

Single-crystal neutron diffraction and Raman spectroscopic study of hydroxylherderite, $\text{CaBePO}_4(\text{OH},\text{F})$

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ABSTRACT

The crystal structure, H bonding and chemical composition of hydroxylherderite from the Bennett pegmatite, Buckfield, Oxford County, Maine, USA were investigated by single-crystal X-ray diffraction and neutron Laue diffraction, electron microprobe analysis in wavelength-dispersive mode, inductively coupled plasma-atomic emission spectrometry and polarized Raman spectroscopy [$\text{Ca}(\text{Na}_{0.01}\text{Ca}_{1.01})_{\Sigma 1.02}(\text{Be}_{0.98}\text{Li}_{0.01})_{\Sigma 0.99}(\text{Si}_{0.03}\text{P}_{0.98})_{\Sigma 1.01}\text{O}_4(\text{OH}_{0.67}\text{F}_{0.33})_{\Sigma 1}$, $Z = 4$, $a = 9.7856(5)$, $b = 7.6607(5)$, $c = 4.8025(3)$ Å, $\beta = 90.02(3)^\circ$, $V = 360.02(4)$ Å³, space group $P2_1/a$]. The neutron-structure refinement converged with fully anisotropic displacement parameters to give a final agreement index $R_1 = 0.0363$ for 85 refined parameters and 1614 unique reflections with $F_o > 4\sigma(F_o)$. The structure refinement was used to determine the H position and geometry of H bonding in the structure. One H site was found on the O5 anion with an O–H interatomic distance, corrected for “riding motion”, of 0.996(2) Å. The H bond of hydroxylherderite is bifurcated with O2 and O4 acceptors forming H bonds with $\text{O5}\cdots\text{O2} = 3.163(1)$ Å, $\text{H}\cdots\text{O2} = 2.544(2)$ Å and $\text{O5} - \text{H}\cdots\text{O2} = 121.8(1)^\circ$; $\text{O5}\cdots\text{O4} = 3.081(1)$ Å, $\text{H}\cdots\text{O4} = 2.428(2)$ Å and $\text{O5} - \text{H}\cdots\text{O4} = 124.4(1)^\circ$. The highly non-linear O–H $\cdots$ O hydrogen bonds in hydroxylherderite and in the isotypic datolite [ideally $\text{CaBSiO}_4(\text{OH})$] are constrained by the tetrahedral network topology. Two main O–H stretching modes were observed in the Raman spectra at 3565 and 3620 cm^{−1}, which are attributed to the bifurcated H bond. Two additional weak bands at 3575 and 3610 cm^{−1} are attributed to Si–P disorder in the tetrahedral sites. Results of this study will contribute to the correlation of H-bonding geometry and O–H stretching frequencies of highly non-linear H bonds.

KEYWORDS: hydroxylherderite, electron microprobe analysis (WDS), inductively coupled plasma-atomic emission spectrometry, Raman spectroscopy, neutron Laue diffraction, hydrogen bonding.

Introduction

BERYLLIUM-CONTAINING minerals are the primary resources of Be for industrial applications, as well as being geologically relevant in understanding

crustal differentiation processes (e.g. Rickers, *et al.*, 2006). Herderite (ideally CaBePO_4F) and hydroxylherderite [ideally $\text{CaBePO}_4(\text{OH})$] are endmembers of a Be-phosphate solid-solution series. Crystals belonging to the herderite–hydroxylherderite series form pseudo-orthorhombic prismatic or thick tabular crystals, or occur more rarely as botryoidal or spheroidal

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aggregates with a radial-fibrous texture. Generally, these minerals are colourless or white, but can rarely display grey, brown, pale yellow, greenish white, light blue, or a purple colour. Single crystals, occurring in miarolitic cavities, may reach 17 cm long and form after alteration of Be or beryllonite during late stage Ca-rich hydrothermal crystallization (Ca-metasomatism). The colour, transparency, refraction indices ($\alpha = 1.595$, $\beta = 1.613$ and $\gamma = 1.624$), hardness (5–5½ Mohs) and large crystal sizes have also led to herderite–hydroxylherderite being considered as a gemmological material. Compositions of the herderite–hydroxylherderite solid solution close to the hydroxylherderite endmember are more common; herderite occurs only in strongly F-enriched Li-Cs-Ta (LCT) granitic pegmatites (Leavens *et al.*, 1978; Dunn and Wight, 1976; Dunn *et al.*, 1979; King and Foord, 1994; Grew, 2002; Harlow and Hawthorne, 2008).

