dimer *C* of 1,3-dimethylthymine (Camerman, Weinblum & Nyburg, 1969).

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The Structure of the Orthorhombic Amphibole Holmquistite

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A two-dimensional refinement of the structure of holmquistite has shown segregation of the cations in different sites. Iron is preferentially concentrated in the sites $M1$ and $M3$ which are internal to the chains, and lithium in the essentially inter-chain site $M4$. It is concluded that aluminum is concentrated in the site $M2$ which has both intra- and inter-chain coordinations.

1. Introduction

Holmquistite is a lithium aluminum amphibole whose ideal formula can be written as

$$Li_2Al_2(Mg,Fe)_3Si_8O_{22}(OH)_2.$$

It was shown by Vogt, Bastiansen & Skancke (1958) to be a member of the orthorhombic series of amphiboles, and it was suggested by Whittaker (1960) that this was associated with the small size of the lithium ion. More recently, Ginsburg (1965) has also found a monoclinic holmquistite.

The structure of orthorhombic holmquistite is of interest for two reasons:

(i) Very little detailed information is available on the structure of any orthorhombic amphibole. The structure of anthophyllite was determined in principle by Warren & Modell (1930), and further work was done on the same mineral by Ito (1950), but no refinement of its structure has been published. No structural study of any other orthorhombic amphibole has been reported.

(ii) In the monoclinic alkali amphiboles in which the alkali ion is sodium, this ion is confined to a single crystallographic site by its size. In magnesio-riebeckite (Whittaker, 1949) and glaucophane II (Ernst, 1963; Colville, Ernst & Gilbert, 1966; Papike & Clark, 1968) the trivalent ion [Fe^{III} and Al respectively] is also ordered to a considerable extent, and its ordering may be regarded as consequential on the effect of the confinement of the monovalent ion to a single neighbouring site. In holmquistite the primary effect of size will not lead to a marked ordering of the lithium into a particular site, and any ordering of the cations among the four available sites will be of considerable interest, as arising from other causes.

2. Material

The specimen studied was from the Benson Pegmatite Mine, Mtoko, Rhodesia, which has been described and analysed by von Knorring & Hornung (1961). Its formula calculated to 24(O,OH,F) is $Na_{0\cdot03}K_{0\cdot01}Ca_{0\cdot03}\,Li_{1\cdot79}\,Mg_{1\cdot76}\,Fe^{2+}_{1\cdot21}\,Fe^{3+}_{0\cdot24}\,Mn_{0\cdot03}\,Ti_{0\cdot02}\,Al^{[6]}_{1\cdot84}\,Si_{7\cdot89}\,Al^{[4]}_{0\cdot11}O_{22}(OH)_{1\cdot86}F_{0\cdot08}O^{2-}_{0\cdot06}$. Apparently single crystals are easily isolated from the rather friable material, but they tend to contain low-angle boundaries and give multiple spots on high layer lines. It proved difficult to choose sufficiently perfect crystals by the criterion of uniformity of extinction in the polarizing microscope, but the ninth crystal selected gave tolerably suitable reflexions. It measured approximately $0\cdot3\times0\cdot1\times0\cdot015$ mm, the major dimension being parallel to c and the minor dimension parallel to a.

