radiation	Mo/K
Na	0.21	Crystal	0.09 × 0.09
K	0.02	Dimensions	× 0.22 mm
M site Σ	6.99	No. of F _o	1383
		$> 4\sigma$ F _o	1383
		Final R (obs)	3.7%
		Final R (all data)	4.4%
$R_w = \frac{\sum w(F_o - F_c)^2}{\sum w F_o ^2}^{1/2}$, w = 1			
Temp. factor form used: $\exp(-\sum_{i=1}^3 \sum_{j=1}^3 h_i h_j \beta_{ij})$			

doublet in the low-velocity part of the spectrum as is indicated by the chemical analysis, and an attempt was made to fit four doublets to the spectrum. The spectrum was fitted using the program of Stone (1967).

Starting parameters were estimated visually from the experimental spectrum. The position of the lower velocity component of the octahedral Fe^{3+} doublet was estimated from isomer shift and quadrupole splitting values in other amphiboles (Bancroft & Burns 1969; Ernst & Wai 1970). The positions and intensities of the hidden Fe^{3+} doublet components were estimated by examining the residuals obtained from the low-velocity absorption.

During the initial refinement cycles, the area of the most intense peak was varied whilst keeping the area ratios and all other parameters constant in order to scale the peak intensities to the experimental measurements. Attempts to vary all the positions with the constraints of equal half-widths for all peaks and equal area for doublet components resulted in divergence. Examination of the iterations prior to divergence showed that the positions of two peaks (initially assigned as the low-velocity component of the $M(4)$ Fe^{2+} doublet and the low-velocity component of the octahedral Fe^{3+} doublet) were converging on the same value. This was taken as indicative of perfect overlap of these two peaks, and thus they were combined with the intensity of the resulting peak constrained to be equal to the sum of the intensities of their high-velocity counterparts. In addition, all half-widths except that of the 'double' peak were constrained to be equal, and refinement resulted in convergence at a χ^2 -value of 415. The half-width of the 'double' peak was only slightly larger than those of the single peaks (Table 2), thus justifying the assumption of complete overlap.

To check the validity of the fitted spectrum, the low-temperature (liquid nitrogen) spectrum was recorded. The refinement converged to a χ^2 -value of 421 for 8 peaks with the constraint of equal half-widths for all peaks. All attempts to remove this half-width constraint resulted in divergence, and examination of the correlation matrix derived from the least-squares procedure showed that there was extreme correlation between variables of strongly overlapping peaks. Final parameters for both spectra are given in Table 2.

The Mössbauer parameters for the octahedral Fe^{3+} doublet are similar to those determined in alkali (Bancroft & Burns 1969; Ernst & Wai 1970) and calcic amphiboles (unpublished data) for Fe^{3+} occupying the $M(2)$ site. In addition, these parameters do not correspond with those

TABLE 2. MÖSSBAUER RESULTS FOR ZINCIAN TIRODITE

	I.S.*	Q.S.	H.W.	Area Ratio**
<u>Room temperature spectrum</u>				
$\text{Fe}_{M(4)}^{2+}$	1.078	1.775	0.329	1.000
$\text{Fe}_{M(1,2,3)}^{2+}$	1.130	2.808	0.329	3.614
$\text{Fe}_{M(2)}^{3+}$	0.447	0.514	0.329	0.569
$\text{Fe}_{T(2)}^{3+}$	0.111	0.494	0.329	0.618
Constraints:	equal areas for upper & lower velocity peaks; all half-widths equal			
χ^2	423	1% = 308	99% = 435	
<u>Low temperature spectrum</u>				
$\text{Fe}_{M(4)}^{2+}$	1.147	1.743	0.357	1.000
$\text{Fe}_{M(1,2,3)}^{2+}$	1.232	3.076	0.357	3.642
$\text{Fe}_{M(2)}^{3+}$	0.454	0.637	0.357	0.547
$\text{Fe}_{T(2)}^{3+}$	0.118	0.519	0.357	1.620
Constraints:	as above			
χ^2	421	1% = 307	99% = 434	

* Isomer shifts (mm/sec) are relative to zero for iron-foil

** Normalized to $\text{Fe}_{M(4)}^{2+} = 1.0$

TABLE 3. ATOMIC PARAMETERS FOR ZINCIAN TIRODITE

Site	x	y	z	B _{equiv.}
O(1)	0.1138(3)	0.0864(1)	0.2116(5)	0.64(3) Å
O(2)	0.1224(3)	0.1723(1)	0.7198(5)	0.74(3)
O(3)	0.1130(4)	0	0.7104(7)	0.72(5)
O(4)	0.3751(3)	0.2469(1)	0.7767(5)	0.98(4)
O(5)	0.3501(3)	0.1307(2)	0.0673(5)	1.00(4)
O(6)	0.3492(3)	0.1204(2)	0.5616(5)	1.09(4)
O(7)	0.3439(4)	0	0.2787(8)	1.11(6)
T(1)	0.2864(1)	0.08426(5)	0.2784(2)	0.58(1)
T(2)	0.2955(1)	0.16977(5)	0.7853(2)	0.60(1)
M(1)	0	0.08711(6)	1/2	0.70(2)
M(2)	0	0.17744(7)	0	0.72(3)
M(3)	0	0	0	0.73(4)
M(4)	0	0.26251(5)	1/2	0.92(1)

of Fe^{3+} in $M(1)$ and $M(3)$ for hydrous amphiboles (Semet 1973). This indicates that the octahedral Fe^{3+} is ordered into the $M(2)$ site as would be expected from charge-balance criteria. The remaining doublet is a little more problematic; it was tentatively assigned to Fe^{3+} in tetrahedral coordination as indicated by the chemical analysis, and the following X-ray refinement results are marginally improved by inclusion of this amount of tetrahedral Fe^{3+} . In addition, the isomer-shift values are in good agreement with values obtained for a doublet in the spectra of titanium-zirconium garnets (Dowty 1971) which was assigned to tetrahedral Fe^{3+} . However, these values are low when compared with the isomer shifts of Fe^{3+} in *RE* iron garnets ($< \text{I.S.} > = 0.30$ mm/sec, Nicholson & Burns 1964), spinel-type

