

## A THREE-AMPHIBOLE ASSEMBLAGE FROM THE TALLAN LAKE SILL, PETERBOROUGH COUNTY, ONTARIO

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### ABSTRACT

The three-amphibole assemblage gedrite-cummingtonite-hornblende occurs in an amphibolite sequence at the margin of the Tallan Lake sill, Peterborough County, Ontario. Mutual contacts, coarse, oriented intergrowths and mutual exsolution suggest a stable equilibrium association. Electron-microprobe analyses and calculation on the basis of 23 oxygens *per* formula unit using a  $Fe^{3+}/(Fe^{2+} + Fe^{3+})$  ratio of 0.15 gave the following compositions: gedrite ( $K_{0.009} Na_{0.441} (Na_{0.133} Ca_{0.122} Mg_{3.312} Mn_{0.061} Fe^{2+}_{2.119} Fe^{3+}_{0.374} Ti_{0.064} Al_{0.815}) (Si_{6.366} Al_{1.634}) O_{22} (OH,F)_2$ ; cummingtonite, ( $K_{0.002} Na_{0.013} (Na_{0.013} Ca_{0.123} Mg_{4.247} Mn_{0.056} Fe^{2+}_{2.329} Fe^{3+}_{0.166} Ti_{0.015} Al_{0.051}) (Si_{7.751} Al_{0.249}) O_{22} (OH,F)_2$ ; hornblende, ( $K_{0.022} Na_{0.457} (Na_{0.134} Ca_{1.422} Mg_{2.676} Mn_{0.036} Fe^{2+}_{1.535} Fe^{3+}_{0.271} Ti_{0.086} Al_{0.840}) (Si_{6.372} Al_{1.628}) O_{22} (OH, F)_2$ . Cell dimensions, measured on a single-crystal diffractometer and by precession photography, are: for gedrite,  $a$  18.696(5),  $b$  17.913(4),  $c$  5.278(2) Å; for cummingtonite,  $a$  9.51,  $b$  18.12,  $c$  5.32 Å,  $\beta$  101.9°; for hornblende,  $a$  9.832(3),  $b$  18.037(5),  $c$  5.302(1) Å,  $\beta$  105.01(2)°. Single-crystal photographs of gedrite show split reflections indicative of unmixing into an intimate intergrowth of gedrite and anthophyllite. Basal thin sections of gedrite show fine lamellae of anthophyllite parallel to (010) and (230). Three-dimensional counter-collected single-crystal X-ray data and a full-matrix least-squares method were used to refine the crystal structure and cation-ordering pattern of the calcic amphibole phase. The final  $R$  index for 1098 observed reflections is 4.8%. Comparison of mean bond lengths and constituent ionic radii, the  $A$ -site cation occupancy and  $R$ -index criteria suggest an  $Fe^{3+}/(Fe^{2+} + Fe^{3+})$  ratio of  $\sim 0.15$  for the calcic amphibole phase, showing it to be a tschermakitic hornblende. This value was used to calculate the cell contents for the gedrite and hornblende given above; the calculated cell contents are supported by the fact that the  $Mg/(Mg + Fe^{2+} + Mn)$  ratios in all

three phases are very similar ( $\sim 0.63$ ). Considerable  $Fe^{2+}$  occurs at the  $M(4)$  site in the tschermakitic hornblende, indicative of a considerable cummingtonite component in solid solution.

**Keywords:** coexisting amphiboles, crystal-structure refinement, cell dimensions, site populations, tschermakitic hornblende, Tallan Lake sill, Ontario.

### SOMMAIRE

Les trois amphiboles gédrite-cummingtonite-hornblende se trouvent réunies dans une suite amphibolitique en bordure du filon-couche du lac Tallan, dans le comté de Peterborough (Ontario). Leurs contacts mutuels, intercroissances orientées et exsolutions mutuelles indiquent un assemblage en équilibre stable. L'analyse à la microsonde, recalculée pour 23 oxygènes et pour un rapport  $Fe^{3+}/(Fe^{2+} + Fe^{3+})$  de 0.15, donne les formules suivantes: gédrite, ( $K_{0.009} Na_{0.441} (Na_{0.133} Ca_{0.122} Mg_{3.312} Mn_{0.061} Fe^{2+}_{2.119} Fe^{3+}_{0.374} Ti_{0.064} Al_{0.815}) (Si_{6.366} Al_{1.634}) O_{22} (OH,F)_2$ ; cummingtonite, ( $K_{0.002} Na_{0.013} (Na_{0.013} Ca_{0.123} Mg_{4.247} Mn_{0.056} Fe^{2+}_{2.329} Fe^{3+}_{0.166} Ti_{0.015} Al_{0.051}) (Si_{7.751} Al_{0.249}) O_{22} (OH,F)_2$ ; hornblende, ( $K_{0.022} Na_{0.457} (Na_{0.134} Ca_{1.422} Mg_{2.676} Mn_{0.036} Fe^{2+}_{1.535} Fe^{3+}_{0.271} Ti_{0.086} Al_{0.840}) (Si_{6.372} Al_{1.628}) O_{22} (OH,F)_2$ . Les dimensions de la maille ont été mesurées sur diffractomètre à cristal unique et par clichés de précession: gédrite  $a$  18.696(5),  $b$  17.913(4),  $c$  5.278(2) Å; cummingtonite  $a$  9.51,  $b$  18.12,  $c$  5.32 Å,  $\beta$  101.9°; hornblende  $a$  9.832(3),  $b$  18.037(5),  $c$  5.302(1) Å,  $\beta$  105.01(2)°. En précession, la gédrite montre des réflexions dédoublées, indication d'une démixtion en gédrite et anthophyllite intimement mélangées; les lames minces de gédrite taillées suivant (001) montrent de fines lamelles d'anthophyllite parallèles à (010) et (230). Les données tridimensionnelles obtenues sur diffractomètre à compteur et traitées par la méthode des moindres carrés à matrice entière, ont servi à l'affinement de la structure et de la mise en ordre des cations dans l'amphibole calcique. Le résidu  $R$  pour les 1098 réflexions observées atteint 4.8%. D'après (1) une comparaison des longueurs moyennes de liaison et des rayons ioniques appropriés, (2) l'occupation de la position cationique  $A$  et (3)

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les trois amphiboles. La forte proportion de  $\text{Fe}^{2+}$  serait d'environ 0.15 dans cette amphibole, qui serait donc une hornblende tschermakitique. L'hypothèse que le même rapport s'applique à la gédrite et à la hornblende est étayée par les rapports très semblables ( $\sim 0.63$ )  $\text{Mg}/(\text{Mg} + \text{Fe}^{2+} + \text{Mn})$  dans les trois amphiboles. La forte proportion de  $\text{Fe}^{2+}$  en  $M(4)$  indique l'importance du pôle cummingtonite dans la solution solide qu'est la hornblende tschermakitique.

