

A Three-Dimensional Refinement of the Structure of Holmquistite

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The structure of holmquistite has been refined by least-squares calculations to an R value of 0.056. The cation distribution is dominated by the preferential occupation of M(4) by Li and of M(2) by trivalent ions, mainly Al. Fe^{2+} avoids M(4) and shows a significant concentration into M(3) rather than M(1). The small degree of disordering of Al and Mg between M(2) and M(1) + M(3) has been estimated from bond lengths. The chain geometry is very similar to that in anthophyllite and gedrite, but the two chains are more alike and the tetrahedral rotations are smaller than in gedrite.

Introduction

A two-dimensional refinement of the structure of a holmquistite crystal from the Benson Pegmatite Mine, Mtoko, Rhodesia (Whittaker, 1969) showed that the lithium was preferentially concentrated in the inter-chain site M(4) and that the iron was preferentially concentrated in the internal sites M(1) and M(3). This work was based on photographic intensity measurements, and led to an R of 0.085. A full three-dimensional refinement of the structure has now been carried out with intensity data from the same crystal but measured on a linear diffractometer. This has substantially confirmed the two-dimensional results, and provided more extensive information on the structure, which can be compared in detail with the results of structure refinements for two other orthorhombic amphiboles that have been published since 1968, anthophyllite (Finger, 1970) and gedrite (Papike & Ross, 1970). When the present work was virtually complete our attention was drawn to a paper by Litvin, Ginzburg, Egorova & Ostapenko (1973) describing a three-dimensional refinement of another specimen of holmquistite. Although Litvin *et al.* reached similar conclusions to ours regarding ionic segregation into the different sites, some of our results reported here differ significantly from theirs, and others provide more detailed information. Our results are based on a larger number of observed independent reflexions (1160 against 580) and the refinement reached a lower R (0.056 against 0.091).

The crystal used was from a specimen whose analysis was given by von Knorring & Hornung (1961) and corresponds to the formula $\text{Na}_{0.03}\text{K}_{0.01}\text{Ca}_{0.03}\text{Li}_{1.79}\text{Mg}_{1.76}\text{Fe}_{1.21}^{2+}\text{Fe}_{0.24}^{3+}\text{Mn}_{0.03}\text{Ti}_{0.02}\text{Al}_{1.84}^{61}\text{Si}_{7.89}\text{Al}_{1.11}^{41}\text{O}_{22}(\text{OH})_{1.86}\text{F}_{0.08}\text{O}_{0.06}$. Intensity data were collected with Mo $K\alpha$ radiation and a system of balanced filters on a Hilger and Watts linear diffractometer, on a series of eight levels from $hk0$ to $hk7$. 5389 reflexions were measured (twice each) of which 2969 were independent. 915 of these (mostly very small) were rejected for negativity, unequal backgrounds at the two sides of the reflexions, or poor reproducibility between the repeat measurements. A further 894 differed from the background by

less than 3σ (based on counting statistics) and were discarded for the main part of the refinement, which was therefore based on 1160 independent reflexions. The value of R for internal consistency of equivalent reflexions was 0.0277. Absorption corrections were based on an ellipsoidally shaped crystal with major axes equal to the dimensions given previously. The absorption coefficient was 24.8 cm^{-1} .

Refinement

The refinement was performed by a full-matrix least-squares process with equal weights using G. M. Sheldrick's program (1973, private communication) on the ICL 1906A computer. The atomic scattering factors used were from Cromer & Waber (1965), which include anomalous scattering effects.

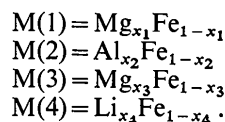
The initial refinement was based on the results of the earlier two-dimensional refinement (Whittaker, 1969). The latter was performed in the two-dimensional space group cm , which has an a axis of only half that of the true cell, and whose origin was taken at a pseudo two-fold rotation point that lies on the mirror plane of space group $Pnma$, but which does not correspond to a projection of any true symmetry element of the space group.

The positional parameters given by Whittaker (1969) therefore have to be modified as follows:

- (1) generate additional independent sites for oxygen and silicon atoms at $-x/a, y/b$;
- (2) halve the values of x/a ;
- (3) shift the origin to $(-\frac{1}{8}, -\frac{1}{4})$ in terms of the old coordinates to coincide with the centre of symmetry in $Pnma$.

