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Foggite, $Ca(H_2O)_2[CaAl_2(OH)_4(PO_4)_2]$: Its Atomic Arrangement and Relationship to Calcium Tschermak's Pyroxene

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Abstract

Foggite, $Ca(H_2O)_2[CaAl_2(OH)_4(PO_4)_2]$, space group $A2_122$, a 9.270(2)Å, b 21.324(7)Å, c 5.190(2)Å, $Z = 4$, is structurally related to the pyroxenes. $R(hkl) = 0.059$ for 888 non-equivalent reflections.

The underlying feature is an $Al(OH)_2(Op)_2$ octahedral edge-sharing zig-zag chain which runs parallel to the c axis. Its tetrahedral envelope and closely associated $Ca(1)O_8$ polyhedron lead to a sheet oriented parallel to {010} which possesses the composition $[CaAl_2(OH)_4(PO_4)_2]^{2-}$. Equivalent sheets are weakly linked along [010] by $Ca(2)(Op)_4(H_2O)_4$ polyhedra, the water molecules possessing a disordered character.

Metrically, foggite's *ac* plane (9.3 × 5.2 Å) corresponds to the *ac* plane (9.6 × 5.3 Å) in the structure of calcium Tschermak's pyroxene. Their structural similarity becomes further apparent by writing their formulae as:

Calcium Tschermak's pyroxene: $[CaAl_2T_2O_{12}]\cdot CaT_2$
Foggite : $[CaAl_2P_2O_8(OH)_4]\cdot Ca(H_2O)_2$

The bracketed region in foggite is obtained by eliminating alternate tetrahedra in the pyroxene chain. The "free" vertices are thus replaced by $(OH)^-$ anions. Average interatomic distances are $^{[8]}Ca(1)$–O 2.46 Å, $^{[4]-[7]}Ca(2)$–O 2.40 Å, $^{[6]}Al(1)$–O 1.91 Å, $^{[6]}Al(2)$–O 1.89 Å, $^{[4]}P$–O 1.54 Å.

Introduction

Recently, Moore, Irving, and Kampf (1975) announced three new species from the Palermo No. 1 pegmatite in North Groton, New Hampshire. This locality, the most prolific pegmatite source of diverse species in the world, has provided good single crystals of species involving Ca^{2+}, Al^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, and P^{5+} cations and the opportunity to study their structures—many of which involve novel octahedral clusters—in detail.

Foggite, $CaAl(OH)_2(H_2O)(PO_4)$, owing to its rather simple composition, was a likely candidate for further investigation, the results of which indicate that the structure is related to the pyroxenes in a rather simple way.

Experimental

Weissenberg and precession single crystal photography and least-squares refinement based on twenty high angle reflections from the PICKER diffractometer afforded a 9.270(2)Å, b 21.324(7)Å, c 5.190(2)Å, space group $A2_122$. The cell contents proposed by Moore, Irving, and Kampf (1975) are $8[CaAl(OH)_2(H_2O)(PO_4)]$. The space group, unusual for a mineral structure, was confirmed in the final three-dimensional refinement of the atomic coordinates.

The very thin tabular aspect of the crystals presented considerable difficulty in finding a suitable crystal for study. A tablet, measuring 0.22 × 0.01 × 0.13 mm along the three crystallographic axes, yielded sharp reflections of low mosaic spread. Utilizing a PICKER automated diffractometer; graphite monochromatized Mo$K\alpha$ radiation ($\lambda = 0.7093$Å); scan speed of 1.0°/minute; scan range of 2.0°; background counting times of 20 seconds on each side of the peak; and maximum $2\theta = 60°$, eight hundred eighty eight non-equivalent averaged reflections were obtained. Prior to averaging, careful measurement of the crystal provided the correction for absorption by the Gaussian integral method described by Burnham (1966). For $I(hkl) < 2\sigma$ of $I(hkl)$, the reflections were set as $\sigma\ I(hkl)$. Structure

TABLE 1. Foggite. Cell Multiplicities (M), Atom Coordinates, and Isotropic Thermal Vibration Parameters*

Atom	M	x	y	z	B(Å^2)
Ca(1)	4	0.0000	0.3614(1)	0.0000	0.66(3)
Ca(2)	4	.2500	.50000	.0870(4)	1.35(4)
Al(1)	4	.0000	.1945(1)	.0000	.52(4)
Al(2)	4	.0000	.2622(1)	.5000	.49(4)
P	8	.2143(2)	.3833(1)	.5702(3)	.48(3)
O(1)	8	.3756(5)	.3680(2)	.6243(9)	.71(7)
O(2)	8	.1255(5)	.3233(2)	.6339(9)	.68(7)
O(3)	8	.1653(5)	.4324(2)	.7659(9)	.76(7)
O(4)	8	.1881(5)	.4040(2)	.2922(9)	.87(7)
OH(1)	8	.1067(5)	.2015(2)	.6844(9)	.62(7)
OH(2)	8	-.0995(5)	.2608(2)	.8205(9)	.57(7)
OW(1)	½(8)	.5000	.4512(10)	.0000	3.34(40)
OW(2a)	¼(16)	.4780(25)	.4741(9)	.2165(44)	1.26(34)
OW(2b)	¼(16)	.4617(21)	.4793(9)	.3513(38)	.93(28)

*Estimated standard errors refer to the last digit.

factor magnitudes, F(obs), were then obtained through standard computational procedures.

Solution of the Structure

Three dimensional Patterson synthesis revealed that most of the electron density was concentrated in the structure at the levels $z = 0$ and $1/2$. In addition, all evidence suggested five non-equivalent strong scatterers in the asymmetric unit. Based on the cell contents, this meant that three distinct atomic species were distributed over four independent special positions of equipoint rank number four and one over the general position of rank number eight.

A plausible solution which satisfied all the prominent vectors on the map was used as input into the β synthesis of Ramachandran and Srinivasan (1970). Owing to similarities in atomic numbers for Ca^{2+}, Al^{3+}, and P^{5+}, no attempt was made to distinguish these species at that stage of the analysis. Several repeated β syntheses revealed the essential outline of the structure and the cations could be appropriately assigned. A final γ' synthesis retrieved all the non-hydrogen atoms in the structure. Two positions—corresponding to the water molecules OW(1) and OW(2)—were of low electron density and possessed broad contours on the Fourier maps. Three-dimensional refinement of all non-hydrogen atomic positions and site occupancies for OW(1) and OW(2) permitted a more detailed analysis of the disordered water molecules. OW(1) appeared as a broad but reasonably spherical distribution but OW(2) was split into a dumbbell-shaped distribution, the two maxima denoted as OW(2a) and OW(2b). Site multiplicity refinement indicated that OW(1) was approximately half occupied, and the split OW(2a) and OW(2b) each about one-quarter occupied. As we shall discuss further on, the principal feature of the structure is not seriously affected by these disordered water molecules.

