Atti Accademia Nazionale dei Lincei

Classe Scienze Fisiche Matematiche Naturali

Rendiconti

Carmelo Giacovazzo, Silvio Menchetti

The crystal structure of prosopite

Atti della Accademia Nazionale dei Lincei. Classe di Scienze Fisiche, Matematiche e Naturali. Rendiconti, Serie 8, Vol. **47** (1969), n.1-2, p. 55–68.

Accademia Nazionale dei Lincei

<http://www.bdim.eu/item?id=RLINA_1969_8_47_1-2_55_0>

Atti della Accademia Nazionale dei Lincei. Classe di Scienze Fisiche, Matematiche e Naturali. Rendiconti, Accademia Nazionale dei Lincei, 1969.

Mineralogia. — *The crystal structure of prosopite* (*). Nota (**) di CARMELO GIACOVAZZO e SILVIO MENCHETTI, presentata dal Socio G. CAROBBI.

RIASSUNTO. — La prosopite, $CaAl_2(F, OH)_8$, cristallizza nel sistema monoclino, gruppo spaziale C 2/c, con quattro unità stechiometriche nella cella elementare. Le costanti reticolari hanno i seguenti valori: $a = 6{,}70$, $b = 11{,}13$, $c = 7{,}33$ Å, $\beta = 95°00'$.

Utilizzando un cristallo proveniente da St. Peter's Dome, El Paso County, Colorado, sono stati registrati fotograficamente 468 riflessi indipendenti, facendo uso di una camera di Weissenberg. Le coordinate degli atomi di Ca e Al sono state determinate mediante l'esame della sintesi tridimensionale di Patterson e la risoluzione completa della struttura è avvenuta tramite Fourier tridimensionali. La struttura è stata successivamente raffinata fino ad un valore di R 0,067, relativo a tutti i 326 riflessi osservati.

I poliedri di coordinazione del Ca sono costituiti da antiprismi distorti, legati l'un l'altro tramite uno spigolo a comune in modo da formare catene parallele all'asse *c*. Ambedue gli atomi indipendenti di Al presentano coordinazione ottaedrica. Gli ottaedri condividono uno spigolo e formano catene parallele alla diagonale *a c*. Catene adiacenti di ottaedri sono collegate fra di loro dagli antiprismi del Ca. Le distanze di legame rientrano nella norma.

Sulla base della analisi dei massimi Fourier, delle distanze catione–anione, dell'andamento dei fattori termici e dei legami idrogeno che probabilmente si stabiliscono nella struttura, vengono formulate alcune ipotesi sulla non equivalenza strutturale degli anioni F , OH; approssimando a 1 il valore del rapporto F : OH (che secondo le analisi chimiche relative a campioni del Colorado ha il valore di 1,17) è molto probabile che la formula chimica da attribuire alla prosopite sia $CaAl_2F_4(OH)_4$.

INTRODUCTION.

Prosopite is a basic alumino-fluoride of calcium, which was first described as a new mineral by Scheerer [22].

It has been found at Altenberg, Saxony, at Schlaggenwald, Bohemia, at St. Peter's Dome, El Paso County, Colorado etc.

Palache [18] assigned prosopite to the monoclinic system on the basis of goniometric measurements on crystals from St. Peter's Dome, Colorado. The first data on the X–ray crystallography have been determined by Berman and Wolfe [3] and later confirmed by Ferguson [8].

Chemical and physical properties of this mineral are summarized in Dana's System of Mineralogy [19].

Preliminary results of the structural study on prosopite are given in our previous paper [9].

From the results of the present paper, an ordered distribution F, OH in prosopite seems to be very likely.

(*) Paper presented at the 2nd Congress of the Associazione Italiana di Cristallografia, Parma, October 17–19, 1968.

Lavoro eseguito nell'Istituto di mineralogia dell'Università di Bari.

(**) Pervenuta all'Accademia il 10 luglio 1969.

Experimental.

Among the samples of the Mineralogical Museum of our Institute, only the ones from St. Peter's Dome, Colorado, show unaltered prosopite crystals associated with massive pachnolite. Owing to the small amount of available substance, a new chemical analysis was not performed.

A tabular transparent colorless crystal was chosen for the structural study. It was not possible to obtain a spherical or cylindrical shape but only an irregular tabular-prismatic crystal fragment elongated [100].

The lattice parameters used in this work are the ones given by Berman and Wolfe [3].

Crystal data:

$$(\lambda\,(\mathrm{CuK}\alpha) = 1.5418\ \text{Å})$$

Chemical formula (accepted before this work) = $CaAl_2(F, OH)_8$

Monoclinic, space group $C2/c$,

$$a = 6.70\ \text{Å} \quad ; \quad b = 11.13 \quad ; \quad c = 7.33 \quad ; \quad \beta = 95°00'$$

$$V = 544.5\ \text{Å}^3 \quad ; \quad Z = 4$$

$$D_m = 2.880\ \text{g cm}^{-3} \quad ; \quad D_x = 2.909\ \text{g cm}^{-3} \quad ; \quad \mu = 134\ \text{cm}^{-1}.$$

The experimental density value 2.880 is given in Dana's System of Mineralogy, for a sample from St. Peter's Dome.

The intensities of the reflections were obtained from integrated Weissenberg photographs, taken around the a axis (h from 0 to 5), using the multiple-film exposure. A total of 468 independent reflections were collected, of which 142 were below the observational limit. The intensities were evaluated by means of a microdensitometer, and the different Weissenberg levels were put approximately on the same relative scale taking into account the exposure time.

The data were then corrected for the Lorentz-polarisation factor and for the $\alpha_1 - \alpha_2$ spot doubling effect. No correction was applied for the transmission factor because of the difficulty arising from the irregular shape of the crystal; on the other hand this effect is nearly negligible owing to the low value of μ and the smallness of the crystal.

All calculations have been carried out on a I.B.M. 360/65 computer.

Structure determination and refinement.

A three-dimensional Patterson synthesis was computed from the complete set of observed reflections.