An initial set of three-dimensional parameters was then completed by taking the z values obtained for anthophyllite by Finger (1970). Initial values for the site occupancies and independent isotropic temperature factors were taken directly from Whittaker (1969). The initial R (after adjustment of the scale factor) was 0.6960. Temperature factors and occupancy parameters were refined in alternating groups of cycles. The occupation of each of the four cation sites was refined in

terms of an occupancy parameter x such that the scattering factor at each site was equivalent to:



When R reached 0.0617 anisotropic temperature factors were introduced and finally led to a reduction of R to 0.0558. However, the anisotropic temperature factors for the oxygen atoms were subject to large standard deviations, and, although very anisotropic, their departures from isotropy were not significant, and three of them were hyperbolic. For this reason Table 2 gives the anisotropic results for the cations only, together with the best isotropic temperature factors for the oxygen atoms. The final atomic coordinates are given in Table 1. The coordinates of the heavier cations were stable to within 0.001 Å, those of oxygen to 0.003 Å [except for O(3) which was still unstable by up to 0.016 Å] and M(4) to 0.01 Å. The occupancy parameters are given in assignment 1 of Table 4 and were stable to 0.01. The list of structure factors is given in Table 3.

Table 1. Atomic coordinates

	x/a	y/b	z/c
M(1)	0.1248 (2)	0.1590 (1)	0.3944 (6)
M(2)	0.1255 (2)	0.0687 (2)	-0.1045 (7)
M(3)	0.1255 (2)	0.2500	-0.1061 (8)
M(4)	0.1221 (10)	-0.0086 (8)	0.3988 (37)
T(1A)	0.2695 (2)	0.1621 (2)	0.0673 (6)
T(1B)	-0.0190 (2)	0.1622 (2)	-0.2770 (6)
T(2A)	0.2738 (2)	0.0761 (2)	-0.4265 (6)
T(2B)	-0.0244 (2)	0.0769 (2)	0.2146 (6)
O(1A)	0.1803 (5)	0.1562 (5)	0.0492 (6)
O(1B)	0.0698 (5)	0.1563 (5)	-0.2611 (15)
O(2A)	0.1848 (5)	0.0747 (5)	-0.4087 (17)
O(2B)	0.0653 (5)	0.0744 (5)	0.1971 (18)
O(3A)	0.1822 (8)	0.2500	-0.4468 (24)
O(3B)	0.0683 (7)	0.2500	0.2322 (24)
O(4A)	0.1873 (5)	0.0042 (4)	0.0612 (15)
O(4B)	0.0653 (5)	0.0013 (5)	-0.2692 (16)
O(5A)	0.1943 (4)	0.1146 (5)	0.3373 (14)
O(5B)	0.0548 (4)	0.1134 (5)	0.0505 (15)
O(6A)	0.2034 (4)	-0.1297 (5)	-0.1686 (16)
O(6B)	0.0462 (4)	-0.1335 (5)	-0.4494 (15)
O(7A)	-0.2054 (7)	0.2500	-0.5451 (21)
O(7B)	-0.0424 (7)	0.2500	-0.2424 (23)

Further investigations

(a) The absences not related to the space group

As was pointed out by Whittaker (1969), the $hk0$ reflexions of holmquistite with $h+2k \neq 4n$ were unobservable photographically at least up to the 34th orders of h and k within the range of Mo $K\alpha$ radiation. Because the least-squares refinement does not take any account of weak reflexions which differ from zero by less than 3σ , it was considered desirable to check that the structure determined did not violate this observation.

Table 2. Temperature factors

(a) Anisotropic		Direction cosines with respect to crystallographic axes			
	Ellipsoid axis	$U(\text{Å}^2)$	x y z		
			x	y	z
M(1)	r_1	0.00575	0.925	0.297	-0.236
	r_2	0.00668	-0.279	0.954	0.110
	r_3	0.01148	0.258	-0.036	0.965
M(2)	r_1	0.00578	0.508	-0.853	-0.117
	r_2	0.00739	-0.783	-0.401	-0.475
	r_3	0.00993	-0.359	-0.333	0.872
M(3)	r_1	0.00540	-0.000	1.000	-0.000
	r_2	0.00861	0.973	0.000	0.230
	r_3	0.01219	-0.230	0.000	0.973
M(4)	r_1	0.00429	-0.057	-0.353	0.934
	r_2	0.02205	0.919	-0.383	-0.089
	r_3	0.03065	-0.389	-0.853	-0.346
T(1A)	r_1	0.00294	-0.628	-0.704	0.332
	r_2	0.00485	0.778	-0.584	0.232
	r_3	0.00851	0.030	0.404	0.914
T(1B)	r_1	0.00209	0.979	-0.201	-0.024
	r_2	0.00459	-0.200	-0.978	0.057
	r_3	0.00872	0.035	0.051	0.998
T(2A)	r_1	0.00121	0.743	-0.635	-0.211
	r_2	0.00654	0.668	0.725	0.170
	r_3	0.00805	-0.045	0.267	-0.963
T(2B)	r_1	0.00279	-0.928	-0.247	-0.278
	r_2	0.00514	0.248	-0.968	0.033
	r_3	0.00887	-0.277	-0.039	0.960