3. Unit cell and space group

Approximate unit-cell dimensions, obtained from oscillation and zero-layer Weissenberg photographs about the c axis, were: $a=18\cdot29$, $b=17\cdot67$, $c=5\cdot28$ Å. Systematic absences agree with the space group *Pnma* assigned to anthophyllite by Warren & Modell (1930). There is an additional non-space-group absence in that $hk0$ is present only for $h+2k=4n$ (including $h00$ only for $h=4n$). Warren & Modell reported 200 and 600 as weak and 10,0,0 and 14,0,0 as absent, although it is difficult to reconcile the presence of 200 and 600 with the structure proposed by these authors. $h00$ reflexions with $h\neq4n$ could occur only if the two silicate double chains in each talc-like strip of the amphibole structure were at different distances from the metal cations sandwiched between them. Any such departure from equality would be expected to be very small, and would therefore lead to weak high-order reflexions of this type, and absent low-order ones, rather than *vice versa*. In the present work the complete absence of $hk0$ for $h+2k\neq4n$, up to at least 34 orders of h and k shows that in holmquistite this non-space-group symmetry is very precise. As a result, the projection down the c axis has the two-dimensional space-group *cm* with an a axis which is half of that of the three-dimensional cell. This two-dimensional space-group is identical with that of the c axis projection of the monoclinic amphiboles.

4. Two-dimensional refinement

The intensities of the $hk0$ reflexions were measured from a range of multiple film exposures on a Weissenberg goniometer using Cu $K\alpha$ radiation, and again using Mo $K\alpha$ radiation. The absorption coefficients for these radiations were 187 and 24·8 respectively. Absorption corrections were made on the KDF9 computer by means of a program based on the method of Busing & Levy (1957) and modified by T. Blundell. In spite of the small size of the crystal, the absorption corrections for Cu $K\alpha$ radiation were large, and, in view of uncertainties in the crystal dimensions and in the adequacy of the program for such large corrections, the corrected Cu $K\alpha$ data were not considered very reliable. It was for this reason that the data were collected again with Mo $K\alpha$ radiation. However, as a check on the reliability of the results, the structure was refined independently from these two independent sets of data by means of a least-squares program based on that of Mills & Rollett (1961).

In view of the considerations in section 3, refinement was carried out in the two-dimensional space-group *cm* starting from estimated atomic positions based on clino-amphibole structures. In the following discussion the nomenclature of the sites follows that which is customary for clino-amphiboles (see, for example, Fig. 2 of Whittaker, 1960), not that introduced by Warren & Modell (1930) for anthophyllite.

The main interest of the two-dimensional refinement lies in the occupation of the cation sites $M3$, $M1$, $M2$ and $M4$ (listed in sequential order from the centres to outer edges of the cation bands). It was obviously desirable to start from the assumption of completely random occupation of the four sites by all the available cations. Since it is not practicable to refine more than one occupation parameter per site, such a situation was simulated by assuming all sites to be occupied by $0\cdot6\,Li+0\cdot4\,Fe$, which gives an atomic scattering factor approximating to random occupancy by all the cations in the formula. Refinement of a single occupation paremeter for each of the four sites (together with an overall temperature factor and the variable positional parameters permitted by the two-dimensional space-group) could then be expected to indicate any preferential occupation of a site in terms of relative average scattering factors. The results from the first cycles of refinement showed the scattering factor at $M4$ to be so small that this site must be almost entirely occupied by Li. The scattering factors at $M1$ and $M3$ were so large that

Table 1. *Occupation of cation sites from least-squares refinement*

	Cu data	Mo data	σ_{Cu}	σ_{Mo}	Interpretation to accord with formula
$M1$	$Mg_{0\cdot61}Fe_{0\cdot39}$	$Mg_{0\cdot56}Fe_{0\cdot44}$	0·06	0·04	$Mg_{0\cdot52}Fe_{0\cdot48}$
$M2$	$Al_{1\cdot14}Fe_{-0\cdot14}$	$Al_{1\cdot01}Fe_{-0\cdot01}$	0·06	0·04	$Al_{0\cdot92}Mg_{0\cdot08}$
$M3$	$Mg_{0\cdot68}Fe_{0\cdot32}$	$Mg_{0\cdot49}Fe_{0\cdot51}$	0·08	0·05	$Mg_{0\cdot46}Fe_{0\cdot54}$
$M4$	$Li_{0\cdot80}Mg_{0\cdot15}$	$Li_{0\cdot94}Mg_{0\cdot01}$	0·08	0·06	$Li_{0\cdot90}Mg_{0\cdot05}Na_{0\cdot03}$
A	$Ca_{0\cdot08}$	$Ca_{-0\cdot03}$	0·06	0·02	$(Ca,K)_{0\cdot04}$

