Hydroxyapophyllite, a new mineral, and a redefinition of the apophyllite group

I. Description, occurrences, and nomenclature

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II. Crystal structure

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Abstract

Apophyllite, KCanSirOro(F,OH)·8HrO, has been redefined in terms of a solid-solution series between the two phases hydroxyapophyllite, KCanSirOro(OH)·8HrO, and fluorapophyllite, KCanSirOroF·8HrO. The pure hydroxyl end-member is tetragonal, P4/mnc, with a = 8.978(3), c = 15.83(1) Å, and two formula weights per unit cell. The observed and calculated densities are 2.37 and 2.36 g/cm³, respectively. Optically it is uniaxial positive with ε = 1.543 and ω = 1.542. The type locality is the Ore Knob mine, Jefferson, Ashe County, North Carolina. Due to the similarity of their properties, hydroxy- and fluorapophyllite can only be distinguished by chemical means. Nomenclature revisions are presented.

A refinement of the crystal structure of hydroxyapophyllite has been carried out using 757 X-ray reflections and least-squares, the final residual being 0.038. The structure is not significantly different from that reported for fluorapophyllite, except for the OH for F substitution. The unconventional formula KCan(SirOro)zFr-(HF)x(H2O)8-(OH)z with x = 1, previously proposed for fluorapophyllite from Centreville, Virginia, is shown on the basis of new chemical data to be invalid.

Part I. Description, occurrences, and nomenclature

Pete J. Dunn, Roland C. Rouse and Julie A. Norberg

Introduction

Since much apophyllite forms in basaltic amygdalules and is associated with prehnite and many zeolites such as stilbite, heulandite, and chabazite, we suspected that a fluorine-free member of the apophyllite group might exist. A comprehensive search of the literature did reveal the existence of older analyses with low fluorine contents, and a systematic search was begun for a pure end-member in which hydroxyl substitutes totally for fluorine. Analysis of 50 specimens labelled apophyllite resulted in the discovery of the sought-after end-member. We have named the new species hydroxyapophyllite for the composition. The mineral and the name were approved by the Commission on New Minerals and New Mineral Names, I.M.A., prior to publication. The I.M.A. Commission voted on a revision of the nomenclature of the apophyllite group. The majority vote ruled that the nomenclature should be as follows:

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* Contribution #334, Mineralogical Laboratory, University of Michigan
fluorapophyllite—for determined K\(\text{Ca}_4\text{Si}_8\text{O}_{20}\text{F} \cdot 8\text{H}_2\text{O}\)
where \(\text{F} > (\text{OH})\)

hydroxyapophyllite—for determined K\(\text{Ca}_4\text{Si}_8\text{O}_{20}\)
\((\text{OH}) \cdot 8\text{H}_2\text{O}\) where \((\text{OH}) > \text{F}\)
apophyllite—for undetermined members of the series.

Holotype material of hydroxyapophyllite is deposited in the Smithsonian Collection under catalog 
\#115268.

Physical properties and morphology

Hydroxyapophyllite is colorless to white with occasional tinges of light yellow and light green. Some specimens from Great Notch, New Jersey, are chalky white, slightly decomposed, and may represent a hydrothermal alteration of apophyllite. Cleavage is perfect and easily produced on \{001\}. The Mohs hardness is about 4½ to 5, and the streak is white. The mineral does not respond to ultraviolet radiation. The density, determined by Berman Balance with temperature correction, is 2.37 g/cm³, in excellent agreement with the calculated value of 2.36 g/cm³. Optically, the type specimen of hydroxyapophyllite is uniaxial positive with \(\epsilon = 1.543, \omega = 1.542\), and low birefringence.

Hydroxyapophyllite occurs as equant or tabular euhedral crystals ranging up to 25 mm in size at some localities. Forms present are \{100\}, \{001\}, and \{111\}. The luster of \{100\} is vitreous, and of \{001\} pearly, with some crystals having striations on \{100\} parallel to \{001\}. The morphology of hydroxyapophyllite is identical to that of fluorapophyllite, and the species cannot be distinguished by visual examination.

Chemistry

Hydroxyapophyllite, K\(\text{Ca}_4\text{Si}_8\text{O}_{20}(\text{OH}) \cdot 8\text{H}_2\text{O}\) with two formula weights per unit cell, is the hydroxyl analog of fluorapophyllite, K\(\text{Ca}_4\text{Si}_8\text{O}_{20}(\text{F}) \cdot 8\text{H}_2\text{O}\). Both phases exist as pure end-members.

