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A Neutron Diffraction and Thermogravimetric Study of the Hydrogen Bonding and Dehydration Behavior in Fluorapophyllite, $KCa_4(Si_8O_{20})F.8H_2O$, and its Partially Dehydrated Form*

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Abstract

Single-crystal neutron diffraction studies have been performed on natural fluorapophyllite at 295 and 373 K, and on partially dehydrated fluorapophyllite (PDFA), $KCa_4(Si_8O_{20})F.7{\cdot}4H_2O$, at 295 K. Space group $P4/mnc$, $Z = 2$, $a = 8{\cdot}970\,(1)$, $c = 15{\cdot}792\,(4)$, $\lambda = 1{\cdot}1598\,(1)$ Å at 295 K, $a = 8{\cdot}985\,(1)$, $c = 15{\cdot}800\,(6)$, $\lambda = 1{\cdot}1598\,(1)$ Å at 373 K and $a = 8{\cdot}962\,(1)$, $c = 15{\cdot}790\,(3)$, $\lambda = 1{\cdot}0505\,(1)$ Å for PDFA. Using 1235, 854 and 1208 unique reflections resulted in $R = 0{\cdot}050$, 0·040 and 0·054 for the 295 K, 373 K and PDFA data sets respectively. Heating to 460 K under atmospheric conditions for 1 h reproducibly but irreversibly removed 0·61 (3) water molecules per formula unit. A new water position, observed subsequently at 295 K, with the oxygen in the mirror plane and occupied to 0·12, gives two strong hydrogen bonds $H\cdots O = 1{\cdot}82\,(2)$ Å as compared to one strong [1·765 (2) Å] and one weak [2·264 (3) Å] bond in the original positions. The dehydration of fluorapophyllite is described as a three-step reaction: (1) loss of one water per f.u. (PDFA); (2) loss of another three waters per f.u. (step 2 requires a rearrangement of the K^+ coordination, and destroys the single crystal); (3) loss of the remaining water. This step leaves an amorphous residue. The refined neutron scattering length for Ca gave a revised value of $0{\cdot}465\,(3) \times 10^{-14}$ m.

Introduction

Apophyllite, $KCa_4Si_8O_{20}(F,OH).8H_2O$, has been subject to numerous chemical, crystallographic and thermodynamic investigations. The crystal structure was first determined by Taylor & Náray-Szabo (1931). Parallel refinements by Colville, Anderson & Black (1971), Chao (1971) and Prince (1971) confirmed the major features of the original structure determination. Localization of the H atoms by Chao (X-ray study) and Prince (neutron study) clarified the hydrogen-bonding situation in apophyllite. Residual scattering

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densities in the vicinity of the F site led Prince (1971) to suggest the occurrence of 'free' HF and the formula $KCa_4Si_8O_{20}F_{1-x}(HF)_x$$[(H_2O)_{8-x}(OH)_x]$. Later work has strongly disputed this result. Bartl & Pfeifer (1976) in a neutron study proposed the more probable $[F_{1-x},(OH)_x]$ exchange to explain the residual scattering densities. In an extensive search for the OH end member of apophyllite, Dunn, Rouse & Norberg (1978) confirmed the $[F_{1-x},(OH)_x]$ exchange. The crystal structure of the pure OH form was found to be not significantly different from the F form (Rouse, Peacor & Dunn, 1978). These authors suggested the following nomenclature for the apophyllites: fluorapophyllite when F > OH; hydroxyapophyllite when OH > F; and apophyllite with undetermined F/OH ratio.

Studies of the dehyration behavior of apophyllite have given very different results. From thermogravimetric analysis (TGA) under maximum dehydration conditions Cavinato (1927) claimed a one-step dehydration reaction, while Gossner & Kraus (1928) found a two-step behavior. Later studies using constant heating rates all show a two-step reaction, although with different characteristic temperatures and curve forms (Colville, Anderson & Black, 1971; Chao, 1971; Bartl & Pfeifer, 1976; Larsen, 1981). However, the experimental conditions are in most cases poorly described.

This work is an attempt, by means of neutron diffraction and TGA, to clarify the structural effects of the dehydration of apophyllite and the differences in appearances in the previous thermal investigations. Precise neutron diffraction data at 295 and 373 K on a pure and unperturbed fluorapophyllite has provided a firm ground for the structural discussion.

Experimental

Four-circle neutron diffraction data were collected at the Brookhaven National Laboratory High Flux Beam Reactor, using natural single crystals of fluorapophyllite from Nasik, India. The same single crystal was used at 295 and 373 K. The partially dehydrated crystals (PDFA) were sealed in quartz bulbs and data collected at 295 K. The higher temperature was attained with a locally built furnace. The crystals were colorless, transparent, square prisms, bound by {001} and {110} and slightly truncated by $(\bar{1}0\bar{1})$, $(0\bar{1}\bar{1})$, $(10\bar{1})$ and $(01\bar{1})$.

