

The crystal chemistry of the amphiboles. III: Refinement of the crystal structure of a sub-silicic hastingsite

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SUMMARY. Three-dimensional counter-diffractometer data and a full-matrix least-squares method have been used to refine the crystal structure of a sub-silicic hastingsite in the space group $C2/m$. The chemical composition of the amphibole is $\text{Na}_{0.85}\text{K}_{0.80}\text{Ca}_{1.74}(\text{Mg}_{1.17}\text{Fe}_{3.17}^{2+}\text{Mn}_{0.04}\text{Ti}_{0.39}\text{Fe}_{0.79}^{3+}\text{Al}_{0.58})\text{Si}_{5.27}\text{Al}_{2.73}\text{O}_{22.56}(\text{OH})_{1.44}$ with cell parameters $a = 9.8659(4)$, $b = 18.0139(8)$, $c = 5.3545(2)\text{\AA}$, and $\beta = 105.082(1)^\circ$. Unit weights were used throughout the refinement and the final R -factor for 1263 observed non-equivalent reflections was 4.1%. The mean tetrahedral bond length for aluminous amphiboles varies linearly with the total amount of tetrahedral Al. Curves are derived relating individual mean bond lengths with Al occupancy. The positional disorder on the A -site of the aluminous amphiboles appears to be partly related to the amount of substitution of Al into the $T(2)$ tetrahedron.

AMPHIBOLES of the pargasite-ferrohastingsite series may be represented by the general formula $\text{NaCa}_2(\text{Mg}, \text{Fe}^{2+})_4(\text{Al}, \text{Fe}^{3+})\text{Si}_6\text{Al}_2\text{O}_{22}(\text{OH}, \text{F})_2$ with complete solid solution between the Mg and Fe^{2+} end members. They have an extremely wide range of paragenesis and extensive substitution of edenitic and tschermakitic components occur. However, the amount of tetrahedral Al rarely exceeds 2.0 atoms per formula unit; this 'limiting composition' may be rationalized (Gibbs, 1969) if all the tetrahedral Al is ordered into the $T(1)$ site and the Al avoidance rule (Loewenstein, 1954; Goldsmith and Laves, 1955) is observed. However, recent refinements of aluminous amphiboles (Robinson, 1971; Kitamura and Tokonami, 1971; Hawthorne and Grundy, 1973a, b) have shown that small amounts of Al can also substitute into the $T(2)$ tetrahedron. Therefore, the existence of sub-silicic amphiboles with a tetrahedral Al content in marked excess of 2.0 atoms per formula unit are possible that obey the Al avoidance rule, providing the Al population on the $T(1)$ site is limited to 0.5. Sub-silicic amphiboles are typically found in igneous rocks (Leake, 1968) whereas metamorphic amphiboles containing less than 6.2 Si per formula unit are rare. This might suggest a temperature dependence for the substitution of tetrahedral Al into the clino-amphibole structure. However, recent work has revealed that metamorphic amphiboles in sub-silicic environments can contain large amounts of tetrahedral aluminium, exceeding that found in amphiboles of igneous origin. These amphiboles provide an opportunity to test the applicability of the Al avoidance rule in the clino-amphiboles and also to check the stereochemistry of the double chain element of the structure.

Experimental details. The sub-silicic hastingsite used in this investigation was kindly supplied by Dr. E. C. Appleyard of the University of Waterloo, Ontario. It occurs in an 'iron formation' (Appleyard, 1967) in the Wolfe Belt, a sequence of banded nepheline gneisses (Appleyard, 1967, 1969), and is typically associated with scapolite, apatite, magnetite, and spinel. Single-crystal precession photographs display diffraction symmetry $2/mC-/-$ consistent with space groups $C2$, Cm , and $C2/m$; in line with previous work, the centrosymmetric space

group was adopted. Unit-cell parameters were determined by a least-squares method from reflections collected on a 4-circle single-crystal diffractometer. These are presented in Table I together with the unit cell contents and other information pertinent to data collection and refinement.