(b) Isotropic

	$U(\text{Å}^2)$		$U(\text{Å}^2)$
O(1A)	0.00814 (17)	O(4B)	0.00982 (18)
O(1B)	0.00909 (19)	O(5A)	0.00763 (16)
O(2A)	0.00797 (15)	O(5B)	0.00754 (16)
O(2B)	0.01154 (19)	O(6A)	0.01159 (18)
O(3A)	0.01053 (27)	O(6B)	0.00907 (15)
O(3B)	0.00787 (26)	O(7A)	0.00766 (25)
O(4A)	0.00989 (17)	O(7B)	0.01206 (26)

Of the 109 reflexions of this class within the range of observation, 49 were actually observed on the diffractometer, although all of them differed from zero by less than 3σ and had therefore been rejected. One cycle of refinement was therefore performed with all the observable reflexions in order to compare F_o and F_c for this class $hk0$ with $h+2k \neq 4n$. The maximum and average values of $|F_o|$ for these reflexions were 21 and 10, and the corresponding values for $|F_c|$ were 20 and 6.

(b) The possible occupation of the A site

In view of the possibility of a split A site, as observed by Papike, Ross & Clark (1969) in clino-amphiboles, the position of the A site was initially refined without any constraint other than that the y coordinate should lie on the mirror plane, with a fixed occupancy equivalent to $Ca_{0.02} + K_{0.02}$. The coordinates obtained were very unstable and shifted to quite unacceptable values, corresponding to positions up to 2.4 Å from the ideal A site and within 0.4 Å of O(3B). Fourier and difference Fourier syntheses failed to show any distinguishable electron density at or near the A site amongst the background fluctuations of $\pm 0.5 \text{ e Å}^{-3}$. By comparison with the cation peaks this suggests that the occupancy

Table 3. *Observed and calculated structure factors*
 The individual columns give $h, k, l, |F_o|$, and F_c in that order.