Two analyses of hydroxyapophyllite are given in Table 1. The samples were analyzed with an ARLESMQ electron microprobe using an operating voltage of 15kV and a beam current of 150 nA. The fluorapatite analyzed by P. M. Black (Colville et al. 1971) was used as a standard for Si, K, and Ca; hornblende for Na and Al; and fluorapatite for fluorine. Water was determined by the Penfield method. The absence of fluorine, as determined by microprobe, was confirmed by a modified Berzelius method followed by precipitation as PbClF, and titration of chlorine according to Volhard’s method (Hillebrand et al., 1953, p. 207, 939).

In addition, two wet-chemical analyses of hydroxyapophyllite are given in Table 2. The North Carolina material (#115268) was analyzed using modified classical analytical methods outlined by Hillebrand et al. (1953) and Peck (1964). Silica, calcium, total iron, and aluminum were determined gravimetrically: silica by dehydration from HCl, calcium by precipitation with oxalic acid, total iron by titration, and aluminum by precipitation with 8-hydroxyquinoline. Sodium and potassium were determined by flame

<table>
<thead>
<tr>
<th>Table 1. Microprobe analyses of hydroxyapophyllite</th>
</tr>
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<tbody>
<tr>
<td>(\text{K}_4\text{Ca}_4\text{Si}<em>8\text{O}</em>{20}(\text{OH}) \cdot 8\text{H}_2\text{O}) (theoretical)</td>
</tr>
<tr>
<td>(\text{Si}_2\text{O}_5)</td>
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<tr>
<td>(\text{Al}_2\text{O}_3)</td>
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<td>(\text{CaO})</td>
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<td>(\text{K}_2\text{O})</td>
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<tr>
<td>(\text{Na}_2\text{O})</td>
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<tr>
<td>(\text{H}_2\text{O}**)</td>
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<tr>
<td>100.00</td>
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*On the basis of 8 (Si,Al).

**\(\text{H}_2\text{O}\) determined by the Penfield method.
photometry. Total H$_2$O was obtained using the Penfield method. The mineral was analyzed in triplicate.

Microprobe analyses of over 100 samples of fluorapophyllite and hydroxyapophyllite resulted in the following general observations. The substitution of aluminum for silicon is quite limited and in most cases does not exceed 1.5 percent Al$_2$O$_3$. The substitution of divalent cations for calcium is negligible. Sodium does substitute for potassium, most notably in specimens of hydroxyapophyllite from Guanajuato, Mexico, up to ~1 percent Na$_2$O. The Na/K ratio does not exceed unity in any specimens examined. Owing to this common K = Na substitution, which is apparently unrelated to the OH/F substitution, optical methods do not suffice to distinguish hydroxyapophyllite from fluorapophyllite. The substitution of sodium for potassium lowers the refractive indices, whereas the substitution of hydroxyl for fluorine raises the refractive indices.

**X-ray crystallography**

Precession and cone-axis photographs of hydroxyapophyllite from North Carolina showed the mineral to be tetragonal, $P4_{1}2_{1}2_{1}$ or $P4/mnc$, with approximate unit-cell parameters $a = 8.9$ and $c = 15.9$Å. Subsequent analysis of the crystal structure established $P4/mnc$ as the correct space group. A least-squares refinement of the above cell parameters using powder diffractometer data gathered with monochromatized CuK$\alpha$ radiation and a quartz ($a = 4.9133$, $c = 5.4049$Å) internal standard yielded the values $a = 8.978$ esd 0.003 and $c = 15.83$ esd 0.01Å. The cell volume is 1276 esd 1Å$^3$, and the axial ratio $c/a$ is 1.763. A similar refinement yielded the same parameters for South African hydroxyapophyllite. By way of comparison, fluorapophyllite also has symmetry $P4/mnc$ and cell dimensions of $a = 8.965$ esd 0.002 and $c = 15.768$ esd 0.002Å (Colville et al., 1971). The cell volume is 1268.8Å$^3$, a negligible 0.5 percent smaller than that of hydroxyapophyllite.