Full-matrix least-squares refinement converged to

$$R(hkl) = \frac{\sum ||F(\text{obs})| - |F(\text{calc})||}{\sum |F(\text{obs})|} = 0.059$$

for all 888 non-equivalent reflections. We employed scattering curves selected from the data of Cromer and Mann (1968) for Ca^{2+}, Al^{3+}, P^0, and O^{1-}.

Atomic coordinates and isotropic thermal vibration parameters are presented in Table 1, and the structure factor data are listed in Table 2.

Discussion of the Structure

Foggite possesses a new type of Al–O octahedral polymerization for the basic phosphates studied thus far (Fig. 1). The underlying feature is an octahedral edge-sharing chain—$Al(OH)_2(Op)_2$ (where Op = PO_4 oxygen)—which runs parallel to the c axis and which is bridged to symmetry equivalent chains along [100] by the PO_4 tetrahedra, defining a dense sheet of composition $[Al(OH)_2(PO_4)]^{2-}$ which is oriented parallel to {010}. Directly connected to this sheet is the $Ca(1)O_8$ polyhedron, a distorted square antiprism. For structural reasons, it is appropriate to define the dense sheet with composition $[CaAl_2(OH)_4(PO_4)_2]^{2-}$. Symmetry equivalent sheets are weakly linked along [010] by a $Ca(2)(Op)_4(H_2O)_4$ polyhedron, where the water molecules at most occupy only half their sites. In consonance with the observations of Moore, Irving, and Kampf (1975), the crystals exhibit perfect {010} cleavage.

The ordered $[CaAl_2(OH)_4(PO_4)_2]^{2-}$ sheet is the essence of the structure. Spatially, the *ac* plane (9.3 × 5.2 Å) corresponds to the *ac* plane (9.6 × 5.3 Å) in the structure of calcium Tschermak's pyroxene, $CaAl[AlSiO_6]$, recently reported by Okamura, Ghose, and Ohashi (1974). To facilitate the visualization of the relationship, the structurally similar region of the pyroxene is shown in Figure 2. The zigzag chains of Al-O octahedra in the two structures are geometrically similar as are the CaO_8 and TO_4 polyhedra on one side of the chain. In fact, the relation between the two structures is so striking that the similarity between a pyroxene and a phosphate which crystallized under quite different conditions would suggest that the equivalent configurations in the two structures are probably electrostatically favorable entities. To proceed from the pyroxene to foggite, alternate tetrahedral centers in the pyroxene chains are eliminated as well as half the calcium atoms.