4	0	0	0	03	00	13	4	1	43	-43	5	0	1	53	-53	3	0	2	42	41	20	5	3	19V	001	4	4	4	10	020	0	3	3	60	63	10	2	0	20	20
8	0	0	0	09	00	16	4	1	37	-35	6	0	1	65	-62	4	0	2	83	82	21	6	3	18V	001	4	4	4	10	020	0	3	3	60	63	10	2	0	20	20
12	0	0	0	15	00	18	4	1	34	-30	8	0	1	64	-60	6	0	2	83	82	21	6	3	18V	001	4	4	4	10	020	0	3	3	60	63	10	2	0	20	20
16	0	0	0	18	00	18	4	1	34	-30	8	0	1	64	-60	6	0	2	83	82	21	6	3	18V	001	4	4	4	10	020	0	3	3	60	63	10	2	0	20	20
20	0	0	0	21	00	18	4	1	34	-30	8	0	1	64	-60	6	0	2	83	82	21	6	3	18V	001	4	4	4	10	020	0	3	3	60	63	10	2	0	20	20
24	0	0	0	24	00	18	4	1	34	-30	8	0	1	64	-60	6	0	2	83	82	21	6	3	18V	001	4	4	4	10	020	0	3	3	60	63	10	2	0	20	20
28	0	0	0	27	00	18	4	1	34	-30	8	0	1	64	-60	6	0	2	83	82	21	6	3	18V	001	4	4	4	10	020	0	3	3	60	63	10	2	0	20	20
32	0	0	0	30	00	18	4	1	34	-30	8	0	1	64	-60	6	0	2	83	82	21	6	3	18V	001	4	4	4	10	020	0	3	3	60	63	10	2	0	20	20
36	0	0	0	33	00	18	4	1	34	-30	8	0	1	64	-60	6	0	2	83	82	21	6	3	18V	001	4	4	4	10	020	0	3	3	60	63	10	2	0	20	20
40	0	0	0	36	00	18	4	1	34	-30	8	0	1	64	-60	6	0	2	83	82	21	6	3	18V	001	4	4	4	10	020	0	3	3	60	63	10	2	0	20	20
44	0	0	0	39	00	18	4	1	34	-30	8	0	1	64	-60	6	0	2	83	82	21	6	3	18V	001	4	4	4	10	020	0	3	3	60	63	10	2	0	20	20
48	0	0	0	42	00	18	4	1	34	-30	8	0	1	64	-60	6	0	2	83	82	21	6	3	18V	001	4	4	4	10	020	0	3	3	60	63	10	2	0	20	20
52	0	0	0	45	00	18	4	1	34	-30	8	0	1	64	-60	6	0	2	83	82	21	6	3	18V	001	4	4	4	10	020	0	3	3	60	63	10	2	0	20	20
56	0	0	0	48	00	18	4	1	34	-30	8	0	1	64	-60	6	0	2	83	82	21	6	3	18V	001	4	4	4	10	020	0	3	3	60	63	10	2	0	20	20
60	0	0	0	51	00	18	4	1	34	-30	8	0	1	64	-60	6	0	2	83	82	21	6	3	18V	001	4	4	4	10	020	0	3	3	60	63	10	2	0	20	20
64	0	0	0	54	00	18	4	1	34	-30	8	0	1	64	-60	6	0	2	83	82	21	6	3	18V	001	4	4	4	10	020	0	3	3	60	63	10	2	0	20	20
68	0	0	0	57	00	18	4	1	34	-30	8	0	1	64	-60	6	0	2	83	82	21	6	3	18V	001	4	4	4	10	020	0	3	3	60	63	10	2	0	20	20
72	0	0	0	60	00	18	4	1	34	-30	8	0	1	64	-60	6	0	2	83	82	21	6	3	18V	001	4	4	4	10	020	0	3	3	60	63	10	2	0	20	20
76	0	0	0	63	00	18	4	1	34	-30	8	0	1	64	-60	6	0	2	83	82	21	6	3	18V	001	4	4	4	10	020	0	3	3	60	63	10	2	0	20	20
80	0	0	0	66	00	18	4	1	34	-30	8	0	1	64	-60	6	0	2	83	82	21	6	3	18V	001	4	4	4	10	020	0	3	3	60	63	10	2	0	20	20
84	0	0	0	69	00	18	4	1	34	-30	8	0	1	64	-60	6	0	2	83	82	21	6	3	18V	001	4	4	4	10	020	0	3	3	60	63	10	2	0	20	20
88	0	0	0	72	00	18	4	1	34	-30	8	0	1	64	-60	6	0	2	83	82	21	6	3	18V	001	4	4	4	10	020	0	3	3	60	63	10	2	0	20	20
92	0	0	0	75	00	18	4	1	34	-30	8	0	1	64	-60	6	0	2	83	82	21	6	3	18V	001	4	4	4	10	020	0	3	3	60	63	10	2	0	20	20
96	0	0	0	78	00	18	4	1	34	-30	8	0	1	64	-60	6	0	2	83	82	21	6	3	18V	001	4	4	4	10	020	0	3	3	60	63	10	2	0	20	20
100	0	0	0	81	00	18	4	1	34	-30	8	0	1	64	-60	6	0	2	83	82	21	6	3	18V	001	4	4	4	10	020	0	3	3	60	63	10	2	0	20	20
104	0	0	0	84	00	18	4	1	34	-30	8	0	1	64	-60	6	0	2	83	82	21	6	3	18V	001	4	4	4	10	020	0	3	3	60	63	10	2	0	20	20
108	0	0	0	87	00	18	4	1	34	-30	8	0	1	64	-60	6	0	2	83	82	21	6	3	18V	001	4	4	4	10	020	0	3	3	60	63	10	2	0	20	20
112	0	0	0	90	00	18	4	1	34	-30	8	0	1	64	-60	6	0	2	83	82	21	6	3	18V	001	4	4	4	10	020	0	3	3	60	63	10	2	0	20	20
116	0	0	0	93	00	18	4	1	34	-30	8	0	1	64	-60	6	0	2	83	82	21	6	3	18V	001	4	4	4	10	020	0	3	3	60	63	10	2	0	20	20
120	0	0	0	96	00	18	4	1	34	-30	8	0	1	64	-60	6	0	2	83	82	21	6	3	18V	001	4	4	4	10	020	0	3	3	60	63	10	2	0	20	20
124	0	0	0	99	00	18	4	1	34	-30	8	0	1	64	-60	6	0	2	83	82	21	6	3	18V	001	4	4	4	10	020	0	3	3	60	63	10	2	0	20	20
128	0	0	0	102	00	18	4	1	34	-30	8	0	1	64	-60	6	0	2	83	82	21	6	3	18V	001	4	4	4	10	020	0	3	3	60	63	10	2	0	20	20
132	0	0	0	105	00	18	4	1	34	-30	8	0	1	64	-60	6	0	2	83	82	21	6	3	18V	001	4	4	4	10	020	0	3	3	60	63	10	2	0	20	20
136	0	0	0	108	00	18	4	1	34	-30	8	0	1	64	-60	6	0	2	83	82	21	6	3	18V	001	4	4	4	10	020	0	3	3	60	63	10	2	0	20	20
140	0	0	0	111	00	18	4	1	34	-30	8	0	1	64	-60	6	0	2	83	82	21	6	3	18V	001	4	4	4	10	020	0	3	3	60	63	10	2	0	20	20
144	0	0	0	114	00	18	4	1	34	-30	8	0	1	64	-60	6	0	2	83	82	21	6	3	18V	001	4	4	4	10	020	0	3	3	60	63	10	2	0	20	20
148	0	0	0	117	00	18	4	1	34	-30	8	0	1	64	-60	6	0	2	83	82	21	6	3	18V	001	4	4	4	10	020	0	3	3	60	63	10	2	0	20	20
152	0	0	0	120	00	18	4	1	34	-30	8	0	1	64	-60	6	0	2	83	82	21	6	3	18V	001	4	4	4	10	020	0	3	3	60	63	10	2	0	20	20
156	0	0	0	123	00	18	4	1	34	-30	8	0	1	64	-60	6	0	2	83	82	21	6	3	18V	001	4	4	4	10	020	0	3	3	60	63	10	2	0	20	20
160	0	0	0	126	00	18	4	1	34	-30	8	0	1	64	-60	6	0	2	83	82	21	6	3	18V	001	4	4	4	10	020	0	3	3	60	63	10	2	0	20	20
164	0	0	0	129	00	18	4	1	34	-30	8	0	1	64	-60	6	0	2	83	82	21	6	3	18V	001	4	4	4	10	020	0	3	3	60	63	10	2	0	20	20
168	0	0	0	132	00	18	4	1	34	-30	8	0	1	64	-60	6	0	2	83	82	21	6	3	18V	001	4	4	4	10	020	0	3	3	60	63	10	2	0	20	20
172	0	0	0	135	00	18	4	1	34	-30	8	0	1	64	-60	6	0	2	83	82	21	6	3	18V	001	4	4	4	10	020	0	3	3	60	63	10	2	0	20	20
176	0	0	0	138	00	18	4	1	34	-30	8	0	1	64	-60	6	0	2	83	82	21	6	3	18V	001	4	4	4	10	020	0	3	3	60	63	10	2	0	20	20
180	0	0	0	141	00	18	4	1	34	-30	8	0																												

