

A neutron powder diffraction study of partially dehydrated fluorapophyllite, $\text{KCa}_4\text{Si}_8\text{O}_{20}\text{F} \cdot 6.9\text{H}_2\text{O}$

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Abstract: Fluorapophyllite, $\text{KCa}_4\text{Si}_8\text{O}_{20}\text{F} \cdot n\text{H}_2\text{O}$, $n(\text{H}_2\text{O}) = 8$, was dehydrated at 473 K to an average of $n(\text{H}_2\text{O}) = 4$. Rietveld analysis of neutron powder diffraction data from the partially dehydrated sample showed no evidence of a crystalline hemi-dehydrated form of fluorapophyllite. The dehydration process is described as a two step reaction. The first step leads to $n(\text{H}_2\text{O}) \approx 7$. One water out of eight in the original K coordination sphere is expelled, the remaining water of a mirror related pair assumes a new position in the mirror plane. In the second step, continued dehydration then destabilizes the K and Ca coordinations, which connect the silicate layers, and a non-diffracting amorphous phase is formed. The sample under study is thus a mixture of the crystalline form with $n(\text{H}_2\text{O}) \approx 7$ and the amorphous form. The frequently observed step-wise dehydration behaviour is explained as a kinetic (diffusion controlled) effect. Partially dehydrated fluorapophyllite, $n(\text{H}_2\text{O}) = 6.9(1)$, is tetragonal, space group $P4/mnc$, $Z = 2$, with unit cell constants of $a = 8.9639(9)$ and $c = 15.754(2)$ Å at 295 K. With the exception of the water content, the crystal structure is not significantly different from that found by Ståhl *et al.* (1987).

Key-words: fluorapophyllite, dehydration, neutron powder diffraction.

Introduction

The dehydration process of apophyllite has been under debate since the discovery of the mineral and its first classification as a zeolite in the late eighteenth century. The structure determination by Taylor & Naray-Szabo (1931) conclusively settled the general features of the crystal structure. Apophyllite, $\text{KCa}_4\text{Si}_8\text{O}_{20}(\text{F},\text{OH}) \cdot 8\text{H}_2\text{O}$, is a layer silicate, where silicate tetrahedra connect to form squares and compressed octagons. The silicate layers are connected through Ca-coordination of silicate oxygens from adjacent layers, and through K-coordination of water also coordinated by Ca and hydrogen bonded to silicate oxygens. Apophyllite is a solid solution with respect to the (F,OH) content; designated fluorapophyllite when $\text{F} > (\text{OH})$, hydroxyapophyllite when $(\text{OH}) > \text{F}$, and apophyllite when (F,OH) is undetermined (Rouse *et al.*, 1978). Based on the step-wise dehydration behaviour at constant heating rate, the existence of a hemi-dehydrated form has been suggested (Chao, 1971; Bartl &

Pfeifer, 1976; Ståhl *et al.*, 1987). However, the nature of the dehydration process has been disputed since Cavinato (1927) found a smooth dehydration curve when the sample was allowed to equilibrate between heating steps (*cf.* Fig. 1). In a study of partially dehydrated single crystals using neutron diffraction, Ståhl *et al.* (1987) found an intermediate form with $n(\text{H}_2\text{O}) \approx 7$ and a new water site. On further dehydration the single crystals were destroyed. The present investigation, by means of neutron powder diffraction, of a sample dehydrated to an average of $n(\text{H}_2\text{O}) = 4$ was conducted in an attempt to finally clarify the dehydration process in fluorapophyllite.

Experiments

Natural fluorapophyllite from Poona, India, was ground, sieved and then heated to 473 K for approximately one hour to reach an average water content of 4.0 H_2O per formula unit. The dehydrated sample was immediately packed and

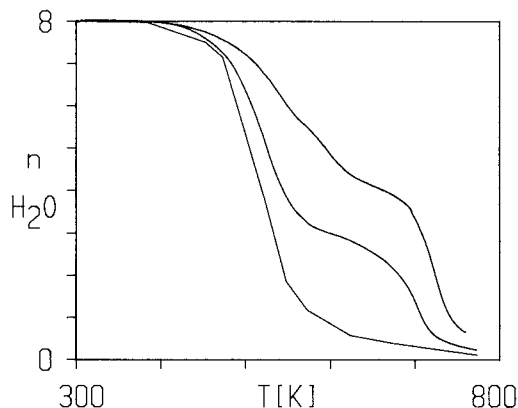


Fig. 1. Thermogravimetric analysis of the dehydration process of fluorapophyllite. From top to bottom: constant heating rate of 10 K/min (Ståhl *et al.*, 1987), constant heating rate of 1 K/min (Ståhl *et al.*, 1987), stepwise heating with equilibration between steps (Cavinato, 1927).

sealed in the vanadium sample holder of 11 mm diameter and 40 mm height used for the data collection. The powder diffraction spectrum was collected at the Neutron Research Laboratory, Studsvik, Sweden, with $\lambda = 1.470(1)$ Å (calibrated with an Al_2O_3 standard), at 295 K, in the range $6.52^\circ < 2\theta < 112.92^\circ$ in 1312 steps; each step was measured for approximately 2 min (monitor controlled) with an array of 10 detectors.

