Compositional and refractive index variations of the herderite–hydroxyl-herderite series

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Abstract

The compositional range of the herderite–hydroxyl-herderite series, CaBePO₄(F,OH), has not been well-established. Microprobe analysis of 41 herderite series samples from 19 localities gave compositions between 98 and 53 mole percent hydroxyl-herderite. The only specimen of true herderite known to us is a cut gem at the Smithsonian Institution with 60 mole percent herderite. Nineteenth-century analyses of specimens from Stoneham, Maine, reporting high fluorine contents and widely cited, must be considered doubtful. Indices of refraction of 12 samples show a linear decline with increasing F content, and least-squares linear regression analysis of the data gave

\[ \alpha = 1.615 - 0.00059(\% H) \quad r = -0.991 \]

\[ \beta = 1.634 - 0.00056(\% H) \quad r = -0.994 \]

\[ \gamma = 1.644 - 0.00055(\% H) \quad r = -0.994 \]

where \( \% H \) is the mole percent herderite in the specimen, and \( r \) is the correlation coefficient of the indices with composition for the fitted lines. The X-ray diffraction pattern of hydroxyl-herderite shows no perceptible shifts with composition.

Introduction

Herderite, CaBePO₄F, and hydroxyl-herderite, CaBePO₄(OH), are end-members of an isomorphous series. Herderite was first discovered in the tin veins of Ehrenfriedersdorf, Saxony (Haidinger, 1828); hydroxyl-herderite was first described from a pegmatite at Paris, Maine, as hydro-herderite by Penfield (1894). The actual composition of the Ehrenfriedersdorf herderite has never been established. Winkler, in Weisbach (1884), gave two analyses, with 6.59 weight percent and 6.54 weight percent H₂O, greater than the theoretical amount of water in pure hydroxyl-herderite, and only a “doubtful reaction” for fluorine, but Genth (1884) felt that Winkler’s methods were totally inadequate for the detection of fluorine. The division of the series into herderite and hydroxyl-herderite was made by Palache et al. (1951, p. 820).

Most analyses of herderite date from the nineteenth century and suffer from the difficulties of fluorine analysis by the wet-chemical methods in use at the time. Optical data on analysed herderites are sparse. This paucity of recent and reliable data prompted us to analyse a large number of herderites and to determine indices of refraction for a number of these. A summary of our results, with a detailed discussion of hydroxyl-herderite from two Brazilian localities, is presented elsewhere (Dunn et al., 1979).
Occurrence

The herderite series minerals occur typically in pegmatites, as crystals in cavities formed during the late, replacement stage of crystallization. Crystals are usually only a few mm across, but in one Brazilian locality reach 15 cm (Dunn et al., 1979). The most commonly associated minerals are crystalline quartz, albite, muscovite, and clays. Microcline, if present, is etched, as at Topsham, Maine (Yatsevitch, 1935), and Virgem da Lapa, Minas Gerais, Brazil (Dunn et al., 1979). Hydroxyl-herderite may form by the alteration of beryl (Yatsevitch, 1935; Perham, 1964) or of beryllonite (Palache and Shannon, 1928). It rarely shows alteration, but occurs as bright, euhedral crystals implanted on the other minerals.

Chemistry

Forty-one samples of herderite series minerals were analysed with an ARL-SEMQ electron microprobe using an operating voltage of 15kV, a beam current of 0.15 μA, and a 10 μ beam. The standards were fluorapatite for Ca, P, and F; hornblende for Si, Al, Fe, and Mg; and manganite for Mn. The data were corrected for background, backscatter, absorption, and fluorescence using a computer program employing the Bence-Albee factors. The analyses are presented in Table 1, along with the fluorine analysis of a faceted green gem herderite in the Smithsonian Gem Collection (Dunn and Wight, 1976).

The analyses are averages; the fluorine content of single crystals varied by as much as 20 percent relative at different sample points. Indices of refraction of different fragments of single crystals show corresponding variation. In addition, different samples from the same locality are in some cases quite different in average composition. No attempt was made to map possible zonal distribution of fluorine in any of the specimens.

