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THE CRYSTAL STRUCTURE OF PACHNOLITE

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ABSTRACT

The crystal structure of pachnolite [$NaCaAlF_6 \cdot H_2O$; *F2/d*, *a* 12.117(4), *b* 10.414(3), *c* 15.680 (4) Å, β 90.37(2)°, *Z* = 16] has been solved by Patterson and Fourier techniques, and refined by a full-matrix least-squares method using three-dimensional counter-diffractometer X-ray data. The final (conventional) *R* index for 1356 observed reflections is 4.8%. The pachnolite structure consists of edge-sharing $[Ca_2F_{12}(H_2O)_2]^{8-}$ dimers linked by $(AlF_6)^{3-}$ octahedra to form sheets parallel to (001). These sheets are stacked along [001] with further dimer-octahedron linkage and interstitial Na atoms holding the sheets together. Both pachnolite and thomsenolite contain the $[Ca_2F_{12}H_2O)_2]^{8-}$ dimer girdled by six $(AlF_6)^{3-}$ octahedra; different tilts of the octahedra produce a slight difference in the coordination of Na in the two structures.

Keywords; pachnolite, crystal-structure determination, aluminofluoride, mineral.

SOMMAIRE

La structure cristalline de la pachnolite [$NaCaAlF_6 \bullet H_2O$; *F2/d*, *a* 12.117(4), *b* 10.414(3), *c* 15.680 (4) Å, β 90.37(2)°, *Z* = 16], résolue par technique de Patterson et de Fourier, a été affinée par la méthode des moindres carrés avec matrice entière, sur données tridimensionnelles du diffractomètre à compteur. Le résidu (conventionnel) final, pour 1356 réflexions observées, est de 4.8%. La structure se compose de dimères $[Ca_2F_{12}(H_2O)_2]^{8-}$ reliés en feuillets (001) par des octaèdres $(AlF_6)^{3-}$. Ces feuillets s'empilent suivant [001] grâce à d'autres liaisons dimère-octaèdre et aux atomes de Na qui les unissent. La pachnolite et la thomsenolite contiennent toutes deux le dimère ceint de ses six octaèdres $(AlF_6)^{3-}$; certaines différences d'orientation dans les octaèdres conduisent à deux polyèdres de coordination du Na quelque peu différents.

Mots-clés: pachnolite, alumino-fluorure, détermination de structure cristalline, minéral.

INTRODUCTION

Pachnolite is a monoclinic hydrated aluminofluoride of calcium and sodium: $NaCaAlF_6 \bullet H_2O$. It is dimorphous with thomsenolite, and both minerals generally occur together as alteration products of cryolite Na_3AlF_6. The morphological crystallography of both these species was summarized by Ferguson (1946). The unit cell of pachnolite derived in that study resulted in the indexing of the principal forms as {110} and {111}. In the present study we found that this cell is F-centred; however, the original orientation should be retained, as it gives the simplest indexing of forms.

The crystal structure of thomsenolite was reported by Cocco *et al.* (1967). The structural relationship between these two minerals is of interest because of their dimorphous nature. In addition, these minerals show two unusual types of intergrowth (Böggild 1913). This led Ferguson (1946) to propose an oriented relationship between the two structures; the current study was undertaken to test this hypothesis.

EXPERIMENTAL

Single-crystal X-ray precession photographs of pachnolite exhibit monoclinic symmetry. Using the unit cell proposed by Ferguson (1946), the observed reflections obey the conditions *hkl*, $h+k = 2n$, $h+l = 2n$, $k+l = 2n$; *h0l*, $h+l = 4n$, consistent with the space group *F2/d*. Cell dimensions were determined by least-squares refinement of 15 reflections automatically aligned on a 4-circle diffractometer. The values obtained (Table 1) agree closely with those of Ferguson (1946).

An equidimensional fragment of ~0.10 mm diameter was used to collect the intensity data according to the experimental method of Hawthorne & Grundy (1976). Two standard reflections were monitored every 50 reflections; no significant change in their intensities occurred during data collection. A total of 1661 reflections was measured over one asymmetric unit to a maximum 2θ of 60° ($\sin\theta/\lambda = 0.704$). The data were corrected for Lorentz, polarization and background effects, and reduced to structure factors. No absorption corrections were performed, as preliminary calculations showed them to be negligible for this crystal. A reflection was considered as observed if its intensity exceeded that of three standard deviations based on counting statistics; application of this criterion resulted in 1356 observed reflections.