The more striking features of the maps were represented by the highest peaks at $u, w = 0,\ 1/4,\ 1/2,\ 3/4$. This suggests that, besides the calcium,

the aluminium atoms are also likely to occupy special positions, namely symmetry centres or twofold axes. Among the four symmetry centres *a*, *b*, *c*, *d*, (according to the Wyckoff notation) one Ca or Al atom can lie only on the centre *c* or on the equivalent *d*, while on the twofold axis, with coordinates 0, *y*, 1/4, two more atoms (Ca and Al or Al(1) and Al(2) respectively) can lie.

On the basis of these considerations two attempts were performed. The second one gave a *R* index value = 0.38 and the subsequent Fourier synthesis allowed the attribution of the coordinates to all the other nonhydrogen atoms. *R* value dropped to 0.14.

The atomic scattering factors used in this work for Ca^{2+} and Al^{3+} are the ones given by Cromer and Waber [6]; the scattering factor curve of (F^-, O^-) was constructed by interpolation between F^- and O^- according to the chemical analysis 3 in Dana's System of Mineralogy.

The refinement was carried out by two more Fourier syntheses and later by the least-squares method. The weighing scheme used in the least-squares calculations was:

$$W_{(hkl)} = 1/[a + b\mathrm{KF_0} + c\,(\mathrm{KF_0})^2]$$

where *a* is nearly the minimum observed F_0, *b* is nearly 1, and *c* is nearly the reciprocal of the maximum observed F_0.

The least-squares calculations were carried out using a program originally written for the I.B.M. 7040 computer by Albano *et al.* [1]. This program uses a block-diagonal approximation to the least-squares matrix (4×4 blocks for isotropic atoms, 9×9 blocks for anisotropic atoms).

Anisotropic thermal parameters were taken into account during the final least-squares cycles.

TABLE I.

Atomic coordinates, their standard deviations (in parentheses) and equivalent isotropic thermal parameters according to HAMILTON [12].

Atom	*x/a*	*y/b*	*z/c*	B_H
Ca	0.5	0.5395(2)	0.25	0.6
Al(1)	0.75	0.25	0.5	0.6
Al(2)	0.0	0.3588(3)	0.25	0.7
(F, O) (1)	0.9755(11)	0.3468(6)	0.5047(8)	1.0
F(2)	0.5769(9)	0.3811(5)	0.4614(7)	1.1
F(3)	0.1830(9)	0.4758(5)	0.2865(7)	1.4
O(4)	0.7990(11)	0.2365(5)	0.2506(8)	0.7

On the basis of stereo-chemical considerations (see below) some hypotheses on the structural non equivalence of F^- and OH^- anions were made and the atomic scattering factors were consequently varied. The better agreement between F_o and F_c has been reached assuming two anions as fluorine, one as oxygen and only one anion with scattering factor curve intermediate between F^- and O^-.

The final R value for all the observed reflections was 0.067.

The atomic and thermal parameters with their standard deviations are given in Table I. The observed and calculated structure factors are listed in Table II. Bond distances and angles are given in Tables III and IV. The standard deviations are: for Ca—O and Al—O: 0.009 Å, for O—O: 0.012 Å, for O—$\widehat{Ca}$—O and O—$\widehat{Al}$—O: 0.3°. For typographic clearness the anion (F, O) (1) is afterwards indicated as O (1).

TABLE II.

Observed and calculated structure factors.

h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc
4	0	0	112.8	125.9	1		—4	25.4	—25.6	0		2	96.7	—98.0
0		2	64.9	—63.5	3		4	39.5	38.6	2		2		—5.2
2		2	54.9	49.8	3		—4	17.0	14.6	2		—2	42.1	—42.0
4		2	32.2	—33.2	5		4		—6.8	4		2	80.8	—72.5
0		4	201.7	230.2	5		—4		—3.6	4		—2	40.0	—42.2
2		4	63.4	53.9	1		5	58.6	—49.5	0		3	18.6	18.3
2		—4	38.7	37.4	1		—5		—11.7	2		3		—3.5
4		4	164.2	155.3	3		5		4.2	2		—3	17.6	—17.2
4		—4	64.4	58.5	3		—5		12.6	4		3	27.7	—28.8
0		6	38.7	—38.2	5		5	80.5	—88.4	4		—3		0.1
2		6		—2.6	5		—5		14.3	0		4	20.0	—15.6
2		—6	70.2	—71.9	1		6	43.5	—39.0	2		4	50.3	44.1
4		—6	21.9	—23.4	1		—6		—13.1	2		—4	73.5	79.1
0		8	85.6	79.5	3		6		—7.2	4		4		6.1
2		8	28.0	31.6	3		—6	43.4	—43.3	4		—4	30.3	—30.7
2		—8	20.3	17.9	5		6		—7.4	0		5	36.4	34.1
4		—8	37.8	38.5	5		—6	28.3	—28.9	2		5		14.2
3	1	0	54.8	57.4	1		7	22.3	20.4	2		—5	26.1	—27.6
5		0	26.0	—26.8	1		—7	56.7	—64.5	4		5		3.7
1		1	135.8	—122.5	3		7	29.6	31.4	4		—5		10.9
3		1	14.9	—12.8	3		—7		4.3	0		6	44.2	—38.8
3		—1	14.3	—13.7	5		—7	39.5	—39.6	2		6		—3.1
5		1	116 3	—114.0	1		8	23.2	23.1	2		—6	31.3	—35.5
1		2	31.9	—24.5	1		—8		—11.5	4		6	59.1	—61.7
1		—2	16.4	4.3	3		8		10.4	4		—6	21.2	—21.2
3		2	64.3	—57.6	3		—8		—1.0	0		7		15.1
3		—2	91.1	—95.2	5		—8	13.7	12.8	2		7		11.0
5		2		—13.7	1		—9		—0.3	2		—7		9.5
5		—2	35.5	—34.3	3		—9	14.2	14.4	4		7		—6.1
1		3	23.9	22.2	2	2	0	72.9	70.2	4		—7		11.9
1		—3	122.1	—132.6	4		0	20.9	—20.7	0		8	23.2	—21.1
3		3		12.8	0		1	32.2	30.8	2		8	42.2	37.6
3		—3		—7.4	2		1	26.2	—25.6	2		—8	43.9	49.9
5		3		—5.1	2		—1	39.1	—42.8	4		—8		—11.8
5		—3	86.1	—80.0	4		1		—12.9	1	3	0	69.8	69.1
1		4	56.0	53.3	4		—1	13.7	—14.6	3		0	124.6	137.8