(Traduit par la Rédaction)

**Mots-clés:** amphiboles coexistantes, affinement de la structure cristalline, dimensions de la maille, mise en ordre des cations, hornblende tschermakitique, filon-couche du lac Tallan, Ontario.

### INTRODUCTION

There has recently been considerable interest in the occurrence and composition of coexisting amphiboles that appear to form equilibrium assemblages in metamorphic rocks. A large number of different coexisting amphibole pairs has been reported, by far the most common being various combinations of anthophyllite, gedrite,

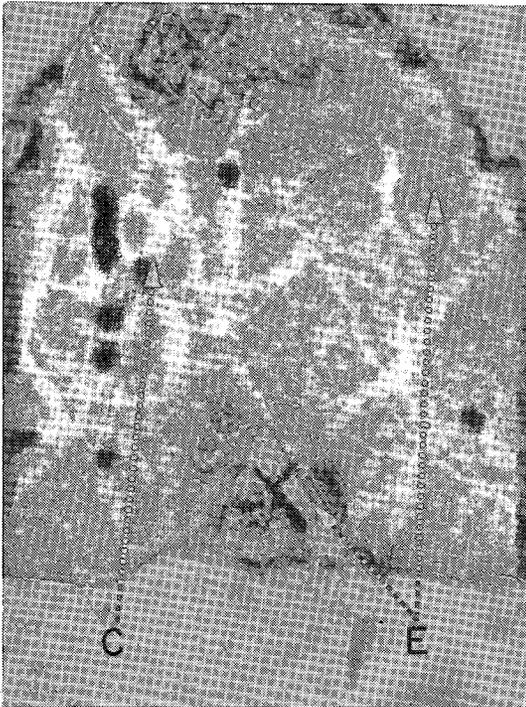


FIG. 1. Basal section of gedrite crystal with characteristic (210) cleavage (C) and patchy development of exsolution lamellae (E) of anthophyllite parallel to (010) and (120).

cummingtonite and hornblende (Klein 1968). Although a considerable body of data is available on coexisting pairs of these amphiboles, three- and four-phase combinations are far less common. Milton (1961) described an assemblage containing cummingtonite-gedrite-hornblende, and Robinson *et al.* (1969) reported an assemblage including cummingtonite, anthophyllite and hornblende in the sillimanite-orthoclase zone of the Ordovician in the Windsor Dam Quadrangle, Massachusetts. The remaining combinations cummingtonite-anthophyllite-gedrite, anthophyllite-gedrite-hornblende and cummingtonite-anthophyllite-gedrite-hornblende have been reported by Stout (1970, 1971, 1972) from the amphibolite-facies Precambrian basement rocks of the Telemark area, Norway. Detailed chemical and crystallographic data are available for all combinations except cummingtonite-gedrite-hornblende. Another occurrence of this assemblage was found in amphibolite-facies rocks in Chandos Township, Ontario, and a detailed account is given here.

The Tallan Lake sill (Shaw 1962) is an extensive stratiform body of amphibolite of apparently igneous derivation (Shaw & Kudo 1965, Griep 1975) occurring in Chandos and Anstruther townships, Peterborough County, Ontario. The specimen described here was collected from the marginal part of the sill where it outcrops in a roadcut on Highway 28.

### PETROGRAPHY

The three-amphibole assemblage (specimen 1317) is found at the margin of the sill where it is in contact with a 20-metre-thick sequence of feather amphibolites. At the margin of these two bodies, the following succession of assemblages is observed: (1217): plagioclase ( $\text{An}_{18}$ ) - quartz - hornblende - cummingtonite - ilmenite - biotite - calcite; (1317): plagioclase ( $\text{An}_{20-22}$ ) - hornblende - cummingtonite - gedrite - ilmenite - biotite; (1417): plagioclase ( $\text{An}_{21-26}$ ) - hornblende - gedrite - ilmenite - biotite; (1517): plagioclase ( $\text{An}_{19-28}$ ) - hornblende - ilmenite.

A dramatic decrease in the size of the amphiboles is apparent towards the contact; from  $> 3$  mm in specimen 1217, the amphibole grain size is reduced to  $< 0.4$  mm in 1517. This change from a normal porphyroblastic feather amphibolite to a dense hornfels occurs within a 5-metre zone encompassing the contact.

In thin section (specimen 1317), the three amphiboles are easily distinguished on the basis of their optical properties. Cummingtonite is

colorless and typically shows exsolution lamellae of a second phase parallel to (101). Gedrite is pleochroic (X tan, Y pale grey, Z medium grey), and is also easily recognizable by its straight extinction. Basal sections of gedrite show fine exsolution lamellae. In some cases, these are parallel to (010), as noted by Robinson *et al.* (1971), and (120), as noted by Gittos *et al.* (1976); lamellae also form rather irregular wormy intergrowths, as illustrated in Figure 1. Hornblende is pleochroic (X tan, Y olive green, Z bluish green) and typically shows colorless exsolution lamellae parallel to (101). Intercrystalline contacts among all phases are sharp and well defined. Two-phase contacts for all combinations of phases present in the assemblage are common. Although less common, three-amphibole contacts and three-amphibole grains do occur, suggesting on the basis of texture alone that the phases do constitute an equilibrium assemblage. Exsolution lamellae are far more numerous in hornblende than in cum-

TABLE 1. ELECTRON-MICROPROBE ANALYSES OF COEXISTING AMPHIBOLES CUMMINGTONITE-GEDRITE-HORNBLLENDE AND ANALYSIS OF WHOLE ROCK 1317

	Cummingtonite	Gedrite	Hornblende	1317	Av. Spilitite <sup>1</sup>	
SiO <sub>2</sub>	53.88	43.46	43.89	SiO <sub>2</sub>	47.90	49.65
Al <sub>2</sub> O <sub>3</sub>	1.77	14.18	14.42	TiO <sub>2</sub>	1.68	1.57
TiO <sub>2</sub>	0.14	0.58	0.79	Al <sub>2</sub> O <sub>3</sub>	15.18	16.00
FeO <sup>2</sup>	20.74	20.35	14.87	Fe <sub>2</sub> O <sub>3</sub>	3.94	3.85
MnO	0.46	0.49	0.29	FeO <sup>3</sup>	8.80	6.08
MgO	19.81	15.17	12.37	MgO	9.20	5.10
CaO	0.80	0.78	9.14	MnO	0.20	0.15
K <sub>2</sub> O	0.01	0.05	0.12	CaO	6.08	6.62
Na <sub>2</sub> O	0.09	2.02	2.10	Na <sub>2</sub> O	4.52	4.29
	<u>97.72</u>	<u>97.07</u>	<u>97.99</u>	K <sub>2</sub> O	0.08	1.28
				H <sub>2</sub> O	1.60	3.49
				P <sub>2</sub> O <sub>5</sub>	0.29	0.26
					<u>99.60</u>	<u>98.34</u>

<sup>1</sup>Vallance (1960)

mingtonite, suggesting that the cummingtonite limb of the solvus is far steeper than the hornblende limb.