these sites must contain most of the iron, while the occupancy of $M2$ was compatible with Mg or Al (the alternative of a mixture of Li and Fe at $M2$ being ruled out by the limited amount of Li available for attribution to $M4$). Further refinement was then carried out with Mg+Fe at $M1$ and $M3$, Al+Fe at $M2$ and Li+Mg at $M4$. The initial ratios of these ions in these sites were chosen to be in line both with the formula and with the results of the first refinement based on Li+Fe only.

Because it seems improbable that the large cations K, Na, and Ca could be accommodated in the $M4$ site of an orthorhombic amphibole, an open-ended parameter was introduced in one cycle of the refinement to permit the placing of these ions at the vacant A site. Refinement did not lead to a significant non-zero occupancy for this site.

The process of refinement described above led to R values of 0·198 and 0·165 for the Cu $K\alpha$ and Mo$K\alpha$ data respectively. Further refinement of positional and independent isotropic temperature factors (holding occupancies constant) led to a further reduction of R to 0·085 for the Mo $K\alpha$ data. This further refinement was not carried out for the Cu $K\alpha$ data.

The final occupancies derived from the two sets of data are shown in Table 1, and are mutually confirmatory, at least in general outline.

The positional parameters derived from the Cu $K\alpha$ data were quite evidently less satisfactory than those from the Mo $K\alpha$ data. For example, the projected Si1–O1 and Si2–O2 distances were noticeably unequal. These irregularities were not confirmed by the Mo $K\alpha$ data, and accordingly the atomic positions given in Table 2 are those derived from the Mo $K\alpha$ data only.

Table 2. *Atomic positions and isotropic temperature factors*

	x/a	y/b	B
O1	0·110	0·095	0·31
O2	0·119	0·175	0·37
O3	0·115	0	0·88
O4	0·122	0·249	0·36
O5	0·143	0·364	0·49
O6	0·156	0·382	0·32
O7	0·165	0·500	0·41
Si1	0·289	0·087	0·13
Si2	0·299	0·173	0·30
$M1$	0	0·091	0·37
$M2$	0	0·182	0·02
$M3$	0	0	0·16
$M4$	0	0·262	1·07

5. Discussion

The results of the refinements of the occupancies of the cation sites, given in columns 2 and 3 of Table 1, take no specific account of the numbers of atoms available as given by the formula. They were refined subject only to the condition that in $M1$, $M2$ and $M3$, the number of Fe atoms is $1-x$, where x is the number of Mg atoms (or Al atoms as the case may be). Negative numbers of Fe atoms in $M2$ merely imply scattering power at that site lower than that of Al.