of the A site does not exceed about one tenth of that originally assumed, as this would correspond to a peak between 2 and 3 times the background fluctuations. In the final refinement it was omitted.

(c) *The position of hydrogen*

The hydrogen atoms could not be located on the difference Fourier synthesis amongst the background fluctuations in electron density.

Cation distribution

The occupancy parameters used during the refinement provided an interpretation of the scattering power at M(1) and M(3) in terms of Mg^{2+} and Fe^{2+} , at M(2) in terms of Al^{3+} and Fe^{2+} , and at M(4) in terms of Li^+ and Fe^{2+} . These may confidently be expected to be the major species present at M(1), M(2) and M(3) (except that Fe at M(2) is likely to be Fe^{3+} , but the difference in scattering factor for the small amount present will be negligible). The two-dimensional refinement showed Li to be the predominant species at M(4), and the occupancy parameter for Fe at this site was used simply as a measure of the presence of ions heavier than Li. All the occupancies require re-interpretation in terms of species of equivalent scattering power consistent with the formula, and these were calculated on the basis of the relative f values at $\sin \theta/\lambda = 0.3$. The formula obtained from the analysis by von Knorring & Hornung (1961) contains 6.96 cations for the seven M sites. The formula is therefore quite compatible with the emptiness of the A sites discussed above, but it was felt that there might be some difficulty in envisioning the presence of $(K, Na, Ca)_{0.07}$ at M(4), amounting as it does to 0.28 of these rather large cations per unit cell. The reality of this cannot be ruled out, but it was noted that the amount would be reduced if the analysed holmquistite had been slightly contaminated with the co-existing hornblende. An upper limit to such contamination would be 2%, which would account for the whole of the reported Ca (and Ti) content of the holmquistite. An alternative formula for the holmquistite based on this extreme correction was therefore evaluated, giving $Na_{0.02}K_{0.01}Li_{1.82}Mg_{1.75}Fe_{1.20}Fe^{3+}_{0.24}$

$Mn_{0.03}Al^{[6]}_{1.85}Si_{7.91}Al^{[4]}_{0.09}O_{22}(OH)_{1.86}F_{0.08}O^{2-}_{0.06}$. The occupancies were interpreted in terms of both formulae. The very small K content is not affected and was ignored in both cases as being near the tolerance for the A site.

The total iron given by the occupancy parameters ($Fe_{1.60}$) exceeds the (Fe, Mn, Ti) in the formula by 0.10, the Li exceeds that in the formula by 0.13, and the Mg is deficient by 0.14. If the corrected formula is accepted, these figures become 0.14, 0.12 and 0.13 respectively. Most of these discrepancies can be accounted for by the following sequence of adjustments at M(4):

(i) insert the required number of vacancies at M(4), keeping the scattering power constant by reducing Li and very slightly increasing Fe;

(ii) replace appropriate proportions of Li and Fe at M(4) by the required numbers of Na and Ca, keeping the scattering power constant;

(iii) reduce the Li to that required by a further balanced exchange of Li and Fe for Mg [this is not pos-

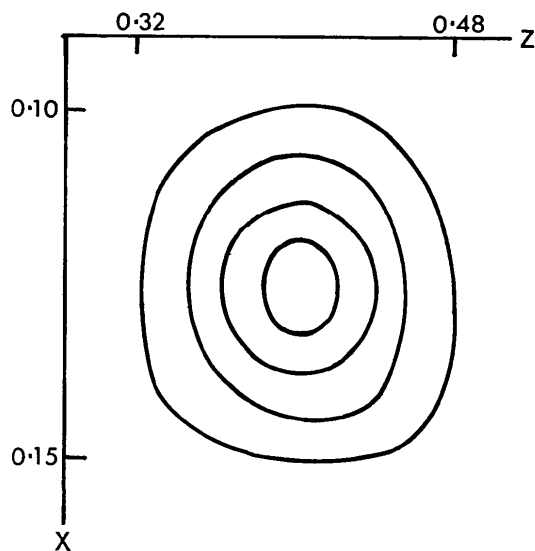


Fig. 1. Electron density in the M(4) site on the plane $y=0.51$; contours at 0, 3, 6 and $9 e \text{ \AA}^{-3}$.