SOLUTION AND REFINEMENT OF THE STRUCTURE

Scattering curves for neutral atoms were taken from Cromer & Mann (1968), with anomalous dispersion corrections from Cromer & Liberman (1970). *R* indices are of the form given in Table 1 and expressed as percentages.

TABLE 1. MISCELLANEOUS INFORMATION

a	12.117(4)Å	Crystal size	∿0.10 mm
b	10.414(3)	Rad/Mono	Mo/C
c	15.680(4)	Total No. of $\|F_o\|$	1661
	90.37(2)°	No. of $\|F_o\|>3\sigma$	1356
V	1978.6(9)Å^3	Final R (obs.)	4.8%
Space Group	F2/d	Final R_w(obs.)	5.1%
Unit cell contents		16[$NaCaAlF_6 \cdot H_2O$]	

Temperature factor form used: $\exp\left[-\sum_{i=1}^{3}\sum_{j=1}^{3} h_i h_j \beta_{ij}\right]$

$R = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$

$R_w = \left[\Sigma w(|F_o|-|F_c|)^2/\Sigma w F_o^2\right]^{\frac{1}{2}}$; w = 1

TABLE 3. ANISOTROPIC TEMPERATURE-FACTORS (x10^5)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Al	87(6)	180(8)	57(3)	5(7)	6(4)	5(5)
Ca(1)	94(7)	195(8)	76(4)	0	13(4)	0
Ca(2)	94(7)	191(8)	61(3)	0	6(4)	0
Na	238(12)	397(16)	189(7)	59(13)	29(7)	16(9)
F(1)	150(16)	282(21)	156(9)	46(15)	15(9)	-17(11)
F(2)	208(18)	288(21)	143(9)	-82(16)	54(9)	-17(11)
F(3)	265(17)	395(23)	65(7)	-75(17)	- 6(9)	5(11)
F(4)	295(17)	368(23)	66(7)	-24(17)	- 7(9)	-12(11)
F(5)	137(16)	293(21)	148(9)	57(15)	-19(9)	-23(12)
F(6)	170(18)	298(21)	212(11)	-106(16)	33(10)	-31(13)
O	230(20)	319(24)	91(9)	3(21)	1(11)	-10(14)

Examination of the three-dimensional Patterson synthesis, *P*(*uvw*), showed multiple occupation of the special positions ⅜, *y*, ⅛; these were assigned to Ca. Systematic examination of high-intensity peaks for Ca–Al vectors produced an Al position for each set of Ca positions. One of the models thus produced gave an *R* index of 38%, and a subsequent difference-Fourier synthesis yielded all the remaining non-hydrogen atom positions. Full-matrix least-squares refinement eventually converged to an *R* index of 6.5% for an isotropic thermal model. Temperature factors were converted to anisotopic of the form given in Table 1, and two cycles of least-squares refinement reduced the *R* index to 5.1%. At this stage, an empirical bond-strength table was prepared; an examination of this, along with the O–F distances and the expected geometry of the water molecule, allowed a sensible scheme of hydrogen bonding to be derived. Inspection of a difference-Fourier map revealed two peaks close to the derived positions. Insertion of these two hydrogen atoms into the structure model, together with full-matrix least-squares refinement of all variables (with the exception of the hydrogen-atom temperature factors, which were fixed at 1.0 Å^2) resulted in convergence at *R* indices of 4.8 (observed data) and 6.2% (all reflections) and R_w indices of 5.1 (observed data) and 6.5% (all reflections). Observed and calculated structure-factors may be obtained from The Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2. Final atomic positions and equivalent isotropic temperature-factors are given in Table 2, and the anisotropic temperature-factors are given in Table 3. Interatomic distances and angles and the magnitudes and orientations of the principal axes of the thermal ellipsoids, calculated with the program ERRORS (L.W. Finger, pers. comm.) are presented in Tables 4 and 5.