A first attempt to dehydrate apophyllite directly in the diffractometer furnace at 460 K resulted in an opaque and non-diffracting crystal. Continued dehydration experiments on single crystals were carried out in a separate furnace in air, during controlled periods of time, with subsequent rapid cooling to room temperature in dry air. The degree of dehydration was measured through careful weighing of the single crystals before and after heating. When the weight loss reached 2·5 (1)% the crystals turned white on the surface, increasingly so at 3·0 (1)%. These partially dehydrated crystals showed only insignificant water absorption during prolonged exposure to humid air. At 9% weight loss the crystals were completely opaque and also non-diffracting. The total water content corresponds to 15·9% by weight.

Table 1. *Crystal data, data collection, reduction and least-squares refinement details for fluorapophyllite and partially dehydrated fluorapophyllite, space group* $P4/mnc$, $Z = 2$

			PDFA
Temperature (K)	295 (1)	373 (1)	295 (1)
a (Å)	8·970 (1)	8·985 (1)	8·962 (1)
c (Å)	15·792 (4)	15·800 (6)	15·790 (3)
V (Å^3)	1270·6 (4)	1275·6 (5)	1268·3 (4)
M_r	907·2	907·2	896·4
D_x (g cm^{-3})	2·371	2·362	2·347
μ (cm^{-1})	1·055	1·051	0·966
Crystal size (mm)	1·7 × 1·7 × 2·5	1·7 × 1·7 × 2·5	2·6 × 2·6 × 1·7
Range of transmission factors	0·80–0·86	0·80–0·86	0·78–0·87
λ(Å)	1·1598 (1)	1·1598 (1)	1·0505 (1)
Monochromator	Ge(220)	Ge(220)	Be(002)
Max. $(\sin\theta)/\lambda$ (Å^{-1})	0·727	0·717	0·789
Number of symmetry allowed reflections			
recorded	1377	935	1372
unique in final LS cycle, m	1235	854	1208
Number of parameters in final LS cycle, n	70	70	88
$R(F^2)$ (%)	5·02	3·96	5·44
$R_o(F^2)$* (%)	5·67	4·26	6·33
$wR(F^2)$ (%)	4·65	6·34	5·24
$R(F)$ (%)	5·05	3·70	5·40
$S = [\sum w(F_o^2 - F_c^2)^2/(m-n)]^{1/2}$	1·23	1·30	1·06
c (in weighting function)	0·007	0·025	0·015

* Including zero-weighted reflections.

The thermogravimetric analyses were made on a Cahn system 113 electrobalance on a fluorapophyllite sample from Poona, India. The samples, ~50 mg, were heated from 300 to 775 K in a dry air flow of 20 ml min^{-1}. The samples consisted of small, 0·1–2 mm^3 crystals ('unground' in Fig. 6) or crystals ground with mortar and pestle ('ground' in Fig. 6). Completed dehydrations indicated no significant water loss during grinding.

Unit-cell parameters were determined from least-squares fitting of 61 or 32 (PDFA) sin 2θ values with $45 < 2\theta < 60°$. Inspection of heavily exposed precession films from PDFA showed no evidence of reflection broadening or streaks, but confirmed the space group $P4/mnc$, which was accordingly assumed in data collection and refinement. Intensity data were collected in a wedge of reciprocal space limited by $0 \le h \le 12$, $0 \le k \le 14$, $0 \le l \le 24$ and $h \le k$. The 373 K data collection was further limited by furnace obstructions. ω–2θ step scans were used: $\Delta 2\theta = 3°$, $2\theta \le 60°$ and $\Delta 2\theta = (1·15 + 3·70 \tan\theta)°$, $2\theta \ge 60°$ at 293 and 373 K, and $\Delta 2\theta = 3·2°$, $2\theta \le 60°$ and $\Delta 2\theta = (2·50 + 3·50 \tan\theta)°$, $2\theta \ge 60°$ for PDFA. The first and last tenths in a scan were used for background calculations. Two standard reflections measured every 50 reflections showed no systematic intensity variations during any of the data collections. The data sets were

Table 2. *Final atomic parameters* ($\times 10^5$) *with e.s.d.'s for fluorapophyllite and partially dehydrated fluorapophyllite*