Continued: TABLE II.

h	*k*	*l*	Fo	Fc	*h*	*k*	*l*	Fo	Fc	*h*	*k*	*l*	Fo	Fc
5	3	0	51.9	51.3	2		3	78.2	72.7	3		6	29.3	—28.8
1		1	25.8	—23.8	2		—3	62.2	—69.7	3		—6		—1.4
1		—1	54.5	62.1	4		3		17.7	5		6	19.0	—20.4
3		1	127.8	—127.3	4		—3	56.1	—54.7	5		—6		—12.0
3		—1	15.4	—13.4	0		4	31.2	28.1	1		7	27.0	—26.5
5		1	21.8	—22.4	2		4	131.2	—127.9	1		—7	20.9	—25.4
5		—1	34.0	35.3	2		—4	50.6	—50.8	3		7	22.8	22.5
1		2	68.8	—61.0	4		4		12.6	3		—7	27.3	25.9
1		—2		—9.3	0		5	26.6	—21.6	5		—7	32.1	—24.0
3		2	86.9	—78.4	2		5	64.5	—59.9	1		8	19.9	20.9
3		—2	60.3	—64.7	2		—5	29.7	28.9	1		—8		13.5
5		2		0.7	4		5	30.8	—32.1	3		—8	16.3	14.7
5		—2		—1.8	4		—5	30.2	31.2	0	6	0		7.4
1		3	90.1	73.7	0		6		—12.7	2		0	74.6	78.0
1		—3	55.2	—58.5	2		6	26.3	—25.3	4		0		1.1
3		3		4.5	2		—6		—7.6	0		1	63.1	—67.0
3		—3	96.2	—101.5	4		—6	34.1	31.0	2		1	65.8	—61.0
5		3	26.4	28.9	0		7	34.6	31.0	2		—1	87.7	97.0
5		—3		3.2	2		7	44.3	43.4	4		1	38.6	—36.4
1		4	89.3	79.8	2		—7	27.9	—31.0	4		—1	78.9	78.5
1		—4	49.1	49.4	4		7	15.2	15.3	0		2	26.2	—26.9
3		4	74.6	72.8	4		—7	33.1	—30.8	2		2	26.3	25.9
3		—4	98.3	103.1	0		8	20.9	22.4	2		—2	15.9	16.4
5		4	30.3	34.9	2		8	55.6	—53.6	4		2	24.6	—25.1
5		—4	52.0	50.8	2		—8		—12.2	4		—2		—8.5
1		5	22.1	21.1	4		—8		12.3	0		3	39.3	37.4
1		—5	40.7	43.4	1	5	0	19.2	—22.3	2		3	85.3	78.9
3		5	82.6	—82.5	3		0	33.2	31.3	2		—3	23.9	—26.1
3		—5		8.5	5		0	24.1	24.6	4		3	60.7	62.7
5		5		—18.2	1		1	63.3	—54.9	4		—3	55.6	—57.5
5		—5	31.2	29.4	1		—1	32.5	36.4	0		4		—1.0
1		6	52.3	—49.9	3		1	88.2	87.6	2		4	59.5	54.0
1		—6		—1.5	3		—1	28.7	31.3	2		—4	74.8	74.9
3		6	47.0	—41.6	5		1	42.2	—41.8	4		4		7.2
3		—6	26.8	—25.7	5		—1	31.5	33.8	4		—4		—6.5
5		6	17.3	—18.7	1		2	72.8	—67.5	0		5	78 0	—74.2
5		—6	17.8	—17.4	1		—2	24.1	—28.4	2		5	71.4	—67.0
1		7	55.3	51.8	3		2	49.9	—49.3	2		—5	44.3	46.4
3		7	28.0	26.9	3		—2	26.0	—26.8	4		5	26.7	—26.8
3		—7	51.3	—51.4	5		2		—2.5	4		—5	50.8	48.0
5		—7	13.0	12.3	5		—2		—0.0	0		6		—9.5
1		8	62.6	56.8	1		3	21.1	—19.7	2		6		15.0
1		—8	31.9	39.7	1		—3	40.5	—45.9	2		—6		2.4
3		8	33.7	35.0	3		3	32.5	32.3	4		6	25.6	—27.8
3		—8	44.5	44.3	3		—3	69.2	73.6	4		—6		—5.2
1		—9	20.9	27.3	5		3	34.9	39.8	0		7	35.0	34.3
0	4	0	30.9	32.8	5		—3	35.1	—36.8	2		7	33.3	31.1
2		0	129.9	—148.2	1		4		7.5	2		—7	18.4	—19.2
4		0	23.3	25.1	1		—4		—3.2	4		—7	52.3	—47.7
0		1	15.2	—14.1	3		4		—3.5	0		8		—6.1
2		1	98.3	—101.0	3		—4	36.6	36.9	2		8	34.0	38.7
2		—1	58.8	64.6	5		4		6.4	2		—8	40.5	45.8
4		1	57.7	—53.7	5		—4	30.4	30.0	1	7	0	55.8	—57.5
4		—1	32.0	32.4	1		5	41.0	—38.0	3		0	26.4	—25.3
0		2	112.7	—113.1	3		5	38.0	36.4	5		0	60.6	—58.3
2		2	41.1	—36.8	3		—5	23.2	21.6	1		1		—2.9
2		—2	19.5	—22.9	5		5	30.7	—32.9	1		—1	84.1	96.4
4		2		—3.3	5		—5		9.5	3		1	37.9	—36.8
4		—2	39.9	40.9	1		6	43.2	—41.0	3		—1	18.5	18.5
0		3	30.9	29.9	1		—6		0.4	5		1		—0.9