The analytical data indicate very little replacement of Ca by Fe, Mg, or Mn in the herderite-hydroxyl-herderite series. Most samples conform quite well to the theoretical content for Ca and P. The analytical data indicate that herderite is a very rare species. All the samples studied herein are hydroxyl-herderite; none were found with a fluorine content which would indicate F > OH. The only herderite known to us is the gemstone described by Dunn and Wight (1976).

A number of the analyzed specimens have been studied in the past, and some comments about these are in order.

In his description of hydro-herderite from Paris, Maine, Penfield (1894) noted that a prism of the mineral was cut to determine the index of refraction by the method of minimum deviation. This prism and a specimen labelled “hydro herderite, Paris, Maine” (Brush #1973) are preserved in the Brush collection of Yale University and were made available for this study. Penfield (1894) found a “trace” of fluorine, but microprobe analysis shows that this hydroxyl-herderite actually contains about 1 percent F by weight, and is 91 mole percent hydroxyl-herderite, rather than the pure end-member. Penfield was a meticulous analyst; the presence of 1 percent F undetected in the sample despite his care is evidence of the difficulty of F analysis by the methods he used.

Ford (1911) described a herderite mineral from Auburn, Maine. He included a chemical analysis for water and fluorine, which yielded F = 6.04 percent, H₂O = 3.62 percent, corresponding to 48 mole percent and 65 mole percent hydroxyl-herderite respectively. A twinned crystal of the described material (Yale #3772) was examined in this study. It has one end sawn and is presumably the analysed specimen. Microprobe analysis gave 4.20 percent F, corresponding to 64 mole percent hydroxyl-herderite, compatible with the H₂O value reported by Ford.

Hydroxyl-herderite from the Golconda Mine, Minas Gerais, Brazil (NMNH #121024) was used by Lager and Gibbs (1974) for a detailed crystal-structure analysis. They treated it as pure hydroxyl-herderite, but our analysis of fragments from the same specimen, a single crystal 7 x 5 x 4 cm, showed 3.39 percent F, corresponding to 71 mole percent hydroxyl-herderite.

Complete analyses of herderite minerals for which F > OH were published by Hidden and Mackintosh (1884) and by Genth (1884), both on material from Stoneham, Maine. Since all six samples from Stoneham which we analysed are hydroxyl-herderite, these early analyses must be reconsidered. Hidden and Mackintosh (1884) gave 11.32 percent F and stated only that “the fluorine was calculated from the excess of lime.” They did not state that they made direct tests for fluorine or for water. Although they stated that they had no doubt that the formula calculated from their analysis represented the true composition of the mineral, it is in fact uncertain with respect to F. Genth (1884) in summarizing his analytical data, stated, “somewhat doubtful is the exact amount of fluorine which it contains.” Although Genth thought his F content (8.93 percent) too low, it is clear that he was doubtful of the analytical procedures for F determination in use at that time. Penfield and Harper
(1886) analysed a specimen from Stoneham, and using the ratio of F to H₂O in the analysis, concluded that their material was 60 mole percent hydroxyl-herderite. They considered that their analysis superseded those of Hidden and Mackintosh and Genth. Thus the composition of Stoneham material was a herderite. Their analysis supports that of Penfield and Harper, and in the absence of more confirmatory data, the existence of herderite from Stoneham must be considered doubtful. We were unable to obtain samples of the actual material analysed by Hidden and Mackintosh or by Genth.

The specimen from Epprechtstein, Fichtelgebirge, West Germany, with 59 mole percent hydroxyl-herderite, is a single crystal, illustrated by Dürrfeld and Harper.
Newry and the King's Mountain material are in-probe, and the lack of any effervescence of this hydroxyl-herderite in HCl indicates low, if any, substitution of CO₂ for PO₄. The X-ray powder patterns of both the phosphates. The summations of the analyses are quite low, however, and there appear to be other problems in the chemistry of these specimens. A microprobe scan failed to reveal other detectable elements, although Li, Be, and B cannot be detected on the probe, and the lack of any effervescence of this hydroxyl-herderite in HCl indicates low, if any, substitution of CO₂ for PO₄. The King's Mountain hydroxyl-herderite also has a high SiO₂ content—3.35 percent. The X-ray powder patterns of both the Newry and the King's Mountain material are indistinguishable from those of the other hydroxyl-herderites X-rayed in this study.