TABLE 2. ATOMIC POSITIONS AND EQUIVALENT ISOTROPIC TEMPERATURE-FACTORS FOR PACHNOLITE

	x	y	z	B(Å^2)
Al	0.34562(9)	0.1259(1)	0.37241(7)	0.62(2)
Ca(1)	3/8	0.1736(1)	1/8	0.71(2)
Ca(2)	3/8	0.5694(1)	1/8	0.66(2)
Na	0.6292(2)	0.1274(2)	-0.0040(1)	1.66(3)
F(1)	0.0542(2)	-0.0009(3)	0.1396(2)	1.21(4)
F(2)	0.2599(2)	-0.0093(3)	0.1014(2)	1.29(4)
F(3)	0.3145(2)	0.1138(3)	0.2602(1)	1.30(4)
F(4)	0.3792(2)	0.1430(3)	0.4852(1)	1.33(4)
F(5)	0.1982(2)	0.2505(3)	0.1039(2)	1.18(4)
F(6)	-0.0092(2)	0.2530(3)	0.1341(2)	1.46(4)
O	0.3930(3)	0.3753(3)	0.0349(2)	1.21(4)
H(1)	0.351(4)	0.371(7)	-0.000(4)	1.0*
H(2)	0.461(6)	0.360(7)	0.027(4)	1.0*

*fixed during refinement

DISCUSSION

There are two symmetrically distinct Ca positions in the pachnolite structure. In each position, Ca is surrounded by six fluorine atoms and two water molecules in an arrangement that is intermediate between a square antiprism and a triangular dodecahedron. These Ca-polyhedra link together to form an edge-sharing dimer of composition $[Ca_2F_{12}(H_2O)_2]^{8-}$. Aluminum is surrounded by six fluorine atoms in a slightly distorted octahedral arrangement. The observed <Al–F> distance of 1.807 Å is typical of both naturally occurring and synthetic

TABLE 4. INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN PACHNOLITE

Al-F(1)	1.791(3)	Ca(1)-F(2)	2.388(3) x2
Al-F(2)	1.812(3)	Ca(1)-F(3)	2.331(2) x2
Al-F(3)	1.802(3)	Ca(1)-F(5)	2.309(3) x2
Al-F(4)	1.821(3)	Ca(1)-O	2.542(4) x2
Al-F(5)	1.814(3)	<Ca(1)-O,F>	2.393
Al-F(6)	1.800(3)		
<Al-F>	1.807	Ca(2)-F(1)	2.301(3) x2
		Ca(2)-F(4)	2.323(2) x2
Na-F(1)	2.374(3)	Ca(2)-F(6)	2.375(3) x2
Na-F(2)	2.382(3)	Ca(2)-O	2.476(4) x2
Na-F(3)	2.353(3)	<Ca(2)-O,F>	2.369
Na-F(3)′	2.641(4)		
Na-F(4)	2.412(3)		
Na-F(5)	2.845(3)		
Na-F(6)	2.547(3)		
Na-F(6)′	2.774(4)		
Na-F(6)″	2.790(4)		
	Al octahedron		
F(1)-F(2)	2.569(4)	F(1)-Al-F(2)	91.0(1)
F(1)-F(3)	2.520(4)	F(1)-Al-F(3)	89.1(1)
F(1)-F(4)	2.587(4)	F(1)-Al-F(4)	91.5(1)
F(1)-F(5)	2.591(3)	F(1)-Al-F(5)	91.9(1)
F(2)-F(3)	2.596(3)	F(2)-Al-F(3)	91.8(1)
F(2)-F(4)	2.567(4)	F(2)-Al-F(4)	89.9(1)
F(2)-F(6)	2.485(4)	F(2)-Al-F(6)	86.9(1)
F(3)-F(5)	2.598(4)	F(3)-Al-F(5)	91.9(1)
F(3)-F(6)	2.554(4)	F(3)-Al-F(6)	90.3(1)
F(4)-F(5)	2.489(4)	F(4)-Al-F(5)	86.4(1)
F(4)-F(6)	2.542(4)	F(4)-Al-F(6)	89.2(1)
F(5)-F(6)	2.562(4)	F(5)-Al-F(6)	90.3(1)
<F-F>	2.555	<F-Al-F>	90.0
	Ca(1) polyhedron		
F(2)-F(2)′	2.882(6)	F(2)-Ca(1)-F(2)′	74.2(1)
F(2)-F(3)	2.874(4) x2	F(2)-Ca(1)-F(3)	75.0(1) x2
F(2)-F(3)′	3.046(4) x2	F(2)-Ca(1)-F(3)′	80.4(1) x2
F(2)-F(5)	2.807(4) x2	F(2)-Ca(1)-F(5)	73.4(1) x2
F(3)-F(5)	3.158(4) x2	F(3)-Ca(1)-F(5)	85.8(1) x2
F(3)-O	2.861(4) x2	F(3)-Ca(1)-O	71.7(1) x2
F(5)-O	2.909(4) x2	F(5)-Ca(1)-O	73.5(1) x2
F(5)-O′	2.896(4) x2	F(5)-Ca(1)-O′	73.1(1) x2
O -O′	2.862(6)	O -Ca(1)-O′	68.5(1)
<F,O-F,O>	2.928	<F,O-Ca(1)-F,O>	75.5
	Ca(2) polyhedron		
F(1)-F(4)	3.330(4) x2	F(1)-Ca(2)-F(4)	92.1(1) x2
F(1)-F(6)	2.755(4) x2	F(1)-Ca(2)-F(6)	72.2(1) x2
F(1)-O	2.851(4) x2	F(1)-Ca(2)-O	73.2(1) x2
F(1)-O′	2.968(4) x2	F(1)-Ca(2)-O′	76.7(1) x2
F(4)-F(6)	2.925(4) x2	F(4)-Ca(2)-F(6)	77.0(1) x2
F(4)-F(6)′	2.768(4) x2	F(4)-Ca(2)-F(6)′	72.2(1) x2
F(4)-O	2.899(4) x2	F(4)-Ca(2)-O	74.2(1) x2
F(6)-F(6)′	2.818(6)	F(6)-Ca(2)-F(6)′	72.8(1)
O -O′	2.868(6)	O -Ca(2)-O′	70.6(2)
<F,O-F,O>	2.917	<F,O-Ca(2)-F,O>	76.2
	Hydrogen bonds		
H(1)-O	0.75(6)		
H(2)-O	0.85(7)		
H(1)-H(2)	1.40(8)	H(1)-O-H(2)	122(6)
H(1)-F(5)	2.14(7)	O -H(1)-F(5)	142(7)
O -F(5)	2.765(4)	O -H(2)-F(4)	170(7)
H(2)-F(4)	1.95(7)		
O -F(4)	2.787(4)		

