

THE REFINEMENT OF THE CRYSTAL STRUCTURE
OF APOPHYLLITE
II. DETERMINATION OF THE HYDROGEN POSITIONS
BY X-RAY DIFFRACTION

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ABSTRACT

The crystal structure of apophyllite has been refined by a least squares method, using three dimensional X-ray diffraction data. The structure determined by Taylor and Náráy-Szabó is essentially correct. The water molecules are found to be hydrogen-bonded to two oxygen atoms in the Si_3O_{20} sheets. The two-stage dehydration in apophyllite is interpreted as the result of the transformation from $\text{KCa}_4\text{Si}_8\text{O}_{20}(\text{F}, \text{OH}) \cdot 8\text{H}_2\text{O}$ to $\text{KCa}_4\text{Si}_8\text{O}_{20} \cdot 4\text{H}_2\text{O}$ at 250°C.

INTRODUCTION

The dehydration behavior of apophyllite, $\text{KCa}_4\text{Si}_8\text{O}_{20}(\text{F}, \text{OH}) \cdot 8\text{H}_2\text{O}$, has long been discussed by mineralogists. Differential thermal and thermal gravimetric analyses of apophyllite always show two stages of dehydration, one at near 330°C and the other near 440°C (Mason and Greenberg, 1953; Koizumi, 1953 and Aumento, 1965), strongly suggesting that the water molecules in apophyllite have two structural environments. This cannot easily be explained on the basis of the structural model determined by Taylor and Náráy-Szabó (1931). A refinement of the structure of apophyllite was therefore carried out.

CRYSTAL DATA

Small euhedral crystals from Mont. St. Hilaire, Quebec, were used in this study. Morphological analysis as well as Weissenberg and precession photographs taken of these crystals indicate no deviation from the previously reported space group $P4/mnc$ (Taylor and Náráy-Szabó, 1931). The cell dimensions derived from single crystal work were refined by a least squares method, using powder diffraction data obtained at 20°C, with metallic Si as an internal standard. The refined values are $a = 8.965$ (3) Å and $c = 15.767$ (7) Å. A small euhedral crystal (0.06 mm) with well developed pinacoid $\{001\}$, prism $\{110\}$, and bipyramids $\{101\}$ and $\{103\}$ (?), thus dimensionally approaching a sphere, was used for collecting the intensity data. A Supper manual single-crystal diffractometer was employed, using $\text{MoK}\alpha$ radiation. A total of 965 symmetry-independent reflections within the limit of $\sin \theta = 0.50$ were considered but only 817 reflections were measurable. Corrections for Lorentz and polarization factors were applied in the usual manner. No attempt was

made to correct the absorption because of the small size of the crystal used.

REFINEMENT OF THE STRUCTURE

The positional parameters of Taylor and Náray-Szabó were used as the starting point. Scattering curves in the *International Tables for X-ray Crystallography* were used. The refinement was carried out using a full-matrix least squares program. The following steps were taken:

- (1) Ten least squares cycles with isotropic thermal parameters for all atoms reduced the residual R from 0.29 to 0.063. Bond lengths and angles were calculated at this stage, and no unreasonable values were found.
- (2) Five least squares cycles of refinement with anisotropic thermal parameters for all atoms further reduced R to 0.053.
- (3) Site-occupancy factors for all atoms were introduced at this stage as least squares variables. At the end of the first least squares cycle it was discovered that the correlation coefficients between the scale factor and the occupancy factors approached 1.0 causing the matrix to become singular. The occupancy factor of O(3) was then deleted and the refinement was resumed without further difficulty. After five cycles of least squares refinement, deleting the occupancy factor of O(2) and O(3) alternately in each cycle, the value of R decreased to 0.048.
- (4) A three-dimensional difference synthesis was computed. Two significant maxima (approximately $0.9 e/\text{\AA}^3$) were found at H(1) (0.45, 0.18, 0.08) and H(2) (0.21, 0.44, 0.15). These were assumed to be due to the hydrogen atoms.
- (5) Five more cycles of least squares refinement with the hydrogen atoms included were carried out. Isotropic thermal parameters were used for the hydrogen atoms H(1) and H(2). At the end of the third cycle, H(1) settled down but the shifts of H(2) were still relatively large. Further refinement resulted in oscillations of the shifts of H(2). The refinement was therefore terminated. The final value of R for these 817 reflections is 0.047; and it is 0.058 if the 148 reflections designated as unobserved are included. The slight improvement in R from 0.048 to 0.047 is significant according to Hamilton's significance test on R (Hamilton, 1965), the R index ratio being 1.021, compared with the significant point 1.015 at the 0.005 level.