Refinements

The Rietveld analysis program employed in this study is essentially the LHMP1 program described by Hill & Howard (1986) modified to fit the local I/O formats and to include Chebyshev polynomials for background fitting. The program minimizes the quantity $\sum w_i(Y_{io} - Y_{ic})^2$ with $w_i = 1/Y_{io}$. The data were corrected for absorption with a calculated absorption coefficient of 0.29 cm^{-1} . The refinements were started with parameters from Ståhl *et al.* (1987). A total of 16 profile and global parameters were refined: three halfwidth $[U + V \cdot \tan\theta + W \cdot \tan^2\theta]^{1/2}$, truncated at five halfwidths), two peak shape (pseudo-Voigt, with Lorentzian component, $\gamma = \gamma_1 + \gamma_2 \cdot 2\theta$), one asymmetry (for $2\theta < 42^\circ$), one preferred orientation (001), 2 zero point and eight background (Chebyshev type I, order 0 to 7) param-

eters. The 21 structural parameters comprised two unit cell parameters, one over-all scale factor, fractional coordinates of all non-H atoms and occupancy factors for the water molecules. The hydrogen coordinates were coupled to the corresponding oxygen atoms except for $z[\text{H}(3)]$, which was refined independently. Independent refinements of the hydrogen positions did not improve the overall fit, but caused severe correlation between water atom parameters. Anisotropic temperature factor coefficients were taken from Ståhl *et al.* (1987) and kept constant during the refinements. The refinements were considered converged when the maximum shift/e.s.d. was less than 0.2, resulting in $R_p = 0.0148$, $R_{wp} = 0.0188$, $\text{GOF} = 1.18$ and $R_{I,\text{Bragg}} = 0.0057$, $R_{F,\text{Bragg}} = 0.0027$ (from 510 reflections). Neutron scattering lengths were taken from Koester *et al.* (1981) except for Ca, where the value from Ståhl *et al.* (1987), $b = 4.65 \text{ fm}$, was used. The observed and calculated powder diffraction pattern and the final difference pattern is shown in Fig. 2. The refined structural parameters are given in Table 1. Complete lists of refined profile parameters, observed step intensities and derived Bragg intensities may be obtained from the author (or through the E.J.M. Editorial Office - Paris, France).

Discussion

In the present study, where the sample was dehydrated to an average of $n(\text{H}_2\text{O}) = 4$, the crystalline part of the sample still contains $6.9(1)$

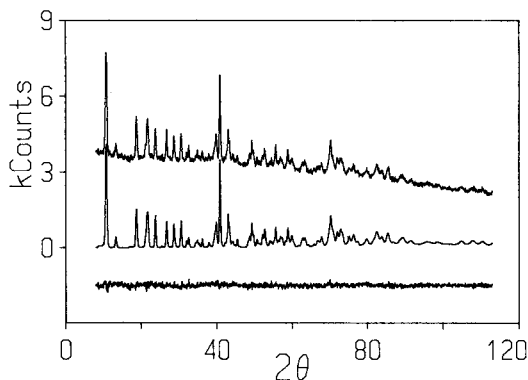


Fig. 2. Observed, calculated (background subtracted) and final difference powder diffraction pattern for partially dehydrated fluorapophyllite.

Table 1. Final fractional coordinates ($\times 10^4$) and occupancy factors (g) for partially dehydrated fluorapophyllite, $\text{KCa}_4\text{Si}_8\text{O}_{20}\text{F}\cdot n\text{H}_2\text{O}$, $n = 6.9(1)$, space group $P4/mnc$, $Z = 2$, $a = 8.9639(9)$, $c = 15.754(2)$ Å.

	x	y	z	g
F	0	0	0	0.125
K	0	0	5000	0.125
Ca	1150(18)	2402(15)	0	0.500
Si	2317(14)	873(15)	1917(5)	1.000
O(1)	3624(10)	1376	2500	0.500
O(2)	894(12)	1915(9)	2159(4)	1.000
O(3)	2663(9)	1021(10)	923(5)	1.000
O(4)	2132(15)	4489(14)	903(6)	0.69(1)
H(1)	4465	1722	894	0.69
H(2)	2209	4257	1492	0.69
O(5)	1848(44)	4878(35)	0	0.17(1)
H(3)	1574	5505	366(22)	0.34

water molecules per formula unit. The refined crystal structure is not significantly different from that found by Ståhl *et al.* (1987), except that

these authors determined a higher water content, $n(\text{H}_2\text{O}) = 7.39(3)$. A selection of bond distances and angles is given in Table 2. The exceptionally

Table 2. Bond distances (Å) and angles ($^\circ$) in partially dehydrated fluorapophyllite.