aluminofluoride structures (Cocco *et al.* 1967, Geller 1971, Hawthorne & Ferguson 1975, Giuseppetti & Tadini 1978, Burns *et al.* 1968); the restricted range of Al–F distances and F–Al–F angles also is typical of these structures. The co-ordination number of Na is not immediately obvious; it is surrounded by four fluorine atoms at a distance between 2.35 and 2.41 Å. Considering longer bonds, there is no obvious break in the distances out to more than 3 Å. Examination of the empirical bond-valences (Table 6) suggests a co-ordination number of eight or nine, as both values lead to acceptable bond-valence sums around both Na and the fluorine anions.

TABLE 5. VIBRATION ELLIPSOIDS

	R.M.S. Displacement	Angle to X-axis	Angle to Y-axis	Angle to Z-axis
Al	0.078(3)Å	29(17)°	91(8)°	120(17)°
	0.085(3)	118(18)	79(9)	149(17)
	0.100(2)	84(8)	11(9)	81(8)
Ca(1)	0.080(3)	22(6)	90	113(6)
	0.100(2)	112(6)	90	157(6)
	0.104(2)	90	0	90
Ca(2)	0.082(3)	30(16)	90	120(16)
	0.089(2)	120(16)	90	150(16)
	0.103(2)	90	0	90
Na	0.123(4)	30(4)	117(5)	102(5)
	0.147(3)	101(6)	133(8)	45(9)
	0.162(3)	63(4)	55(7)	47(8)
F(1)	0.096(6)	30(7)	117(7)	101(5)
	0.130(5)	119(7)	148(11)	102(17)
	0.141(4)	87(10)	106(16)	16(14)
F(2)	0.096(6)	40(4)	58(7)	112(7)
	0.124(5)	82(7)	133(8)	135(7)
	0.156(4)	51(4)	120(5)	53(6)
F(3)	0.090(5)	87(5)	91(5)	3(4)
	0.126(5)	141(6)	129(6)	88(6)
	0.160(5)	129(6)	39(6)	87(3)
F(4)	0.090(5)	86(4)	85(4)	7(4)
	0.139(5)	120(17)	149(17)	83(4)
	0.151(4)	30(17)	120(17)	91(4)
F(5)	0.091(6)	25(6)	114(6)	84(6)
	0.125(5)	104(7)	136(10)	131(10)
	0.144(4)	70(5)	55(9)	139(10)
F(6)	0.086(7)	37(4)	54(4)	93(3)
	0.139(5)	60(5)	136(5)	119(7)
	0.169(4)	71(4)	111(5)	29(7)
O	0.106(5)	90(10)	82(10)	8(10)
	0.131(6)	161(109)	71(108)	93(18)
	0.133(5)	71(109)	21(101)	97(11)