TABLE 2. Foggite. Calculated and Observed Structure Factors

H = 0			
0	2	44.7	55.3
0	4	34.8	41.9
0	6	13.0	20.9
1	7	25.1	9.9
1	5	22.3	25.5
1	3	31.3	35.3
1	1	23.3	23.8
2	0	44.2	54.7
2	2	31.0	31.9
2	4	27.7	31.9
2	6	76.1	83.1
3	7	23.3	25.9
3	5	59.7	63.8
3	3	12.8	12.4
3	1	124.7	150.9
4	0	52.3	77.0
4	2	47.2	46.8
4	4	4.0	1.3
4	6	28.5	28.1
5	7	74.3	79.4
5	5	50.8	54.0
5	3	85.1	88.8
5	1	70.2	81.9
6	0	3.0	2.0
6	2	82.5	84.1
6	4	51.5	54.1
6	6	8.2	2.1
7	7	36.5	31.6
7	5	33.7	33.2
7	3	108.7	116.2
7	1	46.2	51.7
8	0	135.7	144.0
8	2	115.3	118.8
8	4	21.8	26.9
8	6	26.6	25.2
9	5	13.9	12.0
9	3	49.9	52.6
9	1	31.9	34.9
10	0	63.0	65.8
10	2	10.6	10.5
10	4	31.1	35.3
10	6	42.1	42.7
11	5	70.8	71.5
11	3	3.8	7.1
11	1	9.5	13.0
12	0	14.2	20.7
12	2	52.2	55.5
12	4	15.8	11.8
12	6	13.5	2.2
13	5	35.5	34.8
13	3	8.8	11.0
13	1	117.9	118.6
14	0	3.5	4.4
14	2	6.3	4.3
14	4	19.5	20.7
14	6	4.7	2.1
15	5	29.4	26.5
15	3	10.5	12.2
15	1	64.2	65.9
16	0	144.3	144.6
16	2	65.0	65.5
16	4	7.8	6.7
16	6	20.7	16.6
17	5	10.5	3.3
17	3	38.2	41.1
17	1	62.0	66.8
18	0	17.8	19.0
18	2	4.1	2.8
18	4	54.1	55.2
19	5	26.7	28.2
19	3	4.1	0.9
19	1	41.6	39.4
20	0	17.1	14.8
20	2	11.6	8.2
20	4	28.2	26.0
21	5	42.7	42.8
21	3	7.8	5.3
21	1	58.1	54.8
22	0	8.9	6.2
22	2	29.0	25.6
22	4	9.9	3.6
23	3	81.4	82.4
23	1	55.7	52.2
24	0	8.5	4.5
24	2	4.3	4.1
24	4	44.6	42.5
25	3	87.3	88.8
25	1	40.3	40.9
26	0	31.6	26.7
26	2	39.9	40.7
27	3	11.5	9.3
27	1	7.6	7.4
28	0	4.7	5.2
28	2	4.8	2.1
29	1	57.2	52.7
30	0	51.2	41.9
H = 1			
28	2	26.6	22.6
28	0	23.2	24.1
27	1	25.3	26.9
27	3	26.2	23.3
26	2	37.0	35.2
26	0	17.5	15.4
25	1	9.8	11.0
25	3	9.8	9.8
24	4	22.5	22.8
24	2	41.5	38.6
24	0	6.2	11.4
23	1	32.8	32.6
23	3	26.5	24.6
22	4	6.9	13.5
22	2	7.5	4.9
22	0	12.8	14.8
21	1	64.2	66.0
21	3	42.2	39.4
21	5	36.4	35.0
20	4	28.0	28.4
20	2	26.1	24.0
20	0	36.2	35.4
19	1	56.8	58.3
19	3	48.9	47.1
19	5	10.3	9.2
18	4	58.4	58.3
18	2	48.3	44.6
18	0	57.4	61.6
17	1	71.8	75.1
17	3	26.5	28.1
17	5	37.0	34.8
16	6	9.9	13.2
16	4	38.9	40.0
16	2	81.4	82.6
16	0	72.0	74.5
15	1	40.5	43.6
15	3	47.8	49.2
15	5	10.3	5.2
14	6	37.4	36.7
14	4	20.7	20.0
14	2	11.7	16.3
14	0	76.1	82.0
13	1	78.6	79.4
13	3	101.4	106.4
13	5	33.9	36.9
12	6	51.0	55.9
12	4	71.0	75.7
12	2	46.2	49.1
12	0	100.2	104.1
11	1	49.6	52.1
11	3	61.6	64.4
11	5	22.5	22.6
10	6	31.3	29.2
10	4	74.7	78.4
10	2	88.2	97.7
10	0	8.3	9.0
9	1	86.2	85.1
9	3	76.6	81.2
9	5	21.4	25.4
8	6	22.2	22.4
8	4	68.9	68.7
8	2	99.6	100.4
8	0	23.6	19.6
7	1	19.2	20.5
7	3	82.0	81.5
7	5	23.0	23.4
7	7	16.7	20.4
6	6	28.0	28.4
6	4	53.4	56.0
6	2	90.0	91.1
6	0	93.2	89.2
5	1	113.9	116.0
5	3	134.2	134.4
5	5	59.0	58.8
5	7	42.2	37.9
4	6	11.5	5.9
4	4	64.7	61.3
4	2	35.1	35.5
4	0	20.7	21.9
3	1	65.5	66.7
3	3	127.5	123.7
3	5	22.0	22.4
3	7	31.3	34.1
2	6	13.4	10.6
2	4	78.1	76.2
2	2	33.9	32.1
2	0	63.8	72.5
1	1	32.6	34.4
1	3	39.5	37.9
1	5	29.6	29.6
1	7	16.9	20.2
0	6	5.0	8.5
0	4	82.1	76.5
0	2	200.6	184.2
H = 2			
0	0	6.4	11.9
0	2	91.3	82.6
0	4	105.1	98.5
0	6	128.2	121.2
1	7	5.3	8.7
1	5	26.2	27.5
1	3	28.8	29.0
1	1	43.5	48.1
2	0	178.7	179.7
2	2	71.9	68.3
2	4	59.7	58.5
2	6	14.3	11.4
3	7	27.3	24.9
3	5	38.7	41.2
3	3	3.6	7.5
3	1	115.2	113.1
4	0	84.5	81.2
4	2	33.5	34.9
4	4	12.8	13.6
4	6	9.6	12.4
5	7	26.9	23.4
5	5	11.0	9.4
5	3	61.5	62.0
5	1	186.8	181.8
6	0	33.9	29.9
6	2	37.9	36.3
6	4	35.6	36.1
6	6	28.2	29.2
7	7	34.5	31.7
7	5	65.3	69.3
7	3	92.1	93.1
7	1	141.6	132.8
8	0	59.1	58.5
8	2	45.1	47.0
8	4	57.0	56.1
8	6	57.7	59.0
9	5	26.5	27.2
9	3	18.8	20.1
9	1	86.3	85.2
10	0	129.3	133.4
10	2	57.7	59.2
10	4	6.7	6.7
10	6	36.0	38.2
11	5	7.8	5.6
11	3	46.8	48.2
11	1	94.2	94.2
12	0	38.1	38.9
12	2	17.8	17.9
12	4	31.3	34.3
12	6	25.6	23.1
13	5	47.9	51.9
13	3	50.4	47.9
13	1	71.7	73.0
14	0	3.6	8.5
14	2	40.0	42.9
14	4	35.5	37.5
14	6	11.6	14.5
15	5	29.0	29.5
15	3	47.4	50.7
15	1	5.0	10.3
16	0	30.7	27.6
16	2	61.5	67.1
16	4	43.0	43.6
16	6	53.8	54.0
17	5	33.2	36.8
17	3	28.7	30.9
17	1	19.2	20.9
18	0	135.6	137.8
18	2	84.4	89.0
18	4	28.6	31.5
19	5	24.8	21.5
19	3	13.3	15.9
19	1	34.2	36.6
20	0	5.9	13.7
20	2	26.9	29.5
20	4	34.1	36.1
21	5	36.5	34.1
21	3	27.1	28.5
21	1	66.2	63.8
22	0	25.6	31.8
22	2	36.7	42.5
22	4	30.6	27.9
23	3	38.5	38.0
23	1	25.2	29.8
24	0	57.1	51.5
24	2	48.3	45.3
24	4	14.3	12.3
25	3	36.3	37.9
25	1	39.1	37.1
26	0	50.1	44.6
26	2	36.1	32.3
27	1	9.7	11.5
28	0	27.1	23.1
28	2	19.0	18.9
H = 3			
28	2	55.5	56.4
28	0	35.4	39.1
27	1	16.8	13.1
26	2	52.9	51.4
26	0	11.5	10.7
25	1	28.0	32.9
25	3	8.6	11.8
24	4	26.3	28.2