Intensity data. A euhedral cleavage fragment was mounted on a Syntex PI-4 circle X-ray diffractometer and exposed to graphite-monochromated Mo- $K\alpha$ radiation. The resulting diffraction intensities were measured using a scintillation counter and the θ - 2θ scan method. All reflections in one asymmetric unit were collected out to a maximum 2θ of 65° . Two standard reflections were measured after every fifty reflections and their intensities were found to be constant throughout the data collection period. The data were corrected for absorption using an eight point Gaussian quadrature procedure, also for background and Lorenz and polarization effects; equivalent reflections were then averaged to produce an asymmetric set. The resulting F_s were classed as observed if their magnitude was greater than four standard deviations based on counting statistics. Of the 1826 reflections collected 1263 unique reflections were designated as being observed and used in the refinement.

Refinement of the structure. In what follows scaling of the observed data was accomplished through a scale factor that was included as a parameter in the refinement and allowed to vary at all times. Also, where not stated, all computer programs used are from *X-ray 73, Program System for X-ray Crystallography*, by J. M. Stewart, University of Maryland, adapted by H. D. Grundy for the CDC6400. Copies of intensity data are available from the authors. Initial positional parameters and isotropic temperature factors were those of ferrotschermakite (Hawthorne and Grundy, 1973a); atomic scattering factors for neutral atoms were taken from Doyle and Turner (1968).

A full matrix least-squares refinement was made by varying the atomic positions, the isotropic temperature factors, and also the occupancies of the octahedral sites. The refinement converged at an R -factor ($R = \sum |F_o - F_c| / \sum |F_o|$) of 7.7%. Fourier and difference-Fourier maps made at this stage showed a partially disordered A site consistent with previous work on the clino-amphiboles (Hawthorne and Grundy, 1972, 1973a, b). Split positional parameters were read from the Fourier maps and included in the refinement in place of the current A site parameters. Subsequent refinement of all parameters resulted in an R -factor of 6.3% and a reduction in the weighted R factor ($R_w = \sum_w (|F_o| - |F_c|)^2 / \sum |F_o|^2$, $w = 1$) from 7.7% to 6.4%.

The temperature factors were then converted to the anisotropic form

$$\exp\left\{-\sum_{i=1}^3 \sum_{j=1}^3 h_i h_j \beta_{ij}\right\}$$

and further cycles of refinement resulted in convergence at an R -factor of 4.7%. At this stage, the refinement was continued using the least-squares program RFINE (Finger, 1969a, b), which allowed the sum of the site chemistries to be constrained to the chemical analysis (Table I). Because of the chemical complexity of most clino-amphiboles, not all site-occupancies of cations can be refined. Some chemical species must be assigned to sites on the basis of crystal-chemical criteria and previous experience; the criteria used here have been discussed previously (Hawthorne and Grundy, 1973a). All Ca^{2+} was assigned to $M(4)$ together with the excess octahedral cations; the remaining fraction of the $M(4)$ site was assigned to Na^+ . All Ti and octahedral Al^{3+} was assigned to the $M(2)$ site. Na^+ and K^+ in the A -sites were combined and expressed as Na; Fe^{2+} , Fe^{3+} , and Mn^{2+} were combined and expressed as neutral Fe; initial tetrahedral Al occupancies were calculated by method 2 of Papike, Ross, and Clark (1969). The distribution of Mg-Fe over the octahedral sites, the distribution of Na over the A -sites, and the distribution of Al-Si over the T -sites were then refined using the bulk chemical

constraints. An isotropic extinction correction (Zachariasen, 1968) was also included with the extinction coefficient as a variable in the refinement (Larson, 1967). Further cycles of refinement, gradually increasing the number of variables, resulted in convergence at an R -factor of 4.1% and an R_w -factor (unit weights) of 4.4%. The final positional parameters and equivalent isotropic temperature factors are presented in Table II. Interatomic distances and angles were calculated using the program ERRORS (L. W. Finger, personal communication) and are given in Tables III and IV. Final anisotropic temperature factor coefficients are given in Table V (available from the authors) and the magnitude and orientation of the principal axes of the thermal ellipsoids are given in Table VI (also available from the authors).