The final positional and thermal parameters and the occupancy factors are given in Table 1 and a number of selected bond lengths and angles are listed in Table 2. The low occupancy factor for Na may be due to a substantial replacement of Na by K, and the slightly low occupancy factor for Si may be due to Al substitution.

DISCUSSION

The structure of apophyllite determined by Taylor and Náray-Szabó is essentially correct. The H₂O molecules in the structure are hydrogen-bonded to two oxygen atoms (O(2) and O(3)) in the "puckered" Si₈O₂₀ sheets. The results agree well with those reported by Colville *et al.* (1971) in paper I, and by Prince (1971) in paper III, except that in my determination the hydrogen atom H(2) has large estimated standard deviations for all of its parameters. Moreover, on the final

$$\frac{T}{A} \frac{B}{L} \frac{E}{L} \frac{L}{L}$$

Final atomic fractional coordinates, thermal parameters^a ($10^6 x$) and site occupancy factors.
(E.S.D. in parentheses)

Occupancy Factor	\bar{x}	\bar{y}	\bar{z}	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Si	0.970(10)	0.2256(1)	0.0865(1)	0.1900(1)	2285(97)	2039(97)	959(29)	33(142)	-59(88)
Ca	1.013(10)	0.1094(1)	0.2466(1)	0	2773(98)	3202(101)	976(28)	45(152)	---
K	0.940(15)	0	0	$\frac{1}{2}$	7615(457)	7615(457)	4376(163)	---	---
O(1) ^b	1.013(16)	0.3631(5)	0.1369(5)	$\frac{1}{4}$	3936(435)	3936(435)	1327(120)	-631(626)	-275(512)
O(2)	1.009(13)	0.0846(3)	0.1891(3)	0.2178(2)	3412(268)	4789(283)	1965(91)	1246(458)	-653(271)
O(3)	1.005(15)	0.2636(3)	0.1026(3)	0.0923(2)	5001(288)	4314(274)	1135(76)	55(442)	-582(257)
O(4)	0.955(16)	0.2131(4)	0.4491(4)	0.0898(2)	8905(422)	4494(309)	1449(99)	88(569)	-202(345)
F	0.984(23)	0	0	0	2674(753)	2674(753)	2580(265)	---	---
H(1)	0.955	0.4515(87)	0.1770(86)	0.0775(48)	$B_{\text{isotropic}} = 3.49(1.79)$				
H(2)	0.955	0.2362(144)	0.4706(172)	0.1198(75)	$B_{\text{isotropic}} = 13.54(5.42)$				

^a Thermal parameters are expressed in the form:

$$T = \exp \left\{ - \left(h^2 B_{11} + k^2 B_{22} + l^2 B_{33} + 2hk B_{12} + 2hl B_{13} + 2kl B_{23} \right) \right\}$$

^b Coordinates here, as in Colville, Anderson and Black (1971) and Prince (1971) are $x, \frac{1}{2} + x, \frac{1}{4}$.

T A B L E 2Selected interatomic distances (\AA) and bond angles ($^{\circ}$) in apophyllite

(E.S.D. in parentheses)

SiO_4	Tetrahedron	Ca(O,F)_7	Polyhedron
Si-O(1)	1.618 (4)	Ca-O(3)	2.386 (3) (2X)
Si-O(2)	1.628 (3)		2.398 (3) (2X)
Si-O ¹ (2)	1.623 (3)	Ca-O(4)	2.483 (3) (2X)
Si-O(3)*	1.585 (3)	Ca-F	2.418 (3)
O(1)-O(2)	2.590 (5)		
O(1)-O ¹ (2)	2.576 (5)		
O(1)-O(3)	2.660 (3)	KO_8	Polyhedron
O(2)-O ¹ (2)	2.626 (3)	K-O(4)	2.971 (3) (8X)
O(2)-O(3)	2.663 (3)	O(4)-O(4)	2.837 (4)
O ¹ (2)-O(3)	2.679 (3)		3.694 (5)
O(1)-Si-O(2)	106.1 (2)	H_2O	Molecules
O(1)-Si-O ¹ (2)	105.0 (2)		
O(1)-Si-O(3)	112.3 (2)	H(1)-O(3)	1.827
O(2)-Si-O ¹ (2)	107.7 (2)	H(1)-O(4)	0.968
O(2)-Si-O(3)	112.2 (2)	O(3)-O(4)	2.760 (4)
O ¹ (2)-Si-O(3)	113.0 (2)	O(3)-H(1)-O(4)	161.0
Si-O(1)-Si	140.1 (2)	H(2)-O(2)	2.693
Si-O(2)-Si	140.8 (2)	H(2)-O(4)	0.552
		O(2)-O(4)	3.173
		O(2)-H(2)-O(4)	147.7
*non-bridging		H(1)-H(2)	1.102
		H(1)-O(4)-H(2)	88.6