A powder diffractometer pattern complete to 70$^o$ 20 was obtained from the North Carolina material as above but using silicon ($a = 5.4306$Å) as an internal standard, to avoid the coincidence of several quartz and hydroxyapophyllite reflections. Indexing was accomplished with the assistance of the single-crystal intensity data. As expected, the pattern (Table 3) is similar to that of apophyllite (JCPDS 19-944 and 944A), but with one important difference. The apophyllite pattern contains numerous minimum or near-minimum intensity reflections which are not observed from hydroxyapophyllite. However, the reality of at least some of these reflections is suspect, since their assigned indices are not permitted by $P4/mnc$, which is the space group given on JCPDS 19-944. For example, reflections 100 at 8.944 and 113 at 4.13Å should be extinguished by the n- and c-glides, respectively. Either $P4/mnc$ is not the correct space group for this apophyllite sample, or its powder pattern has been improperly interpreted. By contrast, all observed reflections in the pattern of hydroxyapophyllite can be satisfactorily indexed in accord-
Land with the requirements of $P4/mnc$. The powder diffraction pattern has been submitted to the Joint Committee on Powder Diffraction Standards.

**Occurrence**

Hydroxyapophyllite is an abundant mineral, and specimens undoubtedly repose in most of the major mineral collections in the world. The type specimen is from the Ore Knob mine, Jefferson, Ashe County, North Carolina. At this locality, hydroxyapophyllite occurs as a 1.0 cm coating of multiply-twinned white crystals on a pyrrhotite and chalcopyrite ore. A second pure hydroxyapophyllite occurs at Kimberley, South Africa. At this locality the hydroxyapophyllite crystals are colorless, transparent, and tabular on {001}. As a general rule, both fluorapophyllite and hydroxyapophyllite may be present on a single specimen, and frequently are.

Many zeolite localities have both fluorapophyllite and hydroxyapophyllite present. The following observations may be of some assistance to collectors and curators concerned with correct nomenclature. Aside from Jefferson, North Carolina, and Kimberley, South Africa, only one other locality provides specimens which consistently have OH $>$ F. This locality is Guanajuato, Mexico, which has provided many excellent hydroxyapophyllite exhibit specimens. The majority of the apophyllites from the New Jersey basalt zeolite deposits are indeed fluorapophyllite with F $>$ OH. The exception is the chalky white, slightly decomposed material from Great Notch, which is hydroxyapophyllite. Most of the Indian material from the Poona District and other occurrences in the Deccan basalts is fluorapophyllite. Some specimens from near Bombay are hydroxyapophyllite.

**Part II. Crystal structure**

**ROLAND C. ROUSE, DONALD R. PEACOR AND PETE J. DUNN**

**Introduction**

The chemical and crystallographic data presented in Part I of this study suggest that the crystal structures of fluor- and hydroxyapophyllite are identical except for the OH$^{-} = F^{-}$ substitution. However, since cases exist in which this substitution produces a structural change, e.g. hexagonal fluorapatite vs. monoclinic hydroxyapatite (Elliot et al., 1973), a structure determination of the pure hydroxyl end-member has been undertaken, the results of which are presented here. In addition, Prince (1971) has proposed that the fluorine in fluorapophyllite from Centreville, Virginia, is present as HF “molecules” rather than F$^{-}$ ions. We shall examine this hypothesis in the light of new chemical data on Centreville apophyllite.

**Experimental methods and results**

The X-ray diffraction study was performed on a square cleavage plate of dimensions 0.58 $\times$ 0.53 $\times$ 0.12 mm obtained from a crystal (#93040) from Kimberley, South Africa. A chemical analysis of this material is presented in Part I. Unit-cell parameters are $a = 8.979$ esd 0.004 and $c = 15.83$ esd 0.01 A. These are essentially the same as those of the North Carolina material and were obtained by the same method. The intensities of 1409 reflections having $\sin \theta \leq 0.460$ and constituting two asymmetric units in reciprocal space were measured with a Supper-Pace diffractometer system employing Weissenberg equi-inclination geometry, graphite crystal monochromatized MoK$\alpha$ radiation, a scintillation counter, and a scanning rate of 2$^\circ$/min. The intensities were then converted to structure factor amplitudes by correction for Lorentz, polarization, and absorption effects ($\mu_l = 14.8$ cm$^{-1}$). Unobserved reflections were assigned intensities of $I_{int} = I_{obs}^{\frac{1}{3}}$, where $I_{obs}$ is the minimum observable intensity. Equivalent amplitudes $|F|_{hhl}$ and $|F|_{hhl}$ showed excellent agreement, and the latter were deleted from the data set, leaving 757 reflections of which 696 are observed.