TABLE I. *Crystal data; analysis by Appleyard (see Leake, 1968) recalculated to 24(O,OH,F)*

Si	5.27	} 8.00	a	9.8659(4) Å
Al ^{iv}	2.73		b	18.0139(8)
Al ^{vi}	0.58	} 5.14	c	5.3545(2)
Fe ³⁺	0.79		β	105.082(1)°
Fe ²⁺	2.17	} 2.99	Space group	$C2/m$
Mg	1.17		Z	2
Mn	0.04		V	918.35 Å ³
Ti	0.39		μ	37.8 cm ⁻¹
Ca	1.74	} 2.99	Crystal size	0.08 × 0.09 × 0.18 mm
Na	0.95		Final R (unit weights)	0.041
K	0.30		Average $\sigma_{ F }$	2.70

TABLE II. *Atom site positions and populations*

Site	x	y	z	B_{equiv}	Population	Site	x	y	z	B_{equiv}	Population
O(1)	0.1035(3)	0.0935(1)	0.2109(5)	0.77(4)	1.00 0^{2-}	M(1)	0	0.09076(6)	$\frac{1}{2}$	0.66(3)	{ 0.691(8) Fe*
O(2)	0.1180(3)	0.1766(1)	0.7455(6)	0.79(4)	1.00 0^{2-}		{ 0.309(8) Mg				
O(3)	0.1111(4)	0	0.7097(8)	0.91(6)	1.00 0^{2-}	M(2)	0	0.17904(6)	0	0.63(3)	{ 0.301(8) Fe*
O(4)	0.3717(3)	0.2518(1)	0.7946(5)	0.79(4)	1.00 0^{2+}		{ 0.214(8) Mg				
O(5)	0.3526(3)	0.1401(1)	0.1155(6)	0.88(4)	1.00 0^{2-}		{ 0.290 Al				
							{ 0.195 Ti				
O(6)	0.3418(3)	0.1181(1)	0.6105(6)	0.98(4)	1.00 0^{2-}	M(3)	0	0	0	0.64(3)	{ 0.839(12) Fe*
O(7)	0.3328(4)	0	0.2807(9)	1.29(7)	1.00 0^{2-}		{ 0.161(12) Mg				
T(1)	0.2789(1)	0.08693(5)	0.3042(2)	0.46(4)	{ 0.51(11) Si	M(4)	0	0.28193(7)	$\frac{1}{2}$	0.81(2)	{ 0.060 Na
					{ 0.49(11) Al		{ 0.870 Ca				
T(2)	0.2920(1)	0.17394(6)	0.8188(2)	0.43(4)	{ 0.81(11) Si	A(2)	0	0.4848(5)	0	1.93(12)	{ 0.070(15) Fe*
					{ 0.19(11) Al		{ 0.000(15) Mg				
A(m)	0.0391(24)	$\frac{1}{2}$	0.0908(52)	1.82(11)	Na _{0.70} -x+						Na _z +K _y
					K _{0.80} -y						Fe* = Fe ²⁺ + Fe ³⁺ + Mn

Discussion

The basic features of the clino-amphibole structure are well known and have been discussed in detail elsewhere (Whittaker, 1960; Papike, Ross, and Clark, 1969; Papike and Ross, 1970). The site-nomenclature used in Tables III to VI and in the following discussion is that of Papike, Ross, and Clark (1969).

The distribution of tetrahedral Al. Due to the marginal difference in the atomic scattering factors of Al and Si, the relevant normal equations of the design matrix are sub-parallel and extreme correlations occur between the site-populations, which in turn results in extremely large standard deviations for the refined populations. In addition, the resolution of the ordering is extremely dependent on the elimination of systematic errors in the intensity data. Thus it is desirable to be able to assign Al^{iv} occupancies by an alternative method. Because of the difference in ionic radius between {Al³⁺}^{iv} and {Si⁴⁺}^{iv}, the variation in mean tetrahedral bond