EXPERIMENTAL

Mineral analyses were carried out on an

TABLE 2. UNIT-CELL DATA FOR THREE COEXISTING AMPHIBOLES

	Hornblende				Gedrite				Cummingtonite		
	Min. <sup>1</sup>	Max. <sup>1</sup>	Int. <sup>1</sup>	Best <sup>2</sup>	Min.	Max.	Int.	Best	Min.	Max.	Int.
FeO	14.87	1.10	7.99	12.64	20.35	6.25	13.31	17.30	19.68	19.03	19.36
Fe <sub>2</sub> O <sub>3</sub>	0.00	15.31	7.65	2.48	0.00	15.66	7.83	3.39	1.17	1.90	1.54
Si	6.410	6.184	6.295	6.372	6.418	6.184	6.299	6.366	7.757	7.744	7.751
Al	1.590	1.816	1.705	1.628	1.582	1.816	1.701	1.634	0.243	0.256	0.249
Σ IV	<u>8.000</u>	<u>8.000</u>	<u>8.000</u>	<u>8.000</u>	<u>8.000</u>	<u>8.000</u>	<u>8.000</u>	<u>8.000</u>	<u>8.000</u>	<u>8.000</u>	<u>8.000</u>
Al	0.892	0.579	0.733	0.840	0.887	0.563	0.722	0.815	0.058	0.044	0.051
Ti	0.087	0.084	0.085	0.086	0.064	0.062	0.063	0.064	0.015	0.015	0.015
Mg	2.692	2.597	2.644	2.676	3.339	3.217	3.277	3.312	4.251	4.243	4.247
Mn	0.036	0.035	0.035	0.036	0.061	0.059	0.060	0.061	0.056	0.056	0.056
Fe <sup>2+</sup>	1.816	0.129	0.958	1.535	2.513	0.744	1.613	2.119	2.370	2.288	2.329
Fe <sup>3+</sup>	-	1.623	0.826	0.271	-	1.677	0.854	0.374	0.127	0.205	0.166
Σ VI	<u>5.523</u>	<u>5.046</u>	<u>5.281</u>	<u>5.444</u>	-	-	-	-	-	-	-
Σ VI-5	0.523	0.046	0.281	0.444	-	-	-	-	-	-	-
Ca	1.430	1.380	1.405	1.422	0.123	0.119	0.121	0.122	0.123	0.123	0.123
Na	0.046	0.574	0.315	0.134	0.011	0.557	0.289	0.133	-	0.025	0.013
Σ M(4)	<u>2.000</u>	<u>2.000</u>	<u>2.000</u>	<u>2.000</u>	<u>7.000</u>	<u>7.000</u>	<u>7.000</u>	<u>7.000</u>	<u>7.000</u>	<u>7.000</u>	<u>7.000</u>
Na	0.548	-	0.269	0.457	0.567	-	0.278	0.441	0.025	-	0.013
K	0.022	0.022	0.022	0.022	0.009	0.009	0.009	0.009	0.002	0.002	0.002
Σ A	<u>0.570</u>	<u>0.022</u>	<u>0.291</u>	<u>0.479</u>	<u>0.577</u>	<u>0.009</u>	<u>0.288</u>	<u>0.450</u>	<u>0.027</u>	<u>0.002</u>	<u>0.015</u>
Fe <sup>3+</sup>	0.00	0.93	0.46	0.15	0.00	0.69	0.35	0.15	0.00	0.08	0.04
Fe <sup>2+</sup> +Fe <sup>3+</sup>											
Mg	0.59	0.94	0.73	0.63	0.56	0.80	0.66	0.61	0.64	0.64	0.64
Mg+Fe <sup>2+</sup> +Mn											
a (Å)		9.832(3)				18.696(5)				9.51	
b (Å)		18.037(5)				17.913(4)				18.12	
c (Å)		5.302(1)				5.278(2)				5.32	
β (°)		105.01(2)				90				101.9	
V (Å <sup>3</sup> )		908.2				1767.6				897	
Sp. Group		C2/m				Prma				C2/m	

<sup>1</sup>calculated using the method of Papike *et al.* (1974); <sup>2</sup>calculated using the Fe<sup>3+</sup>/Fe<sup>2+</sup>+Fe<sup>3+</sup> ratio derived from the crystal structure refinement.

ARL-EMK electron microprobe; an accelerating potential of 15 kV was used with a sample current of 0.04  $\mu$ A, following the method outlined by Rucklidge *et al.* (1970). Synthetic standards were used for all elements except Ti and Na, for which aenigmatite and sodic amphibole R2088 (Rucklidge *et al.* 1971) were used. Data reduction was performed with the program EMPADR (Rucklidge & Gasparrini 1969). The resultant analyses are given in Table 1 together with the whole-rock analysis. Cell contents were calculated on a basis of 23 oxygens, following the method of Papike *et al.* (1974), to provide an initial estimate of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  in each amphibole; the results are given in Table 2, where they can be compared with the final values calculated using the  $\text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$  ratio of 0.15 derived from the crystal-structure refinement. Robinson *et al.* (1971) have shown that the amount of tetrahedrally coordinated Al is strongly correlated with the monovalent cation *A*-site occupancy in amphiboles of the anthophyllite-gedrite series and the actinolite-"hornblende" series. The "Int" (intermediate) cell-content values for gedrite and hornblende shown in Table 2 deviate significantly from these relationships in that they have insufficient *A*-site Na for their calculated  $\text{Al}^{\text{IV}}$  content. Conversely, the "Best" cell-content values agree very well with the trends shown in Robinson *et al.* (1971), giving further support for the structure-refinement results.

Cell dimensions of hornblende and gedrite were determined from 15 reflections aligned automatically on a 4-circle diffractometer using Mo  $K\alpha$  radiation. Cell dimensions of cumingtonite were derived from precession photographs of multiple grains, using the refined hornblende cell parameters as internal standards. Cell dimensions are given in Table 2. The epitactic relationships are surprisingly coincident in multiple grains. X-ray-precession photographs of three-amphibole grains show virtually identical structural alignment in each phase, the fainter reciprocal lattice nets being due to the exsolved phases. Careful examination of high-angle  $0k0$  reflections of gedrite revealed a splitting of the reflections that is characteristic of unmixing into a microscopic or sub-microscopic intergrowth of anthophyllite and gedrite (Robinson *et al.* 1969, Robinson & Jaffe 1969, Röss *et al.* 1969, Christie & Olsen 1974). No splitting was discernible along  $h00$  or  $00l$ , and consequently the anthophyllite (the minor phase) has *a* and *c* dimensions identical with those of gedrite (Table 2) but a *b* dimension of

18.05 Å, approximately 1% longer than in gedrite.