24	2	35.0	35.9
24	0	42.8	41.0
23	1	49.9	51.3
23	3	36.6	34.1
22	4	10.0	16.9
22	2	22.7	24.7
22	0	10.9	9.8
21	1	20.7	19.5
21	3	48.3	47.9
20	4	31.4	28.7
20	2	44.8	47.7
20	0	61.3	68.6
19	1	11.4	13.9
19	3	20.0	20.1
19	5	53.4	56.8
18	4	33.0	33.8
18	2	60.4	63.9
18	0	9.2	12.0
17	1	29.4	28.8
17	3	48.5	50.4
17	5	29.1	32.0
16	4	47.4	50.4
16	2	27.0	27.1
16	0	48.7	48.7
15	1	18.5	21.7
15	3	33.2	34.7
15	5	32.3	31.4
14	6	6.9	11.6
14	4	36.3	35.3
14	2	69.9	72.9
14	0	17.1	18.5
13	1	44.7	43.8
13	3	90.8	94.4
13	5	51.2	51.5
12	6	39.2	38.3
12	4	35.9	35.0
12	2	93.4	94.1
12	0	118.6	122.5
11	1	91.3	91.2
11	3	38.4	35.9
11	5	26.8	25.4
10	6	39.3	38.7
10	4	65.2	62.7
10	2	54.8	53.6
10	0	87.8	87.6
9	1	42.8	43.6
9	3	31.8	28.7
9	5	16.8	17.3
8	6	11.6	11.4
8	4	62.8	62.7
8	2	68.8	68.1
8	0	59.8	57.9
7	1	71.3	67.6
7	3	22.9	23.8
7	5	30.5	29.2
6	6	43.2	41.4
6	4	35.4	36.3
6	2	34.9	36.6
6	0	78.5	71.3
5	1	122.3	123.0
5	3	112.9	115.1
5	5	65.1	66.1
5	7	26.7	26.7
4	6	32.1	36.6
4	4	29.7	30.2
4	2	58.1	54.4
4	0	97.5	90.2
3	1	73.9	70.8
3	3	52.9	54.0
3	5	41.5	40.3
3	7	8.0	8.1
2	6	40.3	43.2
2	4	8.0	3.9
2	2	132.8	125.0
2	0	93.9	89.5
1	1	88.3	84.0
1	3	22.2	25.3
1	5	22.9	21.4
1	7	12.2	17.5
0	6	11.9	9.8
0	4	117.6	112.9
0	2	24.8	19.9
H = 4			
0	0	73.1	72.9
0	2	221.2	209.6
0	4	97.4	91.1
0	6	10.4	0.9
1	5	20.3	22.8
1	3	34.3	32.7
1	1	62.7	62.2
2	0	96.9	86.9
2	2	72.1	69.1
2	4	105.1	99.9
2	6	29.7	27.7
3	5	33.9	32.6
3	3	36.8	38.3
3	1	27.7	28.9
4	0	20.2	16.0
4	2	16.8	14.0
4	4	43.8	43.1
4	6	16.0	14.8
5	5	80.3	79.2
5	3	48.1	46.1
5	1	20.9	19.8
6	0	39.2	41.5
6	2	33.1	33.2
6	4	47.4	46.9
6	6	9.1	10.2
7	5	45.4	43.4
7	3	53.0	51.3
7	1	139.3	138.6
8	0	127.9	127.7
8	2	46.7	45.5
8	4	32.8	32.1
8	6	22.4	22.7
9	5	19.9	20.4
9	3	13.6	9.9
9	1	49.4	50.6
10	0	39.6	37.9
10	2	27.5	28.1
10	4	47.5	49.5
10	6	46.5	47.5
11	5	42.6	44.0
11	3	75.0	74.1
11	1	36.5	37.0
12	0	13.1	13.5
12	2	25.9	29.3
12	4	28.1	32.1
12	6	10.6	14.2
13	5	25.7	25.4
13	3	30.0	29.3
13	1	69.9	69.4
14	0	21.7	20.1
14	2	53.0	52.1
14	4	10.6	11.0
14	6	26.3	24.5
15	5	17.8	19.9
15	3	40.9	41.1
15	1	67.8	68.2
16	0	41.4	37.8
16	2	74.4	73.0
16	4	39.2	40.3
17	5	30.4	30.5
17	3	47.3	50.8
17	1	29.9	32.2
18	0	9.2	10.7
18	2	29.4	29.7
18	4	62.5	65.8
19	5	27.7	28.7
19	3	19.5	18.3
19	1	42.1	43.8
20	0	39.4	38.1
20	2	37.1	40.1
20	4	11.5	16.6
21	3	8.8	9.4
21	1	26.2	27.1
22	0	17.0	15.1
22	2	19.5	21.4
22	4	29.8	34.5
23	3	14.9	17.2
23	1	90.9	94.9
24	0	6.2	6.4
24	2	25.9	24.0
25	3	17.1	20.7
25	1	61.7	68.4
26	0	57.5	53.4
26	2	23.8	23.5
27	1	14.7	16.2
28	0	10.5	5.2
H = 5			
27	1	38.8	38.2
26	2	38.6	36.0
26	0	4.7	4.5
25	1	10.1	13.8
24	2	16.2	14.2
24	0	9.4	6.1
23	1	39.5	45.7
23	3	51.4	53.9
22	4	10.2	13.7
22	2	10.5	7.6
22	0	7.0	7.2
21	1	11.8	8.7
21	3	45.4	45.7
20	4	25.1	27.8
20	2	34.3	32.8
20	0	8.5	11.7
19	1	66.7	65.4
19	3	49.2	47.9
18	4	30.3	30.8
18	2	65.2	69.0
18	0	9.8	11.5
17	1	44.5	45.0
17	3	31.1	32.7
17	5	41.5	38.0
16	4	29.5	28.6
16	2	47.2	45.0
16	0	10.6	12.6
15	1	62.1	64.4
15	3	28.2	25.9
15	5	16.6	16.0
14	4	44.6	44.0
14	2	30.4	30.1
14	0	42.0	41.0
13	1	52.7	52.6
13	3	38.4	39.4
13	5	71.9	73.6
12	6	44.1	40.3
12	4	46.6	47.7
12	2	66.0	64.9
12	0	32.4	31.7
11	1	16.2	13.2
11	3	32.3	34.2
11	5	55.8	52.8
10	6	7.2	4.1
10	4	30.3	30.0
10	2	103.6	106.0
10	0	97.4	98.6
9	1	63.2	62.0
9	3	29.3	31.2
9	5	12.7	11.4
8	6	18.8	20.1
8	4	40.0	37.9
8	2	51.6	52.8
8	0	51.1	47.9
7	1	127.4	125.3
7	3	43.5	42.8
7	5	23.4	23.6
6	6	6.6	2.8
6	4	29.7	30.0
6	2	88.6	84.2
6	0	144.1	137.2
5	1	71.7	69.6
5	3	67.7	69.1
5	5	71.1	69.6
4	6	25.0	23.4
4	4	6.2	6.7
4	2	26.5	26.8
4	0	37.0	38.4
3	1	36.7	34.5
3	3	33.9	35.2
3	5	49.6	49.0
2	6	14.1	15.9
2	4	21.2	22.8
2	2	59.9	58.2
2	0	152.4	147.9
1	1	60.0	57.1
1	3	25.4	25.8
1	5	30.9	30.0
0	6	31.5	30.9
0	4	38.1	37.9
0	2	13.0	18.6
H = 6			
0	0	71.1	63.7
0	2	55.7	53.6
0	4	109.4	109.9
0	6	52.2	49.9
1	5	32.1	31.3
1	3	48.8	47.4
1	1	9.8	7.3
2	0	26.0	28.0
2	2	123.5	118.5
2	4	59.3	53.4
2	6	14.2	9.9
3	5	35.2	35.5
3	3	63.1	62.4
3	1	35.6	36.6
4	0	68.9	68.3
4	2	21.0	18.3
4	4	21.1	21.1
4	6	15.5	15.1
5	5	22.1	25.1
5	3	45.6	44.0
5	1	101.1	98.6
6	0	43.0	42.5
6	2	59.6	56.1
6	4	57.1	51.9
6	6	28.0	30.8
7	5	64.4	64.0
7	3	77.0	77.1
7	1	69.6	68.1
8	0	50.6	48.3
8	2	25.5	23.1
8	4	29.6	29.8
8	6	36.0	39.7
9	5	18.5	18.5
9	3	19.7	19.6
9	1	87.5	85.9
10	0	57.8	57.6
10	2	79.2	78.2
10	4	36.6	35.7
10	6	9.9	11.0
11	5	33.1	29.0
11	3	66.8	62.8
11	1	63.6	62.5
12	0	25.4	22.8
12	2	34.3	34.5
12	4	22.0	21.2
13	5	28.8	29.4
13	3	22.1	22.8