Herderite was reported for the first time by Haidinger (1828) from Sn-bearing pegmatites at Ehrenfriedersdorf (Erzgebirge, Germany). The unit-cell constants and space group of herderite were determined by Strunz (1936) and its crystal structure was solved by Pavlov and Belov (1959). Structure refinements of herderite were carried out by Lager and Gibbs (1974) and Harlow and Hawthorne (2008) by single-crystal X-ray diffraction (XRD). Herderite is isostructural with datolite, $\text{CaBSiO}_4(\text{OH})$, e.g. Rinaldi *et al.* (2010). The structure of herderite consists of sheets of corner-sharing PO_4 and $\text{BeO}_3(\text{OH},\text{F})$ tetrahedra, parallel to (001), linked by sheets of edge-sharing $\text{CaO}_6(\text{OH})_2$ polyhedra (slightly distorted tetragonal antiprisms) (Fig. 1). The sheet made by alternating PO_4 and $\text{BeO}_3(\text{OH},\text{F})$ units contains four- and eight-membered rings of tetrahedra. The edge-sharing $\text{CaO}_6(\text{OH})_2$ polyhedra form a sheet of six-membered rings (Fig. 1). The most recent X-ray structure refinements by Harlow and Hawthorne (2008; with 0.483 and 0.748 F atoms per formula unit (a.p.f.u.) did not report the H position in herderite. Thus, the geometry of H bonding in hydroxylherderite remains to be determined.

Rickers *et al.* (2006) listed Raman modes for herderite at 584, 595, 983 and 1005 cm^{-1} in the characterization of mineral and melt inclusions in pegmatite quartz, but did not present spectra or provide band assignments. Frezzotti *et al.* (2012) assigned the bands from the study of Rickers *et al.* (2006) to the PO_4^{3-} group as ν_4 out-of-plane bending (584 and 595 cm^{-1}), ν_1 symmetric

stretching (983 cm^{-1}) and ν_3 antisymmetric stretching (1005 cm^{-1}). Recently, Frost *et al.* (2014) presented a detailed Raman, infrared and near-infrared spectroscopic study of herderite and hydroxylherderite, which is used to discuss band assignments and draw comparisons with the current study. In the O–H stretching region, Frost *et al.* (2014) observed two main bands in Raman, one intense band at 3623 cm^{-1} and a second at $\sim 3570\text{ cm}^{-1}$, which was composed of two bands, at 3568 and 3578 cm^{-1} . Frost *et al.* (2014) interpreted the presence of two strong O–H stretching peaks as evidence for two non-equivalent OH sites in the herderite–hydroxylherderite series, although structure data from X-ray or neutron diffraction on H positions were not available at that time.

On this basis, the aim of the present study is to investigate the crystal structure and crystal chemistry of hydroxylherderite at ambient conditions by means of electron microprobe analysis in wavelength-dispersive (EPMA-WDS) mode, inductively coupled plasma-atomic emission spectrometry (ICP-AES), polarized Raman spectroscopy and single-crystal X-ray diffraction and neutron Laue diffraction, in order to: (1) locate the proton site(s) and determine the H-bonding geometry; (2) test for potential F/OH ordering; and (3) provide a list of the principal Raman-active modes. As previous single-crystal XRD studies were unable to locate the proton site, single-crystal neutron diffraction was used to investigate the H bonding in hydroxylherderite in a similar fashion to a series of recent studies on other Be-bearing hydrous minerals (e.g. Gatta *et al.*, 2008, 2012, 2014; Geiger *et al.*, 2012). A comparison between the crystal structure of hydroxylherderite and that of datolite (Rinaldi *et al.*, 2010) is presented.

Sample description and mineralogy

A gem-quality, colourless, single-crystal of hydroxylherderite 7 mm long and 4 mm in diameter from the private collection of one of the authors (P.V., catalog # 2831), collected from the Bennett pegmatite, Buckfield, Oxford County, Maine, USA, Latitude: $44^\circ 17' 35''\text{N}$, Longitude: $70^\circ 25' 35''\text{W}$, was used in the current multi-methodological study. From this locality, stout prismatic crystals of hydroxylherderite, showing a whitish-yellow alteration surface, were found perched on cleavelandite and associated with secondary quartz crystals and lepidolite books.