Table 4. *Assignments of metals to the M sites*

Assignment	M(1)	M(2)	M(3)	M(4)
1	$Mg_{0.59}Fe_{0.41}$	$Al_{0.92}Fe_{0.08}$	$Mg_{0.44}Fe_{0.56}$	$Li_{0.97}Fe_{0.03}$
2	—	—	—	$Li_{0.911}Mg_{0.039}Na_{0.015}Ca_{0.015}\square_{0.02}$
3	—	—	—	$Li_{0.909}Mg_{0.040}Fe_{0.004}Na_{0.011}\square_{0.03}$
4	$Mg_{0.605}Fe_{0.390}$	$Al_{0.920}Fe^{3+}_{0.080}$	$Mg_{0.44}Fe_{0.56}$	$Li_{0.895}Mg_{0.055}Na_{0.015}Ca_{0.015}\square_{0.03}$
5	$Mg_{0.609}Fe_{0.390}$	$Al_{0.935}Fe^{3+}_{0.065}$	$Mg_{0.44}Fe_{0.56}$	$Li_{0.910}Mg_{0.049}Na_{0.011}\square_{0.03}$
6	$Mg_{0.60}Fe_{0.40}$	$Al_{0.93}Fe^{3+}_{0.07}$	$Mg_{0.44}Fe_{0.56}$	$Li_{0.91}Mg_{0.05}Na_{0.01}\square_{0.03}$
7	$Mg_{0.52}Al_{0.08}Fe^{2+}_{0.37}Fe^{3+}_{0.03}$	$Al_{0.81}Fe^{3+}_{0.07}Mg_{0.12}$	$Mg_{0.36}Al_{0.08}Fe^{3+}_{0.04}Fe^{2+}_{0.52}$	$Li_{0.91}Mg_{0.05}Na_{0.01}\square_{0.03}$

(1) Computed occupancies. (2) Occupancy of M(4) to give the same scattering factor as in (1) but with the correct numbers of vacancies, Na, Ca and Li to agree with the original formula. (3) As (2) but calculated to agree with the corrected formula. (4) Assignments of ions from the original formula on the basis that all vacancies, Na, Ca and Li are at M(4) (together with sufficient Mg to complete it), all Al and sufficient Fe^{3+} are at M(2), that M(3) corresponds to the computed occupancy, and the remaining ions are at M(1). (5) As (4) but calculated with the corrected formula. (6) Suggested occupancies to accord with both analysis and diffraction results. (7) Adjustment of (6) to take account of M-O distances.

sible when the original formula is used because there is no Fe left in M(4) after (ii)].

The results of these adjustments are shown in assignments 2 and 3 of Table 4. Assignments 4 and 5 were obtained from the original and corrected formula (respectively) on the assumption that all vacancies, Na, Ca and Li are in M(4), that M(2) is occupied by all the Al together with some Fe, and that M(3) has the occupancy obtained from the refinements. Thus the only diffraction results used in assignments 4 and 5 are the occupancy of M(3) and the avoidance of M(4) by Fe. Agreement between (2) and (4) and between (3) and (5) is within 0.02 of each ion at each site.

The results confirm the conclusions from the two-dimensional refinement that Li is ordered at M(4), that Fe avoids M(4), and that M(3) accepts Fe to a somewhat greater extent than M(1). It eliminates the anomaly in the two-dimensional refinement which gave M(2) a lower scattering power than pure Al; the new results show a small amount of Fe at M(2) as would be expected.

Evidence for the ordering of Al at M(2) relative to Mg at M(1) and M(3) cannot be obtained from an occupancy refinement, because equivalent scattering powers (within small errors at different scattering angles) could be obtained for any distribution of Mg and Al over these sites with small adjustments in the Fe occupancies. However, the assignment of Al to M(2) is confirmed by the fact that the M(2)–O distances are much smaller than the M(1)–O and M(3)–O distances. Both the size of the site and the preference of M(2) sites for trivalent ions (Whittaker, 1971) lead to the conclusion that the Fe in M(2) will be in the ferric state. However, this leaves a small amount of Fe³⁺ (0.08 in total) in M(1)+M(3), and suggests incomplete ordering of the trivalent ions into M(2). The same conclusion regarding the Al is indicated by Table 5. Mean M–O distances calculated from the occupancies in assignment 6 of Table 4 on the basis of the weighted mean ionic radii (Whittaker & Muntus, 1969) are too large for M(1) and M(3) and too small for M(2). If 0.24 atoms of Al are exchanged for Mg between the two M(2) sites and the three [M(1)+M(3)] sites, the agreement is much better. Assignment 7 of Table 4 shows the final occupancies after making this change.