(*a*) Positional parameters

$$B_{\rm iso} = \tfrac{4}{3}\textstyle\sum_i \sum_j \beta_{ij}\,\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm iso}$ (Å^2)	g
295 K					
F	0	0	0	1·24 (4)	
K	0	0	50000	2·54 (9)	
Ca	11045 (12)	24639 (12)	0	0·64 (2)	
Si	22635 (9)	8612 (9)	18985 (5)	0·48 (1)	
O(1)	36376 (7)	13622 (7)	25000	0·74 (1)	
O(2)	8490 (7)	18964 (7)	21761 (4)	1·04 (1)	
O(3)	26476 (7)	10127 (7)	9211 (4)	0·87 (1)	
O(4)	21411 (10)	44899 (9)	8978 (5)	1·74 (2)	
H(1)	44943 (16)	17193 (18)	8875 (10)	2·47 (3)	
H(2)	22149 (25)	42610 (19)	14844 (10)	3·62 (4)	
373 K					
F	0	0	0	1·54 (4)	
K	0	0	50000	3·12 (11)	
Ca	10930 (14)	24600 (15)	0	0·80 (2)	
Si	22580 (10)	8683 (10)	18975 (6)	0·56 (2)	
O(1)	36263 (8)	13736 (8)	25000	0·87 (1)	
O(2)	8393 (9)	18967 (9)	21738 (6)	1·25 (2)	
O(3)	26406 (9)	10212 (9)	9207 (5)	1·05 (1)	
O(4)	21400 (13)	44939 (11)	8973 (7)	2·27 (2)	
H(1)	44934 (19)	17181 (22)	8857 (13)	2·97 (4)	
H(2)	22121 (35)	42640 (25)	14830 (14)	4·39 (6)	
PDFA					
F	0	0	0	1·40 (4)	
K	0	0	50000	3·01 (10)	
Ca	11008 (12)	24576 (13)	0	0·80 (2)	
Si	22675 (9)	8618 (9)	18967 (5)	0·58 (1)	
O(1)	36384 (7)	13615 (7)	25000	0·88 (1)	
O(2)	8475 (8)	18961 (8)	21695 (5)	1·23 (1)	
O(3)	26541 (8)	10166 (8)	9172 (4)	1·04 (1)	
O(4)	21554 (11)	44915 (10)	8967 (6)	1·81 (2)	0·865 (4)
H(1)	44891 (20)	17242 (23)	8878 (15)	2·54 (4)	0·865
H(2)	22327 (29)	42595 (22)	14857 (12)	3·58 (6)	0·853 (7)
O(5)	18890 (126)	49450 (115)	0	1·94 (24)	0·059 (3)
H(3)	16147 (193)	55722 (164)	4696 (92)	2·79 (34)	0·119

(*b*) Thermal parameters

The temperature factor is of the form:

$$\exp-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl).$$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
295 K						
F	230 (12)	230 (12)	223 (10)	0	0	0
K	553 (28)	553 (28)	417 (25)	0	0	0
Ca	197 (11)	207 (11)	63 (3)	7 (9)	0	0
Si	148 (7)	134 (7)	53 (2)	1 (6)	−15 (4)	−9 (4)
O(1)	207 (5)	207 (5)	90 (2)	−6 (7)	−48 (3)	−48 (3)
O(2)	180 (6)	348 (7)	143 (2)	95 (6)	−18 (3)	−47 (3)
O(3)	343 (7)	322 (7)	48 (2)	16 (5)	−17 (3)	−7 (3)
O(4)	806 (10)	375 (8)	141 (3)	−4 (7)	−11 (5)	−67 (4)
H(1)	595 (16)	940 (19)	246 (5)	−14 (14)	60 (8)	−15 (9)
H(2)	1837 (32)	900 (21)	204 (5)	14 (21)	−56 (11)	3 (9)
373 K						
F	275 (14)	275 (14)	285 (11)	0	0	0
K	728 (35)	728 (35)	468 (28)	0	0	0
Ca	230 (13)	277 (13)	78 (4)	34 (10)	0	0
Si	150 (9)	162 (9)	68 (3)	−1 (7)	−23 (4)	−16 (5)
O(1)	242 (6)	242 (6)	104 (3)	−6 (8)	−53 (4)	−54 (4)
O(2)	209 (7)	419 (9)	173 (3)	119 (6)	−22 (4)	−63 (4)
O(3)	417 (9)	381 (8)	58 (2)	10 (6)	−22 (4)	−6 (4)
O(4)	1048 (14)	464 (11)	194 (4)	12 (9)	−10 (6)	−89 (5)
H(1)	676 (21)	1069 (23)	329 (8)	−16 (18)	81 (10)	14 (11)
H(2)	2291 (45)	1037 (27)	241 (8)	72 (28)	−70 (16)	−7 (12)
PDFA						
F	298 (13)	298 (13)	228 (10)	0	0	0
K	709 (33)	709 (33)	448 (27)	0	0	0
Ca	243 (11)	266 (12)	76 (3)	41 (9)	0	0
Si	165 (8)	185 (8)	61 (2)	−12 (6)	−16 (4)	−12 (4)
O(1)	246 (5)	246 (5)	106 (3)	−5 (7)	−45 (3)	−46 (3)
O(2)	218 (6)	408 (7)	169 (2)	105 (6)	−25 (4)	−63 (3)
O(3)	395 (7)	386 (7)	61 (2)	0 (5)	−15 (3)	−14 (3)
O(4)	829 (13)	397 (11)	150 (4)	7 (8)	−2 (5)	−75 (5)
H(1)	576 (21)	976 (24)	263 (8)	−64 (17)	78 (11)	5 (13)
H(2)	1850 (40)	870 (27)	202 (7)	100 (24)	−43 (13)	13 (11)
O(5)	933 (147)	378 (108)	162 (42)	82 (93)	0	0
H(3)	1253 (220)	802 (178)	178 (48)	162 (139)	1 (95)	−11 (85)