TABLE 6. EMPIRICAL BOND-STRENGTH TABLE FOR PACHNOLITE*

	Ca(1)	Ca(2)	Na	Al	H(1)	H(2)	Σ
F(1)		$0.306^{x2}_{\downarrow}$	0.153	0.512			0.971
F(2)	$0.245^{x2}_{\downarrow}$		0.151	0.487			0.883
F(3)	$0.283^{x2}_{\downarrow}$		0.159 0.097	0.498			1.037
F(4)		$0.290^{x2}_{\downarrow}$	0.143	0.476		(0.2)**	1.109
F(5)	$0.300^{x2}_{\downarrow}$		0.070	0.484	(0.2)		1.054
F(6)		$0.253^{x2}_{\downarrow}$	0.078 0.113 0.076	0.501			1.021
O	$0.212^{x2}_{\downarrow}$	$0.243^{x2}_{\downarrow}$			(0.8)	(0.8)	2.055
Σ	2.080	2.184	1.040	2.958	(1.0)	(1.0)	

*calculated from the bond-strength parameters of Brown & Wu (1976) and I.D. Brown (pers. comm.).

**values in parentheses are assumed.

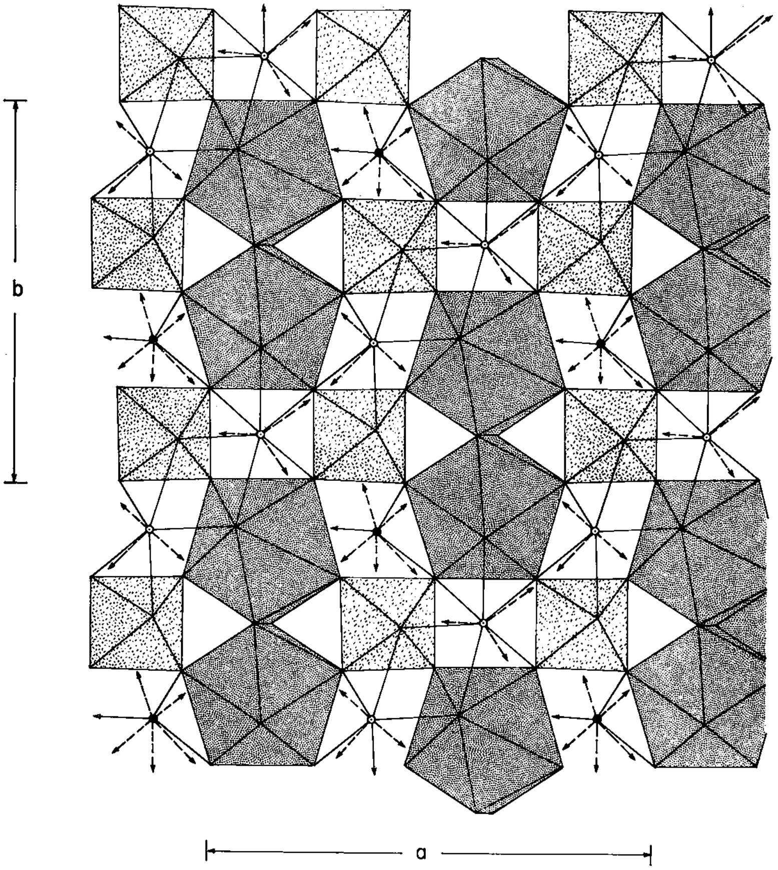

FIG. 1. The structure of pachnolite, projected onto (001). $Ca\varnothing_8$ polyhedra are dotted, AlF_6 polyhedra are dashed, and the Na co-ordination is indicated by Na-$\varnothing$ bonds; Na atoms below the sheet are filled circles, Na atoms above the sheet are hollow circles. $\varnothing$: unspecified anionic group.