difference map there is no evidence of H(3) which Prince has found by neutron diffraction. The structure is shown in three projections in Figure 1, 2, and 3. To avoid repetition, the detailed descriptions of the

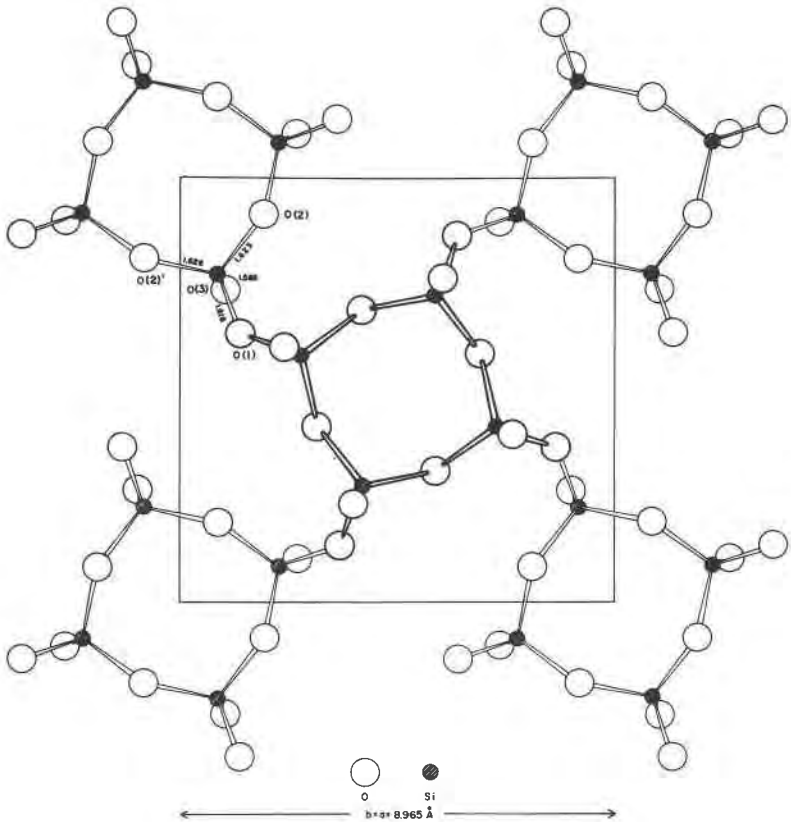


FIG. 1. The Si_8O_{20} sheet in apophyllite projected on (001).

structure that have been given in the other two papers are omitted here, and the discussions are centered on the interpretation of the thermal behavior of apophyllite on the basis of the refined structure.

Differential thermal analyses of apophyllite from Mont. St. Hilaire, Quebec (Fig. 4), heated in air at the rate of $12^\circ\text{C}/\text{min.}$, showed two endothermic peaks at 350° and 468°C . The peak at 350°C is smaller and broader, with an auxiliary hump at 375°C , similar to that described by Aumento (1965). The two main peaks are separated by a saddle at 400°C . Thermal gravimetric analyses, conducted in air at the heating rate of $6^\circ\text{C}/\text{min.}$, showed an 8.0 percent weight loss at 400°C and a further loss of 8.3 percent at between 400° and 1100°C . The major weight loss in the second stage took place between 400° and 500°C .