13	1	27.9	28.7
14	0	4.0	5.3
14	2	58.5	57.5
14	4	31.1	29.4
15	5	54.4	54.1
15	3	34.1	35.5
15	1	18.5	20.6
16	0	4.1	9.7
16	2	22.5	20.0
16	4	58.5	58.9
17	3	23.8	23.7
17	1	41.9	41.5
18	0	68.8	68.0
18	2	66.4	66.1
18	4	35.3	38.2
19	3	27.2	24.5
19	1	24.0	26.5
20	0	4.4	9.9
20	2	34.0	35.5
20	4	26.4	24.6
21	3	13.4	18.2
21	1	43.5	39.7
22	0	12.2	12.5
22	2	24.7	24.9
23	3	32.7	36.1
23	1	27.5	29.7
24	0	55.6	53.6
24	2	33.9	33.3
25	1	53.2	54.3
26	0	32.0	30.0
H = 7			
24	0	48.8	46.7
23	1	22.7	26.5
22	2	28.3	26.4
22	0	16.8	15.4
21	1	13.6	9.0
21	3	27.8	24.5
20	2	55.5	59.1
20	0	45.8	47.2
19	1	14.7	11.8
19	3	32.2	31.6
18	4	32.0	31.6
18	2	7.6	7.2
18	0	8.4	3.5
17	1	43.6	40.2
17	3	24.8	25.2
16	4	5.0	13.3
16	2	33.8	34.5
16	0	31.5	25.3
15	1	42.1	43.6
15	3	11.2	7.8
14	4	13.4	17.9
14	2	60.0	58.2
14	0	66.1	61.9
13	1	66.3	67.2
13	3	25.9	26.5
13	5	20.4	20.0
12	4	61.0	60.7
12	2	67.8	67.7
12	0	82.8	87.0
11	1	81.3	77.9
11	3	42.1	41.7
11	5	10.0	11.0
10	4	52.7	50.0
10	2	39.9	37.5
10	0	37.2	38.4
9	1	16.0	17.5
9	3	32.9	36.7
9	5	27.3	26.8
8	4	20.4	21.0
8	2	33.8	34.0
8	0	47.2	44.7
7	1	45.0	41.5
7	3	40.7	40.0
7	5	45.5	45.8
6	4	61.2	59.0
6	2	26.5	26.9
6	0	36.2	34.6
5	1	102.8	101.6
5	3	56.9	57.4
5	5	30.0	26.6
4	6	6.2	4.2
4	4	18.0	16.8
4	2	24.7	24.5
4	0	17.8	16.3
3	1	88.8	84.9
3	3	41.5	41.6
3	5	8.0	7.8
2	6	44.3	41.1
2	4	45.9	47.4
2	2	17.7	17.5
2	0	44.0	39.8
1	1	56.5	56.4
1	3	37.4	35.4
1	5	17.4	19.8
0	6	11.1	5.3
0	4	28.4	26.9
0	2	98.5	98.1
H = 8			
0	0	130.4	129.3
0	2	88.4	88.6
0	4	15.2	14.3
1	5	21.5	19.5
1	3	38.9	38.7
1	1	37.0	37.2
2	0	59.9	57.0
2	2	35.1	35.8
2	4	54.9	55.3
3	5	36.4	36.1
3	3	51.9	48.6
3	1	33.3	34.8
4	0	33.3	36.9
4	2	13.2	16.0
4	4	11.6	4.1
5	5	39.7	40.9
5	3	38.3	38.0
5	1	52.4	49.9
6	0	75.9	77.3
6	2	40.9	39.2
6	4	37.5	36.0
7	5	40.6	37.5
7	3	79.1	76.6
7	1	62.9	63.6
8	0	36.7	37.5
8	2	30.1	28.2
8	4	19.11	18.0
9	5	28.2	27.9
9	3	34.0	32.4
9	1	28.8	29.1
10	0	13.1	11.4
10	2	30.2	32.8
10	4	37.1	37.4
11	5	36.7	35.9
11	3	37.1	38.8
11	1	48.9	47.6
12	0	4.2	0.8
12	2	14.5	13.5
12	4	43.8	44.5
13	3	7.4	7.4
13	1	23.3	26.0
14	0	36.5	37.2
14	2	28.5	27.7
14	4	43.4	39.7
15	3	44.0	44.9
15	1	33.7	36.9
16	0	64.0	62.9
16	2	47.4	43.3
16	4	7.7	8.2
17	3	6.3	3.4
17	1	17.7	18.2
18	0	39.5	39.8
18	2	41.6	43.6
19	3	43.2	41.3
19	1	34.8	34.7
20	0	20.4	19.7
20	2	28.5	29.2
21	1	13.6	9.2
22	0	49.5	49.7
22	2	34.6	35.6
23	1	30.7	30.2
H = 9			
21	1	25.2	21.3
20	2	6.8	10.3
20	0	9.0	10.9
19	1	63.8	59.9
18	2	21.2	22.6
18	0	42.6	46.5
17	1	32.3	35.4
17	3	34.2	34.9
16	2	10.3	8.5
16	0	66.2	62.6
15	1	41.7	46.2
15	3	22.1	22.2
14	4	28.3	27.6
14	2	24.0	21.7
14	0	24.5	25.1
13	1	39.3	35.3
13	3	35.9	34.4
12	4	47.9	47.9
12	2	44.3	42.9
12	0	24.4	21.5
11	1	18.2	16.5
11	3	29.8	30.1
10	4	47.5	43.6
10	2	43.1	43.7
10	0	72.2	72.6
9	1	6.9	10.7
9	3	49.4	52.1
8	4	17.3	15.2
8	2	9.7	7.9
8	0	12.0	8.8
7	1	42.2	45.9
7	3	62.4	61.0
7	5	13.1	15.5
6	4	41.3	41.0
6	2	57.4	56.7
6	0	82.1	76.1
5	1	34.8	33.1
5	3	46.4	42.3
5	5	36.7	38.1
4	4	43.9	44.8
4	2	16.2	20.8
4	0	4.2	4.5
3	1	30.9	34.1
3	3	18.4	19.5
3	5	26.9	27.6
2	4	4.6	1.4
2	2	63.1	64.8
2	0	32.7	34.5
1	1	4.2	6.7
1	3	35.2	36.4
1	5	33.8	29.5
0	4	4.6	2.3
0	2	17.3	20.4
H = 10			
0	0	104.3	98.8
0	2	54.4	50.7
0	4	49.9	50.9
1	3	21.3	19.3
1	1	28.7	31.1
2	0	78.4	82.2
2	2	34.1	34.2
2	4	30.8	25.3
3	3	23.3	23.9
3	1	4.3	9.0
4	0	38.6	42.0
4	2	35.6	35.1
4	4	8.7	6.4
5	3	46.7	45.2
5	1	17.2	20.4
6	0	34.8	37.1
6	2	13.2	11.1
6	4	24.7	27.2
7	3	46.9	46.9
7	1	15.3	12.5
8	0	34.3	30.6
8	2	15.8	16.1
8	4	23.1	24.2
9	3	23.1	22.0
9	1	45.5	45.9
10	0	10.0	10.7
10	2	28.0	27.3
10	4	31.5	28.0
11	3	15.7	13.2
11	1	45.8	47.1
12	0	49.5	49.4
12	2	39.2	40.1
13	3	13.7	13.9
13	1	31.9	31.7
14	0	33.5	32.9
14	2	11.0	4.8
15	1	6.5	14.4
16	0	16.2	13.5
16	2	43.6	41.7
17	1	54.9	53.3
18	0	42.6	45.1
H = 11			
16	0	21.3	15.8
15	1	11.6	16.8
14	0	51.5	45.2
13	1	23.0	23.8
12	2	54.3	54.8
12	0	70.1	66.6
11	1	26.8	25.5
10	2	18.2	17.6
10	0	30.1	25.7
9	1	8.5	15.8
9	3	33.3	35.4
8	2	27.9	25.2
8	0	12.4	7.6
7	1	39.7	41.2
7	3	20.3	20.0
6	2	18.9	18.3
6	0	18.1	17.4
5	1	49.1	47.3
5	3	49.4	46.4
4	2	37.4	41.5
4	0	13.3	18.8
3	1	28.1	28.3
3	3	38.9	37.0
2	2	25.8	31.7
2	0	4.3	3.7
1	1	32.7	33.7
1	3	52.1	56.7
0	2	41.7	35.7
H = 12			
0	0	20.8	22.5
0	2	30.3	27.0
1	1	55.2	56.1
2	0	13.2	4.8
2	2	32.5	32.3
3	1	22.0	20.8
4	0	54.1	56.0
4	2	18.1	20.5
5	1	37.4	35.5
6	0	4.7	4.2
6	2	27.7	30.0
7	1	71.9	71.8
8	0	12.5	5.2
8	2	13.2	12.9
9	1	27.0	28.7
10	0	22.2	20.5
11	1	19.3	17.0