The $[Ca_2F_{12}(H_2O)_2]^{8-}$ dimers are linked together by corner-sharing with $[AlF_6]^{3-}$ octahedra to form continuous sheets parallel to (001), as illustrated in Figure 1. These sheets stack along the Z axis, held together by interstitial Na atoms (Fig. 2) and further linkage between $[AlF_6]^{3-}$ octahedra and the $[Ca_2F_{12}(H_2O)_2]^{8-}$ dimers. The refined H positions allow a reasonable hydrogen-bond arrangement that provides additional linkage both within and between the sheets (Fig. 3). The observed O–H bond-lengths are typically too short, but the geometry of the arrangement is compatible with the range of values found by neutron diffraction in many hydrates (Baur 1972). Empirical bond-valence sums around the individual anions also are compatible with this arrangement.

The structures of pachnolite and thomsenolite are very similar, as is shown in Figure 4. Both contain the $[Ca_2F_{12}(H_2O)_2]^{8-}$ dimer girdled by six $[AlF_6]^{3-}$ octahedra; it is apparent from Figure 4 that the only significant difference in this unit between the two structures lies in the relative attitude of the $[AlF_6]^{3-}$ octahedra, which are tilted differently relative to the $[Ca_2F_{12}(H_2O)_2]^{8-}$ dimer. This results in a change in the co-ordination of Na, from [8] in thomsenolite to [9] in pachnolite.

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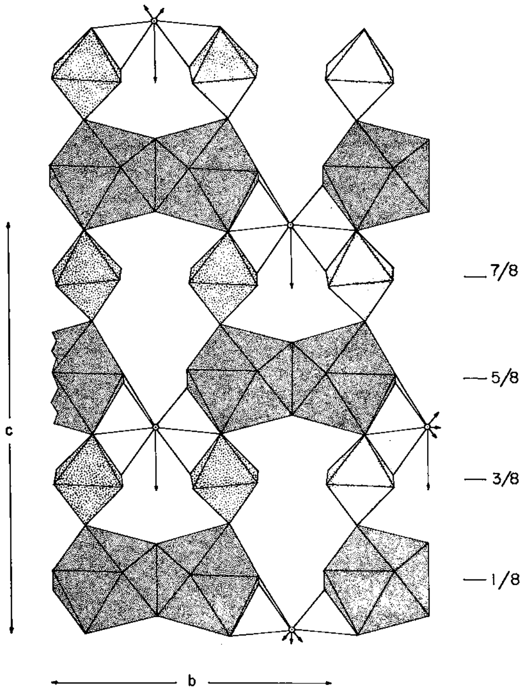

FIG.2. The structure of pachnolite, projected onto (100). The sheets (as shown in Figure 1) occur at $z \sim \frac{1}{8}$ and $\frac{5}{8}$.

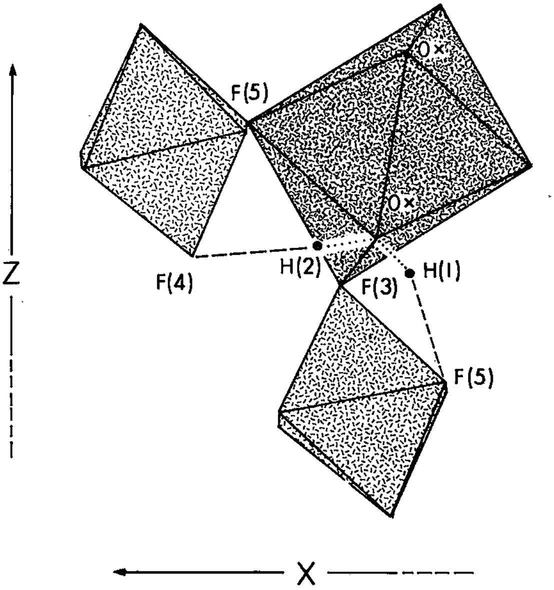

FIG. 3. Proposed hydrogen-bonding scheme in pachnolite.