TABLE IIIa. *Interatomic distances in Å, with bond multiplicities*

<i>T</i> (1) tetrahedron		<i>T</i> (2) tetrahedron		<i>M</i> (1) octahedron		<i>M</i> (2) octahedron	
<i>T</i> (1)-O(1)	1 1·675(3)	<i>T</i> (2)-O(2)	1 1·660(3)	<i>M</i> (1)-O(1)	2 2·065(4)	<i>M</i> (2)-O(1)	2 2·023(4)
<i>T</i> (1)-O(5)	1 1·688(3)	<i>T</i> (2)-O(4)	1 1·630(3)	<i>M</i> (1)-O(2)	2 2·163(4)	<i>M</i> (2)-O(2)	2 2·010(4)
<i>T</i> (1)-O(6)	1 1·692(4)	<i>T</i> (2)-O(5)	1 1·661(4)	<i>M</i> (1)-O(3)	2 2·120(3)	<i>M</i> (2)-O(4)	2 1·907(4)
<i>T</i> (1)-O(7)	1 1·669(2)	<i>T</i> (2)-O(6)	1 1·668(3)	Mean	2·116	Mean	1·980
Mean	1·681	Mean	1·655				
<i>M</i> (3) octahedron		<i>A</i> (2) polyhedron		<i>A</i> (<i>m</i>) polyhedron		Conventional <i>A</i> site	
<i>M</i> (3)-O(1)	4 2·135(3)	<i>A</i> (2)-O(5)	2 2·834(8)	<i>A</i> (<i>m</i>)-O(5)	2 3·057(9)	<i>A</i> -O(5)	4 3·055(4)
<i>M</i> (3)-O(3)	2 2·122(5)	<i>A</i> (2)-O(5)	2 3·285(8)	<i>A</i> (<i>m</i>)-O(5)	2 3·146(11)	<i>A</i> -O(6)	4 3·101(4)
Mean	2·131	<i>A</i> (2)-O(6)	2 3·295(8)	<i>A</i> (<i>m</i>)-O(6)	2 2·737(19)	<i>A</i> -O(7)	2 2·504(5)
		<i>A</i> (2)-O(6)	2 2·921(8)	<i>A</i> (<i>m</i>)-O(6)	2 3·510(14)	<i>A</i> -O(7)	2 3·775(6)
		<i>A</i> (2)-O(7)	2 2·519(6)	<i>A</i> (<i>m</i>)-O(7)	1 2·501(15)	Mean for 12	3·099
		<i>A</i> (2)-O(7)	2 3·785(8)	<i>A</i> (<i>m</i>)-O(7)	1 2·620(17)		
		Mean for 12	3·106	<i>A</i> (<i>m</i>)-O(7)	1 3·273(19)	<i>M</i> - <i>M</i>	
		Mean for 8	2·889	<i>A</i> (<i>m</i>)-O(7)	1 4·285(19)	<i>M</i> (1)- <i>M</i> (1)	3·270(2)
				Mean for 12	3·132	<i>M</i> (1)- <i>M</i> (2)	3·114(1)
				Mean for 8	2·875	<i>M</i> (1)- <i>M</i> (3)	3·137(1)
						<i>M</i> (1)- <i>M</i> (4)	3·444(1)
<i>A</i> - <i>T</i>		Miscellaneous		<i>T</i> (1)- <i>T</i> (2)		<i>M</i> (2)- <i>M</i> (3)	3·225(1)
<i>A</i> (<i>m</i>)- <i>T</i> (1)	3·446(13)	<i>A</i> (<i>m</i>)- <i>A</i> (<i>m</i>)	1·07(6)	<i>T</i> (1)- <i>T</i> (2)		<i>M</i> (2)- <i>M</i> (4)	3·256(1)
<i>A</i> (<i>m</i>)- <i>T</i> (2)	3·523(11)	<i>A</i> (2)- <i>A</i> (2)	0·55(2)	through O(6)	3·143(1)		
<i>A</i> (2)- <i>T</i> (1)	3·306(6)	<i>A</i> (<i>m</i>)- <i>A</i> (2)	0·60(2)	<i>T</i> (1)- <i>T</i> (2)			
<i>A</i> (2)- <i>T</i> (2)	3·506(8)			through O(5)	3·066(1)		
				<i>T</i> (1)- <i>T</i> (1)			
				across mirror	3·132(2)		