Single-crystal-precession photographs of the calcic amphibole displayed diffraction symmetry  $2/mC-/-$ , consistent with the space group  $C2/m$ , which was adopted and found to be adequate during the subsequent structure-refinement. Numerous crystals were examined, and all showed the presence of a second exsolved phase. The crystal chosen for the collection of single-crystal intensity data was a cleavage fragment with dimensions 0.04 x 0.06 x 0.11 mm. Comparison of the relative intensities of the two diffraction patterns apparent in the  $h0l$  photograph indicated that the amount of the exsolved phase was  $\sim 2\%$ . This crystal was mounted on a Syntex P1 automatic four-circle diffractometer; intensity data were collected according to the experimental procedure of Hawthorne & Ferguson (1975). Two standard reflections were monitored every 50 reflections; no significant change in their intensities was observed during data collection. A total of 1557 reflections were measured over one asymmetric unit out to  $2\theta = 65^\circ$ . The data were corrected for absorption (for polyhedral crystal-shape), Lorentz, polarization and background effects. A reflection was considered as observed if its intensity exceeded that of three standard deviations based on counting statistics. Application of this criterion resulted in 1098 observed reflections.

#### STRUCTURE REFINEMENT

Scattering curves for neutral atoms were taken from Cromer & Mann (1968) together with anomalous dispersion coefficients from Cromer & Liberman (1970). The final coordinates and equivalent isotropic temperature factors of ferrotschermakite (Hawthorne & Grundy 1973a) were used as initial input to the least-squares program RFINE (Finger 1969a). The five distinct scattering species at the octahedral sites were initially represented by the two species  $\text{Mg}^*$  ( $=\text{Mg}+\text{Al}$ ) and  $\text{Fe}^*$  ( $=\text{Fe}+\text{Mn}+\text{Ti}$ ), which were assumed to be completely disordered over the  $M(1)$ ,  $M(2)$ ,  $M(3)$  and part of the  $M(4)$  sites. The amount of  $\text{Fe}^*$  in the formula unit was used as a linear constraint in the refinement procedure (Finger 1969b). The site chemistry initially assigned in the refinement represented the unit formula calculated assuming the intermediate  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio (Table 2). Several cycles of full-matrix refinement, gradually increasing the number of variables, resulted in convergence at an *R* fac-

tor of 7.0% for an isotropic thermal model. Several features of the refinement were not considered satisfactory at this stage: (1) The  $\text{Fe}^{3+}$  content of the cell greatly exceeded the  $\text{Fe}^*$  content of the  $M(2)$  site (0.826 versus 0.426 atoms per formula unit), whereas the  $\langle M(1)-O \rangle$  and  $\langle M(3)-O \rangle$  bond lengths did not indicate any significant occupancy of these sites by  $\text{Fe}^{3+}$ . (2) The  $A$ -site temperature factor of  $3.3 \text{ \AA}^2$  is significantly less than that generally encountered in amphiboles (Hawthorne & Grundy 1972, 1973a, b, 1978, Papike *et al.* 1969), suggesting that the  $A$ -site occupancy assigned was too small.

Both the total  $\text{Fe}^{3+}$  content and the  $A$ -site Na content derived from the cell-content calculation are a function of the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratio, which suggested that the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio was not correct. In an attempt to estimate a realistic  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio, the refinement was repeated for a variety of  $\text{Fe}_2\text{O}_3/(\text{FeO} + \text{Fe}_2\text{O}_3)$  values; pertinent parameters from these refinements are presented in Table 3. Inspection of Table 3 suggests that the intermediate formula of Table 2 overestimated the amount of  $\text{Fe}^{3+}$  in the unit formula. The  $R$  and  $R_w$  factors are lowest for  $\text{Fe}_2\text{O}_3/(\text{FeO} + \text{Fe}_2\text{O}_3) = 0$ , but the  $A$ -site temperature factor of 7.0(6)  $\text{\AA}^2$  is slightly larger than that usually encountered in amphiboles (5.5–6.0  $\text{\AA}^2$ ). An  $\text{Fe}^{3+}/\text{Fe}^{2+} + \text{Fe}^{3+}$  value of 0.15 was used to proceed further; refinement for an isotropic thermal model with the  $A$ -site cations occupying the  $A(2/m)$  position converged to  $R$  and  $R_w$  factors of 6.7 and 6.6%, respectively. At this stage, difference-Fourier sections through the  $A$  site were calculated with the  $A$ -site cations removed from the refinement (Fig. 2). In the (100) section, the maximum density occurs in the 4g position [ $A(2)$  site: Hawthorne & Grundy 1978], whereas in the (010) section the electron density is strongly elongate approximately in the (102) direction. A section through the  $A$  site in the direction of elongation shows that the maximum density is actually confined to the 4g position and is not in the 8j position, a fact that is not apparent from the (100) section. Figure 2 thus indicates that the  $A$ -site cations are strongly ordered in the  $A(2)$  site with slight occupancy of the  $A(m)$  site; alternatively, if the cations occupy the  $A(1)$  site (8j position) the displacement from the  $A(2)$  site (4g position) must be very small. Using starting positional parameters taken from the refinement of potassic ferritaramite (Hawthorne & Grundy 1978), full-matrix least-squares refinement of all variables resulted in convergence at  $R$  and

TABLE 3. SELECTED PARAMETERS FROM ISOTROPIC REFINEMENTS OF AMPHIBOLE WITH THE CELL CONTENTS CALCULATED FOR THE  $\text{Fe}_2\text{O}_3/(\text{FeO} + \text{Fe}_2\text{O}_3)$  RATIOS GIVEN

	$\frac{\text{Fe}_2\text{O}_3}{\text{FeO} + \text{Fe}_2\text{O}_3}$	0.00	0.10	0.20	0.30	0.40	0.50
$A1^{IV}$		0.398	0.404	0.410	0.416	0.423	0.429
$Na^A$		0.583	0.522	0.461	0.402	0.340	0.283
$B^A$		7.0(6)	6.2(6)	5.5(6)	4.7(6)	4.0(6)	3.2(6)
$Fe^M(4)$		0.165	0.164	0.163	0.163	0.162	0.162
$Mg^M(4)$		0.097	0.071	0.045	0.020	-0.006	-0.031
$A1^M(2)$		0.446	0.429	0.411	0.395	0.377	0.361
$T1^M(2)$		0.044	0.043	0.043	0.043	0.042	0.042
$Fe^*M(2)$		0.211	0.212	0.212	0.212	0.213	0.213
$Mg^M(2)$		0.299	0.316	0.334	0.350	0.368	0.384
$Fe^p.f.u.$		0.000	0.181	0.360	0.539	0.715	0.891
$Fe^*M(2)$		0.646	0.637	0.628	0.627	0.630	0.633
$R(\%)$		6.659	6.696	6.745	6.808	6.888	6.975
$R_w(\%)$		6.605	6.642	6.696	6.765	6.858	6.966
$\langle T-O \rangle$		1.653 $\text{\AA}$				$\langle M(1)-O \rangle = 2.093$	
$\langle M(2)-O \rangle$		2.030 $\text{\AA}$				$\langle M(3)-O \rangle = 2.085\text{\AA}$	

\* cation radius calculated assuming all  $\text{Fe}^{3+}$  is in  $M(2)$  except when  $\text{Fe}^*M(2) < \text{Fe}^{3+}/2$ .