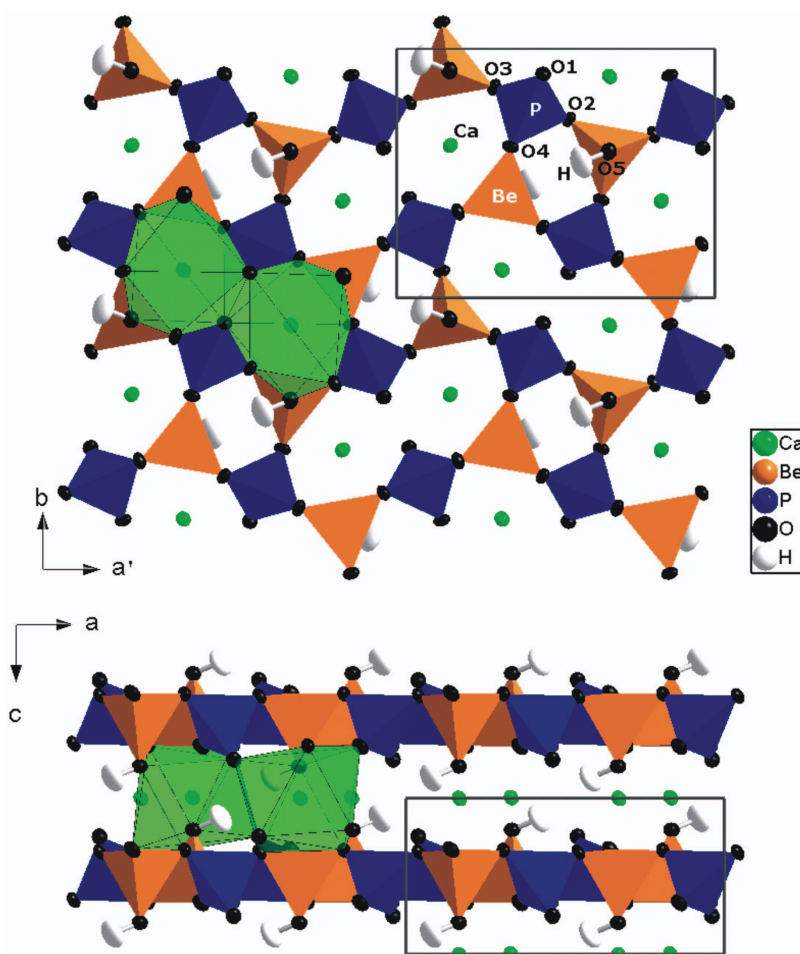


FIG. 1. Two views of the crystal structure of hydroxylherderite based on the neutron structure refinement of this study. Displacement ellipsoid probability factor: 90%.

The Bennett quarry, opened in 1920, was mined for ceramic feldspar and contained a great number of miarolitic pockets up to 4 m in diameter which produced noteworthy gem material and collectibles. The most famous specimen, found in 1989, was a giant morganite (gem variety of pink beryl) crystal 40 cm in diameter and 20 cm thick, called 'The Rose of Maine'. The Bennett is a highly evolved LCT pegmatite of the spodumene subtype in the classification of Černý and Ercit (2005). The accessory minerals occur mainly in miarolitic cavities, which are lined with cleavelandite and contain elbaite, columbite-group minerals, hydroxylherderite and cookeite (Falster and Simmons, 2013).

Experimental methods

Chemical analysis

The chemical composition of the hydroxylherderite from Bennett quarry was investigated by EPMA-WDS and ICP-AES. Quantitative EPMA-WDS analyses were performed on a polished crystal (2 mm × 2 mm × 2 mm), optically free of defects, using a Jeol JXA-8200 electron microprobe. The system was operated using a defocused electron beam ($\varnothing$ 5 μ m), an accelerating voltage of 15 kV, a beam current of 5 nA measured by a Faraday cup and counting times of 30 s on the peaks and 10 s on the backgrounds. Natural crystals of grossular (for Ca, Si and Al),

forsterite (for Mg), fayalite (for Fe), rhodonite (for Mn), omphacite (for Na), apatite (for P), cancrinite (for Cl) and hornblende (for F) were used as standards. The results were corrected for matrix effects using a conventional $\Phi\rho Z$ routine as implemented in the JEOL suite of programs. The crystal was found to be homogeneous within the analytical error. The chemical formula, obtained by averaging 20 point analyses, is given in Table 1.

A further chemical analysis of the sample of hydroxylherderite used in this study was performed by ICP-AES using a PerkinElmer Optima 7000 DV spectrometer. In this apparatus, the sample-introduction unit includes a cyclonic spray chamber and a MEINHARD-type concentric glass nebulizer. The cyclonic spray chamber was used to provide both high sample transfer into the ICP and fast sample rinse-in and rinse-out times. The concentric nebulizer provided excellent sensitivity and precision for aqueous solutions. Only the F content in aqueous solution was measured using an ion selective electrode perfectION[®] (METTLER TOLEDO). A total mass of 94 mg of hydroxylherderite was used for the chemical analysis. Sample preparation, standardization, quantification of uncertainty

in measurement and analytical methods were performed using the guidelines of the following international protocols: EN ISO 10058 (2009) (parts 1, 2 and 3), 26845 (2008); EPA 3052 (1996), 6010c (2007), 9214 (1996); JGCM 100 (2008). The preliminary dissolution tests show that hydroxylherderite is not soluble in HCl (as is usually expected for phosphates), H₂SO₄, HNO₃, HF, CH₃COOH, or in any mixture of these, at room-*T* or at high-*T* and microwave assisted. Hydroxylherderite was then melted with a mixture of Na₂CO₃ + H₃BO₃ (or K₂CO₃ + H₃BO₃) and dissolved finally in a HCl + H₂SO₄ mixture. The chemical composition of hydroxylherderite, along with further details pertaining to the analytical methods, are given in Table 2.