Continued: TABLE II.

h	*k*	*l*	Fo	Fc	*h*	*k*	*l*	Fo	Fc	*h*	*k*	*l*	Fo	Fc
5	7	—1	50.2	49.0	4		6	22.4	24.8	2		4	20.2	—19.5
1		2	34.1	31.7	4		—6		3.9	2		—4	23.7	—23.9
1		—2	31.6	36.2	0		7		—3.6	4		4	57.7	—62.5
3		2		2.9	2		7	24.2	24.3	4		—4	66.5	—58.2
3		—2		—9.9	2		—7		—3.1	0		5		3.0
5		2	27.8	27.0	1	9	0		18.2	2		5		—9.7
5		—2	17.0	18.1	3		0		—8.3	2		—5	18.4	—16.6
1		3	46.5	42.0	5		0		—10.5	4		—5	16.7	16.2
3		—3	32.4	—36.0	1		1	90.1	—88.3	0		6		12.7
5		3	60.0	63.3	1		—1	32.8	35.3	2		6	32.8	35.8
5		—3		—3.9	3		1		—11.2	2		—6	21.9	24.7
1		4	40.7	—36.3	3		—1	25.0	24.7	1	11	0		—10.3
1		—4	51.0	—56.8	5		1	91.2	—92.5	3		0		3.1
3		—4	29.3	—28.7	5		—1	30.4	28.3	1		1		12.3
5		4	43.8	—48.2	1		2	53.6	49.5	1		—1	22.0	23.4
5		—4	43.6	—40.0	1		—2	37.8	41.2	3		1	27.8	—25.7
1		5		—3.4	3		2	45.5	41.8	3		—1	31.7	—29.4
1		—5	67.3	76.3	3		—2	25.9	23.6	5		1		3.9
3		5	54.7	—56.2	5		2		11.7	5		—1	23.2	22.8
3		—5		11.1	5		—2		—0.4	1		2		10.6
5		5		2.7	1		3	25.5	24.4	3		2		1.9
5		—5	15.7	15.6	1		—3	90.1	—99.4	3		—2		6.4
1		6		12.3	3		3	36.5	37.6	5		—2	21.5	20.6
3		6		12.6	3		—3		—9.6	1		3	21.2	21.5
3		—6		—4.0	5		3	28.0	29.0	3		3	20.5	—19.2
5		—6	12.6	12.0	5		—3	67.4	—67.0	1		4		—12.3
1		7		13.5	1		4		15.9	3		4		1.0
3		7	14.1	16.1	3		4		3.8	3		—4		5.0
3		—7	41.0	—41.8	3		—4	22.9	—21.1	1		5	30.6	29.5
1		—8	31.4	—34.7	5		4		0.6	1		—5	19.7	19.3
0	8	0	78.9	91.7	5		—4		—9.0	3		—5	11.3	—9.7
2		0	24.3	—23.7	1		5	50.6	—47.1	0	12	0	17.7	—18.2
4		0	20.5	21.7	1		—5	27.2	28.1	2		0	53.8	—52.4
0		1	23.7	22.0	3		5		—16.0	4		0		—3.6
2		1	36.3	—33.3	3		—5	29.2	26.9	0		1		4.4
2		—1	49.4	51.4	5		—5	20.4	18.6	2		1	50.7	—46.9
4		1		8.1	1		6	27.1	26.4	2		—1	28.1	24.9
4		—1	26.9	28.7	3		6	36.6	40.0	4		1	21.2	—24.9
0		2	25.1	24.7	3		—6	13.7	12.0	4		—1		8.0
2		2		16.5	1		7	15.1	16.6	0		2	40.1	40.1
2		—2		—6.7	1		—7	57.7	—62.1	2		2		9.9
4		—2		7.2	0	10	0	75.3	—86.0	2		—2	21.8	21.2
0		3	22.8	—22.9	2		0	24.0	—23.6	4		2	47.3	48.0
2		3	54.7	49.7	4		0	76.4	—72.5	4		—2	52.0	49.3
2		—3		—9.7	0		1		4.7	0		3		5.1
4		3		13.5	2		1	31.3	—26.5	2		3	35.0	35.1
4		—3		—8.1	2		—1		—11.3	2		—3	37.3	—35.5
0		4	61.4	58.5	4		1	21.3	—24.7	0		4		—9.2
2		4		—13.8	4		—1		2.3	2		4	49.7	—51.5
2		—4	28.4	—32.3	0		2	21.6	20.7	2		—4	39.7	—37.7
4		4	36.7	39.4	2		2	48.0	45.8	1	13	0	53.9	—49.9
4		4		5.6	2		—2	36.9	38.9	3		0	50.6	—51.7
0		5		—3.7	4		2		10.4	1		1		—3.3
2		5	32.6	—32.8	4		—2		6.5	1		—1	20.3	—21.1
2		—5	21.7	22.3	0		3		16.9	3		1	43.2	44.9
4		5		11.4	2		3		9.8	3		—1		—9.0
4		—5	26.2	24.0	2		—3		—14.8	1		2		6.9
0		6		6.8	4		3		—10.9	3		—2	32.0	34.6
2		6		10.2	4		—3	28.3	—25.4	1		3	31.8	—31.3
2		—6	21.1	—19.2	0		4	76.5	—73.9	0	14	0	32.0	—30.2

TABLE III.

Interatomic distances in prosopite.