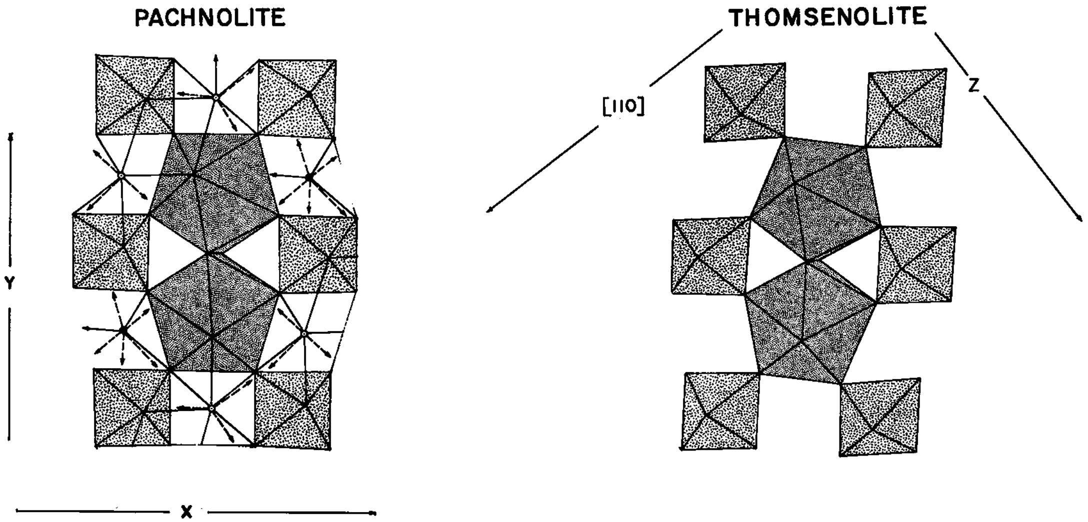

FIG. 4. A comparison of the structure of pachnolite and thomsenolite, drawn so as to emphasize the $[Ca_2F_{12}(H_2O)_2]^{8-}$ dimer and its girdle of six $[AlF_6]^{3-}$ octahedra, present in both structures.

REFERENCES

BAUR, W.H. (1972): Prediction of hydrogen bonds and hydrogen atom positions in crystalline solids. *Acta Cryst.* **B28,** 1456-1465.

BÖGGILD, O.B. (1913): Boebachtungen über die Mineralien der Kryolithgruppe. *Z. Krist. Mineral.* **51,** 591-613.

BROWN, I.D. & WU, KANG KUN (1976): Empirical parameters for calculating cation–oxygen bond valences. *Acta Cryst.* **B32,** 1957-1959.

BURNS, J.H., TENNISSEN, A.C. & BRUNTON, G.D. (1968): The crystal structure of α-Li_3AlF_6. *Acta Cryst.* **B24,** 225-230.

COCCO, G., CASTIGLIONE, P.C. & VAGLIASINDI, G. (1967): The crystal structure of thomsenolite. *Acta Cryst.* **23,** 162-166.

CROMER D.T. & LIBERMAN, D. (1970): Relativistic calculation of anomalous scattering factors for X rays. *J. Chem. Phys.* **53,** 1891-1898.

______ & MANN, J.B. (1968): X-ray scattering factors computed from numerical Hartree-Fock wave functions. *Acta Cryst.* **A24,** 321-324.

FERGUSON, R.B. (1946): On the crystallography of thomsenolite and pachnolite. *Roy. Soc. Can. Trans., Ser. III, Sect. IV,* **40,** 11-25.

GELLER, S. (1971): Refinement of the crystal structure of cryolithionite, $\{Na_3\}[Al_2](Li_3)F_{12}$. *Amer. Mineral.* **56,** 18-23.

GIUSEPPETTI, G. & TADINI, C. (1978): Re-examination of the crystal structure of weberite. *Tschermaks Mineral. Petrog. Mitt.* **25,** 57-62.

HAWTHORNE, F.C. & FERGUSON, R.B. (1975): Refinement of the crystal structure of cryolite. *Can. Mineral.* **13,** 377-382.

______ & GRUNDY, H.D. (1976): The crystal chemistry of the amphiboles. IV. X-ray and neutron refinements of the crystal structure of tremolite. *Can. Mineral.* **14,** 334-345.

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