cubic ferrites ($\langle I.S. \rangle = 0.25$ mm/sec, Mizoguchi & Tanaka 1963) and Fe^{3+} -bearing orthoclase ($\langle I.S. \rangle = 0.46$ mm/sec, Brown & Pritchard 1969). Dowty's fitting of the garnet spectra has been criticized by Burns (1972) who states that the isomer shift of the tetrahedral Fe^{3+} doublet is lower than that of tetrahedral Fe^{3+} in sulfides, inferring that the Fe^{3+} -O bond is more covalent than the Fe^{3+} -S bond. Comparison with I.S. values for tetrahedral Fe^{3+} in RE iron garnets and other silicates would indicate that the increased covalent bonding expected in tetrahedral coordination is not, in general, sufficient to produce I.S. values as low as those observed here. However, recent work on synthetic ferri-diopside (Hafner & Huckenholz 1971), natural ferri-augites (Virgo 1972) and synthetic ferri-phlogopite (Annersten *et al.* 1971) has shown peaks with parameters in agreement with those obtained in the present study. In particular, the ferri-phlogopite spectrum consists of a single Fe^{3+} doublet with an I.S. of 0.17 mm/sec. Thus an oxygen environment can produce I.S. values smaller than those generally encountered in sulfides. The reason for this becomes apparent from the crystallography of these minerals. The X-ray results indicate that the Fe^{3+} occurs in the $T(2)$ tetrahedron in zinc-cummingtonite, which is analogous to the tetrahedron in the clinopyroxenes. The most apparent feature of these tetrahedra is their extremely short $T-O(nbr)$ bonds. Brown & Shannon (1973) have suggested that the covalency of a bond is related to its length; accordingly, the $T(2)-O(4)$ and $T(2)-O(2)$ bonds in the amphiboles and the $Si-O(2)$ and $Si-O(1)$ bonds in the pyroxenes will be extremely covalent. This is supported by X-ray photoelectron spectra of the oxygen $1s$ level in ortho- and clinopyroxenes (Yin *et al.* 1971), where the non-bridging anions are observed to have a higher binding energy than the bridging anions, indicating a higher degree of 'covalency'. Hence, the small amounts of Fe^{3+} in these tetrahedra are likely to show very low isomer shifts.

Combining the peak intensities with the chemical analysis gives the site-populations in Table 4. The intensity of the doublet assigned to tetrahedral Fe^{3+} is proportionally much greater at low temperature than at high temperature. Although relative changes in the recoil-free fraction at the octahedral and tetrahedral sites are to be expected, they are unlikely to be of this magnitude, and this effect is probably the result of sample orientation combined with high correlation of variables in the fitting procedure. Thus the area of the tetrahedral Fe^{3+} peak was not used in the site-population calculation. Fe^{3+} was assigned to the $T(2)$ site to fill it and the remaining populations were assigned from the Mössbauer and chemical analysis results. Two different procedures have been used to assign site-populations from peak-intensity data. Bancroft *et al.* (1967a) assumed that the recoil-free fractions of the $M(4)$ and the $M(1)$, $M(2)$ and $M(3)$ sites differ by 10%. Conversely, Hafner & Ghose (1971) assumed that the recoil-free fractions at all four M sites in cummingtonites are equal. In view of the close agreement between the site-populations obtained by X-ray diffraction (Finger 1969a) and Mössbauer spectroscopy (Hafner & Ghose 1971) on the same sample of grunerite, we have assumed that the recoil-free fractions at the four M sites are equal.

CRYSTAL-STRUCTURE REFINEMENT

Scattering factors for neutral atoms were taken from Doyle & Turner (1968) and anomalous dispersion coefficients were taken from Cromer (1965). Quoted R -indices are of the forms given in Table 1 and are expressed as percentages. Atomic coordinates and isotropic temperature factors from the X-ray refinement of C -centred Mn-cummingtonite (Papike *et al.* 1969) were used as input parameters for the least-squares program SORFLS (Stewart 1967). Initial site-occupancies were assigned on the basis of the known crystal-chemical characteristics of ferro-

TABLE 4. SITE-POPULATIONS FOR ZINCIAN TIRODITE

Site	Populations	Standard deviations from least-squares**	
		Method 1	Method 2
T(1)	0.978Si + 0.022Al		
T(2)*	0.998Si + 0.01Fe		
M(1)	0.252Zn + 0.708Mg + 0.039Mn	(0.042)Zn, (0.080)Mg, (0.065)Mn	(0.004)Zn; (0.004)Mg; (0.004)Mn
M(2)*	0.165Fe ²⁺ + 0.020Fe ³⁺ + 0.034Zn + 0.781Mg	(0.053)Zn, (0.053)Mg	(0.004)Zn; (0.004)Mg
M(3)	0.177Zn + 0.722Mg + 0.101Mn	(0.083)Zn, (0.098)Mg, (0.091)Mn	(0.007)Zn; (0.007)Mg; (0.008)Mn
M(4)*	0.710Mn + 0.045Fe ²⁺ + 0.140Ca + 0.105Na		

* Iron assigned from Mossbauer spectra results, ** see text.

magnesian amphiboles (Papike *et al.* 1969). All large cations were assigned to the $M(4)$ site together with Fe^* where $\text{Fe}^* = \text{Fe} + \text{Mn} + \text{Zn}$ and was expressed in terms of the scattering curve for neutral Fe. The remaining Fe^* was assigned as being randomly distributed over $M(1)$, $M(2)$ and $M(3)$.