Table 3. *Observed and calculated structure factors for planes hk*0

k	$\lvert F_o \rvert$	F_c
	h = 0	
4	7332	−7040
6	868	429
8	2552	1985
10	6316	6829
12	10365	11558
14	4149	−4079
16	1354	1132
18	740	−798
20	659	−875
22	5571	5909
24	4108	4072
26	2968	−2767
32	1224	1323
34	3658	3304
	h = 2	
3	967	863
5	2617	2103
7	2784	−2414
9	725	655
11	7379	6696
13	1325	808
15	1501	−1131
21	2333	2659
25	1390	1201
33	2119	1309
	h = 4	
0	2010	−1224
2	698	632
4	4133	3536
8	1546	1275
10	1634	1697
12	611	−748
14	770	501
16	1639	1367
20	2540	2569
24	1678	−1848
26	967	883
32	1333	1697
	h = 6	
1	10122	10534
3	5010	−4639
5	2558	−2150
7	2234	1625
9	1490	1217
11	5948	6130
13	1157	1121
15	289	−304
17	863	795
19	1541	−1731
21	1282	1132
23	4238	4224
33	1653	1743
35	1788	1974
	h = 8	
0	2382	−1683
2	2428	2358
6	740	−650
8	5335	−5409
10	3951	3729
12	3598	3419
16	2360	−2233
20	906	−679
22	2644	2666
26	559	649
28	1059	−1200
34	1646	1538
	h = 10	
1	3979	−3551
3	3724	3435
5	681	616
7	1534	1039
9	2021	1954
11	3406	−3257
13	1496	−1501
15	3394	3508
17	559	−529
19	832	776
21	1305	1334
23	2298	−2193
27	2128	1859
31	877	1188
33	493	173
35	1599	−1568
	h = 12	
0	6836	6725
2	719	556
4	1533	−1310
6	2147	2144
8	1320	1071
10	2397	2265
12	1698	1501
16	1544	1965
18	955	633
22	1939	1955
24	552	807
34	1353	1459
	h = 14	
1	4979	5424
3	2697	−2358
5	919	650
7	3620	−3324
9	2191	−2133
11	8437	8805
13	2254	2353
15	3772	−3461
17	478	−360
19	1625	−1392
21	1735	1622
23	3867	3955
25	445	−491
27	1417	−988
31	894	−608
33	2145	2121
	h = 16	
0	4231	4373
4	943	863
6	1025	−965
8	2131	2059
10	1465	1427
12	1703	1440
16	1488	1414
18	1199	−1219
20	1807	1910
22	1608	1624
32	1802	1912
	h = 18	
1	2761	2767
5	1533	1384
7	1747	1865
9	2060	2024
11	2101	2074
15	537	733
17	2033	2150
19	1160	868
21	1639	1612
	h = 20	
0	6392	6552
4	1246	−946
6	360	81
8	3719	−3484
10	3496	3147
12	5991	6149
14	2519	−2275
16	1249	−1416
22	3321	3358
24	1711	1402
26	2025	−1757
	h = 22	
1	2950	2885
3	827	−582
5	1720	−1639
9	1396	1238
11	2251	2153
17	1357	−1223
21	1943	1879
23	1830	1614
	h = 24	
0	1954	−1714
2	1508	1578
4	1224	958
8	1568	1508
10	1193	1267
12	2244	−2183
14	1270	1341
16	1193	1133
20	1117	1010
24	1227	−1160
26	2149	2247
	h = 26	
5	1230	1296
9	1371	−1362
11	1758	2040
	h = 28	
0	3620	3723
2	559	442
4	1781	−1637
8	818	−432
10	1314	1333
12	1738	1418
18	1209	−1143
20	818	−673
22	2259	2117
	h = 30	
3	1173	1299
9	1309	1373
	h = 32	
0	1460	1200
2	814	−946
4	863	1207
6	991	1129
12	1734	1658
	h = 34	
1	3039	3226
3	2049	−1939
5	790	−341
11	3127	3185
	h = 36	
0	2035	2244

The range of planes listed is extended to include the rather large F_o values for k in the region of 30, although this means that a rather large number of reflexions within this range of indices were unobserved. 63 planes with $F_o=0$ occur within this range and are not listed. Two reflexions, 020 and 210, were at too small an angle to be measured with Mo radiation and are also omitted, although their approximate values are known from the Cu data.

The interpretation in the final column was obtained as follows. The distribution of Al between octahedral and tetrahedral sites, indicated in the formula given in section 2, was derived in the usual way by allocating sufficient Al to tetrahedral sites to make up 8 atoms of $\mathrm{Si}+\mathrm{Al}^{[4]}$. For reasons discussed in the next paragraph, the predominant cation at $M2$ is assumed to be Al, although, of course, the diffraction results do not distinguish between Al and Mg. Therefore all the $\mathrm{Al}^{[6]}$ in the formula is put at $M2$. The total Fe content derived from column 3 (1·39 allowing for multiplicity of sites) is slightly less than the total Fe+Ti+Mn in the formula. The Fe (including Ti+Mn) in $M1$ and $M3$ has therefore been scaled up to fit the formula, and sufficient Mg put in these sites to fill them. The remaining Mg is put at $M2$ and $M4$. All Li available is put at $M4$ and the small amounts of Na, K and Ca, rather arbitrarily and without good evidence, are divided between $M4$ and A.