$R_w$  indices of 6.3 and 6.3%, respectively. Although this reduction is significant at the 0.005 level (Hamilton 1965), one unsatisfactory aspect of the refinement was that both the  $A(2)$ - and  $A(m)$ -site temperature-factors became negative. This indicated that the total  $A$ -site cation-occupancy was still not correct; by inference, neither was the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio. As a temporary measure, the  $A(2)$ - and  $A(m)$ -site temperature-factors were set equal to  $1.3 \text{ \AA}^2$  and kept constant while the site occupancies of both sites were varied, together with all other variables, until convergence occurred at  $R$  and  $R_w$  indices of 6.1 and 6.1%, respectively. The  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio corresponding to the current total  $A$ -site chemistry was calculated, the formula unit of the amphibole was recalculated, and the relevant minor changes in site occupancies were made. Temperature factors were converted to an anisotropic form as given in Table 4, and full-matrix least-squares refinement of all variables resulted in convergence at  $R$  and  $R_w$  indices of 4.9 and 5.1%, respectively. At this stage, the isotropic temperature factors of the  $A(2)$  and  $A(m)$  sites were fixed at a series of values between 1.0 and  $3.0 \text{ \AA}^2$ , and all other variables were refined to convergence. The be-

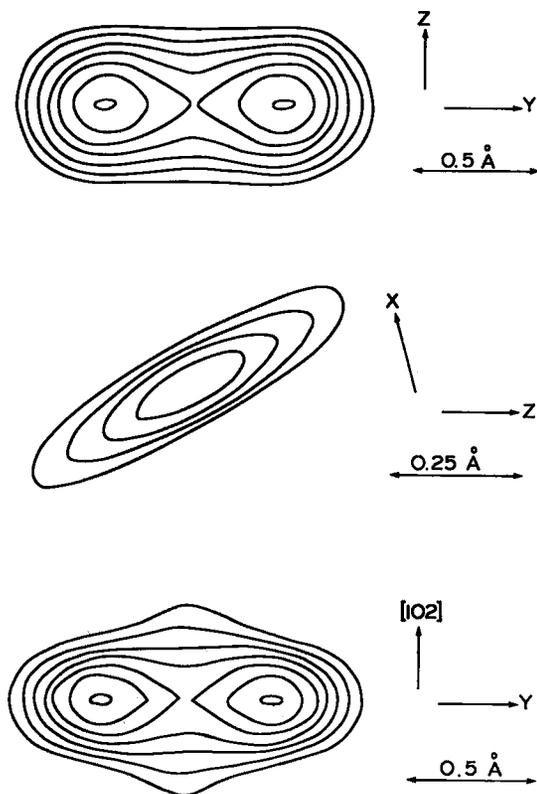


FIG. 2. Difference-Fourier sections through the *A* position in hornblende, calculated with the *A*-site cations removed from the refinement.

havior of the *R* index with the magnitude of the *A*-site temperature-factors is shown in Figure 3, which shows a minimum at 2.1 Å<sup>2</sup>. This corresponds to a total *A*-site occupancy of 0.73 Na\* (≡ Na + 1.8K); this occupancy is larger than the maximum (0.58Na\*) allowed by the chemical analysis, suggesting that the chemical analysis has slightly underestimated the amount of Na<sub>2</sub>O. Final atomic parameters

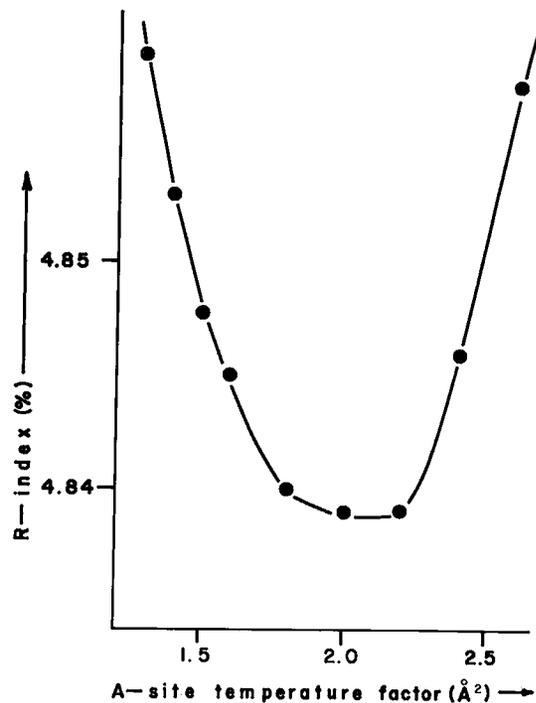


FIG. 3. Variation in *R* index with *A*-site cation isotropic temperature factor.

from the refinement with  $B^{A(m)} = B^{A(2)} = 2.1$  Å<sup>2</sup> are given in Tables 5 and 6. Selected interatomic distances and angles and the magnitudes and orientations of the principal axes of the thermal ellipsoids were calculated with the program ERRORS (L.W. Finger *pers. comm.*) and are given in Tables 7–10. Observed and calculated structure factors may be obtained from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

## DISCUSSION

The site populations obtained from the refinement are given in Table 11. As these site populations are given only in terms of scattering species that differ significantly, it is necessary to turn to more indirect methods for further information in this regard. Hawthorne & Grundy (1977) and Hawthorne (1978) have derived curves relating mean bond-length to cation content or variations in mean cationic radius for the coordination polyhedra of the *C2/m* amphibole structure. Use of the relevant relation-

TABLE 4. MISCELLANEOUS INFORMATION

Space Group	C2/m	$R = \frac{\sum ( F_o  -  F_c )}{\sum  F_o }$
Z	2	
Rad/Mon	Mo/C	$R_w = \left( \frac{\sum w( F_o  -  F_c )^2}{\sum wF_o^2} \right)^{1/2}$
No. of $ F_o $	1557	
No. $ F_o  > 3\sigma$	1098	Temp. factor form used:
Final <i>R</i> (obs)	4.8%	
Final <i>R<sub>w</sub></i> (obs)	5.1%	$\exp \left[ - \sum_{i=1}^3 \sum_{j=1}^3 h_i h_j \beta_{ij} \right]$

TABLE 5. ATOMIC POSITIONS AND EQUIVALENT ISOTROPIC TEMPERATURE FACTORS

Site	x	y	z	$B_{\text{equiv}}(\text{\AA}^2)$
O(1)	0.1061(4)	0.0895(2)	0.2134(7)	0.91(5)
O(2)	0.1203(4)	0.1743(2)	0.7351(7)	0.74(5)
O(3)	0.1094(6)	0	0.7132(11)	1.03(8)
O(4)	0.3696(4)	0.2498(2)	0.7879(8)	1.01(5)
O(5)	0.3506(4)	0.1403(2)	0.1107(7)	0.95(5)
O(6)	0.3436(4)	0.1168(2)	0.6066(8)	1.13(6)
O(7)	0.3394(6)	0	0.2750(12)	1.20(8)
T(1)	0.2812(1)	0.08559(7)	0.3008(3)	0.53(2)
T(2)	0.2921(1)	0.17282(7)	0.8125(3)	0.54(2)
M(1)	0	0.0892(1)	$\frac{1}{2}$	0.67(4)
M(2)	0	0.1773(1)	0	0.54(4)
M(3)	0	0	0	0.56(5)
M(4)	0	0.2783(1)	$\frac{1}{2}$	1.15(3)
A(2)	0	0.5238(13)	0	2.1*
A(m)	0.037(5)	$\frac{1}{2}$	0.088(9)	2.1*