corrected for the Lorentz effect and absorption corrected using Gaussian integration over a $6\times6\times6$ grid. Two complete data sets were collected for PDFA using crystals with 2·5 (1) and 3·0 (1)% weight loss. The data sets gave, within two e.s.d.'s, equivalent refined parameters. Results from the latter will be given below because of slightly lower e.s.d.'s. Further information concerning crystal data, data collection and reduction and least-squares refinements is given in Table 1.

Structure refinements

The full-matrix least-squares refinements minimized $\sum w(F_o^2-F_c^2)^2$, where $w=[\sigma_c^2(F_o^2)+(cF_o^2)^2]^{-1}$ with $\sigma_c(F_o^2)$ determined from counting statistics and c adjusted to give uniform $\langle w(\Delta F^2)\rangle$ in different F_o^2 and $\sin\theta$ intervals. The crystallographic computer programs are described by Lundgren (1983). Neutron scattering lengths were taken from Koester, Rauch, Herkens & Schroeder (1981). The 295 K refinements were started with parameters given by Prince (1971). A new water site in PDFA was located in a difference Fourier map. Six anisotropic (295 K) or one isotropic (373 K and PDFA) extinction parameters [type I, Lorentzian mosaicity (Becker & Coppens, 1974, 1975)] were refined in the initial, but kept constant in the final LS cycles. The final extinction parameters [9·3 (3·3), 11·1 (2·1), 6·5 (2·3), −7·1 (1·8), −4·3 (1·4), 5·3 (1·8) × 10^6 at 295 K, 2·44 (27) × 10^3 at 373 K and 1·4 (12) × 10^3 for PDFA] resulted in maximum extinction corrections (*F_o^2) of 1·22, 1·27 and 1·16 at 295 K, 373 K and for PDFA respectively.

Refined parameters in the final LS cycles include one scale factor, atomic coordinates and anisotropic thermal parameters for all atoms. The occupancy factors of the water atoms were initially refined for all data sets, but did not differ significantly from unity for the 295 and 373 K data sets, and were kept constant in the final LS cycles. The short H(1)–H(3) distance, 0·670 (15) Å, in PDFA resulted in very strong correlations between their occupancy factors and thermal parameters. The occupancy factors of H(1) and H(3) were therefore constrained to the occupancy factors of O(4) and O(5) respectively. Occupancy factors for K, Ca and F were also initially refined. The values did not differ significantly from unity and were kept constant in the final LS cycles. The Ca^{2+} value showed a significant deviation from unity assuming the Ca scattering length of Koester, Rauch, Herkens & Schroeder (1981). A revised Ca scattering length of 0·465 (3) × 10^{-14} m derived from the refined occupancy factor was then assumed, since there is no chemical or structural evidence of lower occupancy or exchange of Ca. This value agrees with other results (Shull, 1972; Kvick, Ståhl & Smith, 1985).

The refinements were considered converged when (parameter shift)/(parameter e.s.d.) $< 0{\cdot}1$. The highest residual peaks in the final difference Fourier maps correspond to $\leq 8\%$ of the absolute H(1) peak heights. Reflections with $|F_o^2/F_c^2| > 4{\cdot}0$ (142, 81 and 165 reflections for the 295 K, 373 K and PDFA data sets respectively) were given zero weight in the final LS cycles. These reflections were all weak and probably affected by multiple scattering. Final atomic parameters are given in Table 2.*

The difference densities along the fourfold axis are very sensitive to the refinement model, Fig. 1. The possible (F_{1-x},OH_x) exchange (*cf.* Prince, 1971; Bartl & Pfeifer, 1976) should therefore be cautiously interpreted, and carefully tested at the final level of the refinements, as illustrated by the following. Parameters of the extra hydrogen, H(6), as proposed by Prince (1971), on the fourfold axis, near the F site in the mirror plane, were refined using different data sets from the same crystal with differing maximum $(\sin\theta)/\lambda$, thermal parameter models (on remaining atoms) and extinction models (Table 3). The H(6) parameters varied were the positional, z, and one occupational, g, parameter with an isotropic temperature factor fixed at the isotropic mean value found for H(2). A dramatic effect on the site occupancy - a variation between 2 (2) and 12 (6)% - may readily result depending on the procedure used. [For comparison, Prince (1971) made no extinction correction and had $(\sin\theta)/\lambda_{\max} = 0{\cdot}62$ Å^{-1}, while Bartl & Pfeifer (1976) used an isotropic extinction model and $(\sin\theta)/\lambda_{\max} = 0{\cdot}70$ Å^{-1}.]