One cycle of refinement varying atomic positions resulted in an R -index of 14.1%. One cycle varying the isotropic temperature factors gave an R -index of 12.1% and a further cycle varying positions and isotropic temperature factors gave an R -value of 8.7%. At this stage, the temperature factors of the octahedral sites were not equal, indicating a non-random distribution of Fe^* . Thus the site-occupancies were varied by refining the formal multiplicity of the four M sites. Several cycles of refinement gradually increasing the number of variables resulted in an R -index of 6.1%. At this stage, the isotropic temperature factors for $M(1)$, $M(2)$ and $M(3)$ were equal within one standard deviation, and the total scattering power of the M sites from the refinement was equivalent to that of the chemical analysis to within less than 1%. This would indicate that the refinement had not departed significantly from the actual composition, as had been observed in some other refinements (Finger 1969a; Burnham *et al.* 1971). However, correlations between site-populations, temperature factors and the scale factor were high, and at this stage the parameters were used as input to the least-squares program RFINE (Finger 1969b). Initial site-occupancies were calculated from the total scattering power at each site from SORFLS, the chemical formula, and mean bond-length considerations. The total scattering power at $M(4)$ indicated that it was completely occupied by Na, Ca, Fe and Mn. Ferrous iron occupancy of $M(4)$ was taken from the Mössbauer results, thus giving unambiguous site-occupancies for the cations occupying this position. Consistent with previous work (Papike & Clark 1968; Hawthorne & Grundy 1973), the octahedral ferric iron was assigned to the $M(2)$ site. The $\langle M(2)\text{-O} \rangle$ distance was 2.092 Å at this stage and the $M(2)$ site-occupancy from the unconstrained refinement was 0.742(8)Mg + 0.258Fe. For the $M(2)$ site, the mean bond length is related to the mean ionic radius of its constituent cations by the equation

$$\langle M(2)\text{-O} \rangle = 1.557 + 0.733 \langle r_{M(2)} \rangle \quad (r = 0.992)$$

(Hawthorne 1973). Using the $\langle M(2)\text{-O} \rangle$ bond length given above, the mean ionic radius of the cations occupying the $M(2)$ site may be calculated. Application of the above relation to the structure of C -centred Mn-cummingtonite (Pa-

pike *et al.* 1969) indicates that there is no Mn in the $M(2)$ site (see next section). If this is assumed to be the case for zincian tirodite, we have three simultaneous equations involving the $M(2)$ site-populations:

$$x^{\text{Mg}} + x^{\text{Fe}^{2+}} + x^{\text{Zn}} + 0.02 (\text{Fe}^{3+}) = 1.0$$

$$(x^{\text{Mg}} \times 0.72) + (x^{\text{Fe}^{2+}} \times 0.78) + (x^{\text{Zn}} \times 0.745) + (0.02 \times 0.645) = \langle r_{M(2)} \rangle$$

$$(x^{\text{Mg}} \times 12) + ((x^{\text{Fe}^{2+}} + 0.02) \times 26) + (x^{\text{Zn}} \times 30) = (0.742 \times 12) + (0.258 \times 26)$$

Solution of these equations indicates that all the octahedral Fe^{2+} is in the $M(2)$ site [$M(2) = 0.758 \text{Mg} + 0.167 \text{Fe}^{2+} + 0.055 \text{Zn} + 0.020 \text{Fe}^{3+}$]. This leaves three species, Mg, Zn and Mn which are distributed over the $M(1)$ and $M(3)$ sites. Initial site-populations were assigned on the basis of bond-length considerations and total scattering powers of each site from the unconstrained refinement. Then all three species were refined over the $M(1)$ and $M(3)$ sites using bulk-chemical constraints (Finger 1969c). Each site was split into two half-occupied sites, each of which may be considered as a combination of two species; thus the sites

$$\begin{array}{lll} M(1) & x^{\text{Mg}} + y^{\text{Zn}} + z^{\text{Mn}} & x + y + z = 1 \\ M(3) & x'^{\text{Mg}} + y'^{\text{Zn}} + z'^{\text{Mn}} & x' + y' + z' = 1 \end{array}$$

become the pairs of sites

$$\begin{array}{lll} M(1) & (x - a)^{\text{Mg}} + y^{\text{Zn}} & x - a + y = 0.5 \\ M(1)' & a^{\text{Mg}} + z^{\text{Mn}} & a + z = 0.5 \\ M(3) & (x' - a')^{\text{Mg}} + y'^{\text{Zn}} & x' - a' + y' = 0.5 \\ M(3)' & a'^{\text{Mg}} + z'^{\text{Mn}} & a' + z' = 0.5 \end{array}$$

The Zn-Mg distribution may be refined for the unprimed sites and the Mn-Mg distribution may be refined for the primed sites, with the following bulk-chemical constraints operative:

$$\begin{array}{l} y' = \text{Zn}^{\text{tot}} - 2y \\ z' = \text{Mn}^{\text{tot}} - \text{Mn}_{M(4)} - z \end{array}$$

Application of this procedure resulted in an R -value of 4.4%. Conversion to anisotropic temperature factors (Table 1), application of a variable isotropic extinction correction (Zachariasen 1968), and several cycles of least-squares refinement gradually increasing the number of variables resulted in convergence at an R -value of 3.9%. Examination of bond lengths calculated at this stage showed a slight change in the mean $M(2)$ bond length, indicating that the assigned populations were no longer quite correct; this was also reflected by the relative magnitudes of the equivalent isotropic temperature factors, $B_{M(1)} = B_{M(3)} < B_{M(2)}$, indicating that the electron density was slightly too high at the $M(2)$ site. Thus the bulk-chemistry constraint for Zn was appropriately modified and the distribution of

Zn was refined over $M(1)$, $M(2)$ and $M(3)$. A subsequent cycle of refinement, refining the distribution of Zn and Mg over $M(1)$, $M(2)$ and $M(3)$ and the distribution of Mn over $M(1)$ and $M(3)$ together with all other variables, resulted in convergence at an R -index of 3.8%. The equivalence of equivalent isotropic temperature factors at $M(1)$, $M(2)$ and $M(3)$ suggests that the derived site-populations are correct.