Bracketing the equivalent regions and placing the remaining ions outside, the relationship is:

Calcium Tschermak's pyroxene:
$[CaAl_2T_2O_{12}]\cdot CaT_2$
Foggite: $[CaAl_2P_2O_8(OH)_4]\cdot Ca(H_2O)_2$.

Thus, in foggite, the hydroxyl groups appear at the locations of the missing tetrahedral vertices when the alternate tetrahedra in the pyroxene are removed. We suggest that the formula of foggite be written $Ca(H_2O)_2[CaAl_2(OH)_4(PO_4)_2]$ so as to more clearly emphasize the compound's crystal chemistry.

Distortions of the polyhedra in foggite adhere to electrostatic repulsion effects. Interatomic distance tabulations (Table 3) show that shared edges are among the shortest for their polyhedra and the OH(1)–OH(2) shared edge of 2.40 Å can be compared with the O1*A*–O1*B*2 edge of 2.52 Å in the

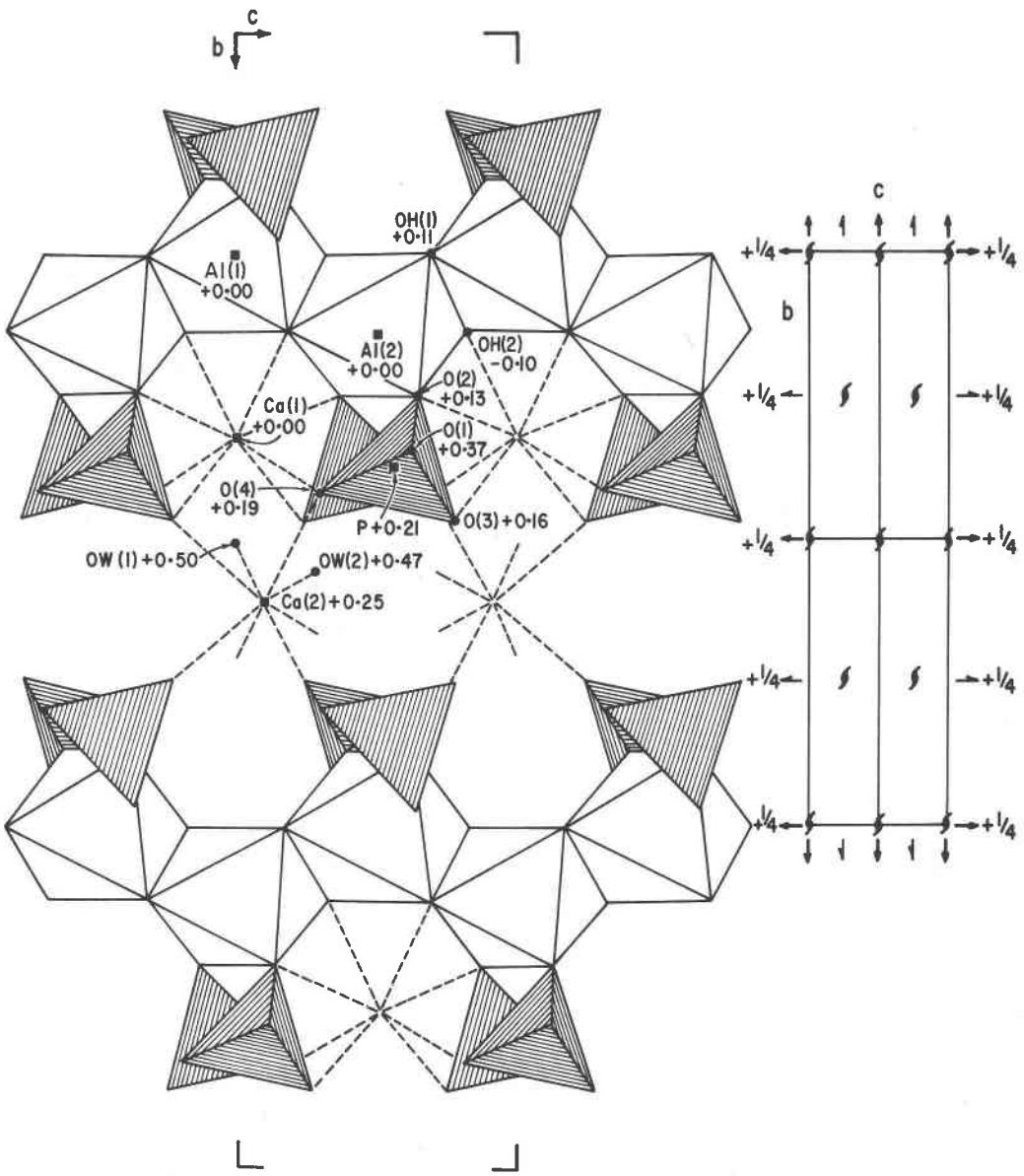

FIG. 1a. Foggite down the *a* axis with accompanying symmetry diagram (half scale). Only the polyhedra between $-1/2 < x < 1/2$ are shown. Heights of atoms are given as fractional coordinates x. The Ca(1)–O and Ca(2)–O bonds are dashed in. The symmetry diagrams accompanying Figures 1a and 1b facilitate visualization of the symmetry equivalent polyhedra which have not been included in the sketches of the structure.