Table 3. H(6) *refinement summary for fluorapophyllite*

T(K)	Thermal parameter type	Extinction parameter type	Max. $(\sin\theta)/\lambda$ (Å^{-1})	$R(F^2)$ (%)	g[H(6)] ($\times 10^4$)	(F,O)–H(6) (Å)
295	Isotropic	None	0·79	11·78	145 (72)	1·31 (20)
295	Anisotropic	None	0·79	5·99	127 (26)	1·39 (11)
295	Anisotropic	Isotropic	0·79	5·05	79 (22)	1·48 (15)
295	Anisotropic	Anisotropic	0·79	5·01	48 (22)	1·59 (23)
295	Anisotropic	Anisotropic	0·70	3·93	53 (23)	1·68 (21)
295	Anisotropic	Anisotropic	0·62	3·25	49 (24)	1·81 (24)
373	Anisotropic	Isotropic	0·71	3·96	29 (29)	0·98 (54)

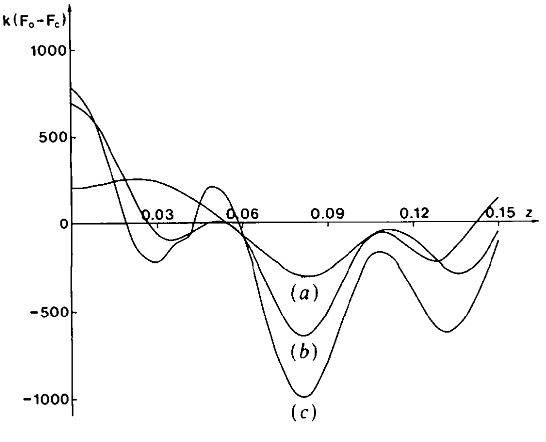

Fig. 1. Difference densities along the z axis using different refinement models and data sets. Curve (a) $T = 373$ K, isotropic extinction correction and max. $(\sin\theta)/\lambda = 0{\cdot}71$ Å^{-1}; curve (b) $T = 295$ K, anisotropic extinction correction and max. $(\sin\theta)/\lambda = 0{\cdot}79$ Å^{-1}; curve (c) $T = 295$ K, no extinction correction and max. $(\sin\theta)/\lambda = 0{\cdot}70$ Å^{-1}.

Discussion

Structure description

The crystal structure of fluorapophyllite is shown in two projections in Fig. 2. A selection of distances and angles is given in Table 4.

The structure consists of infinite silicate $(Si_2O_5^{2-})$ layers held together through Ca^{2+} and K^+ coordination of O atoms and through hydrogen bonding. The puckered silicate layers are perpendicular to 001 and centered on $z = \frac{1}{4}$ and $\frac{3}{4}$. The Ca^{2+}, K^+ and F^- ions are located in the mirror planes $z = 0$ and $\frac{1}{2}$. Ca coordinates four O(3) atoms from the silicate layers, two water O atoms and F^- in a capped trigonal prism, with F^- on a square face (Fig. 5). K^+ coordinates eight water O atoms in a square prism. The $K^+(OH_2)_8$ polyhedron connects to the silicate layers through hydrogen bonding and indirectly through the Ca^{2+}–water coordination. The water molecules in fluorapophyllite are crystallographically equivalent and show one strong [H(1)···O(3)] and one weak [H(2)···O(2)] hydrogen bond, and coordinate to one Ca^{2+} and one K^+ each (Fig. 3).

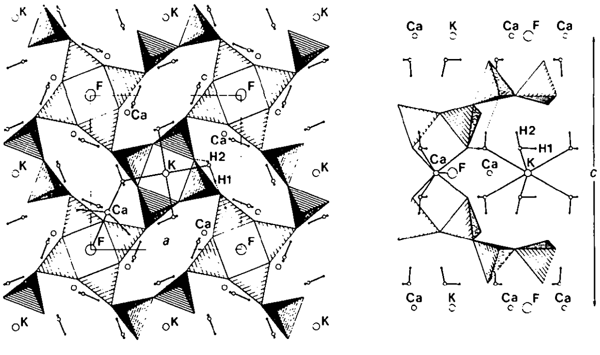

Fig. 2. Sections of the fluorapophyllite structure viewed along **c** (left) and **a** (right).