The correlation coefficients encountered during the site-population refinement were extremely large among the population parameters, with a typical value of ± 0.994 ; however, correlations between site-populations and the scale and temperature factors were without exception very small. This ill conditioning of the matrix of normal equations is not the result of the equations being a poor approximation, as is the case for an unconstrained site-population refinement, but occurs because the solution is only marginally defined. Due to these large correlations, the standard deviations must be extracted from the full matrix. This requirement is extremely important, as the use of a partitioned matrix at this stage will give rise to a substantial underestimation of the errors. This effect was evaluated for the zinc-manganese cummingtonite refinement by performing successive cycles of refinement, whilst varying the site-populations of two of the chemical species at a time, with the third held constant. The final standard deviations for the site-populations are given in Table 4 (method 2), where they are compared with those from the full-matrix refinement (method 1). It is apparent that method 2 gives standard deviations that are too low by at least an order of magnitude, and therefore, those standard deviations in the published literature that have been estimated from partitioned matrices must be viewed with extreme caution.

During the later stages of refinement, cycles of least-squares refinement were performed both with and without the presence of tetrahedral iron. Both bond-length comparison with C -Mn cummingtonite (Papike *et al.* 1969) and crystal-chemical factors suggest that any tetrahedral iron should be ordered into $T(2)$, and this premise is upheld by the refinement results. Without the presence of tetrahedral iron, the equivalent isotropic temperature factor of $T(2)$ was four standard deviations smaller than the equivalent isotropic temperature factor of $T(1)$; inclusion of the amount of tetrahedral (ferric) iron indicated by the analysis resulted in equivalent isotropic temperature factors at $T(1)$ and $T(2)$ that were statistically equal although no reduction in the R -index occurred. Although this is a result of marginal significance, it is compa-

tible with the results of the Mössbauer experiment.

Final atomic positions and equivalent isotropic temperature factors are presented in Table 3, site-populations are given in Table 4 and the final observed and calculated structure factors are listed in Table 5*. Interatomic distances and angles were calculated with the program ERRORS (L. W. Finger, pers. comm.) and are given in Tables 6, 7 and 8. Table 9 lists the final anisotropic temperature factor coefficients and the magnitudes and orientations of the principal axes of the thermal ellipsoids are presented in Table 10.

DISCUSSION

Ordering

The site-populations obtained from the refinements confirm the non-random distribution of Mn in manganoan cummingtonites that is indicated by both infrared spectra (Bancroft *et al.* 1967a) and bond-length considerations (Papike *et al.* 1969). Previous results show a fairly good qualitative agreement with this work; the $M(4)$ site preference of $Mn > Fe > Mg$ is confirmed, and ordering of Fe^{2+} into $M(2)$ is also indicated. In the zincian tirodite, the mean ionic radii (Shannon & Prewitt 1969, 1970) of the cations in $M(2)$ is 0.73 Å; substitution of this into equa-

*Table 5 is available, at a nominal charge, from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Canada K1A 0S2.

TABLE 6. SELECTED INTERATOMIC DISTANCES

Atoms	Distance	Atoms	Distance
T(1)-O(1)	1.618(3) Å	M(1)-O(1)	2.069(4) Å x 2
T(1)-O(5)	1.626(3)	M(1)-O(2)	2.129(4) x 2
T(1)-O(6)	1.632(4)	M(1)-O(3)	2.095(4) x 2
T(1)-O(7)	1.624(2)	Mean M(1)	2.097
Mean T(1)	1.625		
T(2)-O(2)	1.623(3)	M(2)-O(1)	2.155(4) x 2
T(2)-O(4)	1.600(3)	M(2)-O(2)	2.092(4) x 2
T(2)-O(5)	1.637(3)	M(2)-O(4)	2.026(4) x 2
T(2)-O(6)	1.658(3)	Mean M(2)	2.091
Mean T(2)	1.630		
M(4)-O(2)	2.195(4) x 2	M(3)-O(1)	2.092(3) x 4
M(4)-O(4)	2.099(4) x 2	M(3)-O(3)	2.069(5) x 2
M(4)-O(5)	2.109(5) x 2	Mean M(3)	2.084
M(4)-O(6)	2.630(3) x 2		
Mean for 8	2.508	A-O(5)	2.835(4) x 4
Mean for 6	2.397	A-O(6)	3.289(4) x 4
		A-O(7)	2.327(5) x 2
		A-O(7)	3.800(5) x 2
		Mean for 12	3.062
M(1)-M(1)	3.158(2)		
M(1)-M(2)	3.122(1)	T(1)-T(2)	
M(1)-M(3)	3.092(1)	through O(6)	3.094(1)
M(1)-M(4)	3.179(1)	T(1)-T(2)	
M(2)-M(3)	3.216(1)	through O(5)	3.063(1)
M(2)-M(4)	3.073(1)	T(1)-T(1)	
		across mirror	3.055(2)

tion (1) forecasts a $\langle M(2)-O \rangle$ distance of 2.091 Å in agreement with the experimental result (Table 6). Although agreement as exact as this must be considered as fortuitous, this does lend additional weight to the X-ray results that are compatible with complete Fe^{2+} ordering into $M(2)$. As the scattering powers of Fe and Mn are similar and Mn^{2+} is 0.05 Å larger than

Fe^{2+} , any substitution of Mn into the $M2$ site would lead to a less satisfactory agreement between the observed and calculated $\langle M(2)-O \rangle$ distances. It should be noted that application of the above equation to C -centred manganese cumingtonite (Papike *et al.* 1969) indicates that there is no Mn^{2+} in the $M(2)$ site, resulting in $M(2)$ site-population of (0.84 Mg, 0.16 Fe^{2+}).