F-Ca (*4)	2.39(1)	O(4)-H(1)	1.01
-O(3) (*8)	2.94(1)	-H(2)	0.95
		H(1)-O(4)-H(2)	104
K-O(4) (*8)	2.97(1)		
-O(5) (*4)	2.83(4)	O(5)-H(3) (*2)	0.84
		H(3)-O(5)-H(3)	86
Ca-O(3) (*2)	2.34(1)		
-O(3)' (*2)	2.44(2)	H(1)--O(3)	1.73(2)
-O(4) (*2)	2.51(2)	O(4)--O(3)	2.74(2)
-O(5)	2.31(3)	O(4)-H(1)--O(3)	178
Si-O(1)	1.56(1)	H(2)--O(2)	2.27(1)
-O(2)	1.63(2)	O(4)--O(2)	3.19(1)
-O(2)'	1.67(2)	O(4)-H(2)--O(2)	162
-O(3)	1.60(1)		
		H(3)--O(3)	1.93(3)
O(1)-Si-O(2)	106.6(8)	O(5)--O(3)	2.74(3)
-O(2)'	107.6(7)	O(5)-H(3)--O(3)	163
-O(3)	114.0(8)		
O(2)-Si-O(2)'	108.8(9)		
-O(3)	109.5(8)		
O(3)-Si-O(2)'	110.1(8)		

Estimated standard deviations have been omitted for distances and angles involving both water oxygens and hydrogens as they were not independently refined.

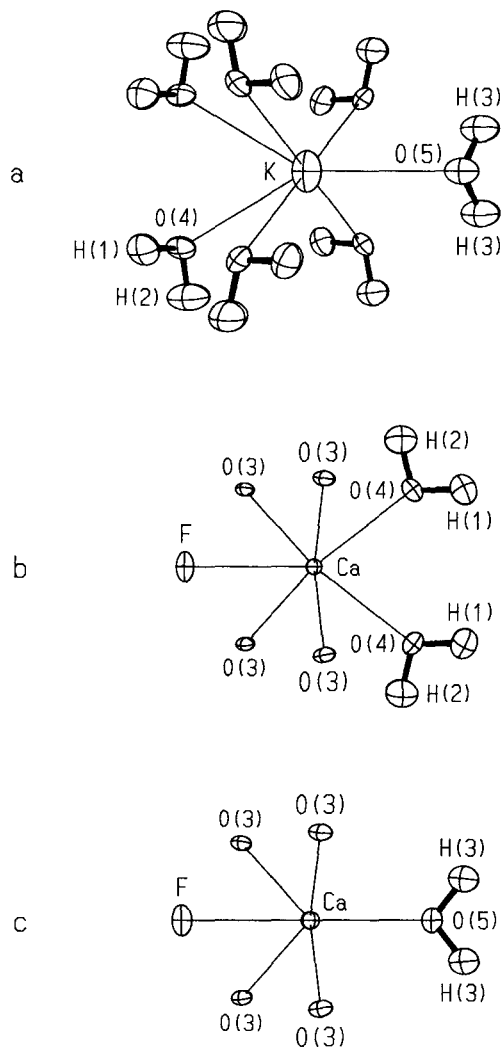


Fig. 3. a) K-coordination in partially dehydrated fluorapophyllite. b) Ca-coordination in fluorapophyllite and to 3/4 in partially dehydrated fluorapophyllite. c) Ca-coordination to 1/4 in partially dehydrated fluorapophyllite.

good fit between the refined model and the data rules out the existence of a crystalline hemi-dehydrated form of fluorapophyllite. The dehydration process of fluorapophyllite can therefore be described as a two step reaction. In a first step the water content will decrease to approximately seven H_2O p.f.u., so that one water molecule of originally eight in the K coordination sphere ($4/m$ symmetry) will have been expelled. The remain-

ing water molecule of a mirror-related pair will assume a new position, with the oxygen (O(5)) in the mirror plane and the hydrogens ($2^*\text{H}(3)$) above and below (Fig. 3a). One quarter of the Ca coordinations, originally forming trigonal Ca-O prisms with F capping one face (Fig. 3b), will now form distorted octahedra (Fig. 3c). As the new compound retains the $P4/mnc$ symmetry, the new water position is of necessity randomly occupied. In a second step, continued water loss causes a collapse of the K coordination, and in turn also of the Ca coordination. As the K and Ca coordinations are crucial in keeping the silicate layers together, the crystal structure is destroyed and the compound becomes amorphous. The remaining water will be trapped inside the amorphous structure and will be expelled on further heating.

Dehydration studies of minerals are complicated by the fact that equilibrium conditions are difficult to attain. When heating a sample in air, the equilibrium water pressure will only very rarely coincide with the ambient water pressure. In addition, the dehydration process is highly diffusion controlled, making heating rate and sometimes particle size important variables. The higher the heating rate and/or the larger the particle size, the higher is the apparent transition temperature (Fig. 1 and Ståhl *et al.*, 1987). In the case of apophyllite the transition to an amorphous form, initially on the outside of the crystallites, will trap a certain fraction of the remaining water inside, and form a diffusion barrier. The thicker the amorphous layer and the lower its water content, the more effective the diffusion barrier becomes, causing a plateau to form in the TGA curve. A lower heating rate will allow a larger fraction of the water to diffuse through the amorphous part, keeping its water content high, and the plateau in the TGA curve will appear at lower temperatures, and with a lower total water content. At an infinitely slow heating rate, the plateau will disappear completely (Cavinato, 1927).

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