Table 5. M–O mean distances and radius sums

	Mean distance observed	Radius sum from Table 3, assignment 6	Radius sum from Table 3, assignment 7
M(1)–O	2.100 (4)	2.124	2.105
M(2)–O	1.932 (4)	1.918	1.941
M(3)–O	2.095 (5)	2.134	2.113

The geometry of the cation sites

Litvin *et al.* found an elongated region of electron density at the M(4) site of holmquistite which they interpreted in terms of a split site having the atoms

separated by 0.67 Å. This has not been observed in any previously studied amphibole structure, and we have not found it in our holmquistite structure. Fig. 1 shows a section through the M(4) atom on the $y=0.51$ plane, and it is not appreciably elongated. The long axis of the ellipsoid of the anisotropic temperature factor for M(4) is oriented at 63° to the long axis of the region indicated by Litvin *et al.*

Table 5 shows that the M(4) site has five close neighbours, O(5A) being very much closer than O(5B). This is exactly in line with the situation in anthophyllite (Finger, 1970) and to a less extent in gedrite (Papike & Ross, 1970). It is notable in connexion with the extra absences among the $hk0$ reflexions not required by the space group that the difference in the distances M(4)–O(5A) and M(6)–O(5B) is almost entirely due to the difference between their separations in the z direction.

Some confirmation is obtained that the departures of the M(1), M(2) and M(3) sites from regular octahedra are systematically similar in the various orthorhombic amphiboles. Thus the largest M(1)–O distance is that to O(2), and this is true in all the four structures. In the M(2) octahedron the M(2)–O(1) is usually the longest distance and M(2)–O(4) is always the shortest, and in the M(3) octahedron M(3)–O(1) is always the longest distance. Bond distances and angles are given in Tables 6 and 7.

Table 6. Bonded distances (Å)

	A chain	B chain
M(1)–O(1)	2.086 (6)	2.079 (9)
M(1)–O(2)	2.123 (9)	2.123 (9)
M(1)–O(3)	2.095 (9)	2.095 (8)
Average	2.101	2.099
M(2)–O(1)	2.013 (9)	2.029 (9)
M(2)–O(2)	1.941 (10)	1.938 (10)
M(2)–O(4)	1.828 (9)	1.841 (10)
Average	1.927	1.936
M(3)–O(1)	2.103 (9)	2.109 (9)
M(3)–O(3)	2.077 (14)	2.070 (13)
Average	2.094	2.096
M(4)–O(2)	2.125 (19)	2.090 (19)
M(4)–O(4)	2.157 (21)	2.045 (21)
M(4)–O(5)	2.314 (19)	2.886 (19)
M(4)–O(6)	3.465 (19)	2.728 (18)
Average	2.52	2.44
T(1)–O(1)	1.638 (10)	1.630 (10)
T(1)–O(5)	1.618 (9)	1.613 (9)
T(1)–O(6)	1.587 (9)	1.610 (9)
T(1)–O(7)	1.623 (5)	1.620 (10)
Average	1.616	1.618
T(2)–O(2)	1.630 (9)	1.645 (9)
T(2)–O(4)	1.589 (8)	1.597 (10)
T(2)–O(5)	1.657 (8)	1.638 (9)
T(2)–O(6)	1.644 (9)	1.643 (9)
Average	1.630	1.631

The structure of the silicate chains

The A and B chains both contain O-type rotations of the tetrahedra in the nomenclature of Thompson

Table 7. *Inter-bond angles* (°)