The attribution of all the Al to the $M2$ position in Table 1 is not strictly demanded by the data, which only indicates an avoidance of $M2$ by Fe, and would be equally satisfied by occupation of that site by Mg. However, the effects of radius, charge and polarizability would all be more likely to lead to an association between Mg and Fe than between Al and Fe, since the latter is predominantly Fe^{II}; and the fact that there is evidence for occupation of $M2$ by the triply-charged ion in riebeckite and glaucophane, when $M4$ is occupied by a singly-charged ion, suggests that a similar situation may be expected here in view of the preferential occupation of $M4$ by Li. The apparent total avoidance of $M2$ by Fe is, however, difficult to understand in view of the presence of $Fe^{3+}_{0\cdot24}$ in the formula. It has been shown by Bancroft, Maddock, Burns & Strens (1966) by means of infrared and Mössbauer spectra that in cummingtonite and anthophyllite Fe^{II} goes into $M4$ and $M2$ (in that order of preference) rather than into $M1$ and $M3$, on account of the greater crystal field stabilization energies arising in the former, less symmetrically coordinated, sites. The avoidance of $M4$ and $M2$ by Fe in holmquistite shows that the ordering observed here must be due to energy differences greater than those which would be involved in such crystal field effects. That the difference does not arise in any way from the presuppositions of the different experimental methods has been shown by infrared examination of holmquistite by Strens (1966). This revealed OH vibration frequencies appropriate to the occupation of $M1$ and $M3$ sites solely by Mg+Fe. Were Fe to be present in $M2$ or $M4$, the composition of the mineral would require a corresponding introduction of Al and Li into $M1$ and $M3$, and this would have led to additional OH vibration frequencies. Strens did not detect any difference in occupancy of the $M1$ and $M3$ sites, and this is in accordance with the fact that the occupancies deduced for these sites in Table 1 do not differ significantly from one another.

Since Li is undoubtedly small enough to fit the $M1$, $M2$ and $M3$ sites of amphibole, and since Mg and Fe are known to be able to enter the $M4$ site in orthorhombic amphiboles, it would seem that the preferential entry of Li into $M4$ must be an effect of electrostatic potential leading to a preference for a low positive charge at $M4$ combined with a high positive charge at $M2$. The preference for a low charge at $M4$ may perhaps be qualitatively correlated with the fact that two of the six oxygen atoms which coordinate this site are already attached to two silicon atoms each, and any electrostatic bonds formed from them to $M4$ necessarily contravene Pauling's second rule. A more quantitative theoretical investigation of electrostatic ordering effects on cations in amphibole structures is in hand.

The relative positions of the atoms in the projection are in accord with the now familiar details of clino-amphibole structures, with the silicate band bending about its mid-line away from the plane of the metal ions. Calculated standard deviations for atomic positions are 0·02 Å for oxygen, 0·01 Å for silicon, $M1$ and $M2$, and 0·06 Å for $M4$ (lithium). It is not worth while seeking to interpret the positions in detail before the completion of a three-dimensional refinement which is in hand. It is, however, worth noting that in spite of the large uncertainty in the y coordinate of $M4$ (arising from the low electron density associated with it), this is very significantly smaller than the corresponding coordinate in the calc-alkali clino-amphiboles in which this site is occupied by Na or Ca. It is, however, very similar to the coordinate of $M4$ found by Ghose (1961) and Fisher (1966) in cummingtonite.

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