The $N(z)$ test of Howells et al. (1950) indicated hydroxyapophyllite to be centrosymmetric, which is consistent with space group $P4/mnc$. A least-squares refinement of the structure was then carried out using the program RFIN 2 of L. W. Finger and commencing with the atomic coordinates in fluorapophyllite given by Colville et al. (1971). Neutral atom scattering factors for K, Ca, Si, and O (Doyle and Turner, 1968) were employed, the 0.1 weight percent Al indicated by the chemical analysis (Part I of this study) being neglected. The reciprocal variances, $1/\sigma^2$, of the structure-factor amplitudes were used as weights in the refinement, except for unobserved reflections which were assigned zero weight.
When the residual, defined as $\sum |F_{\text{obs}} - |F_{\text{calc}}| / \sum |F_{\text{obs}}$, had reached 0.044, a difference synthesis was computed in hopes of locating the hydrogen atoms. In fact, two significant maxima of 0.6 and 0.7 e/Å$^2$ did appear at about the positions found for H(1) and H(2) of the water molecule in the neutron diffraction study of fluorapophyllite (Prince, 1971). No firm indication of the location of H(3), which is part of the hydroxyl ion in hydroxyapophyllite, appeared on the difference map, but this is not surprising considering that there are only two H(3) atoms per cell compared to sixteen each of H(1) and H(2). H(1) and H(2) were included in subsequent least-squares cycles using the hydrogen scattering curve given by Lee and Pakes (1969). The refinement converged at a residual of 0.038 for all reflections or 0.035 for the observed ones alone.

Table 4 contains a list of the observed and calculated structure factor amplitudes on an absolute scale, Table 5 the refined atomic parameters, and Table 6 some selected interatomic distances and angles in hydroxyapophyllite. Not unexpectedly, the values are very similar to those in the fluorine analog. Exceptions are the hydrogen parameters, whose refined values, although close to those found by neutron diffraction in fluorapophyllite (Prince, 1971; Bartl and Pfeifer, 1976), deviate sufficiently to give unreasonable bond parameters for the water molecule, H(1)-O(4)-H(2). The distances H(1)-O(4) and H(2)-O(4) are 1.16(5) and 0.73(4) Å, respectively, while the angle H(1)-O(4)-H(2) is 86(4)$^\circ$. The corresponding and presumably accurate values given by Bartl and Pfeifer (1976) are 0.983 Å, 0.953 Å, and 103.81$^\circ$. A similar problem with the hydrogen parameters was encountered by Chao (1971) in an X-ray diffraction study of fluorapophyllite.

**Discussion**

The atomic parameters, interatomic distances, and angles in hydroxyapophyllite are in good agreement for those reported for fluorapophyllite by Taylor and Náray-Szabó (1931), Colville et al. (1971), Chao (1971), Prince (1971), and Bartl and Pfeifer (1976), although the present refinement gives lower estimated standard deviations and/or a slightly lower residual than previous studies. Of greater interest here is the relationship between hydrogen and fluorine in the

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Table 5. Atomic coordinates and anisotropic temperature factors ($\times 10^3$) in hydroxyapophyllite

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$\beta_{11}$</th>
<th>$\beta_{22}$</th>
<th>$\beta_{33}$</th>
<th>$\beta_{12}$</th>
<th>$\beta_{13}$</th>
<th>$\beta_{23}$</th>
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<tr>
<td>K</td>
<td>0.1108</td>
<td>0.2475</td>
<td>0.2265</td>
<td>0.8637</td>
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<td>0.2166</td>
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<td>Ca</td>
<td>0.2265</td>
<td>0.1896</td>
<td>0.3637</td>
<td>0.2166</td>
<td>0.2166</td>
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<tr>
<td>Si</td>
<td>0.1025</td>
<td>0.0889</td>
<td>0.0894</td>
<td>0.0894</td>
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<td>OH</td>
<td>0.4535</td>
<td>0.1356</td>
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<td>0.1064</td>
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<tr>
<td>H(1)</td>
<td>0.2145</td>
<td>0.4324</td>
<td>0.1342</td>
<td>0.2145</td>
<td>0.4324</td>
<td>0.1342</td>
<td>0.1342</td>
<td>0.1342</td>
<td>0.1342</td>
<td>0.1342</td>
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</tbody>
</table>