\*fixed

TABLE 6. ANISOTROPIC TEMPERATURE-FACTOR COEFFICIENTS\*

Atom	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
O(1)	18(3)	11(1)	55(12)	-1(1)	-2(5)	0(3)
O(2)	14(3)	5(1)	90(12)	0(1)	2(5)	3(2)
O(3)	31(5)	6(1)	117(20)	0	17(8)	0
O(4)	35(4)	5(1)	113(14)	-3(2)	18(5)	2(3)
O(5)	18(3)	10(1)	83(12)	0(1)	1(5)	11(3)
O(6)	23(3)	11(1)	97(13)	3(2)	6(5)	-11(3)
O(7)	33(6)	5(1)	159(22)	0	7(9)	0
T(1)	13(1)	4(1)	53(5)	-1(1)	0(2)	1(1)
T(2)	14(1)	4(1)	51(4)	0(1)	4(2)	4(1)
M(1)	19(2)	7(1)	45(6)	0	7(2)	0
M(2)	14(2)	4(1)	50(6)	0	3(2)	0
M(3)	19(2)	3(1)	49(8)	0	4(3)	0
M(4)	24(1)	13(1)	92(5)	0	25(2)	0

\*  $\beta_{ij} = \beta_{ji} \times 10^4$ 

ships for the tetrahedra give the site populations indicated in Table 11; the total  $\text{Al}^{\text{IV}}$  indicated by these equations agrees reasonably well with that indicated by the chemical analysis (1.69 versus 1.63 atoms per formula unit, respectively). The site preference of aluminum in  $T(1) > T(2)$  exhibited by this amphibole is the same as in all amphiboles so far examined. For the octahedra, the following comparison of observed and calculated mean bond-lengths is obtained, assuming that all available [6]-coordinated trivalent cations are ordered at the  $M(2)$  site:

TABLE 7. SELECTED INTERATOMIC DISTANCES ( $\text{\AA}$ )

Atoms	Distance	Atoms	Distance
T(1)-O(1)	1.664(4)	T(2)-O(2)	1.632(4)
T(1)-O(5)	1.677(4)	T(2)-O(4)	1.605(4)
T(1)-O(6)	1.675(4)	T(2)-O(5)	1.644(4)
T(1)-O(7)	1.664(3)	T(2)-O(6)	1.660(4)
Mean	1.670	Mean	1.635
M(1)-O(1)	2.054(4) x2	M(3)-O(1)	2.088(4) x4
M(1)-O(2)	2.132(4) x2	M(3)-O(3)	2.077(6) x2
M(1)-O(3)	2.096(4) x2	Mean	2.084
Mean	2.094	M(4)-O(2)	2.388(4) x2
M(2)-O(1)	2.065(4) x2	M(4)-O(4)	2.290(4) x2
M(2)-O(2)	2.057(4) x2	M(4)-O(5)	2.646(4) x2
M(2)-O(4)	1.973(4) x2	M(4)-O(6)	2.592(4) x2
Mean	2.032	Mean	2.479
A(2)-O(5)	2.715(16) x2	A(m)-O(5)	3.05(2) x2
A(2)-O(5)	3.421(18) x2	A(m)-O(5)	3.15(2) x2
A(2)-O(6)	2.806(13) x2	A(m)-O(6)	2.72(3) x2
A(2)-O(6)	3.388(15) x2	A(m)-O(6)	3.48(4) x2
A(2)-O(7)	2.448(7) x2	A(m)-O(7)	2.40(4)
A(2)-O(7)	3.783(8) x2	A(m)-O(7)	2.53(4)
Mean 12	3.094	A(m)-O(7)	3.27(5)
Mean 8	2.839	A(m)-O(7)	4.25(5)
A-0(5)	3.058(3) x4	Mean 12	3.10
A-0(6)	3.081(4) x4	Mean 8	2.85
A-0(7)	2.411(3) x2	M(1)-M(1)	3.217(3)
A-0(7)	3.758(3) x2	M(1)-M(2)	3.091(1)
Mean 12	3.075	M(1)-M(3)	3.101(1)
T(1)-T(2)	through O(6)	M(1)-M(4)	3.411(3)
T(1)-T(2)	through O(5)	M(2)-M(3)	3.198(2)
T(1)-T(1)	across mirror	M(2)-M(4)	3.217(1)
		A-A(2)	0.43(2)
		A-A(m)	0.52(10)

 $\langle M(1)-O \rangle$  obs. = 2.093  $\text{\AA}$  calc. = 2.088  $\text{\AA}$  $\langle M(2)-O \rangle$  obs. = 2.030  $\text{\AA}$  calc. = 2.019  $\text{\AA}$  $\langle M(3)-O \rangle$  obs. = 2.085  $\text{\AA}$  calc. = 2.089  $\text{\AA}$ 

The agreement for the  $M(1)$  and  $M(3)$  octahedra is good, but the difference for the  $M(2)$  octahedron is probably significant. Table 3 shows that the mean ionic radius of the cations occupying the  $M(2)$  sites increases as the ferric/ferrous iron ratio decreases. Hence the observed  $\langle M(2)-O \rangle$  suggests a lower  $\text{Fe}^{3+}/\text{Fe}^{2+} + \text{Fe}^{3+}$  than the value of 0.15 that was used. This is also in accord with the  $A$ -site cation population refined in the last cycle. However, the  $\langle T-O \rangle$  distance is compatible with an  $\text{Al}^{\text{IV}}$  value (1.72 atoms per formula unit) that suggests a higher  $\text{Fe}^{3+}/\text{Fe}^{2+} + \text{Fe}^{3+}$  than the value of 0.15 used here. Thus the final composition of the amphibole chosen may be seen as a compromise between the various factors affected by a varying  $\text{Fe}^{3+}/\text{Fe}^{2+} + \text{Fe}^{3+}$  ratio. The fact that the agreements between these factors do not converge on the same  $\text{Fe}^{3+}/\text{Fe}^{2+} + \text{Fe}^{3+}$  value may

TABLE 8. POLYHEDRAL EDGE LENGTHS (Å)