TABLE 7. POLYHEDRAL EDGE LENGTHS

T(1) Tetrahedron		T(2) Tetrahedron	
0(1)-0(5)	2.673(4) Å	0(2)-0(4)	2.737(4) Å
0(1)-0(6)	2.667(8)	0(2)-0(5)	2.646(7)
0(1)-0(7)	2.668(4)	0(2)-0(6)	2.672(5)
0(5)-0(6)	2.637(4)	0(4)-0(5)	2.655(4)
0(5)-0(7)	2.629(3)	0(4)-0(6)	2.551(4)
0(6)-0(7)	2.645(4)	0(5)-0(6)	2.693(4)
Mean 0-0	2.653	Mean 0-0	2.659
M(1) Octahedron		M(3) Octahedron	
0(1 ^u)-0(2 ^d)	2.840(4)	0(1 ^u)-0(1 ^d)	2.774(9)
0(1 ^u)-0(2 ^u)	3.104(4)	0(1 ^u)-0(1 ^u)	3.133(5)
0(1 ^u)-0(3 ^u)	2.788(4)	0(1 ^u)-0(3 ^d)	2.788(4)
0(1 ^u)-0(3 ^u)	3.081(4)	0(1 ^u)-0(3 ^u)	3.090(4)
0(2)-0(2)	2.930(9)	Mean 0-0	2.944
0(2)-0(3)	3.125(3)		
0(3)-0(3)	2.756(9)		
Mean 0-0	2.964		
M(2) Octahedron		M(4) Polyhedron	
0(1)-0(1 ^d)	2.774(9)	0(2)-0(2)	2.930(9)
0(1 ^u)-0(2 ^u)	2.840(4)	0(2 ^u)-0(4 ^u)	3.023(4)
0(1 ^u)-0(2 ^d)	3.060(4)	0(2 ^u)-0(4 ^d)	2.862(4)
0(1)-0(4)	3.022(4)	0(2 ^u)-0(5 ^u)	3.737(4)
0(2 ^u)-0(4 ^u)	2.862(4)	0(4 ^u)-0(5 ^d)	3.337(5)
0(2 ^u)-0(4 ^d)	3.046(4)	0(4 ^u)-0(6 ^u)	2.551(4)
0(4)-0(4)	2.984(9)	0(5 ^u)-0(6 ^u)	2.637(4)
Mean 0-0	2.952	0(5 ^u)-0(6 ^d)	3.128(9)
		0(6 ^u)-0(6 ^d)	3.107(6)
		Mean 0-0	3.037

TABLE 8. SELECTED INTERATOMIC ANGLES

T(1) Tetrahedron		T(2) Tetrahedron	
0(1)-T(1)-0(5)	111.0(2)°	0(2)-T(2)-0(4)	116.3(2)°
0(1)-T(1)-0(6)	110.3(2)	0(2)-T(2)-0(5)	108.5(2)
0(1)-T(1)-0(7)	108.1(2)	0(2)-T(2)-0(6)	109.0(2)
0(5)-T(1)-0(6)	108.1(2)	0(4)-T(2)-0(5)	110.2(2)
0(5)-T(1)-0(7)	108.0(2)	0(4)-T(2)-0(6)	103.0(2)
0(6)-T(1)-0(7)	108.7(2)	0(5)-T(2)-0(6)	109.6(2)
Mean 0-T(1)-0	109.5	Mean 0-T(2)-0	109.4
M(1) Octahedron		M(3) Octahedron	
0(1 ^u)-M(1)-0(2 ^d)	85.2(1)	0(1 ^u)-M(3)-0(1 ^d)	83.0(2)
0(1 ^u)-M(1)-0(2 ^u)	95.4(1)	0(1 ^u)-M(3)-0(1 ^u)	97.0(2)
0(1 ^u)-M(1)-0(3 ^u)	84.0(1)	0(1 ^u)-M(3)-0(3 ^d)	84.1(1)
0(1 ^u)-M(1)-0(3 ^u)	95.4(1)	0(1 ^u)-M(3)-0(3 ^u)	95.9(1)
0(2)-M(1)-0(2)	87.0(2)	Mean 0-M(3)-0	90.0
0(2)-M(1)-0(3)	95.4(2)		
0(3)-M(1)-0(3)	82.2(2)		
Mean 0-M(1)-0	90.0		
M(2) Octahedron		M(4) Polyhedron	
0(1)-M(2)-0(1)	80.1(2)	0(2)-M(4)-0(2)	83.8(2)
0(1 ^u)-M(2)-0(2 ^u)	83.9(1)	0(2 ^u)-M(4)-0(4 ^u)	83.6(1)
0(1 ^u)-M(2)-0(2 ^d)	92.2(1)	0(2 ^u)-M(4)-0(4 ^d)	89.5(1)
0(1 ^u)-M(2)-0(3 ^u)	92.2(1)	0(2 ^u)-M(4)-0(5 ^u)	87.8(2)
0(1 ^u)-M(2)-0(4 ^u)	88.0(1)	0(4 ^u)-M(4)-0(5 ^d)	77.0(1)
0(2 ^u)-M(2)-0(4 ^u)	95.4(1)	0(4 ^u)-M(4)-0(6 ^u)	64.1(1)
0(2 ^u)-M(2)-0(4 ^d)	94.9(2)	0(5 ^u)-M(4)-0(6 ^u)	65.4(1)
0(4)-M(2)-0(4)	89.9	0(5 ^u)-M(4)-0(6 ^d)	53.9(1)
Mean 0-M(2)-0	89.9	0(6 ^u)-M(4)-0(6 ^d)	72.4(1)
		Mean 0-M(4)-0	74.9
A Polyhedron		Tetrahedron	
0(7)-0(7)-0(7)	59.9(1)	T(1)-0(5)-T(2)	139.7(2)
		T(1)-0(6)-T(2)	140.2(2)
		T(1)-0(7)-T(1)	140.3(3)
		0(5)-0(6)-0(5)	172.0(2)
		0(5)-0(7)-0(6)	171.0(2)
Δ^*	0.334		