O(1A)-M(1)-O(1B)	177.3 (4)	O(2B)-M(2)-O(4A)	89.5 (4)
O(2A)-M(1)-O(3B)	173.9 (4)	O(2B)-M(2)-O(4B)	94.7 (4)
O(2B)-M(1)-O(3A)	173.6 (5)	O(4A)-M(2)-O(4B)	101.1 (3)
O(1A)-M(1)-O(2A)	99.2 (3)	O(1A)-M(3)-O(1B')	179.6 (3)
O(1A)-M(1)-O(2B)	78.7 (3)	O(3A)-M(3)-O(3B)	179.6 (6)
O(1A)-M(1)-O(3A)	97.2 (4)	O(1A)-M(3)-O(1A')	104.0 (4)
O(1A)-M(1)-O(3B)	84.3 (4)	O(1A)-M(3)-O(1B)	76.2 (3)
O(1B)-M(1)-O(2A)	78.8 (4)	O(1A)-M(3)-O(3A)	95.7 (4)
O(1B)-M(1)-O(2B)	99.5 (4)	O(1A)-M(3)-O(3B)	84.5 (3)
O(1B)-M(1)-O(3A)	84.8 (4)	O(1B)-M(3)-O(1B')	103.5 (5)
O(1B)-M(1)-O(3B)	97.8 (4)	O(1B)-M(3)-O(3A)	84.6 (3)
O(2A)-M(1)-O(2B)	90.6 (3)	O(1B)-M(3)-O(3B)	95.2 (3)
O(2A)-M(1)-O(3A)	94.8 (4)	O(2A)-M(4)-O(5B)	168.4 (9)
O(2B)-M(1)-O(3B)	95.0 (4)	O(2B)-M(4)-O(5A)	141.3 (10)
O(3A)-M(1)-O(3B)	79.8 (3)	O(4A)-M(4)-O(4B)	168.6 (9)
O(1A)-M(2)-O(4B)	170.1 (4)	O(2A)-M(4)-O(2B)	91.5 (6)
O(1B)-M(2)-O(4A)	168.8 (4)	O(2A)-M(4)-O(4A)	91.4 (7)
O(2A)-M(2)-O(2B)	173.9 (4)	O(2A)-M(4)-O(4B)	78.8 (7)
O(1A)-M(2)-O(1B)	80.1 (3)	O(2A)-M(4)-O(5A)	108.7 (8)
O(1A)-M(2)-O(2A)	90.8 (4)	O(2B)-M(4)-O(4A)	77.3 (7)
O(1A)-M(2)-O(2B)	84.9 (4)	O(2B)-M(4)-O(4B)	97.1 (8)
O(1A)-M(2)-O(4A)	88.8 (4)	O(2B)-M(4)-O(5B)	85.0 (7)
O(1B)-M(2)-O(2A)	84.3 (4)	O(4A)-M(4)-O(5A)	69.7 (6)
O(1B)-M(2)-O(2B)	80.3 (3)	O(4A)-M(4)-O(5B)	77.1 (6)
O(1B)-M(2)-O(4B)	90.1 (4)	O(4B)-M(4)-O(5A)	118.6 (8)
O(2A)-M(2)-O(4A)	94.8 (4)	O(4B)-M(4)-O(5B)	112.6 (7)
O(2A)-M(2)-O(4B)	88.8 (4)		

Table 7 (cont.)

	A chain	B chain
O(1)-T(1)-O(5)	109.3 (4)	109.4 (5)
O(1)-T(1)-O(6)	109.8 (4)	109.6 (5)
O(1)-T(1)-O(7)	109.8 (5)	108.6 (5)
O(5)-T(1)-O(6)	110.1 (5)	111.8 (5)
O(5)-T(1)-O(7)	109.0 (5)	108.7 (5)
O(6)-T(1)-O(7)	108.7 (5)	108.7 (5)
O(2)-T(2)-O(4)	115.8 (5)	117.0 (5)
O(2)-T(2)-O(5)	108.1 (5)	107.5 (5)
O(2)-T(2)-O(6)	107.9 (5)	107.5 (5)
O(4)-T(2)-O(5)	104.1 (5)	109.7 (5)
O(4)-T(2)-O(6)	111.6 (5)	106.1 (5)
O(5)-T(2)-O(6)	109.1 (5)	108.8 (5)
T(1)-O(7)-T(1)	146.1 (9)	146.6 (9)
T(1)-O(5)-T(2)	134.4 (5)	135.0 (5)
T(1)-O(6)-T(2)	144.3 (5)	142.5 (5)

(1970). This again is in agreement with the results for the other orthorhombic amphiboles. However, in holmquistite the amount of the rotation is smaller than in either anthophyllite or gedrite, and the two chains (*A* and *B*) in holmquistite are very much more alike in their degree of rotation (Table 8).

Table 8. *Comparison of the tetrahedral rotations as indicated by the angle O(5)-O(6)-O(5) in holmquistite with those in gedrite and anthophyllite*

	Chain A	Chain B
Holmquistite	166.4°	163.3°
Gedrite 001	162.4	147.5
Gedrite 002	162.5	146.0
Anthophyllite	169.2	157.5

As in the case of the octahedra, there are systematic departures from regularity in the tetrahedra which run through all the four published structures. T(1A)-O(6A), T(2A)-O(4A), and T(2B)-O(4B) are systematically the

shortest distances in their respective tetrahedra, and T(2A)-O(5A) is systematically the longest in the T(2A) tetrahedron. The ranges of the angles in the T(1) tetrahedra are not very large, and comparisons between the structures in this respect are not very significant, but in the T(2A) tetrahedron O(2)-T-O(4) is systematically the largest angle and O(4)-T-O(5) the smallest. In the T(2B) tetrahedron O(2)-T-O(4) is again the largest and O(4)-T-O(6) the smallest.

The dihedral angle between the (approximate) planes of the O(4), O(5), O(6) and O(7) atoms at each side of the symmetry plane is 171°, which agrees well with that in other amphiboles.

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