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* Lists of observed and calculated structure factors together with the Monte-Carlo simulation program have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44221 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Selected distances (Å) and angles (°) in fluorapophyllite and partially dehydrated fluorapophyllite*

		295 K	373 K	PDFA
F–Ca	[4]*	2·4221 (11)	2·4187 (13)	2·4134 (12)
–O(3)	[8]	2·9293 (7)	2·9304 (9)	2·9301 (7)
K–O(4)	[8]	2·9657 (9)	2·9699 (12)	2·9515 (10)
–O(5)	[4]	—	—	2·788 (11)
Ca–O(3)	[2]	2·3929 (11)	2·3919 (13)	2·3881 (11)
–O(3)′	[2]	2·3979 (11)	2·3981 (13)	2·3936 (11)
–O(4)	[2]	2·4854 (12)	2·4969 (15)	2·4941 (14)
–F		2·4221 (11)	2·4187 (13)	2·4134 (12)
–O(5)		—	—	2·338 (10)
Si–O(1)		1·6200 (9)	1·6198 (11)	1·6180 (9)
–O(2)		1·6290 (11)	1·6279 (12)	1·6257 (11)
–O(2)′		1·6320 (11)	1·6338 (12)	1·6322 (11)
–O(3)		1·5875 (10)	1·5871 (13)	1·5910 (10)
O(1)–Si–O(2)		104·90 (5)	104·94 (6)	105·08 (6)
–O(2)′		106·04 (5)	106·06 (6)	106·23 (6)
–O(3)		112·40 (5)	112·51 (6)	112·51 (6)
O(2)–Si–O(2)′		107·85 (6)	107·80 (8)	107·80 (7)
–O(3)		112·71 (6)	112·68 (7)	112·60 (6)
O(2)′–Si–O(3)		112·41 (6)	112·33 (7)	112·14 (6)
O(4)–H(1)		0·9867 (16)	0·9858 (20)	0·9921 (21)
–H(2)		0·9511 (18)	0·9503 (24)	0·9556 (22)
H(1)–O(4)–H(2)		104·01 (16)	104·18 (21)	104·04 (21)
O(5)–H(3)	[2]	—	—	0·962 (16)
H(3)–O(5)–H(3)		—	—	101 (2)
H(1)···O(3)		1·7744 (16)	1·7795 (19)	1·7632 (20)
O(4)···O(3)		2·7602 (11)	2·7642 (13)	2·7544 (12)
O(4)–H(1)···O(3)		176·89 (15)	176·52 (19)	177·03 (21)
H(2)···O(2)		2·2627 (19)	2·2701 (26)	2·2645 (22)
O(4)···O(2)		3·1764 (13)	3·1822 (18)	3·1842 (14)
O(4)–H(2)···O(2)		160·80 (19)	160·60 (26)	161·25 (22)
H(3)···O(3)		—	—	1·820 (15)
O(5)···O(3)		—	—	2·709 (9)
O(5)–H(3)···O(3)		—	—	152 (1)
K–O(4)–Ca		99·41 (4)	99·61 (4)	99·66 (4)
–H(1)		100·44 (10)	100·51 (13)	100·81 (14)
–H(2)		116·03 (15)	116·04 (21)	115·97 (17)
Ca–O(4)–H(1)		121·49 (11)	121·33 (14)	121·15 (15)
–H(2)		115·07 (13)	114·80 (16)	114·90 (14)
K–O(5)–Ca		—	—	108·6 (4)
–H(3)		—	—	104 (1)
Ca–O(5)–H(3)		—	—	119 (1)
Ca–O(4)–H*a*†		140·37 (16)	139·99 (22)	139·78 (19)
K–O(4)–H*a*†		119·94 (16)	120·09 (21)	120·27 (18)
Ca–O(5)–H*b*†		—	—	139 (2)
K–O(5)–H*b*†		—	—	113 (2)
Ca–H(1)		3·1165 (18)	3·1252 (22)	3·1248 (22)
–H(2)		3·0142 (19)	3·0214 (25)	3·0233 (22)
–H(3)		—	—	3·097 (16)
K–H(1)		3·2909 (16)	3·2956 (20)	3·2854 (21)
–H(2)		3·4894 (20)	3·4931 (28)	3·4777 (24)
–H(3)		—	—	3·165 (17)

* Number of symmetry equivalent distances.

† H*a* [H*b*] represents the H(1)–H(2) [H(3)–H(3)] midpoint.

This structure refinement of fluorapophyllite shows some significant differences from hydroxyapophyllite (Rouse, Peacor & Dunn, 1978). The Ca–O(3), Ca–O(3′), and Ca–(F,OH) distances are longer in hydroxyapophyllite [$\Delta = 0{\cdot}010\,(2)$, $0{\cdot}019\,(2)$ and $0{\cdot}011\,(2)$ Å respectively] while the K–O(4) distance is slightly shorter [$\Delta = 0{\cdot}014\,(3)$ Å]. The silicate layers are unchanged. The increased Ca–O(3), Ca–O(3′) and Ca–(F,OH) distances may be explained by a Ca^{2+} to hydroxyl H atom repulsion. The expected Ca···H distance in hydroxyapophyllite is ~2·6 Å, which is very short in combination with a Ca–O–H angle near 90°, compared to Ca···H distances in Ca–water coordinations (Einspahr & Bugg, 1980).

Effects of increased temperature

The effects of increasing the temperature from 295 to 373 K are small, except for a general increase in the temperature factors. Among the significant changes are a widening of the octagonal holes, Fig. 4, and increased Ca^{2+} and K^+ to water oxygen and hydrogen-bonding distances, Table 4.

