

REFINEMENT OF THE CRYSTAL STRUCTURE
OF APOPHYLLITE
III. DETERMINATION OF THE HYDROGEN POSITIONS
BY NEUTRON DIFFRACTION

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ABSTRACT

The crystal structure of apophyllite, a mineral with the ideal formula $\text{KCa}_4(\text{Si}_4\text{O}_{10})_2\text{F} \cdot 8\text{H}_2\text{O}$, has been refined using three-dimensional neutron diffraction data. 671 independent reflections were observed on a 4-circle diffractometer. Of these 516 had observable intensities. A least-squares refinement, with anisotropic temperature factors, led to an R index of 0.046. However, a difference Fourier synthesis revealed a region of negative scattering density in the vicinity of the fluorine atom. Accordingly a further refinement was carried out assuming a model in which 1/8 of the water molecules are replaced by OH^- ions, with the remaining proton bonded to fluorine to form an HF molecule. This model refined quickly to an R value of 0.037. The water molecules and OH ions are hydrogen bonded to the silicate framework. A preliminary mass spectrometric analysis of the gases evolved when apophyllite is heated revealed that the higher temperature specific-heat anomaly is due to the evolution of hydrogen fluoride. This suggests that the structural formula is $\text{KCa}_4(\text{Si}_4\text{O}_{10})_2\text{F}_{1-x}(\text{HF})_x \cdot [(\text{H}_2\text{O})_{8-x}(\text{OH})_x]$ with $x \approx 1$.

INTRODUCTION

Apophyllite, $\text{KCa}_4(\text{Si}_4\text{O}_{10})_2\text{F} \cdot 8\text{H}_2\text{O}$, is a silicate mineral with an unusual sheet structure. The heavy-atom portion of the structure was determined originally by Taylor and Náráy-Szabo (1931), and has recently been refined by Colville, Anderson, and Black (1971, hereinafter referred to as I). An attempt by the latter authors to determine the positions of the hydrogen atoms from the X-ray diffraction data was unsuccessful. However, using valence-summation techniques recently developed by Donnay and Allmann (1970), Donnay (priv. comm.) proposed that one of the hydrogen atoms should be involved in a hydrogen bond between the oxygen atom in the water molecule and an oxygen atom at an unshared vertex of an SiO_4 tetrahedron. The position of the other proton was less clearly defined. She proposed that it should be equally distant from another unshared oxygen atom and an oxygen atom which is shared by two SiO_4 tetrahedra, forming a bifurcated hydrogen bond. This paper describes the results of a neutron diffraction investigation undertaken to locate the hydrogen positions directly and provide experimental verification of the valence-summation technique. It was hoped, further, that an explanation would be found for the fact that gas is evolved in two distinct stages as the mineral is heated.

EXPERIMENTAL

The apophyllite structure is tetragonal, belonging to space group $P4/mnc$ (Taylor and Naray-Szabo, 1931). The approximate lattice constants, $a=8.96$, $c=15.80$ , proved to be sufficiently accurate for computation of diffractometer settings. A crystal with pseudo cubic shape and a volume of approximately 12 cm^3 was chosen from a hand-specimen of apophyllite from Centerville, Va. (kindly furnished by A. A. Colville). It was mounted on a full-circle goniometer with $[001]$ approximately perpendicular to the ϕ axis and $[110]$ making a small angle with the ϕ axis. The diffractometer was set for a neutron wavelength of 1.23  and a maximum 2θ angle of 100° .

A total of 671 independent reflections lie within the limiting sphere specified by the wavelength and the maximum 2θ angle. The automatic diffractometer (Alperin and Prince, 1970) examined all these reflections, and found statistically significant intensity for 516 of them. All reflections except those of the forms $\{hhl\}$ were measured in at least two symmetrically equivalent positions. A detailed comparison of equivalent reflections was not attempted, but a spot check revealed that the vast majority of the structure factors, F , of equivalent reflections lay either within the range expected from counting statistics or within 3 percent of one another, whichever was greater, and none differed by more than 10 percent. There is thus no indication that the assignment of the structure to Laue group $4/mmm$ is incorrect. The reflections were therefore merged into a unique set based on this Laue group.

Because the effective absorption coefficient, actually due almost entirely to incoherent scattering by hydrogen, was small ($\mu r \approx 0.5$) and the shape of the crystal was fairly regular, no absorption corrections were made. Unobservable reflections were assigned magnitudes based on the assumption that the peak intensity was equal to twice the standard deviation of the difference between the measured intensity at the peak position and at background positions on either side.