pyroxene. Such a distortion is particularly strong since the zig-zag chain results in Al–Al nearest neighbor repulsion and additional repulsion by the second nearest neighbors whose central distances are less than those in the linear chain.

The remainder of the structure shall be discussed only briefly. As Figure 1b and Table 1 show, the OW(1), OW(2a), and OW(2b) water molecules are disordered, with OW(1) on the 2-fold rotor half-occupied and OW(2a) and OW(2b) in general positions each about one-quarter occupied. The OW(2a) and OW(2b) loci are actually electron density maxima which merge to the average position denoted OW(2) in the structure drawings. These water molecules reside in large channels in the structure and are partly zeolitic in character. Steric effects require

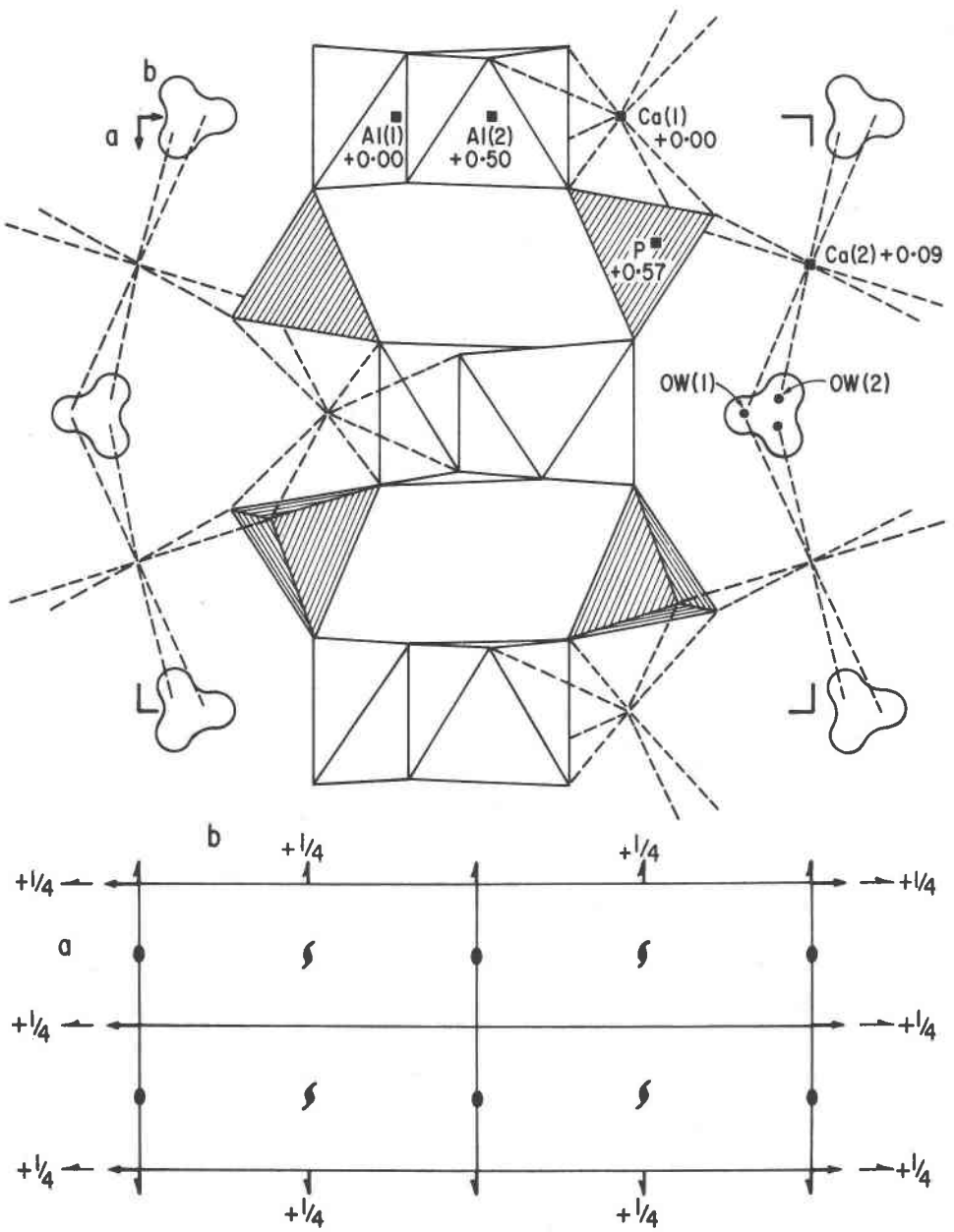

FIG. 1b. Foggite down the *c* axis with accompanying symmetry diagram (half scale). The polyhedral diagram shows only half the cell along *b*. The disordered water molecules, OW(1) and OW(2) occur in large channels. The Ca(1)–O and Ca(2)–O bonds are dashed in.