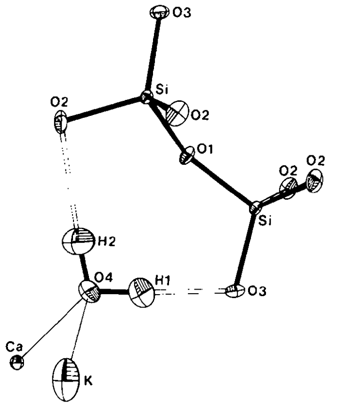
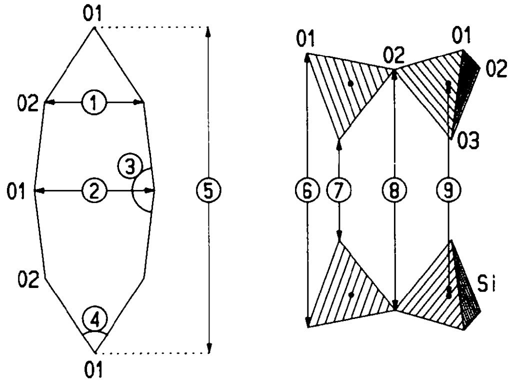


Fig. 3. The water coordination in fluorapophyllite at 295 K. The thermal ellipsoids are scaled to include 50% probability.



No	295 K	373 K	PDFA	
1	3.039(1)	3.056(2)	3.044(1)	[Å]
2	3.457(1)	3.492(2)	3.451(1)	[Å]
3	166.72(4)	166.31(4)	166.81(4)	[°]
4	71.59(3)	71.99(4)	71.68(3)	[°]
5	9.229(2)	9.216(2)	9.223(2)	[Å]
6	7.896(2)	7.900(3)	7.895(2)	[Å]
7	2.909(1)	2.909(2)	2.897(1)	[Å]
8	6.873(2)	6.869(3)	6.851(2)	[Å]
9	5.996(2)	5.996(3)	5.990(2)	[Å]

Fig. 4. A selection of distances and angles within and between the silicate layers in fluorapophyllite and partially dehydrated fluorapophyllite.

Partially dehydrated fluorapophyllite, PDFA

The loss of 0·61 (3) water molecules per formula unit results in a repositioning of the water molecule remaining of a mirror-related pair (Fig. 5). The short H(1)–H(3) distance, 0·670 (15) Å, makes a simultaneous occupancy of the original and new water positions impossible. The new water position with its O atom, O(5), in the mirror plane forms two strong hydrogen bonds compared to one strong and one weak bond in the original position. The coordination to the Ca^{2+} and K^+ ions is retained, but with shorter distances (Fig. 5). The silicate layers are increasingly puckered in PDFA (Fig. 4) and the Ca–O, Ca–F and K–O distances decreased (Table 4). The unaltered space-group symmetry requires the new water position to be distributed over the four equivalent sites about the K^+ ions. The formula for PDFA is probably best written as $KCa_4Si_8O_{20}F.(8-x)H_2O$ ($x = 0-1$), as discussed below.

Dehydration behavior

The thermogravimetric analyses using different heating rates and sample treatments are shown in Fig. 6. The observed differences in curve shape are expected for consecutive reactions, when recorded under non-equilibrium conditions. A 'zero' rate TGA curve [*i.e.* the sample was allowed to reach constant weight after each temperature increase, Cavinato (1927)] will show a one-step behavior using a finely powdered sample, recorded under dry atmospheric conditions, where the equilibrium water pressure is never reached. With increasing heating rate the importance of reaction kinetics and diffusion will increase.

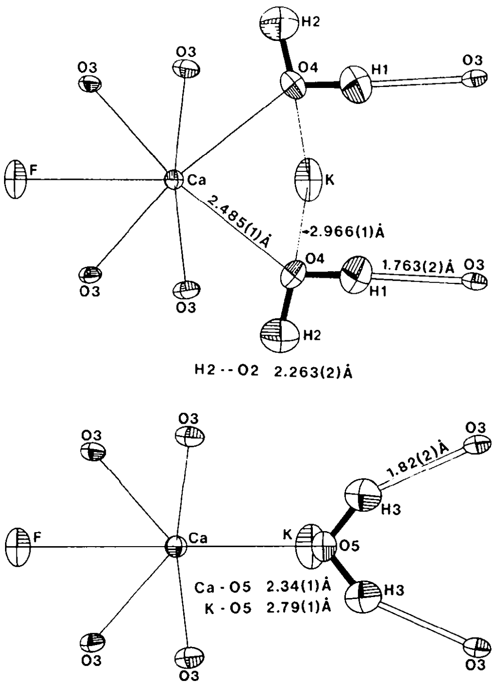


Fig. 5. The Ca coordination in fluorapophyllite at 295 K (top) and showing the new water position in partially dehydrated fluorapophyllite (bottom). The thermal ellipsoids are scaled to include 50% probability.