REFINEMENT OF THE STRUCTURE

The parameters (Col. 3, Table 1) found in the X-ray study for the non-hydrogen atoms were used in the calculation of a three-dimensional Fourier synthesis with the observed F_s . The crystal was assumed to have the ideal formula $\text{KCa}_4(\text{Si}_4\text{O}_{10})_2\text{F}\cdot 8\text{H}_2\text{O}$. However, the neutron scattering factors for potassium and sodium are virtually identical, so that some substitution of potassium by sodium would not affect the results reported here. The Fourier map contained regions of substantial positive density in the positions of the heavy atoms, and regions of significant negative density in positions that, taken together with the position of the oxygen atom $\text{O}(4)$, represented a reasonable configuration for a water molecule. The approximate coordinates of these regions were therefore assigned to two hydrogen atoms, and the resulting parameters used for a least squares refinement with isotropic temperature factors.

In all stages of least-squares refinement a weighting scheme was used which assigned unit weight to all observed reflections whose F values were less than $0.4 F_{\text{max}}$. To allow for possible extinction effects, weights for stronger reflections were calculated from the formula $w = 0.4 F_{\text{max}}/F_0$.

TABLE 1. ATOMIC COORDINATES IN APOPHYLLITE, FOR SEVERAL STAGES OF REFINEMENT BY X-RAY AND NEUTRON DIFFRACTION. IN THIS TABLE, AND IN TABLE 3, THE NUMBERS IN PARENTHESES INDICATE STANDARD DEVIATIONS IN THE LAST QUOTED SIGNIFICANT FIGURE, AS COMPUTED BY THE LEAST-SQUARES PROGRAM

Atom	Parameter	X-ray	Neutron isotropic	Neutron anis. H ₂ O	Neutron anis. HF
F	<i>x, y, z</i>	0, 0, 0	0, 0, 0	0, 0, 0	0, 0, 0
K	<i>x, y, z</i>	0, 0, $\frac{1}{2}$	0, 0, $\frac{1}{2}$	0, 0, $\frac{1}{2}$	0, 0, $\frac{1}{2}$
Ca	<i>x</i>	.1102 (2)	.1114 (5)	.1109 (3)	.1110 (3)
	<i>y</i>	.2460 (2)	.2467 (6)	.2474 (3)	.2473 (3)
	<i>z</i>	0	0	0	0
Si	<i>x</i>	.2258 (2)	.2271 (5)	.2268 (2)	.2267 (2)
	<i>y</i>	.0864 (2)	.0864 (5)	.0865 (2)	.0866 (2)
	<i>z</i>	.1900 (1)	.1898 (2)	.1896 (1)	.1896 (1)
O(1)	<i>x</i>	.3635 (6)	.3639 (7)	.3636 (4)	.3636 (3)
	<i>y</i>	.1365 (6)	.1361 (7)	.1364 (4)	.1364 (3)
	<i>z</i>	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$
O(2)	<i>x</i>	.0845 (4)	.0847 (4)	.0845 (2)	.0846 (2)
	<i>y</i>	.1897 (4)	.1905 (4)	.1899 (2)	.1897 (2)
	<i>z</i>	.2178 (2)	.2168 (2)	.2167 (1)	.2169 (1)
O(3)	<i>x</i>	.2640 (4)	.2655 (4)	.2656 (2)	.2657 (2)
	<i>y</i>	.1023 (4)	.1021 (4)	.1019 (2)	.1018 (2)
	<i>z</i>	.0923 (3)	.0921 (2)	.0923 (1)	.0924 (1)
O(4)	<i>x</i>	.2132 (5)	.2145 (4)	.2155 (2)	.2154 (2)
	<i>y</i>	.4501 (5)	.4498 (4)	.4498 (2)	.4500 (2)
	<i>z</i>	.0901 (3)	.0903 (3)	.0895 (1)	.0893 (1)
H(1)	<i>x</i>	—	.4496 (7)	.4488 (4)	.4490 (4)
	<i>y</i>	—	.1734 (8)	.1728 (4)	.1730 (4)
	<i>z</i>	—	.0889 (4)	.0889 (2)	.0889 (2)
H(2)	<i>x</i>	—	.2251 (9)	.2246 (6)	.2244 (5)
	<i>y</i>	—	.4267 (9)	.4255 (5)	.4255 (4)
	<i>z</i>	—	.1471 (5)	.1477 (3)	.1481 (2)
H(3)	<i>x, y</i>	—	—	—	0, 0
	<i>z</i>	—	—	—	.0651 (12)