In his equilibrium-controlled maximum-dehydration experiments on apophyllite, Aumento (1965) noted that the maximum-dehydration

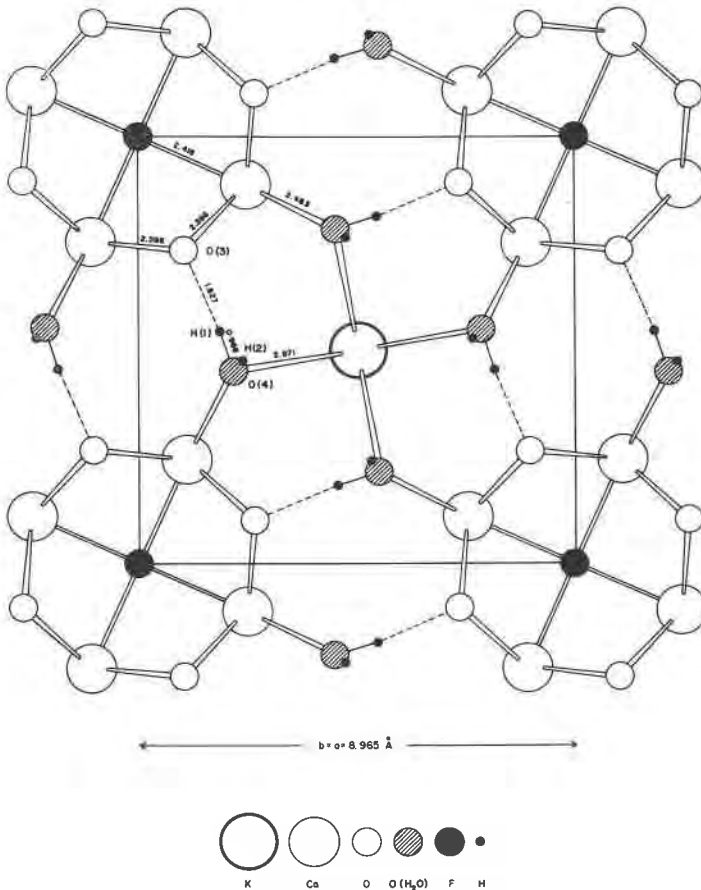


FIG. 2. The K, Ca sheet in apophyllite projected on (001).

curve was similar to the dynamic dehydration curve but was displaced to lower temperatures. He ascertained the two main dehydration temperatures to be 250° and 350°C. X-ray diffraction studies at elevated temperatures (Aumento, 1965) showed a continuous reduction in intensity of reflections with increasing temperature to 360°–370°C, at which the material became amorphous and the pattern completely disappeared. The a parameter increased continuously from 8.994 Å at room temperature to 9.016 Å at 360°C, while c decreased from 15.620 Å at room temperature to a minimum of 15.606 Å at 250°C and then increased to 15.611 Å at 360°C.

The existence of two different structural environments for the water

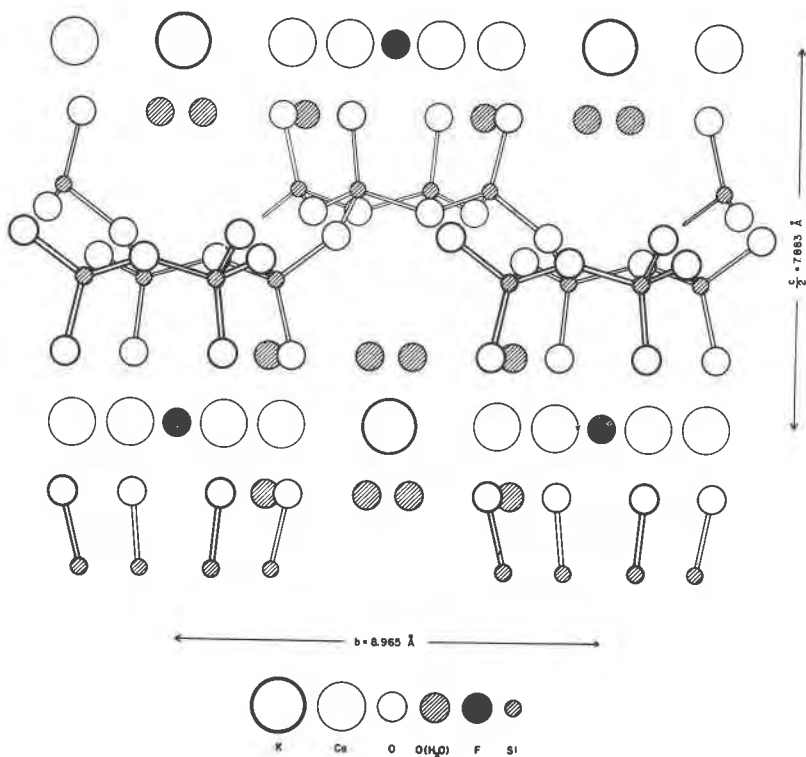


FIG. 3. The structure of apophyllite projected on (100).