TABLE IIIb. *Oxygen-oxygen polyhedral edge lengths*

<i>T</i> (1) tetrahedron		<i>T</i> (2) tetrahedron		<i>M</i> (1) octahedron		<i>M</i> (2) octahedron	
O(1)-O(5)	2·766(4)	O(2)-O(4)	2·798(4)	O(1 ^u)-O(2 ^d)	2·709(4)	O(1)-O(1)	2·622(9)
O(1)-O(6)	2·772(8)	O(2)-O(5)	2·707(8)	O(1 ^u)-O(2 ^u)	3·200(4)	O(1 ^u)-O(2 ^d)	2·709(4)
O(1)-O(7)	2·767(4)	O(2)-O(6)	2·709(4)	O(1 ^u)-O(3 ^d)	2·823(4)	O(1 ^u)-O(2 ^u)	2·942(4)
O(5)-O(6)	2·710(4)	O(4)-O(5)	2·685(4)	O(1 ^u)-O(3 ^u)	3·143(4)	O(1)-O(4)	2·797(4)
O(5)-O(7)	2·698(3)	O(4)-O(6)	2·590(4)	O(2)-O(2)	3·024(10)	O(2 ^u)-O(4 ^d)	2·822(4)
O(6)-O(7)	2·752(4)	O(5)-O(6)	2·707(4)	O(2)-O(3)	3·188(3)	O(2 ^u)-O(4 ^u)	2·757(4)
Mean	2·744	Mean	2·699	O(3)-O(3)	2·699(11)	O(4)-O(4)	2·890(9)
				Mean	2·969	Mean	2·797
<i>M</i> (4) polyhedron		<i>M</i> (4) polyhedron, ctd.		<i>M</i> (3) octahedron			
O(2)-O(2)	3·024(10)	O(4 ^u)-O(6 ^u)	2·590(4)	O(1 ^u)-O(1 ^u)	2·622(9)		
O(2 ^u)-O(4 ^u)	3·191(4)	O(5 ^u)-O(6 ^u)	2·710(4)	O(1 ^u)-O(1 ^u)	3·370(5)		
O(2 ^u)-O(4 ^d)	2·822(4)	O(5 ^u)-O(6 ^d)	3·017(7)	O(1 ^u)-O(3 ^d)	2·823(4)		
O(2 ^u)-O(5 ^u)	3·380(4)	O(6 ^u)-O(6 ^d)	3·615(7)	O(1 ^u)-O(3 ^u)	3·186(4)		
O(4 ^u)-O(5 ^d)	3·317(4)	Mean	3·043	Mean	3·002		

The superscript notation refers to oxygen with an *x* coordinate greater (u) or less (d) than the *x* coordinate of *M*.

length is usually considered to be a good method for determining the Al/Si occupancy (Smith, 1954). On this basis, Papike, Ross, and Clark (1969) developed three methods of assigning tetrahedral site-occupancies in amphiboles, of which 'method 2' has been the most successful. However, increase in the amount of data available has revealed inadequacies in this procedure and a new treatment of this problem is warranted.

Fig. 1 shows the variation in mean *T*-O distance (i.e. $\langle T-O \rangle$) with the total amount of Al^{IV} for the clinoamphiboles listed in Table VII. With the exception of the Kakanui hornblende, the trend is linear. A simple linear regression analysis was made (omitting Kakanui hornblende) and the results are given in fig. 1. Amphiboles with a high richterite component will probably deviate from this relationship because of the increase in mean anion coordination number of the tetrahedra at low Al concentrations. However, this is not the case for the