$$^* \Delta = 90^\circ - [0(7)-0(7)-0(7)] / 90^\circ.$$

TABLE 9. ANISOTROPIC TEMPERATURE FACTORS ($\beta_{ij} \times 10^5$)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
T(1)	194(8)	32(2)	557(27)	3(3)	41(12)	3(6)
T(2)	212(9)	34(2)	546(27)	14(4)	51(12)	1(6)
M(1)	274(12)	34(3)	654(37)	0	117(15)	0
M(2)	257(13)	37(3)	700(39)	0	96(17)	0
M(3)	279(19)	37(5)	667(58)	0	90(23)	0
M(4)	285(9)	86(2)	694(26)	0	226(12)	0
O(1)	182(22)	34(6)	749(74)	12(9)	50(34)	1(17)
O(2)	201(23)	50(6)	779(73)	2(10)	74(32)	1(18)
O(3)	263(34)	37(8)	735(114)	0	145(48)	0
O(4)	327(27)	42(6)	1102(85)	56(10)	78(38)	26(18)
O(5)	255(25)	86(7)	905(81)	6(11)	112(35)	161(19)
O(6)	237(25)	109(8)	893(81)	16(11)	24(35)	128(20)
O(7)	294(39)	25(9)	1839(146)	0	200(60)	0

TABLE 10. VIBRATION ELLIPSOIDS

	R.M.S. Displacement	Angle to a axis	Angle to b axis	Angle to c axis
T(1)	0.072(3) Å ² 0.086(2) 0.096(2)	85(5)° 111(9) 22(8)	7(8)° 83(8) 93(4)	86(7)° 146(9) 124(9)
T(2)	0.073(3) 0.086(2) 0.101(2)	74(4) 98(6) 18(4)	16(3) 87(8) 105(4)	92(8) 159(6) 110(6)
M(1)	0.076(3) 0.093(3) 0.110(2)	90 74(6) 16(6)	0 90 90	90 176(6) 86(6)
M(2)	0.079(4) 0.097(3) 0.107(3)	90 81(12) 9(12)	0 90 90	90 176(12) 94(12)
M(3)	0.079(5) 0.095(4) 0.112(4)	90 86(9) 4(9)	0 90 90	90 171(9) 99(9)
M(4)	0.082(2) 0.118(2) 0.120(2)	128(2) 142(2) 90	90 90 0	25(2) 115(2) 90
O(1)	0.073(7) 0.091(6) 0.104(5)	71(14) 146(18) 117(18)	20(15) 71(15) 86(10)	90(9) 105(19) 15(19)
O(2)	0.091(6) 0.095(5) 0.104(5)	103(66) 159(46) 107(25)	13(68) 103(69) 92(20)	89(20) 95(23) 5(25)
O(3)	0.079(9) 0.095(8) 0.110(7)	90 56(22) 34(22)	0 90 90	90 159(22) 69(22)
O(4)	0.067(7) 0.119(5) 0.136(5)	64(4) 115(11) 143(9)	26(4) 81(7) 66(4)	98(5) 141(12) 52(12)
O(5)	0.077(7) 0.106(5) 0.144(5)	98(9) 171(8) 95(6)	131(3) 88(7) 41(3)	41(4) 87(8) 49(3)
O(6)	0.091(6) 0.102(5) 0.152(5)	82(22) 161(10) 107(4)	60(9) 71(13) 144(4)	36(8) 80(19) 56(4)
O(7)	0.065(11) 0.113(8) 0.158(6)	90 177(7) 93(7)	0 90 90	90 80(7) 10(7)

This strong ordering of Fe^{2+} into $M(2)$ is also shown by analysis of the O-H stretching bands in the infrared region (Bancroft *et al.* 1967a)*.

Thus all evidence in Mn- and Zn-Mn cummingtonites does indicate strong or even complete ordering of Fe^{2+} into the $M(2)$ octahedron. It should be noted that the Fe^{2+} site-preferences in zinc and manganese cummingtonites is in agreement with both Ribbe & Gibbs (1971) and Burns (1970) predictions although each is based on slightly different crystal-field criteria. This distribution of Fe^{2+} differs from that observed in other clinoamphiboles:

1) cummingtonite	$M(4) \gg M(3) \sim M(1) > M(2)$
2) grunerite	$M(4) > M(3) > M(1) > M(2)$
2) glaucophane	$M(3) > M(1) \gg M(2)$
4) actinolite	$M(1) > M(3) > M(2)$
5) ferrotschermakite	$M(3) > M(1) \gg M(2)$
6) arfvedsonite	$M(1) > M(3) \gg M(2)$
7) pargasite	$M(1) = M(3) \gg M(2)$

-
- 1) Ghose (1961); Fischer (1966)
 - 2) Finger (1967, 1969a)
 - 3) Papike & Clark (1968)
 - 4) Mitchell *et al.* (1970, 1971)
 - 5) Hawthorne & Grundy (1973)
 - 6) Hawthorne (1976)
 - 7) Robinson *et al.* (1973)

... the Fe^{2+} distributions of which are difficult to rationalize on the basis of C.F.S.E. predictions (Ribbe & Gibbs 1971). It is apparent that the ordering patterns in the different amphibole species are strongly controlled by anion bond-strength requirements and the presence of additional cations. In glaucophane and arfvedsonite, the occurrence of Na at $M(4)$ leads to a bond-strength deficiency at the O(4) anion that can only be compensated by the occurrence of trivalent cations (Al and Fe^{3+}) at $M(2)$; thus the $M(2)$ site is not available (or only partly available) for occupancy by Fe^{2+} . It is perhaps unrealistic to expect a single criterion to explain the site-distribution patterns of a particular element in different mineral species when no account is taken of the additional cations present.