E.s.d.'s in parentheses refer to last digit. Temperature factors for anisotropically refined atoms are of the form $\exp \left\{ - \frac{3}{3} \sum_{i=1}^{3} \sum_{j=1}^{3} h_i h_j B_{ij} \right\}$. Hydrogen atoms were refined isotropically and the $\beta_{\text{eq}}$ are the equivalent isotropic temperature factors (Hamilton, 1959).
apophyllite structure. On the basis of an \((F_-^5-F_-^t)\) difference synthesis calculated from his neutron diffraction data, Prince (1971) proposed that fluorine is present not as the fluoride ion, as previously supposed, but as hydrogen fluoride “molecules” in which the hydrogen atom \(H(3)\) is located on the 4-fold axis a distance of 1.0 A from the fluorine atom. The result is a new structural formula for fluorapophyllite

\[
KCa_8(SiO_4)_2F_2\cdot[(H_2O)_8\cdot(OH)_2]_x 
\]

with \(x \approx 1\), compared to the conventional \(KCa_8(SiO_4)_2F\cdot8H_2O\). Prince’s interpretation has been challenged by Bartl and Pfeifer (1976), who find on the basis of site occupancy factor refinements that \(H(3)\) is bonded not to fluorine as HF but to oxygen as OH- in crystals of composition \(KCa_8(SiO_4)_2\cdot(OH,F)\cdot8H_2O\).

The above discussion suggests that the crystal used by Prince was not fluorapophyllite but some intermediate composition containing both fluorine and hydroxyl. No chemical analysis is cited by Prince, but the crystal used is stated to be from Centreville, Virginia, and to have a volume of about 12 cm\(^3\). Electron microprobe analyses by one of the authors (PJD) of 12 apophyllite crystals from the Centreville locality revealed two pertinent facts: (1) individual crystals are very inhomogeneous with respect to fluorine content; and (2) the average fluorine content in the crystals ranges from 0.1 percent, or nearly pure hydroxyapophyllite, to 1.6 percent, compared to the theoretical 1.95 percent for fluorapophyllite. In no case was the pure fluorine end-member found, and with a volume of 12 cm\(^3\) it is quite unlikely that Prince’s crystal was hydroxyl-free. It must therefore be concluded that the interpretation of Bartl and Pfeifer (1976) is correct and that the new structural formula proposed by Prince is invalid.

There is one additional comment to be made concerning the hydroxyl ion in hydroxyapophyllite. The thermal ellipsoids of both the oxygen atom of the hydroxyl group and the fluorine atom are prolate along the \(c\) axis, and both Prince (1971) and Bartl and Pfeifer (1976) suggest that these atoms are slightly displaced along the 4-fold axis from their ideal position on equipoint \(2a\) (0,0,0). In hydroxyapophyllite this would require the oxygen atom of the hydroxyl group to be disordered on equipoint 4e, i.e., half at 0,0,2 and half at 0,0,2. Now the rms thermal displacement of OH along \(c\) is, in fact, 0.17(1) Å compared to 0.07(1) Å along \(a\) and \(b\) (Table 7). However, 0.17 Å is not substantially greater than the rms dis-

### Table 6. Interatomic distances and angles in hydroxyapophyllite

<table>
<thead>
<tr>
<th>Polyhedron</th>
<th>(K_0) polyhedron</th>
<th>(CaO) polyhedron</th>
<th>(SiO_3) tetrahedron</th>
<th>(O(4)-H\cdots\cdotO) distances</th>
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</thead>
<tbody>
<tr>
<td>(K-O(4))</td>
<td>2.954(3) Å (8x)</td>
<td>0(4)-0(4) 2.816(6) Å (4x)</td>
<td>0(1)-0(1) 2.583(3) Å</td>
<td>0(4)-0(3) 2.743(4) Å</td>
</tr>
<tr>
<td>(Ca-O(3))</td>
<td>2.403(2) Å (2x)</td>
<td>0(4)-0(4) 2.816(6) Å</td>
<td>0(1)-0(1) 2.583(3) Å</td>
<td>0(4)-0(3) 2.743(4) Å</td>
</tr>
<tr>
<td>(Si-O(3))</td>
<td>1.584(1) Å</td>
<td>0(1)-0(2) 2.650(5) Å</td>
<td>0(1)-0(1) 2.583(3) Å</td>
<td>0(4)-0(3) 2.743(4) Å</td>
</tr>
<tr>
<td>(O(4)-H\cdots\cdotO) distances</td>
<td>0(4)-0(3) 2.743(4) Å</td>
<td>0(4)-0(2) 3.312(4) Å</td>
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</table>

E.s.d.'s in parentheses refer to last digit.
placements of the other oxygen atoms, which average 0.124 Å and range as high as 0.191(4) Å. Moreover, there is no indication of any OH displacement on the difference map. Since the X-ray data provide no unequivocal evidence for positional disorder of the hydroxyl oxygen atom, it was kept at 0,0,0 during the course of the present refinement.

Acknowledgments
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References

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