TABLE IV. Selected interatomic angles

<i>T</i> (1) tetrahedron		<i>T</i> (2) tetrahedron		<i>M</i> (1) octahedron	
<i>O</i> (1)– <i>T</i> (1)– <i>O</i> (5)	110·7(2)°	<i>O</i> (2)– <i>T</i> (2)– <i>O</i> (4)	116·5(1)°	<i>O</i> (1 ^u)– <i>M</i> (1)– <i>O</i> (2 ^d)	79·6(1)°
<i>O</i> (1)– <i>T</i> (1)– <i>O</i> (6)	110·8(3)	<i>O</i> (2)– <i>T</i> (2)– <i>O</i> (5)	109·7(2)	<i>O</i> (1 ^u)– <i>M</i> (1)– <i>O</i> (2 ^u)	98·4(1)
<i>O</i> (1)– <i>T</i> (1)– <i>O</i> (7)	111·7(2)	<i>O</i> (2)– <i>T</i> (2)– <i>O</i> (6)	109·0(2)	<i>O</i> (1 ^u)– <i>M</i> (1)– <i>O</i> (3 ^d)	84·8(1)
<i>O</i> (5)– <i>T</i> (1)– <i>O</i> (6)	106·6(2)	<i>O</i> (4)– <i>T</i> (2)– <i>O</i> (5)	109·3(2)	<i>O</i> (1 ^u)– <i>M</i> (1)– <i>O</i> (3 ^u)	97·3(1)
<i>O</i> (5)– <i>T</i> (1)– <i>O</i> (7)	107·0(2)	<i>O</i> (4)– <i>T</i> (2)– <i>O</i> (6)	103·5(2)	<i>O</i> (2)– <i>M</i> (1)– <i>O</i> (2)	88·7(2)
<i>O</i> (6)– <i>T</i> (1)– <i>O</i> (7)	109·9(2)	<i>O</i> (5)– <i>T</i> (2)– <i>O</i> (6)	108·9(1)	<i>O</i> (2)– <i>M</i> (1)– <i>O</i> (3)	96·2(2)
Mean	109·5	Mean	109·4	<i>O</i> (3)– <i>M</i> (1)– <i>O</i> (3)	79·1(3)
				Mean	90·0
<i>M</i> (3) octahedron		<i>M</i> (4) polyhedron		<i>M</i> (2) octahedron	
<i>O</i> (1 ^u)– <i>M</i> (3)– <i>O</i> (1 ^d)	75·8(2)°	<i>O</i> (2)– <i>M</i> (4)– <i>O</i> (2)	77·1(2)°	<i>O</i> (1)– <i>M</i> (2)– <i>O</i> (1)	80·8(2)°
<i>O</i> (1 ^u)– <i>M</i> (3)– <i>O</i> (1 ^u)	104·2(2)	<i>O</i> (2 ^u)– <i>M</i> (4)– <i>O</i> (4 ^d)	72·5(1)	<i>O</i> (1 ^u)– <i>M</i> (2)– <i>O</i> (2 ^d)	84·4(1)
<i>O</i> (1 ^u)– <i>M</i> (3)– <i>O</i> (3 ^d)	83·1(1)	<i>O</i> (2 ^u)– <i>M</i> (4)– <i>O</i> (4 ^u)	84·0(1)	<i>O</i> (1 ^u)– <i>M</i> (2)– <i>O</i> (2 ^u)	93·7(1)
<i>O</i> (1 ^u)– <i>M</i> (3)– <i>O</i> (3 ^u)	96·9(1)	<i>O</i> (2 ^u)– <i>M</i> (4)– <i>O</i> (5 ^u)	84·4(2)	<i>O</i> (1)– <i>M</i> (2)– <i>O</i> (4)	90·7(2)
Mean	90·0	<i>O</i> (4 ^u)– <i>M</i> (4)– <i>O</i> (5 ^d)	84·1(1)	<i>O</i> (2 ^u)– <i>M</i> (2)– <i>O</i> (4 ^d)	92·1(1)
		<i>O</i> (4 ^u)– <i>M</i> (4)– <i>O</i> (6 ^u)	63·7(1)	<i>O</i> (2 ^u)– <i>M</i> (2)– <i>O</i> (4 ^u)	89·5(1)
Tetrahedral chain		<i>O</i> (5 ^u)– <i>M</i> (4)– <i>O</i> (6 ^d)	71·7(1)	<i>O</i> (4)– <i>M</i> (2)– <i>O</i> (4)	98·5(2)
<i>T</i> (1)– <i>O</i> (5)– <i>T</i> (2)	132·6(2)	<i>O</i> (5 ^u)– <i>M</i> (4)– <i>O</i> (6 ^u)	63·4(1)	Mean	90·0
<i>T</i> (1)– <i>O</i> (6)– <i>T</i> (2)	138·7(2)	<i>O</i> (6)– <i>M</i> (4)– <i>O</i> (6)	90·2(1)		
<i>T</i> (1)– <i>O</i> (7)– <i>T</i> (1)	139·5(3)	Mean	75·9	<i>A</i> polyhedron	
<i>O</i> (5)– <i>O</i> (6)– <i>O</i> (5)	162·6(2)			<i>O</i> (7)– <i>O</i> (7)	64·9(1)°
<i>O</i> (5)– <i>O</i> (7)– <i>O</i> (6)	160·2(2)				$\delta = 0\cdot279$

The superscript notation refers to oxygen with an *x* coordinate greater (u) or less (d) than that of *M*.
 $\delta = 90^\circ - [\text{O}(7) - \text{O}(7) - \text{O}(7)]/90^\circ$.