T(1) Tetrahedron		T(2) Tetrahedron	
0(1)-0(5)	2.756(5)	0(2)-0(4)	2.754(5)
0(1)-0(6)	2.742(5)	0(2)-0(5)	2.671(5)
0(1)-0(7)	2.754(6)	0(2)-0(6)	2.672(5)
0(5)-0(6)	2.682(6)	0(4)-0(5)	2.651(5)
0(5)-0(7)	2.688(4)	0(4)-0(6)	2.573(5)
0(6)-0(7)	2.737(5)	0(5)-0(6)	2.689(6)
Mean	<u>2.727</u>	Mean	<u>2.668</u>
M(1) Octahedron		M(3) Octahedron	
0(1 <sup>u</sup> )-0(2 <sup>d</sup> )	2.772(5)	0(1 <sup>u</sup> )-0(1 <sup>d</sup> )	2.651(7)
0(1 <sup>u</sup> )-0(2 <sup>u</sup> )	3.133(6)	0(1 <sup>u</sup> )-0(1 <sup>u</sup> )	3.227(8)
0(1 <sup>u</sup> )-0(3 <sup>d</sup> )	2.769(5)	0(1 <sup>u</sup> )-0(3 <sup>d</sup> )	2.769(5)
0(1 <sup>u</sup> )-0(3 <sup>u</sup> )	3.096(6)	0(1 <sup>u</sup> )-0(3 <sup>u</sup> )	3.112(6)
0(2)-0(2)	2.959(7)	Mean	<u>2.940</u>
0(2)-0(3)	3.147(3)		
0(3)-0(3)	<u>2.687(11)</u>	M(4) Polyhedron	
Mean	<u>2.957</u>	0(2)-0(2)	3.147(3)
		0(2 <sup>u</sup> )-0(4 <sup>u</sup> )	3.117(5)
		0(2 <sup>u</sup> )-0(4 <sup>d</sup> )	2.895(5)
		0(2 <sup>u</sup> )-0(5 <sup>u</sup> )	3.436(5)
		0(4 <sup>u</sup> )-0(5 <sup>d</sup> )	3.315(5)
		0(4 <sup>u</sup> )-0(6 <sup>u</sup> )	2.573(5)
		0(5 <sup>u</sup> )-0(6 <sup>u</sup> )	2.682(6)
		0(5 <sup>u</sup> )-0(6 <sup>d</sup> )	3.022(5)
		0(6)-0(6)	<u>3.542(6)</u>
		Mean	<u>3.048</u>
M(2) Octahedron			
0(1 <sup>u</sup> )-0(1)	2.651(7)		
0(1 <sup>u</sup> )-0(2 <sup>d</sup> )	2.772(5)		
0(1 <sup>u</sup> )-0(2 <sup>u</sup> )	2.996(6)		
0(1 <sup>u</sup> )-0(4)	2.909(5)		
0(2 <sup>u</sup> )-0(4 <sup>d</sup> )	2.895(5)		
0(2 <sup>u</sup> )-0(4 <sup>u</sup> )	2.855(5)		
0(4)-0(4)	<u>2.941(8)</u>		
Mean	<u>2.871</u>		

TABLE 9. SELECTED INTERATOMIC ANGLES (°)

T(1) Tetrahedron		T(2) Tetrahedron	
0(1)-T(1)-0(5)	111.2(2)	0(2)-T(2)-0(4)	116.6(2)
0(1)-T(1)-0(6)	110.4(2)	0(2)-T(2)-0(5)	109.2(2)
0(1)-T(1)-0(7)	111.7(2)	0(2)-T(2)-0(6)	108.5(2)
0(5)-T(1)-0(6)	106.3(2)	0(4)-T(2)-0(5)	109.3(2)
0(5)-T(1)-0(7)	107.1(2)	0(4)-T(2)-0(6)	104.0(2)
0(6)-T(1)-0(7)	<u>110.1(2)</u>	0(5)-T(2)-0(6)	<u>109.0(2)</u>
Mean	<u>109.5</u>	Mean	<u>109.4</u>
M(1) Octahedron		M(3) Octahedron	
0(1 <sup>u</sup> )-M(1)-0(2 <sup>d</sup> )	82.9(2)	0(1 <sup>u</sup> )-M(3)-0(1 <sup>d</sup> )	78.8(2)
0(1 <sup>u</sup> )-M(1)-0(2 <sup>u</sup> )	97.0(2)	0(1 <sup>u</sup> )-M(3)-0(1 <sup>u</sup> )	101.2(2)
0(1 <sup>u</sup> )-M(1)-0(3 <sup>d</sup> )	83.7(2)	0(1 <sup>u</sup> )-M(3)-0(3 <sup>d</sup> )	83.3(1)
0(1 <sup>u</sup> )-M(1)-0(3 <sup>u</sup> )	96.5(2)	0(1 <sup>u</sup> )-M(3)-0(3 <sup>u</sup> )	<u>96.7(1)</u>
0(2)-M(1)-0(2)	87.9(2)	Mean	<u>90.0</u>
0(2)-M(1)-0(3)	96.2(1)		
0(3)-M(1)-0(3)	<u>79.7(2)</u>	M(4) Polyhedron	
Mean	<u>90.0</u>	0(2)-M(4)-0(2 <sup>d</sup> )	76.6(2)
		0(2 <sup>u</sup> )-M(4)-0(4 <sup>d</sup> )	76.4(1)
		0(2 <sup>u</sup> )-M(4)-0(4 <sup>u</sup> )	83.5(1)
		0(2 <sup>u</sup> )-M(4)-0(5 <sup>u</sup> )	85.9(1)
		0(4 <sup>u</sup> )-M(4)-0(5 <sup>d</sup> )	84.0(1)
		0(4 <sup>u</sup> )-M(4)-0(6 <sup>d</sup> )	63.2(1)
		0(5 <sup>u</sup> )-M(4)-0(6 <sup>u</sup> )	70.5(1)
		0(5 <sup>u</sup> )-M(4)-0(6 <sup>d</sup> )	61.6(1)
		0(6)-M(4)-0(6)	<u>86.2(2)</u>
		Mean	<u>75.8</u>
M(2) Octahedron		Tetrahedral Chain	
0(1)-M(2)-0(1)	79.8(2)	T(1)-0(5)-T(2)	133.8(2)
0(1 <sup>u</sup> )-M(2)-0(2 <sup>d</sup> )	84.5(1)	T(1)-0(6)-T(2)	138.0(2)
0(1 <sup>u</sup> )-M(2)-0(2 <sup>u</sup> )	93.2(2)	T(1)-0(7)-T(1)	136.1(4)
0(1 <sup>u</sup> )-M(2)-0(4 <sup>d</sup> )	92.2(1)	0(5)-0(6)-0(5)	161.6(2)
0(2 <sup>u</sup> )-M(2)-0(4 <sup>u</sup> )	91.8(2)	0(5)-0(7)-0(6)	159.6(2)
0(2 <sup>u</sup> )-M(2)-0(4 <sup>d</sup> )	<u>90.2(2)</u>		
0(4)-M(2)-0(4)	<u>96.4(2)</u>		
Mean	<u>90.0</u>		
A Polyhedron			
0(7)-0(7)-0(7)	62.8(3)		
Δ*	0.302		

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

perhaps be related to the effects of the exsolved cummingtonite phase in the diffraction experiment.