Antiprism		*Octahedra*	
Ca—F(2)	2.374 Å	Al(1)—O(1)	1.853 Å
F(2)$_3$	2.390	F(2)	1.870
F(3)	2.277	O(4)	1.891
O(4)$_3$	2.573		
		O(1)—F(2)	2.689
F(2)—F(2)$_1$	3.179	F(2)$_2$	2.576
F(2)$_3$	2.913	O(4)	2.448
F(3)	3.021	O(4)$_2$	2.834
F(3)$_1$	2.740	F(2)—O(4)	2.755
F(2)$_3$—F(3)	2.832	O(4)$_2$	2.560
O(4)$_3$	2.560		
O(4)$_4$	3.219	Al(2)—O(1)	1.893
O(4)$_4$—F(3)$_1$	3.021	F(3)	1.793
O(4)$_3$	2.694	O(4)	1.915
		O(1)—F(3)	2.634
Hydrogen bonds		F(3)$_1$	2.711
		O(4)	2.448
O(4)$_5$—O(1)	2.850 Å	O(4)$_1$	2.790
O(1)—F(3)$_3$	2.766	F(3)—F(3)$_1$	2.464
		O(4)$_1$	2.681
		O(4)—O(4)$_1$	2.694

DESCRIPTION AND DISCUSSION OF THE STRUCTURE.

Fig. 1 shows the general arrangement of the atoms in prosopite.

The Ca atom binds eight anions on the corners of an irregular antiprism; calcium-anion distances range from a minimum of 2.277 to a maximum of 2.573 Å; the mean distance is 2.403 Å.

These antiprisms are connected to each other by the sharing of one edge (anions 2–2$_3$) so as to form two sets of zig-zag chains running parallel to the *c* axis at *a* approx. 0, *b* approx. 0 and at *a* approx. 0.50, *b* approx. 0.50. The Ca—Ca distance in the chain is 3.77 Å.

Both independent aluminium atoms show octahedral coordination. The equatorial planes of Al(1) and Al(2) octahedra (which contain the anions 1, 1$_2$, 2, 2$_2$ and 3, 3$_1$, 4, 4$_1$ respectively) are nearly perpendicular to the *c* axis.

TABLE IV.

Interatomic angles in prosopite.

Antiprism		*Octahedra*	
F(2)—Ca—$F(2)_1$	84.1°	O(1)—Al(1)—$O(1)_2$	180.0°
$F(2)_3$	75.4	F(2)	92.5
$F(2)_4$	143.2	$F(2)_2$	87.5
F(3)	81.0	O(4)	81.6
$F(3)_1$	72.2	$O(4)_2$	98.4
$O(4)_3$	135.7	F(2)—Al(1)—$F(2)_2$	180.0
$O(4)_4$	123.4	O(4)	94.2
$F(2)_3$—Ca—$F(2)_4$	136.6	$O(4)_2$	85.8
F(3)	74.7	O(4)—Al(1)—$O(4)_2$	180.0
$F(3)_1$	119.6		
$O(4)_3$	62.0	O(1)—Al(2)—$O(1)_1$	171.9°
$O(4)_4$	80.8	F(3)	91.2
F(3)—Ca—$F(3)_1$	143.7	$F(3)_1$	94.7
$O(4)_3$	76.8	O(4)	80.0
$O(4)_4$	139.4	$O(4)_1$	94.2
$O(4)_3$—Ca—$O(4)_4$	63.1	F(3)—Al(2)—$F(3)_1$	86.8
		O(4)	171.1
		$O(4)_1$	92.6
		O(4)—Al(2)—$O(4)_1$	89.4

Coordination polyhedra around the anions.

Al(1)—O(1)—Al(2)	99.4°	$Al(1)_1$—$O(4)_5$—$Al(2)_1$	97.3°
H(1)	94.2	Ca_1	101.8
H(2)	113.4	H(2)	116.8
Al(2)—O(1)—H(1)	124.5	$Al(2)_1$—$O(4)_5$—Ca_1	103.7
H(2)	121.3	H(2)	136.5
H(1)—O(1)—H(2)	100.9	Ca_1—$O(4)_5$—H(2)	95.2
Al(1)—F(2)—Ca	140.8	Ca—F(3)—Al(2)	147.3
Ca_1	109.5	H(1)	104.5
Ca—F(2)—Ca_1	104.6	Al(2)—F(3)—H(1)	108.1

It has been assumed that H *atoms lie on the* O—O *and* O—F *directions.*

The aluminium-anion distances range from 1.793 to 1.915 Å, the mean distances being 1.871 and 1.867 in Al(1) and Al(2) octahedra.

These octahedra are connected to each other by edge-sharing (anions 1–4) to form infinite chains, on the whole running parallel to the [10$\bar{1}$] axis. There are chains at b approx. 1/4 and chains at b approx. 3/4 (see fig. 2). Thus the distance Al—Al is rather short (2.86 Å). Because of the electrostatic repulsion between the cations (the Al—Al distance would be 2.70 Å for regular Al octahedra sharing one edge), the (1)—Al(1)—(4) angle value is 81.6°, the (1)—Al(2)—(4) one is 80.0° and the (1)—(4) distance is rather short (2.45 Å), due to the slight deformation observed in the Al octahedra.