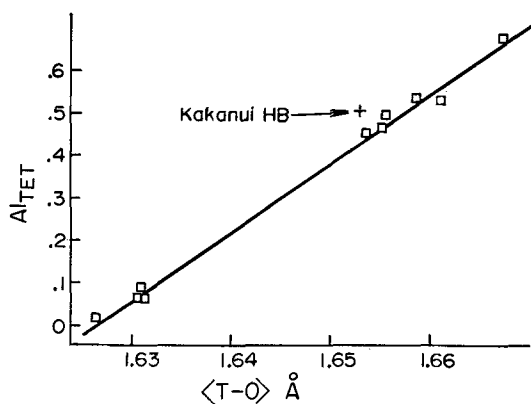


FIG. 1. Variation in mean *T*–*O* distance with total tetrahedral Al. Linear regression analysis gives the result:
 $Al_{TET} = -26\cdot434 + 16\cdot252 \langle T-O \rangle$, $R = 0\cdot997$, $\sigma = 0\cdot019$.

Kakanui hornblende; in addition, the tetrahedral distortions are similar to those of the other amphiboles, and thus the reason for its departure from the linear relationship remains obscure.

Because of the difficulties mentioned above, it was considered desirable to derive bond length *v.* Al-occupancy curves for the individual tetrahedra that were not based on the refined site-populations. In order to do this, it is necessary to make certain assumptions concerning the effect of variable Al occupancy on the mean bond lengths. In this study, it is assumed that the slopes of the curves relating individual mean bond length to Al occupancy are identical to

TABLE VII. *Refined clino-amphiboles with tetrahedral aluminium*

	Al _{T(1)} ^F	Al _{T(1)} ^R	Al _{T(2)} ^F	Al _{T(2)} ^R	
Tremolite	—	—	—	—	Papike, Ross, and Clark (1969)
Actinolite	0·064	0·08(-)	0·004	0·00(-)	Mitchell (1970); Mitchell, Bloss, and Gibbs (1971)
Pargasite	0·444	0·38(-)	0·028	0·09(-)	Robinson (1971)
Titanian pargasite	0·468	0·46(-)	0·062	0·08(-)	Robinson (1971)
Ferrotschermakite	0·432	0·46(3)	0·046	0·04(3)	Hawthorne and Grundy (1973a)
Ferrohastingsite	0·428	0·42(4)	0·017	0·04(4)	In preparation
Oxykaersutite	0·482	0·47(4)	0·089	0·06(4)	Hawthorne and Grundy (1973b)
Alumino-hastingsite	0·490	0·49(11)	0·182	0·19(11)	This study
Tremolite X-ray	0·068	0·06(9)	0·020	0·00(9)	Hawthorne and Grundy (1976)
neutron	0·054	0·04(2)	0·025	0·00(2)	
Kakanui hornblende	—	—	—	—	Papike, Ross, and Clark (1969); Robinson (1971)

F: Forecast from the mean bond lengths using equations given below.

R: Refined values from crystal structure analysis.

each other. Thus the sum of the intercepts of the individual equations will be equal to the intercept of the equation in fig. 1. Comparison of the mean bond lengths in tremolite (Hawthorne and Grundy, 1976) and actinolite with those of hydroxy-tremolite (Papike, Ross, and Clark, 1969) indicates that Al shows a site-preference for $T(1)$. Resolving the individual intercepts from their sum so as to reflect this preference, the following occupancy equations are derived:

$$\text{Al}_{T(1)} = -13\cdot170 + 8\cdot126\langle T(1)\text{-O} \rangle \quad \text{and} \quad \text{Al}_{T(2)} = -13\cdot265 + 8\cdot126\langle T(2)\text{-O} \rangle.$$

The values forecast from these equations are listed in Table VII where they are compared with the values refined or assigned during structure refinement.