However, there is no indication in the data (see Table 2) that any reflections has been significantly affected by extinction, and therefore no extinction corrections have been made. Furthermore, because there is no reason to give less weight to the strong reflections, the *R* index is given as $\Sigma|F_0 - F_c| / \Sigma|F_0|$. Unobserved reflections were assigned zero weight if $F_c < F_0$ and unit weight if $F_c > F_0$. The *R* index dropped, in 3 cycles of isotropic least-squares refinement, to 0.076. The parameters are listed in column 4 of Table 1. The *R* index dropped, after 4 cycles of refinement with anisotropic temperature factors, to 0.046. The parameters given

by this refinement are listed in column 5 of Table 1. The maximum shift in the final cycle was .06 of the standard deviation. The R index ratio (Hamilton, 1965) for refinements with isotropic and anisotropic temperature factors is 1.55, compared with a required ratio of only 1.056 for results of the refinement to be significant at the .005 level.

An (F_o-F_c) difference synthesis using these parameters revealed one very significant feature, a region of negative density lying on the 4-fold axis 1.0 Å distant from the fluorine position. In order to account for this feature a model was assumed in which the hydrogen H(2) was removed from 1/8 of the water molecules, at random, leaving an OH⁻ ion. One half of a hydrogen atom, H(3), was then placed in a position along the c axis 1 Å away from the fluorine position. Because the fluorine occupies a center of symmetry (in the assigned space group), the model assumes that HF molecules are disordered, with half of them pointing up along the c axis and half pointing down. This model quickly refined to an R index of .037. The maximum shift in the last cycle was .07 standard deviation. The R index ratio 1.24 may be compared with 1.011 necessary for significance at the .005 level. Table 2 is a list of observed and calculated structure factors for this model.¹ Table 3 lists the final parameters, and the position parameters are also summarized in column 6 of Table 1. The final difference Fourier map contained no peaks greater than 0.1 of the amplitude of an atom with the minimum scattering amplitude. The largest off-diagonal element of the correlation matrix, the element relating B_{33} of F and B_{33} of H(3), was 0.6872, and four others had magnitudes greater than 0.4.

DISCUSSION

Figure 1 is a stereo pair giving a general view of the apophyllite structure, looking down the c axis. The portion of the structure shown includes one half of the unit cell in the c direction. The infinite sheet of SiO₄ tetrahedra is clearly visible.

Figure 2 is a stereo pair showing the water molecule and its environment H(1) clearly forms a strong hydrogen bond between O(3) and O(4), as predicted. The O(4)-H(2) bond points toward O(2), with an O(4)-H(2)-O(2) bond angle of 161°. Hamilton and Ibers (1968) suggest that an $A-H-B$ linkage can be considered a hydrogen bond if the distance H-B is less than the distance determined by subtracting 0.2 Å from the sum of the van der Waals radii. If the B atom is oxygen, this distance is

¹ To obtain a copy of Table 2, order NAPS Document No. 01482 from National Auxiliary Publications Service of the A.S.I.S., c/o CCM Information Corporation, 909 Third Avenue, New York, New York 10022; remitting \$2.00 for microfiche or \$5.40 for photocopies, in advance payable to CCMIC-NAPS.

Table 3. Final atomic coordinates and anisotropic temperature factors for apophyllite. Temperature factors are given as the coefficients of the form

$$\exp \left[-\left(\frac{1}{4} \right) \left(h^2 a^*{}^2 B_{11} + k^2 b^*{}^2 B_{22} + \frac{c^*{}^2}{2} B_{33} + 2hka^*{}^* B_{12} + 2hla^*{}^* B_{13} + 2klb^*{}^* B_{23} \right) \right].$$

Atom	\bar{x}	\bar{y}	\bar{z}	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
F	0	0	0	0.56(2)	0.56(2)	1.61(2)	0	0	0
K	0	0	1/2	1.4(2)	1.4(2)	3.8(4)	0	0	0
Ca	.1110(3)	.2473(3)	0	0.83(9)	0.79(9)	0.79(8)	-.08(6)	0	0
Si	.2267(2)	.0866(2)	.1896(1)	0.42(6)	0.57(6)	0.66(6)	-.02(6)	-.02(5)	.06(6)
O(1)	.3636(3)	.1364(3)	1/4	0.64(5)	0.64(5)	0.85(6)	-.02(5)	-.20(4)	-.20(4)
O(2)	.0846(2)	.1897(2)	.2169(1)	0.59(5)	1.07(5)	1.38(5)	.34(4)	-.11(7)	-.26(4)
O(3)	.2657(2)	.1018(2)	.0924(1)	1.09(5)	1.05(5)	0.43(5)	-.01(4)	-.03(4)	-.02(4)
O(4)	.2154(2)	.4500(2)	.0893(1)	2.45(7)	1.13(7)	1.47(8)	-.06(5)	.11(6)	-.29(5)
H(1)	.4490(4)	.1730(4)	.0889(2)	2.0(1)	2.6(1)	2.6(1)	-.1(1)	.36(9)	-.06(9)
H(2)	.2244(5)	.4255(4)	.1481(2)	5.0(2)	2.6(1)	1.3(1)	0.0(1)	-.5(1)	.1(1)
H(3)	0	0	.065(1)	7.1(8)	7.1(8)	2.8(8)	0	0	0

* Units are Å².