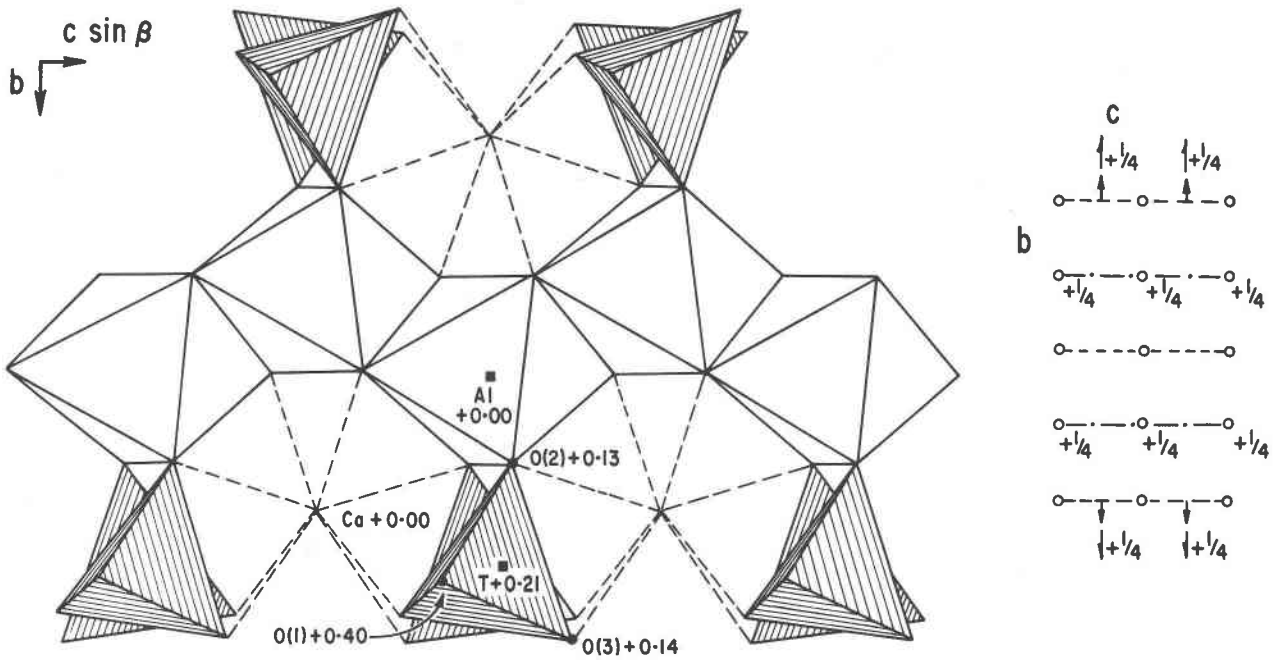

FIG. 2. A portion of calcium Tschermak's pyroxene down the *a* axis and accompanying symmetry diagram (half scale). The coordinates are from Okamura *et al* (1974). Alternate tetrahedra in the chain are omitted. This diagram can be directly compared with Figure 1a.

TABLE 3. Foggite. Polyhedral Interatomic Distances[a]

Al(1)		Al(2)		Ca(1)	
2Al(1) - O(1)^{ii}	1.877Å	2Al(2)- O(2)	1.879	2Ca(1)- O(2)	2.372
2 -OH(1)	1.919	2 -OH(1)	1.890	2 - O(3)	2.473
2 -OH(2)	1.928	2 -OH(2)	1.902	2 - O(4)^{i}	2.483
average	1.908	average	1.890	2 -OH(2)	2.514
				average	2.460
2OH(1) -OH(2)	2.398*	2OH(1)-OH(2)	2.398*		
1OH(2) -OH(2)^{i}	2.622+	2OH(1)- O(2)	2.615	2 O(2)-O(3)	2.452**
1 O(1)^{ii}- O(1)^{iii}	2.643	2 O(2)-OH(2)	2.658+	1OH(2)-OH(2)^{i}	2.622+
2 O(1)^{ii}-OH(1)^{i}	2.727	1 O(2)- O(2)^{i}	2.711	2OH(2)- O(2)	2.658+
2 O(1)^{ii}-OH(2)	2.771	2 O(2)-OH(2)^{i}	2.719	2 O(3)- O(4)	2.806
2 O(1)^{ii}-OH(1)	2.788	1OH(1)-OH(1)^{i}	2.753	2 O(2)-OH(2)^{i}	3.139
2OH(1) -OH(2)^{i}	2.864	2OH(1)-OH(2)^{i}	2.910	2 O(4)-OH(2)^{i}	3.216
average	2.697	average	2.672	2 O(3)- O(4)^{i}	3.345
				2 O(2)- O(4)^{i}	3.400
P		Ca(2)		1 O(3)- O(3)^{i}	3.913
P-O(3)	1.527	2Ca(2)-OW(2a)	2.286(20)	average	3.047
-O(4)	1.528	2 - O(3)	2.340(5)		
-O(1)	1.556	2 - O(4)	2.378(5)	Hydrogen Bonds	
-O(2)	1.557	2 -OW(2b)	2.433(20)		
average	1.542	2 -OW(1)	2.580(20)	OH(1) ...O(4)^{iii}	2.999
		average	2.403	OH(2)^{i}...O(2)^{iii}	3.126
O(2)-O(3)	2.452**				
O(1)-O(3)	2.495				
O(1)-O(2)	2.507				
O(2)-O(4)	2.538				
O(3)-O(4)	2.540				
O(1)-O(4)	2.565				
average	2.516				

[a]Estimated standard errors: Me-O ± 0.005Å, O-O' ± 0.007Å, except where stated in parentheses under Ca(2).

*Al-Al shared edge.

+Al-Ca shared edge.

**Ca-P shared edge.

i = -x, y, -z; ii = 1/2+x, 1/2 -y, 1/2 -z; iii = 1/2 -x, 1/2 -y, 1/2+z referring to the coordinates in Table 1.

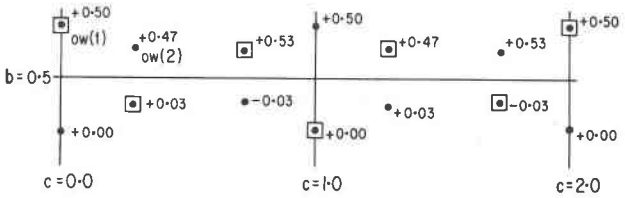

FIG. 3. Loci of the disordered OW(1) and OW(2) molecules in foggite. These positions are on the average only half-occupied. A local cooperative ordering scheme is shown as the squared in positions.

that the OW(1) and averaged OW(2) positions must be ordered in a cooperative way. Such an ordering scheme is shown in Figure 3 and suggests a doubled *c* axis repeat. Since this was not noted on long exposure photographs, the average distribution throughout the crystal is probably statistical.

The steric effects would indicate that Ca(2) probably has a range of coordinations, from a minimum of 4 (provided by O(3) and O(4)) in the absence of the water molecules to a maximum of 7 for the composition $Ca(2):H_2O = 1:2$. Doubtless, this affects the stability of the entire structure. If the water molecules are removable without destruction of the structure, then foggite could conceivably be a rather high temperature phase (500–700°C). The paragenetic setting suggests that foggite formed at low temperature (< 350°C), which would indicate that the water molecules are essential to the stability of the structure.

Geometrical considerations lead to the locations of the hydrogen bonds associated with OH(1) and OH(2). We propose $OH(1) \cdots O(4)^{iii} = 3.00$ Å and $OH(2)^{i}–O(2)^{iii} = 3.13$ Å. Owing to the disordered character of the water molecules, we have not attempted to locate their hydrogen bonds nor have we examined the electrostatic valence balances in detail.

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