Of particular interest are the results for the sub-silicic hastingsite. The $T(1)$ site is almost exactly half-filled with Al, with the 'excess' Al substituting into the $T(2)$ site. Thus it appears that the Al avoidance rule does limit the maximum amount of Al able to substitute into the $T(1)$ site. Potentially, this rule also imposes the same limit on the $T(2)$ site, but it is apparent that another mechanism controls this substitution long before the avoidance rule becomes applicable.

The tetrahedral chain configuration. It was shown in a previous paper (Hawthorne and Grundy, 1973b) that the amount of ditrigonal distortion of the double-chain element was a function of the Al^{iv}. This asymptotic relationship suggested a maximum of two Al^{iv} atoms per formula unit and a minimum O(5)–O(6)–O(5) angle of about 162°. The O(5)–O(6)–O(5) angle of the sub-silicic hastingsite (Table IV) corresponds to this apparent minimum, and thus the increased misfit between the double-chain and octahedral strip elements of the structure must be accommodated elsewhere.

An inspection of the cell dimensions of the amphiboles in Table VII shows that commensurate with its high Al^{iv}, the sub-silicic hastingsite has the largest c dimension, the smallest b dimension and also a comparatively small a dimension. The amounts of Fe²⁺ and Mg in ferrotschermakite, ferrohastingsite, and sub-silicic hastingsite are very similar, and thus the b dimension should be proportional to the mean ionic radius of the cations substituting into the M(2) site (Colville, Ernst, and Gilbert, 1966). The values for this parameter and the b dimensions are: Ferrotschermakite, 0·579Å, b 18·106Å; sub-silicic hastingsite, 0·633Å, b 18·014Å; ferrohastingsite, 0·669Å, b 18·134Å.

It can be seen that the b dimensions do not follow the same sequence. Inspection of the $\langle M(2)-O \rangle$ bond lengths shows that the value for the sub-silicic hastingsite is anomalously low. It appears that in order to articulate with the tetrahedral double chain, the octahedral strip has contracted in the b (and a) directions and extended in the c -direction.

The octahedral sites. In general, the mean octahedral bond lengths in the clinoamphiboles reflect the chemistry of their constituent cations (anions). However, this is not the case with the sub-silicic hastingsite, particularly with respect to the $M(2)$ site. Regression equations developed for the octahedral sites (in preparation) forecast an $\langle M(2)-O \rangle$ distance of 2.021 \AA with a standard error of estimate of 0.005 \AA ; this compares with the observed value of $1.980(2) \text{ \AA}$. Due to the magnitude of the anomaly, it was thought pertinent to check the possibility of systematic errors in the data; in particular that the crystal used in the initial collection of the data was truly representative of the chemical analysis. In order to accomplish this, data was collected from another crystal and the refinement repeated. The resulting parameters were compared with those previously determined using the half-normal-probability method (Abrahams and Keve, 1971; Hamilton and Abrahams, 1972). No significant difference was found between the two sets; the analysis also showed (Abrahams, 1972) that the standard deviations assigned to the data were of the correct magnitude.

As there was no obvious systematic error, the short mean bond length at $M(2)$ may be rationalized by a brief qualitative consideration of the bond strengths in this part of the structure. Substitution of significant amounts of Al into the $T(2)$ tetrahedron increases the formal charge imbalance at the $O(4)$ anion; to compensate for this effect, the bond lengths to $O(4)$ must shorten. However, as the bonds to $O(1)$ and $O(2)$ cannot lengthen due to the bond strength requirements of these anions, an overall contraction of the bond lengths on the $M(2)$ site occurs relative to that expected for the actual size of the constituent cations. The contraction of $M(2)-O(4)$ produces the small b dimension observed for this amphibole.

The A-site. Distinct from all the previous amphiboles that have been refined, the sub-silicic hastingsite shows the site preference $A(2) > A(m)$ for the electron density on the A site. Since the actual site populations cannot be derived from X-ray measurements, the exact mechanism controlling this ordering is not apparent. However, in those amphiboles so far examined (Hawthorne and Grundy, 1973a, b, this study, and in preparation), increase in the Al on the $T(2)$ site is accompanied by a relative increase in the electron density at the $A(2)$ site. This has the effect of compensating for the decrease in bond strength supplied to the bridging anions $O(5)$ and $O(6)$ by the $T(2)$ cations.

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