Coordination of the $M(4)$ site

In his original description of the structure of grunerite, Finger (1967, 1969a) referred to the $M(4)$ site as six-coordinated on the basis of bond lengths. Subsequently, Donnay & Allman (1970) used their bond-strength scheme to 'de-

monstrate' that the $M(4)$ site in grunerite has a one-sided fourfold coordination with no bonding interaction between $M(4)$ and either of the chain-bridging anions O(5) and O(6). Conversely, Brown & Gibbs (1969, 1970) and Mitchell *et al.* (1970, 1971) implicitly assumed that $M(4)$ is eight-coordinated in all non-aluminous clinoamphiboles, and their treatment of Si-O distances was criticized by Baur (1971) because of this. The discussion given by Bragg (1930) would indicate that a one-sided fourfold coordination is highly improbable here. In addition, the supposition of a sharp cutoff in the pairwise interaction of ions is incompatible with all forms of inter-ion potential (Tosi 1964).

Baur's scheme may be used to test a structure for the most likely coordination number; Table 11 shows the observed and calculated bond lengths for the tetrahedral sites in cummingtonite (Cumm), grunerite (Grun) and C-Mn cummingtonite (C-Mn), calculated by the methods outlined by Baur (1971) for [4]-, [6]- and [8]-fold coordination of the $M(4)$ site. The results are rather ambiguous; for C-Mn cummingtonite, a [6]- or [8]-fold coordination is indicated, whereas the grunerite results indicate a [4]-fold coordination; the cummingtonite results show no preference. A similar analysis was made with the bond-strength scheme of Brown & Shannon (1973). Table 12 shows the bond-strength sums around O(5) and O(6) in the cummingtonites for different coordination numbers of $M(4)$. In all cases, the deviations from the ideal value of 2 are least for [8]-fold coordination of $M(4)$. However, inspection of the complete bond-strength tables for the non-aluminous clinoamphiboles (Hawthorne 1973) shows that the best anion sums occur around O(5) and O(6); comparison of the deviations for [4]- and [6]-fold coordination of $M(4)$ with other anion deviations (where the nature of the coordination is not in question) shows them to be of the same order. Hence it is questionable whether significance can be attached to this result.

If the interaction between $M(4)$ and the chain-bridging anions is so weak that a unique coordination number for $M(4)$ cannot be defined in the cummingtonite, the question arises as to whether or not this interaction (if present) can be of any significance in the crystal chemistry of these minerals. There are several factors, unconnected with any theories of chemical bonding, that are pertinent to this question. Ross *et al.* (1968, 1969) and Papike *et al.* (1969) have shown that when significant amounts of Mg occur in the $M(4)$ site in cummingtonite, the structure assumes the space group $P2_1/m$ rather than the $C2/m$ symmetry that is characteristic of more

*There is a misprint in Table 4, page 1021 of this reference; the quoted Fe^{2+} occupancy of $M(2)$ in the unit formula of Mn cummingtonite should read 0.57 NOT 0.07.

TABLE 11. BOND LENGTH CALCULATIONS FOR THE CUMMINGTONITES*

M(4) Coordination		[4]-Coordinate			[6]-Coordinate			[8]-Coordinate		
		Cumm [†]	Grun	C-Mn	Cumm	Grun	C-Mn	Cumm	Grun	C-Mn
T(1)-0(1)	OBS.	1.619	1.637(4)	1.610(3)	1.619	1.637(4)	1.610(3)	1.619	1.637(4)	1.610(3)
	METHOD 1	1.616	1.616	1.616	1.611	1.611	1.611	1.611	1.611	1.611
	METHOD 2	1.619	1.627	1.620	1.611	1.619	1.612	1.608	1.616	1.609
T(1)-0(5)	OBS.	1.614	1.627(5)	1.622(4)	1.614	1.627(5)	1.622(4)	1.614	1.627(5)	1.622(4)
	METHOD 1	1.616	1.616	1.616	1.611	1.611	1.611	1.633	1.633	1.633
	METHOD 2	1.619	1.627	1.620	1.611	1.619	1.612	1.630	1.638	1.631
T(1)-0(6)	OBS.	1.628	1.630(4)	1.633(3)	1.628	1.630(4)	1.633(3)	1.628	1.630(4)	1.633(3)
	METHOD 1	1.616	1.616	1.616	1.641	1.641	1.641	1.633	1.633	1.633
	METHOD 2	1.619	1.627	1.620	1.641	1.649	1.642	1.630	1.638	1.631
T(1)-0(7)	OBS.	1.613	1.613(2)	1.616(2)	1.613	1.613(2)	1.616(2)	1.613	1.613(2)	1.616(2)
	METHOD 1	1.616	1.616	1.616	1.611	1.611	1.611	1.611	1.611	1.611
	METHOD 2	1.619	1.627	1.620	1.611	1.619	1.612	1.608	1.616	1.609
T(2)-0(2)	OBS.	1.625	1.633(4)	1.618(3)	1.625	1.633(4)	1.618(3)	1.625	1.633(4)	1.618(3)
	METHOD 1	1.634	1.634	1.634	1.622	1.622	1.622	1.623	1.623	1.623
	METHOD 2	1.644	1.637	1.640	1.629	1.622	1.625	1.627	1.620	1.623
T(2)-0(4)	OBS.	1.609	1.604(4)	1.595(3)	1.609	1.604(4)	1.595(3)	1.609	1.604(4)	1.595(3)
	METHOD 1	1.604	1.604	1.604	1.592	1.592	1.592	1.585	1.585	1.585
	METHOD 2	1.614	1.614	1.610	1.599	1.592	1.595	1.589	1.582	1.585
T(2)-0(5)	OBS.	1.639	1.611(5)	1.634(3)	1.639	1.611(5)	1.634(3)	1.639	1.611(5)	1.634(3)
	METHOD 1	1.619	1.619	1.619	1.622	1.622	1.622	1.646	1.646	1.646
	METHOD 2	1.629	1.622	1.625	1.629	1.622	1.625	1.650	1.643	1.646
T(2)-0(6)	OBS.	1.643	1.638(5)	1.655(4)	1.643	1.638(5)	1.655(4)	1.643	1.638(5)	1.655(4)
	METHOD 1	1.619	1.619	1.619	1.653	1.653	1.653	1.646	1.646	1.646
	METHOD 2	1.629	1.622	1.625	1.660	1.653	1.656	1.650	1.643	1.646
$\langle \Delta \rangle_1$		0.010	0.010	0.013	0.009	0.013	0.006	0.009	0.014	0.007
$\langle \Delta \rangle_2$		0.009	0.009	0.013	0.008	0.012	0.005	0.009	0.014	0.007