molecules in apophyllite would provide an explanation for the two stages of approximately equal weight loss in the DTA and TGA analyses. The refinement of the structure, however, provides no evidence for the existence of two different structural environments. In addition, the amount of F present in apophyllite is not sufficient to account for the weight loss at either stage. It is therefore suggested that, after losing fifty percent of its water at 250°C (or 350°C if heated at faster rates, as in DTA), apophyllite changes to another compound, the structure of which is identical to apophyllite except for the environment of the water molecules. The water molecules are probably ordered on the mirror planes at $z=0$ and $z=\frac{1}{2}$. However, the possibility that the water molecules are statistically distributed over the water sites of apophyllite cannot be ruled out. The composition of this new compound is then $\text{KCa}_4\text{Si}_8\text{O}_{20}(\text{F},\text{OH}) \cdot 4\text{H}_2\text{O}$. The auxiliary peak at 375°C on the DTA curve may be due to the superposition of a small, sharp, exothermic peak at 360°C (Fig. 4) produced by the ordering of the water molecules which were necessarily disordered

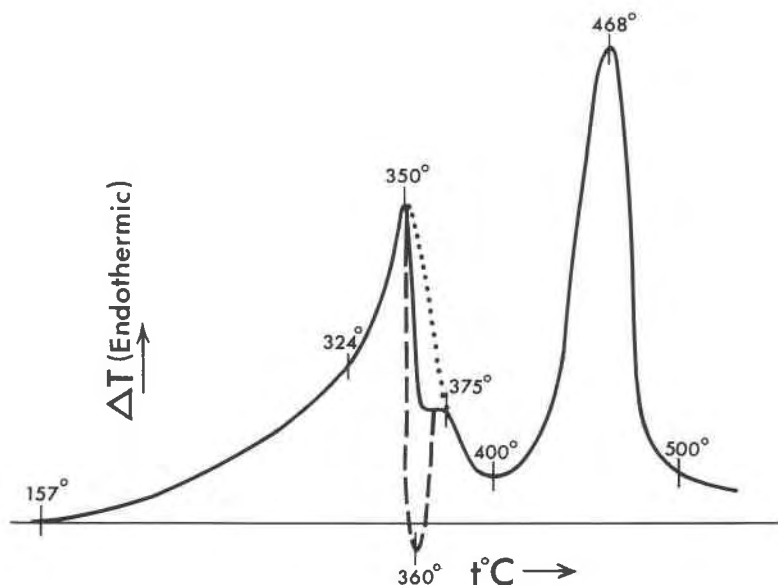


FIG. 4. Differential thermal analysis curve of apophyllite from Mont. St. Hilaire, Quebec. The theoretical curve, in the absence of ordering of H_2O , is represented by the dotted line and the theoretical exothermic peak, due to ordering of H_2O , is represented by the dashed line.

near the end of the first stage of dehydration. A structure determination of the partially dehydrated apophyllite is planned and it is hoped that it will clarify the problem.

On further heating, the newly formed compound loses all of its water between 360° and 370°C . At this point the structure collapses completely and F is evolved, possibly to combine with H_2O to form HF. Thus the HF detected in the analysis of the gas evolved in the dehydration of apophyllite (G. Donnay, personal communication, 1970) may be accounted for.

The variation of the cell parameters of apophyllite with heating may also be explained on this hypothesis. The "puckering" of the Si_3O_{20} sheets (Fig. 3) is in part to accommodate the water molecules. When some of the water molecules are removed on dehydration, the extent of "puckering" will decrease, resulting in a reduction of the c parameter, and at the same time the sheets must expand laterally causing the a parameter to increase. At 250°C (the first stage maximum-dehydration temperature) the c parameter is reduced to the minimum when the remaining water molecules are ordered on the mirror planes in the new compound. On further heating c increases, mainly due to thermal expansion.

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