### Optics

Indices of refraction for a number of analysed samples were determined using the spindle stage designed by Jones (1968). Principal vibration directions were located by observing interference figures in conoscopic light, and refractive indices were measured in sodium light by the Becke line method. Refractive indices of the immersion oils were checked in each case by refractometer. Single index determinations are believed to be precise within ±0.001.

Because the grains analysed by microprobe and those examined optically were not the same, although coming from the same specimen and usually from the same small crystal, and because different grains may show marked variation in composition and refractive indices, refractive indices were determined on two or more grains of most specimens. If differences of 0.003 or greater were found for a given index between grains, the specimen was considered excessively in-homogeneous and the data discarded. As can be seen from the equations below, a difference of 0.003 in refractive index corresponds to a difference of about 5 mole percent F (or OH) in the composition. If differences in index were less than 0.003, the average of the determinations was used. The resultant indices of refraction of 12 samples are recorded in Table 2, along with the indices of the herderite gem, which were determined by refractometer to ±0.002 (Dunn and Wight, 1976). The equations of the best-fit lines determined by least-squares linear regression analysis are:

\[ \alpha = 1.615 - 0.00059(\% H) \quad r = -0.991 \]
\[ \beta = 1.634 - 0.00056(\% H) \quad r = -0.994 \]
\[ \gamma = 1.644 - 0.00055(\% H) \quad r = -0.994 \]

where %H is the mole percent herderite in the specimen, and \( r \) is the correlation coefficient of the indices with composition for the fitted lines.

The herderite series thus shows a significant decrease in indices of refraction with increasing F content. This change provides a useful method for determining the composition of an unknown sample. The variation is not unexpected, for other minerals with F-OH substitution show a decrease in indices of refraction with increasing F content.

Calculated 2V angles show a slight change, from 77° for pure hydroxyl-herderite to 70° for the midpoint composition. Thus 2V is not a useful property...
for determining the composition of members of the series.

Crystallography

Some minerals show changes in unit-cell dimensions with OH–F substitution. In the case of tremolite (Cameron and Gibbs, 1973), the effect is small, amounting to a reduction of about 0.05 Å in the b-axis dimension of synthetic fluor-tremolite as compared to hydroxyl tremolite, with smaller reductions in the other axial dimensions. To test whether a change in lattice dimensions with composition is detectable in hydroxyl-herderite, an X-ray powder photograph was made of hydroxyl-herderite with 98 mole percent OH (Palermo Quarry, N. H.; NMNH #106076-1) mixed with an equal amount of hydroxyl-herderite from Auburn, Maine, with 64 mole percent OH (Ford, 1911; Yale #3772), using nickel-filtered CuKα radiation and a 114.6 mm Debye-Scherrer camera. There was no detectable broadening or splitting of the lines as compared with the pattern of Palermo Quarry hydroxyl-herderite alone; thus, any shift must be slight, and X-ray powder diffraction does not provide a method for determining F content in members of the series. Because OH− and F− have the same number of electrons, their mutual substitution is unlikely to cause intensity changes in the X-ray diffraction pattern. Powder diffraction data of the Palermo hydroxyl-herderite have been submitted independently to the JCPDS.

Penfield (1894) and Ford (1911) investigated the variation of the morphological axial ratios of hydroxyl-herderite with its composition, although each observed that the usual rounding and unevenness of the faces of crystals made precise goniometric measurements difficult. Penfield reported a variation, whereas Ford did not. Dürrfeld (1909) used Penfield’s (1894) data in his study of Epprechtstein hydroxyl-herderite discussed under Chemistry. Our X-ray study did not detect any change in the lattice spacings with composition and hence no change in the axial ratios, supporting the work of Ford (1911).

Acknowledgments

Clifford Frondel first pointed out the problems with the data on the herderite series to the senior author more than 10 years ago; solution of these problems had to wait for adequate methods for analysing for small amounts of F. Horace Winchell made a number of specimens available from the Yale University collections, including documented specimens exceedingly important for this study. Joseph Nelen of the Smithsonian Institution and Jun Ito of the James Franck Institute of the University of Chicago provided preliminary chemical analyses which were useful in the early stages of this study. Frederick Keidel provided a sample of the hydroxyl-herderite from the Keyes Mine.

References


Manuscript received, March 27, 1978; accepted for publication, May 30, 1978.