A simple Monte-Carlo simulation (see deposition footnote) of a plausible dehydration model was performed. Starting from a 100 × 100 sheet of $K(OH_2)_8$ groups the water molecules were randomly removed. It was assumed that the probability of losing a water molecule from a $K(OH_2)_8$ group or from a $K(OH_2)_7$ group was the same. Based on the lack of more than one intermediate step in the dehydration curves it was assumed that the third and fourth water molecules left together with the second in each group. To summarize: the model allows each $K(OH_2)_8$ unit to lose zero, one or four water molecules. $K(OH_2)_8$ units that lost four water molecules were considered 'non-diffracting', *i.e.* not contributing to the single-crystal diffraction intensities, while those that lost zero or one water molecule were considered 'diffracting'. When a certain total water loss was reached, the simulations were interrupted and the water contents in the 'diffracting' units were counted: with a total water loss of 0·5, 1·0, 1·5, 2·0, 3·0 per f.u. the crystallographically observable water contents were 7·70, 7·53, 7·41, 7·32 and 7·20 respectively. The experimentally observed water loss of 1·51 (5) molecules per f.u. resulted in 7·39 (3) crystallographically observable water molecules per f.u.

Based on the above results the dehydration behavior of fluorapophyllite can be described as a three-step reaction:

Step 1: *loss of one water per formula unit.* The formation of PDFA. The effects on the overall structure from this step are only minor, as discussed above,

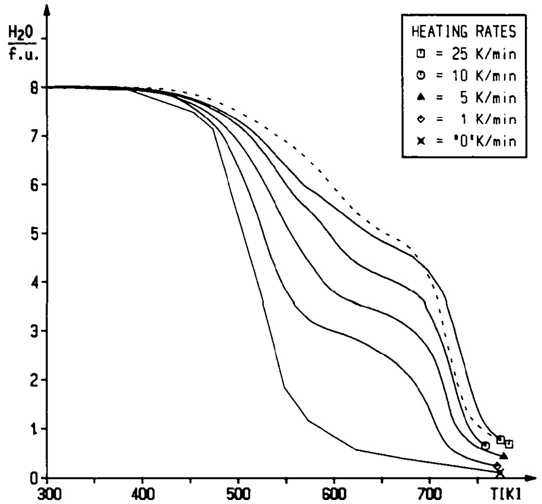


Fig. 6. Thermogravimetric analysis of fluorapophyllite. Broken line: unground sample. Solid lines: ground samples. The '0' rate curve is from Cavinato (1927), assuming 0% weight loss between 300 and 375 K.

and the reaction is apparently rapid. On the TGA curves recorded with the highest heating rates, it is seen as the faster dehydration on the top part of the curves (Fig. 6). Using larger crystal fragments (broken line, Fig. 6) will slow down step 1 because of the growing importance of the diffusion rate.

Step 2: *loss of another three waters per f.u.* During this step, single crystals turned opaque and polycrystalline. A continuation and completion of the step 1 reaction would lead to an unstable square-planar $K(OH_2)_4$ coordination. A tetrahedral water arrangement, using half the original water positions would give either too long K–O distances, or very weakened hydrogen bonds to the silicate layers. To reach a stable K coordination with four waters per f.u., silicate O atoms must be involved. The following mechanism is suggested: as more than one water per f.u. is lost, the K^+ ion tends to move out of the position in the mirror plane towards an O(2) square in the silicate layer above or below. This will trigger the release of two more water molecules per f.u. and finally allow the K^+ ion to take a position between four water O atoms and the O(2) square. The rearranged K coordination will require a change in puckering and spacing of the silicate layers and result in K–O distances of approximately 3·0 Å. An increase in the *a* and a decrease in the *c* axis has been reported (Chao, 1971; Bartl & Pfeifer, 1976). These structural changes explain the breakdown of the single crystals.

Step 3: *loss of the remaining water.* This step leaves an amorphous residue.

A high heating rate experiment performed on hydroxyapophyllite (Larsen, 1981) was interpreted as having an initial step with a 25% water loss and a final step where the rest of the water left. This result may depend on experimental conditions but a difference in the dehydration process between fluorapophyllite and hydroxyapophyllite may not be ruled out until further investigations have been performed.

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Magnesium Bis(hydrogen maleate) Hexahydrate, $[Mg(C_4H_3O_4)_2].6H_2O$, Studied by Elastic Neutron Diffraction and *Ab Initio* Calculations

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Abstract

Magnesium bis(hydrogen maleate) hexahydrate was investigated at room temperature by neutron diffraction, establishing the H positions and H-bonding scheme with great accuracy. The Mg cation at a centre of inversion is surrounded by six water molecules, which are rotated by 9, 28 and 44°, respectively, out of their ideal O_h planes. A slightly asymmetric intramolecular O(3)–H···O(1) bridge is found in the hydrogen maleate ion, together with an asymmetric crystalline environment of the O atoms: O(1) is also

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