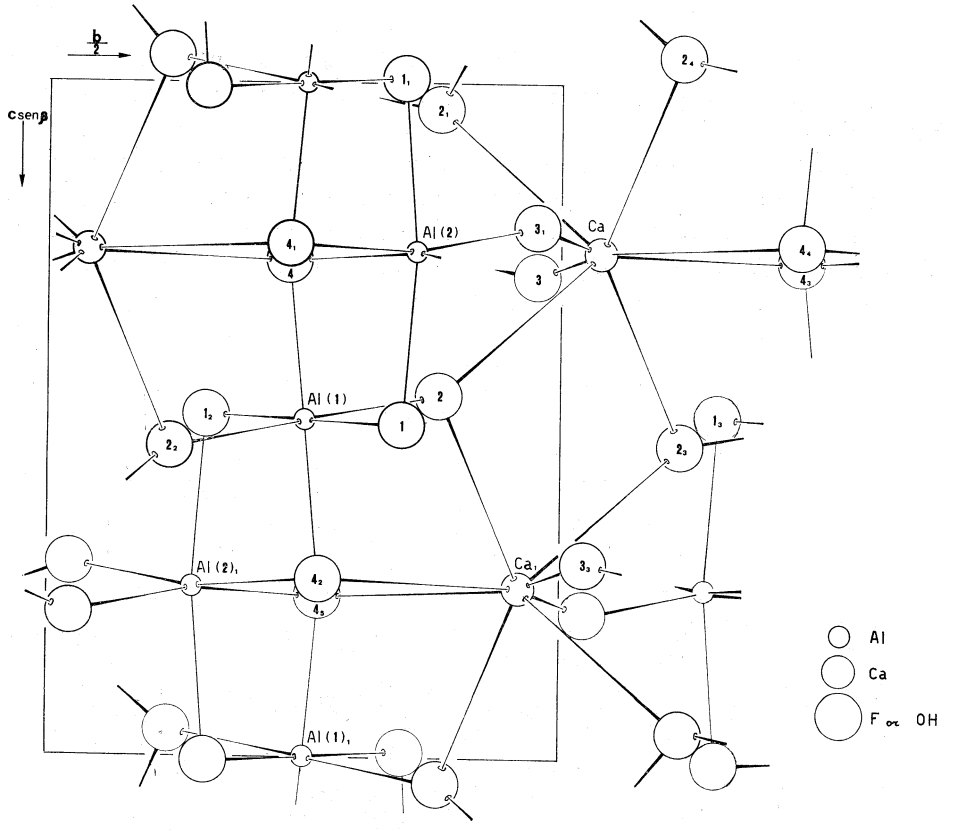

Fig. 1. – The crystal structure of prosopite projected along the a axis.

The connections between one Al chain and the adjacent ones are provided by the Ca coordination polyhedra. In fact each antiprism shares corners and edges with seven adjacent Al octahedra (see fig. 3). The shared edges, belonging to three octahedra of the same chain, (anions 2–4$_2$ (2×), 4$_2$–4$_5$) have lengths of 2.56 (2×) and 2.69 Å respectively. The shared corners (four) belong to octahedra of two Al chains adjacent to the last one mentioned, and equivalent to each other by translation.

From the previous description it arises that the anions are linked to the nonhydrogen cations according to the following scheme:

Anions	Cations	Charge surrounding each anion
(1)	Al (1), Al (2)	1.0
(2)	Al (1), Ca, Ca	1.0
(3)	Al (2), Ca	0.75
(4)	Al (1), Al (2), Ca	1.25

Now let us examine the problem of the isomorphous substitution F, OH; that is to try some hypotheses on the possible structural non equivalence of these anions.

In fact the three chemical analyses given in Dana's System of Mineralogy show F : OH ratios 1.34, 1.17, 1.13 according to the origin of the samples. In the same textbook the following statement is found: "The F and OH substitute mutually over only a narrow range, and these anions may be structurally non equivalent, as in gearksutite, at least in part".

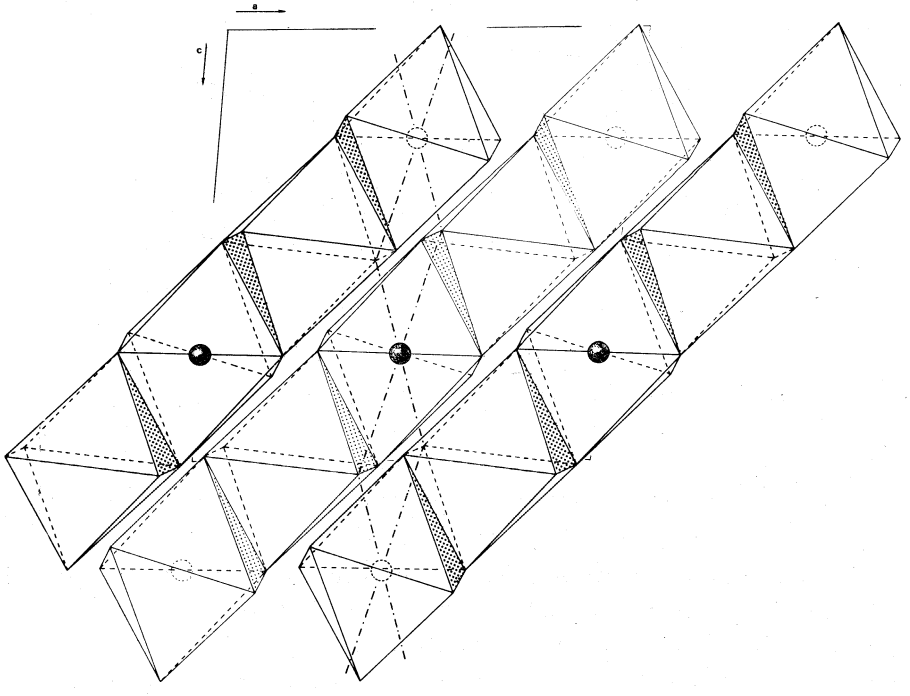

Fig. 2. – Al octahedra chains parallel to [101], projected along the *b* axis. Circles indicate Ca atom positions; for clearness some calcium–anion bonds are not drawn. The sign —·—· indicates one Ca antiprisms chain, parallel to [001].

For this purpose, electron-density distribution was carefully examined. The (1) and (4) atoms appeared to have an almost alike electron-density distribution, but slightly different from the one of (2) and (3) atoms; the peak profile of (2) and (3) being higher and sharper. However this experimental suggestion, taken by itself, was not considered definitive.