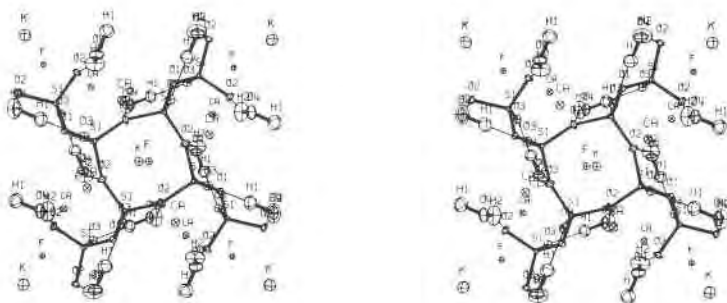


FIG. 1. Stereo pair showing the apophyllite structure. Water molecules are bonded to infinite, two-dimensional sheets of SiO_4 tetrahedra. The hydrogen atom attached to fluorine has been omitted.

about 2.4 \AA , so $\text{O}(4)\text{-H}(2)\text{-O}(2)$ can be considered a weak hydrogen bond. The distance from $\text{H}(2)$ to the other $\text{O}(3)$ in the left of the figure is much too long (3.05 \AA) for there to be any suggestion of a bifurcated hydrogen bond. The $\text{H}(1)\text{-O}(4)$ distance is longer than the $\text{H}(2)\text{-O}(4)$ distance, which is consistent with the fact that $\text{H}(1)$ is involved in a stronger hydrogen bond.

The uncorrected H-F bond distance in the HF group is 1.03 \AA , which is much longer than the value, 0.91 \AA , found by infrared techniques in hydrogen fluoride gas (Hertzberg, 1950). The $\text{H}(3)\text{-O}(3)$ distance is 2.58 \AA , which is too long for a hydrogen bond. Correction of the H-F distance for thermal motion would make it even longer. This may be due to one or both of two factors. First, the fluorine atom is coordinated to four calcium atoms as well as to the hydrogen atom. Therefore the H-F bond may be considerably weaker than it is in the gas. Second, the ellipsoid of motion of the fluorine atom is markedly prolate along the c

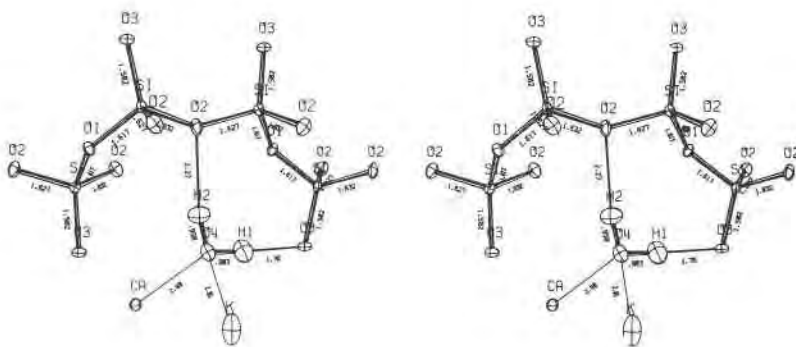


FIG. 2. Stereo pair showing the environment of the water molecule in apophyllite.

axis direction, suggesting the possibility that the position may not be actually at the center of symmetry, but that the fluorines may also be disordered, and displaced toward their associated hydrogen atoms. An attempt was made to refine the structure further by placing one half of a fluorine atom in position $0, 0, z$. The R index went no lower, and the correlation coefficient between the z parameters and B_{33} was -0.9885 , so that the model cannot be justified by the data. However, the bond distance becomes shorter (The uncorrected distance is 0.895 \AA , and the distance, corrected for thermal vibration by the riding model is 0.983 \AA . The standard deviation of this distance is about 0.09 \AA , so that both values are within range of the gas phase value.) and the vibration ellipsoid becomes nearly spherical. Thus the model is plausible, and is consistent with the data.