*Calculated using the methods of Baur (1971); **Method 1 uses the value of $\langle d(\text{Si-O}) \rangle$ calculated from the equation: $\langle d(\text{Si-O}) \rangle = 1.584 + 0.0127 \langle \text{C.N.} \rangle$. Method 2 uses the observed mean bond lengths.

[†]Bond lengths taken from Mitchell et al. (1971).

Fe-rich cummingtonites, and this has since been confirmed by Kisch (1969) and Rice *et al.* (1974). Papike *et al.* (1969) showed that in the $P2_1/m$ structure, the tetrahedral chains distort independently, producing a change in the attitude of the chain-bridging anions adjacent to the $M(4)$ site; they suggest that this change occurs "in order to provide the necessary coordination for the joint Ca/Mg occupancy" of $M(4)$. If this inference is correct, it indicates an interaction between $M(4)$ and the chain-bridging anions. At extremely magnesian compositions, the ferromagnesian amphiboles crystallize with the anthophyllite structure. The change in the double-chain configurations (Finger 1970), when compared to that in C -centred cummingtonite, is accompanied by major changes in the anion arrangement around the $M(4)$ site; a comparison of the relevant interatomic distances is given in Table 13. It is difficult to explain the occurrence of these three different structure types with very similar chemical compositions if the $M(4)$ site in C -centred cummingtonite is considered as [4]-coordinate, as the major structural differences between these structures involve the configuration of the chain-bridging anions in the vicinity of the $M(4)$ site. On the other hand, the relationships among these three structures may be adequately rationalized if $M(4)$ is con-

TABLE 12. BOND STRENGTHS AROUND 0(5) AND 0(6) IN THE CUMMINGTONITES.

M(4) Coordination		UNCORRECTED		CORRECTED FOR ANION COORD.	
		0(5)	0(6)	0(5)	0(6)
CUMM	4	1.980	1.894	1.899	1.855
	6	1.980	2.020	1.899	2.015
	8	2.030	2.020	1.996	2.015
GRUN	4	2.034	1.951	1.932	1.862
	6	2.034	2.038	1.932	2.004
	8	2.066	2.038	2.021	2.004
C-Mn	4	1.984	1.899	1.890	1.818
	6	1.984	2.033	1.890	1.999
	8	2.033	2.033	1.991	1.999
Zn	4	1.972	1.903	1.868	1.818
	6	1.972	2.029	1.868	1.991
	8	2.021	2.029	1.979	1.991

* calculated from the curves of Brown & Shannon (1973); bond strengths in valence units (v.u.).

TABLE 13. INTERATOMIC DISTANCES ($\text{\AA}$) AROUND M(4) IN THE FERROMAGNESIAN AMPHIBOLES.

	$C2/m^*$	$P2_1/m^*$	$Pnma^{**}$	
M(4)-0(2)	2.204(3)	2.195(6)	2.208(6)	2.156(3)
-0(4)	2.109(4)	2.139(8)	2.074(8)	2.044(3)
-0(5)	3.101(3)	3.209(6)	2.932(6)	3.481(3)
-0(6)	2.592(4)	2.511(8)	2.650(8)	2.387(3)

* Papike *et al.* (1969); ** Finger (1970).

sidered as bonding to the chain-bridging anion(s). The anion rearrangements about $M(4)$ that accompany the changes in space group occur as a result of the different bonding requirements of the $M(4)$ cation(s) as the amount of Mg at this site increases. Although this suggests that the coordination of the $M(4)$ site is not [4], it does not indicate whether [6]- or [8]-fold coordination is more realistic.

Another approach to this problem concerns the Mössbauer parameters for Fe^{2+} in the $M(4)$ site. The isomer shift is sensitive to the coordination of the cation, and should give an indication of the $M(4)$ coordination number. Comparison of the values obtained for Fe^{2+} in the $M(4)$ sites of cummingtonite with those obtained for other ferromagnesian silicates suggests that the $M(4)$ site should be considered as [6]-coordinate. The isomer shift is slightly less than that exhibited by Fe^{2+} in regular and slightly distorted octahedra; this could reflect the extremely distorted nature of the $M(4)$ polyhedron when considered as an octahedron, as the bonding will become more covalent as the bond length variation increases (see previous section). However, this does not negate the possibility of $M(4)$ being [8]-coordinate. Although the observed isomer shift of Fe^{2+} in $M(4)$ in cummingtonite is much less than that normally encountered in [8]-fold coordination, the extreme bond-length distortion could lead to a considerable decrease in the isomer shift. As this effect is not very well characterized, this possibility cannot be dismissed.

Despite the fact that bond-strength arguments do not yield a decision among the coordinations [4], [6] and [8] for the $M(4)$ site, the above discussion suggests that a [4]-fold coordination for $M(4)$ is not valid, and that $M(4)$ does bond to the chain-bridging anions. The evidence marginally favors [6]-fold over [8]-fold coordination, although it is certainly not conclusive.

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