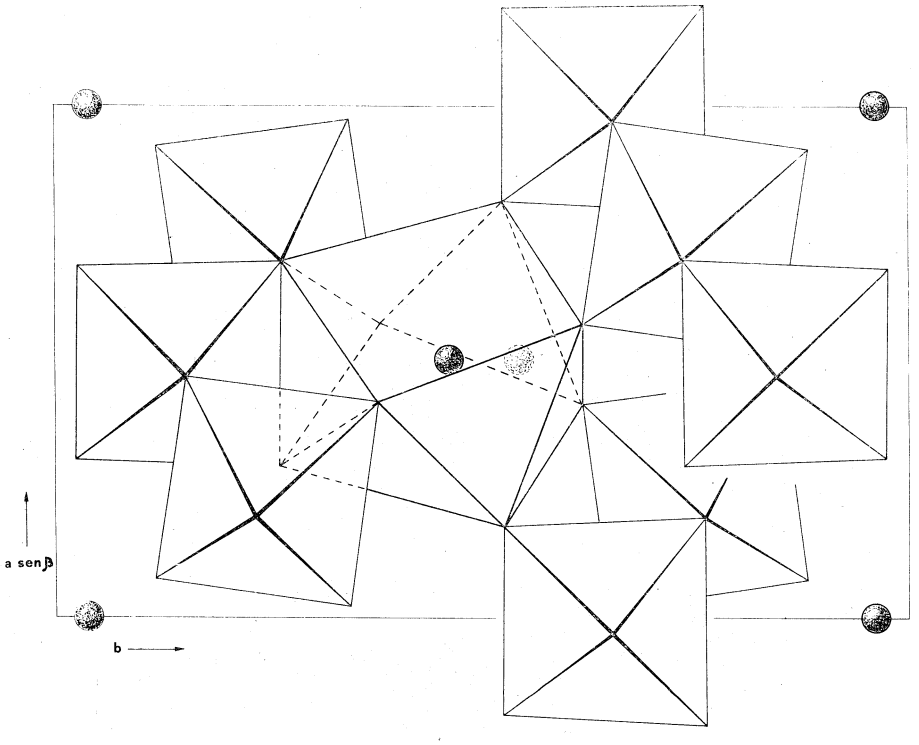

Fig. 3. – Coordination polyhedra for Al and Ca. Circles indicate calcium atom positions. The Ca antiprism connects adjacent Al octahedra chains. For a clearer drawing only one antiprism is represented.

On the other hand, cation-anion bond distance analysis and the examination of the possible hydrogen bonds allowed the following considerations:

– the atom (4) is always the most distant from the cations; besides it can make hydrogen bonds with the atom (1);

– the atom (2) has bond distance shorter than the atom (4); the interanionic distances are not suitable for hydrogen bonds, the shortest distance being of 3.27 Å;

– the atom (3) has always the shortest bond distances from the cations, and can make hydrogen bonds with the atom (1);

– as to the atom (1) no conclusion is possible from cation-anion bond distance analysis. It can make hydrogen bonds with the (3) and (4) atoms.

Though interesting, these experimental indications, taken by themselves, are not definitive. Actually a careful examination on Ca—F, Ca—O, Al—F,

Al—O distance values found in previous papers [2] [4] [5] [7] [10] [11] [14] [15] [16] [17] [20] [23], shows Al—F and Ca—F bond distances almost always shorter than Al—O and Ca—O ones. However the measured values range is rather wide and for Al—F bond distances a numerous set of reliable values is not available.

Owing to the deformation of the coordination polyhedra, arising from the sharing of corners and edges, the analysis of the interanionic distances in the same polyhedron seemed less meaningful for this purpose.

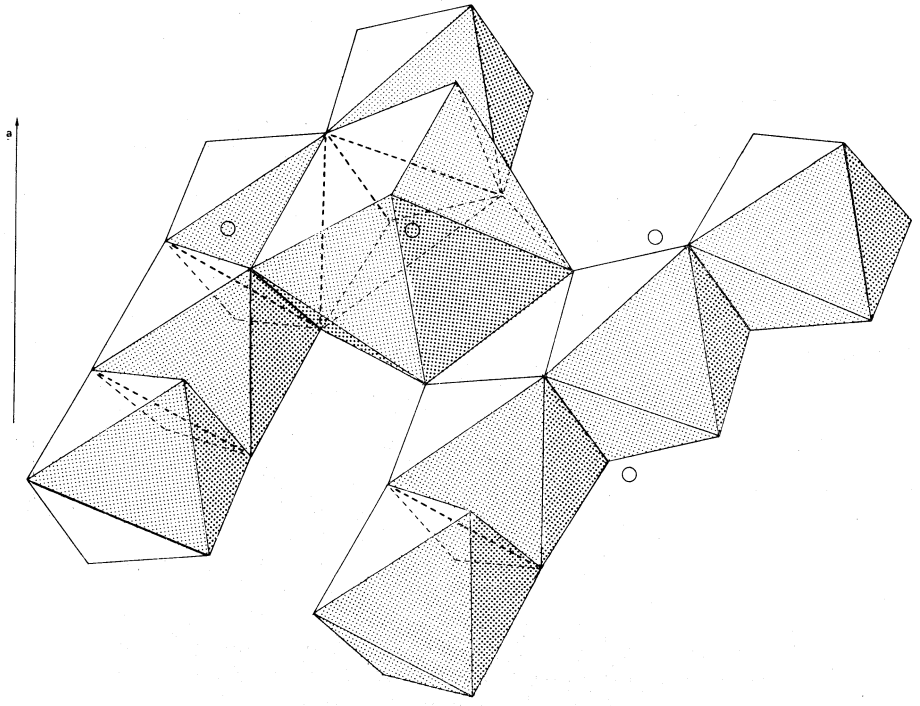

Fig. 4. – The crystal structure of prosopite projected on a plane normal to (111). Circles indicate calcium atom positions. For clearness only one antiprism is drawn.

However on the basis of the previous agreeing indications, the hypothesis of position (4) being completely occupied by oxygen and position (2) by fluorine seemed reasonable.

The inspection of this hypotesis allowed a substantial improvement of R index (from 0.079 to 0.071); temperature factors also showed better values though some anomalous behaviour was persisting. In the following attempt a F : OH ratio = 1 was assumed (oxygen in (1) and (4) positions, fluorine in (2) and (3)). Residual anomalous behaviour of the temperature factors disappeared, and R index value was decreasing, although in a negligible amount. The last attempt was performed on the basis of the F : OH ratio = = 1.17 according to the chemical analysis 3 in Dana's System of Mineralogy;

fluorine atoms in (2) and (3) positions, oxygen in (4) and oxygen + fluorine in (1). R value decreased from 0.069 to 0.067.