The apparent chemistry of this amphibole varies considerably with the  $\text{Fe}^{3+}/\text{Fe}^{2+} + \text{Fe}^{3+}$  ratio used for the cell-content recalculation, as can be seen by comparing  $\text{Al}^{\text{IV}}$ ,  $\text{Al}^{\text{VI}}$ ,  $(\text{Fe}, \text{Mg})^{M(4)}$  and  $\text{Na}^A$  in each of the three cell contents listed in Table 2. The name of the amphibole is also affected; the three cell contents of Table 2 are, respectively, ferroan pargasitic hornblende (Min), tschermakitic hornblende (Int) and ferritschermakite (Max). At the  $\text{Fe}^{3+}/\text{Fe}^{2+} + \text{Fe}^{3+}$  ratio of 0.15, it is a tschermakitic hornblende, but if the slightly higher *A*-site occupancy indicated by the unconstrained refinement is taken into account, the amphibole is a ferroan pargasitic hornblende, albeit with a slightly unbalanced unit formula.

Of particular interest with regard to this amphibole is the  $(\text{Fe}, \text{Mg})$  content of the *M*(4) site, as this represents the amount of cummingtonite component in solid solution in the calcic amphibole. As indicated in Table 3, this is strongly influenced by the  $\text{Fe}^{3+}/\text{Fe}^{2+} + \text{Fe}^{3+}$  ratio

used in the cell-content recalculation. However, in the range of  $\text{Fe}^{3+}/\text{Fe}^{2+} + \text{Fe}^{3+}$  ratios that seem reasonable ( $\sim 0.15$ ), the *M*(4) ( $\text{Fe}, \text{Mg}$ ) occupancy is considerable (0.22), with  $\text{Fe}^{2+}$  strongly ordered at *M*(4) relative to Mg. This is in line with the results of Goldman & Rossman (1977), who showed several calcic amphiboles to have significant  $\text{Fe}^{2+}$  occupancy of the *M*(4) site. It is also in accord with the site occupancies expected for an amphibole that is in part a solid solution between cummingtonite and a calcic amphibole. In the monoclinic  $\text{Fe-Mg-Mn}$  amphiboles,  $\text{Fe}^{2+}$  is very strongly ordered in *M*(4) if significant Mn is not present (Ghose 1961, Finger 1969c, Bancroft *et al.* 1967, Hafner & Ghose 1971). Thus, if an amphibole consists of cummingtonite and a calcic component in solid solution, the  $(\text{Fe}, \text{Mg})$  content of *M*(4) is expected to be predominantly  $\text{Fe}^{2+}$ , as is the case in this study.

Figure 2 shows that the *A*-site cations are primarily ordered at the *A*(2) position. This is in accord with the arguments of Hawthorne & Grundy (1978), who suggested that Na will occupy the *A*(2) sites and K the *A*(*m*) sites in

TABLE 10. MAGNITUDE AND ORIENTATION OF PRINCIPAL AXES OF THERMAL ELLIPSOIDS

Atom	R.M.S. deviation	Angle to x-axis	Angle to y-axis	Angle to z-axis
O(1)	0.075(9) <sup>R</sup>	57(13) <sup>O</sup>	86(6) <sup>O</sup>	48(13) <sup>O</sup>
	0.106(8)	34(13)	80(12)	137(13)
	0.133(6)	100(10)	10(11)	85(9)
O(2)	0.079(9)	25(11)	88(31)	80(12)
	0.091(8)	95(29)	164(13)	74(14)
	0.117(7)	114(9)	74(13)	19(12)
O(3)	0.097(11)	90	0	90
	0.118(10)	175(74)	90	70(74)
	0.125(11)	85(74)	90	21(74)
O(4)	0.079(9)	70(7)	22(7)	103(8)
	0.122(7)	83(41)	101(16)	167(16)
	0.130(6)	22(16)	109(11)	94(43)
O(5)	0.081(9)	56(20)	110(12)	54(14)
	0.099(8)	142(19)	120(11)	57(15)
	0.141(6)	105(7)	37(7)	53(6)
O(6)	0.097(8)	141(109)	59(36)	56(97)
	0.100(8)	123(117)	104(68)	129(91)
	0.153(6)	109(6)	145(6)	57(6)
O(7)	0.089(12)	90	0	90
	0.120(11)	150(14)	90	105(14)
	0.153(10)	120(14)	90	15(14)
T(1)	0.068(4)	42(6)	65(15)	71(9)
	0.079(3)	96(13)	32(14)	118(11)
	0.096(3)	132(6)	71(9)	35(8)
T(2)	0.071(4)	81(15)	131(10)	48(6)
	0.080(3)	152(11)	115(14)	87(13)
	0.095(3)	116(10)	52(7)	42(6)
M(1)	0.077(5)	95(11)	90	10(11)
	0.093(4)	175(11)	90	80(11)
	0.104(4)	90	0	90
M(2)	0.076(5)	50(15)	90	55(15)
	0.083(5)	90	0	90
	0.089(5)	140(15)	90	35(15)
M(3)	0.075(6)	90	0	90
	0.079(6)	103(13)	90	152(13)
	0.097(5)	13(13)	90	118(13)
M(4)	0.086(4)	147(4)	90	42(4)
	0.119(3)	123(4)	90	132(4)
	0.148(3)	90	0	90

TABLE 11. SITE POPULATIONS

From site-occupancy refinement:	
M(1)	0.322(9)Fe <sup>2+</sup> +0.678Mg*
M(2)	0.250(9)Fe <sup>2+</sup> +0.750Mg*
M(3)	0.450(13)Fe <sup>2+</sup> +0.550Mg*
M(4)	0.712Ca+0.067Na+0.167Fe <sup>2+</sup> +0.055Mg*
From examination of mean bond lengths:	
T(1)	0.40A1+0.60Si
T(2)	0.02A1+0.98Si
M(1)	0.32Fe <sup>2+</sup> +0.68Mg
M(2)	0.42A1+0.04Ti+0.14Fe <sup>3+</sup> +0.07Fe <sup>2+</sup> +0.33Mg
M(3)	0.45Fe <sup>2+</sup> +0.55Mg
M(4)	0.71Ca+0.07Na+0.17Fe <sup>2+</sup> +0.05Mg
A(2)	0.26(1)Na*
A(m)	0.11Na*

monoclinic amphiboles. The *A*-site cations are predominantly Na, and the *A*-site electron density is smeared out along the 2-fold axis in this amphibole. In the unconstrained *A*-site population refinement, the *A*(*m*) position also shows a significant occupancy, although much lower than that of the *A*(2) position. This may be an artifact of the refinement; as there was no bulk-chemical constraint used here (for reasons stated above), the parameter correlation was high and the difference-Fourier sections through the *A* position (Figure 2) seem to show the cations almost exclusively occupying the *A*(2) sites.

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