The valence summation used to predict the proton positions assumes that fluorine is present as the F^- ion, and that it participates in the calcium coordination polyhedron. However, if fluorine is bonded to hydrogen in HF molecules, the calcium fluorine interaction is weakened, and the proper valence summation around the calcium ion is quite uncertain. A limiting case can be represented by ignoring the Ca-F interaction, and making the coordination number for calcium six rather than seven. A revised set of computations based on this assumption has been performed by Donnay (priv. comm.) with the results shown in Table 4. Since the proton positions are known, hydrogen is included as a cation, and its valence contributions have been estimated using the Donnay and Allmann formula for the long bond valence, v , and taking the short bond valence, v_s , equal to $1-v$. This procedure gives slightly too much charge to O(3), and not quite enough to O(4), but the agreement is remarkably good. If a large number of similar structures were known, it might be possible to construct an empirical relation connecting the bond valences with the O-H distances.

Colville, Anderson, and Black (I) have presented differential thermal analysis and thermogravimetric analysis data which confirm that, as apophyllite is heated, there is decomposition in two distinct stages. If all of the hydrogen is present in water molecules, this result cannot be explained, because all water molecules are crystallographically equivalent, and therefore will require the same amount of energy to break away from the silicate framework. However, if one of the decomposition products is hydrogen fluoride, the DTA and TGA results can be explained. This hypothesis is supported by preliminary results of a mass spectrometric analysis of the evolved gas at various temperatures (Hoering and Donnay, priv. comm.). At 325°C there is copious evolution of water molecules. If the sample is held at this temperature long enough, all of

Table 4. Bond lengths and estimated bond valences in apophyllite. In each case the bond length, in Å, is above the estimated valence. Roman numbers attached to element symbols indicate coordination numbers.

Cations Anions	K ^{viii}	Ca ^{vi}	Si ^{iv}	H(1) ⁱⁱ	H(2) ⁱⁱ	H(3) ⁱ	Σv
0(1) ⁱⁱ 8(g)	2(b)	8(h)	16(i)	16(i)	.875 x 16(i)	.5 x 4 (e)	1.99
0(2) ⁱⁱⁱ 16(i)			1.617Å 0.996 v.u. 1.633Å 0.965 v.u. 1.627Å 0.977 v.u.		2.269Å 0.055 v.u.		1.99
0(3) ^{iv} 16(i)			1.582Å 1.067 v.u.	1.762Å 0.301 v.u.			2.06
0(4) ^{iv} 16(i)		2.398Å 0.347 v.u. 2.408Å 0.342 v.u.	0.983Å 0.699 v.u.	0.983Å 0.699 v.u.	0.958Å 0.945 v.u.	1.036Å 1.00 v.u.	1.96
F ⁱ 2(a)		2.429Å					1.00
I(Å)	2.950	2.430	1.615	1.372 ₅	1.613 ₅	1.036	
$\Sigma_A v(v.u.)$	1.000	2.000	4.005	1.000	1.000	1.000	

the water is driven off, and the peak on the mass spectrograph disappears. As the temperature is raised further, the mass spectrum of HF appears with a peak height which increases as the temperature increases. Unfortunately, the apparatus on which these measurements were performed is not capable of maintaining temperatures substantially above 350°C for any extended period of time.

In view of the evidence for the presence of hydrogen fluoride in the structure, the structural formula should be written $\text{KCa}_4(\text{Si}_4\text{O}_{10})_2\text{F}_{1-x}(\text{HF})_x \cdot [\text{H}_2\text{O}]_{8-x}(\text{OH})_x$, with $x \approx 1$.

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REFERENCES

- ALPERIN, H. A., AND E. PRINCE (1971) A time-shared computer system for diffractometer control. *J. Res., Nat. Bur. Stand., Sec. C.*, (in press).
- COLVILLE, A. A., C. P. ANDERSON, AND P. BLACK (1971) Refinement of the crystal structure of apophyllite. I. X-ray diffraction and physical properties. *Amer. Mineral.* **56**, 1220-1231.
- DONNAY G., AND R. ALLMANN (1970) How to recognize O^{2-} , OH^- , and H_2O in crystal structures determined by X-rays, *Amer. Mineral.* **55**, 299.
- HAMILTON, W. C. (1965) Significance tests on the crystallographic R factor. *Acta Crystallogr.* **18**, 502-510.
- AND J. A. IBERS (1968) *Hydrogen Bonding in Solids*. W. A. Benjamin, Inc., New York.
- HERTZBERG, G. (1950) *Spectra of Diatomic Molecules*. D. Van Nostrand Co., Inc., Princeton, N. J.
- TAYLOR, W. H., AND ST. NÁRÁY-SZABO (1931) The structure of apophyllite, *Z. Kristallogr.* **77**, 146-158.

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