The attempt of a direct location of the hydrogen atoms on Fourier-difference maps was not successful. However, from anion-anion distance analysis it seems very likely the following hydrogen bonds to be present: $O(4)_1$—H $\cdots$ $O(1)_2$ with O—O distance of 2.85 Å and O(1)—H $\cdots$ $F(3)_3$ with O—F distance of 2.77. The first value falls within the limits quoted in literature for O—H$\cdots$O distances, the second one seems to be slightly higher than the O—H$\cdots$F distance values measured by neutron diffraction [13]. Distributing each hydrogen contribution between oxygen and fluorine atoms, as 3/4 for the linked one and 1/4 for the unlinked atom, the balance of the electrostatic valences is quite satisfactory.

In conclusion, according to the previous experimental indications, the structure of prosopite can be described as follows: Ca atom binds six fluorine and two oxygen atoms, while both Al atoms link two fluorine and four oxygen atoms (approximating to 1 the experimental F : OH ratio = 1.17, that is assuming on position (1) : oxygen = 1, fluorine = 0 instead of oxygen = 0.85, fluorine = 0.15).

The F(2) and F(3) atoms are nearly planar bound to three cations: Al(1), Ca, Ca and Al(2), Ca, H respectively; both O(1), O(4) atoms link four cations with roughly tetrahedral coordination: Al(1), Al(2), H, H and Al(1), Al(2), Ca, H.

The mean cation-anion distances are: Al—O = 1.89, Al—F = 1.83, Ca—O = 2.57, Ca—F = 2.35 Å. These values agree with the mean distance values found in thomsenolite [5] and with the ones calculated on the basis of the " effective ionic radii " values given by Shannon and Prewitt [21].

Therefore it is reasonable to attribute the chemical formula $CaAl_2F_4(OH)_2$ $(OH_{0.85}, F_{0.15})_2$ to prosopite or, assuming a F : OH ratio = 1, the formula $CaAl_2F_4(OH)_4$.

Nevertheless, the foregoing statements have to be considered only highly probable, and not experimentally definitive; that is all the lattice positions (2), (3), (1), (4) could be occupied by oxygen + fluorine, but only with decreasing F : O ratio.

The physical properties of prosopite are well explained by the structural features. The rather homogeneous distribution of the atoms in the cell is surely connected to its low birefringence (0.009). The cleavage {111} is easy explicable upon examining fig. 4, which represents the structure of prosopite projected on a plane normal to (111). It is evident that the cleavage is parallel to the Al octahedra chains and breaks some calcium-anion bonds and some hydrogen bonds.

REFERENCES.

[1] ALBANO A., DOMENICANO A. e VACIAGO A., *Programmi di Strutturistica chimica diffrattometrica per l'elaboratore elettronico I.B.M. 7040*, « Gazz. Chim. Ital. », *96*, 922 (1966).

[2] BAUR W. H., *Die Kristallstruktur des Edelamblygonits*, « Acta Cryst. », *12*, 988 (1959).

[3] BERMAN H. and WOLFE W. C. in *Dana's System of Mineralogy*, *2*, 121, New York 1951.

[4] CANNILLO E., GIUSEPPETTI G. and TAZZOLI V., *The crystal structure of leucophanite*, « Acta Cryst. », *23*, 255 (1967).

[5] COCCO G., CASTIGLIONE P. C. and VAGLIASINDI G., *The crystal structure of thomsenolite*, « Acta Cryst. », *23*, 162 (1967).

[6] CROMER D. T. and WABER J. T., *Scattering factors computed from relativistic Dirac–Slater wave functions*, « Acta Cryst. », *18*, 104 (1965).

[7] DAL NEGRO A., ROSSI G. and UNGARETTI L., *The crystal structure of meliphanite*, « Acta Cryst. », *23*, 260 (1967).

[8] FERGUSON R. B., *Observations on some aluminium fluoride minerals*, « Am. Min. », *34*, 391 (1949).

[9] GIACOVAZZO C. and MENCHETTI S., *The crystal structure of prosopite*, « Naturwiss. », *56*, 86 (1969).

[10] GIUSEPPETTI G., CODA A., MAZZI F. e TADINI C., *La struttura cristallina della liroconite*, « Per. Min. », *31*, 19 (1962).

[11] GUY B. B. and JEFFREY G. A., *The crystal structure of fluellite*, « Am. Min. », *51*, 1579 (1966).

[12] HAMILTON W. C., *On the isotropic temperature factor equivalent to a given anisotropic temperature factor*, « Acta Cryst. », *12*, 609 (1959).

[13] HAMILTON W. C. and IBERS J. A., *Hydrogen Bonding in Solids*, New York, 1968.

[14] *International Tables for X-Ray Crystallography, vol. III*, The Kynoch Press, Birmingham, 1962.

[15] KETELAAR J. A. A., *The crystal structure of the aluminium halides. I. The structure of aluminium trifluoride*, « Zeit. Krist. », *85*, 119 (1933).

[16] MENCHETTI S., *The crystal structure of gaylussite*, « Rend. Acc. Naz. Lincei », *44*, 680 (1968).

[17] NÁRAY-SVABÓ S. and SASVÁZI K., *The structure of cryolite, Na_3AlF_6*, « Zeit. Krist. », *99*, 27 (1938).

[18] PALACHE C. in *Dana's System of Mineralogy 2*, 121, New York 1951.

[19] PALACHE C., BERMAN H. and FRONDEL C., *Dana's System of Mineralogy 2*, 121, New York 1951.

[20] PAVLOV P. W. and BELOV N. V., *Crystal structure of herderite, datolite and gadolinite*, « Dokl. Akad. Nauk. S.S.S.R. », *114*, 884 (1957).

[21] SHANNON R. D. and PREWITT C. T., *Effective ionic radii in oxides and fluorides*, « Acta Cryst. », *25 B*, 925 (1969).

[22] SCHEERER, « Ann. Phys. », *90*, 315 (1853). Fide: *Dana's System of Mineralogy*, *2*, 121.

[23] SWANSON H. E. and TATGE E., *Standard X-ray diffraction powder patterns*, « N.B.S. Circular 539 », *1*, 69 (1962).