Single-crystal X-ray and neutron diffraction experiment

Two crystals of hydroxylherderite (crystal size: 0.33 mm × 0.30 mm × 0.08 mm and 3.1 mm × 2.8 mm × 1.8 mm, respectively), optically free of inclusions under a transmitted-light polarizing microscope, were selected for the diffraction experiments. The unit-cell parameters were measured by single-crystal XRD, using the

TABLE 1. Representative composition of the hydroxylherderite from the Bennett pegmatite, Maine, USA, based on EPMA-WDS analysis (average of 20 data points). The chemical formula calculated on the basis of (OH+F) = 1 a.p.f.u. is: $^{Ca}Ca_{0.99}^{Be}Be_1^{P}(Si_{0.01}P_{0.99})_{\Sigma 1.00}O_4(OH_{0.67}F_{0.33})_{\Sigma 1}$.

	Wt.%	e.s.d.		a.p.f.u. [§]
P ₂ O ₅	43.77	0.50	P	0.994
SiO ₂	0.20	0.17	Si	0.006
Al ₂ O ₃	0.01	0.01		
FeO	0.02	0.02	Al	<0.001
MnO	0.01	0.02	Fe ²⁺	<0.001
CaO	34.54	0.17	Mn ²⁺	<0.001
BeO*	15.50		Ca	0.993
Na ₂ O	0.05	0.04	Na	0.003
H ₂ O**	3.53			
F	3.90	0.49	Be	1.000
Sum	101.50			
–O=F	–1.64		OH [–]	0.669
Total	99.89		F	0.331

Notes: Mg, K and Cl content were below detection limit;

[§] calculated on the basis of (P+Si) = 1 a.p.f.u.;

* calculated on the basis of 1 Be a.p.f.u.;

** calculated on the basis of (OH+F) = 1 a.p.f.u.

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TABLE 2. Chemical composition of the hydroxylherderite from the Bennett pegmatite, Maine, USA, based on ICP-AES analysis. The chemical formula, calculated on the basis of (OH+F) = 1 a.p.f.u., is: ${}^{Ca}_{(Na_{0.01}Ca_{1.01})\Sigma 1.02}{}^{Be}_{(Be_{0.98}Li_{0.01})\Sigma 0.99}{}^P(Si_{0.03}P_{0.98})\Sigma 1.01O_4(OH_{0.67}F_{0.33})\Sigma 1$.

	Wt.%	e.s.d.		a.p.f.u. [§]	λ ICP-AES (nm)	Alkaline fusion	Electrochemical methods
P ₂ O ₅	42.7	0.4	P	0.976	213.617	x	
SiO ₂	1.01	0.09	Si	0.027	251.611	x	
Cr ₂ O ₃	0.14	0.02	Cr	0.003	267.716	x	
Fe ₂ O ₃	0.13	0.02	Fe	0.003	238.204	x	
CaO	34.7	0.6	Ca	1.006	317.933	x	
BeO	15.1	0.3	Be	0.980	313.107	x	
BaO	0.09	0.01	Ba	0.001	233.527	x	
SrO	0.10	0.02	Sr	0.002	407.771	x	
Na ₂ O	0.16	0.03	Na	0.008	589.592	x	
Li ₂ O	0.05	n.d.	Li	0.005	670.784	x	
H ₂ O *	3.69		OH	0.665			
F	3.92	0.26	F	0.335		x	x
Sum	101.79						
–O=F	–1.65						
Total	100.15						

Notes: ZrO₂ <0.01 wt.%, TiO₂ <0.01 wt.%, Al₂O₃ <0.05 wt.%, V₂O₅ <0.01 wt.%, MoO₃ <0.01 wt.%, NiO <0.01 wt.%, MnO <0.01 wt.%, MgO <0.01 wt.%, Tl₂O <0.01 wt.%, K₂O <0.02 wt.%

n.d. = not determined; [§] calculated on the basis of (P+Si) = 1 a.p.f.u.; * calculated on the basis of (OH+F) = 1 a.p.f.u..

smaller crystal, with a KUMA four-circle diffractometer equipped with a point detector. A total of 46 reflections were centred giving a metrically monoclinic unit-cell with: $a = 9.7856(5)$, $b = 7.6607(5)$, $c = 4.8025(3)$ Å, $\beta = 90.02(3)^\circ$ and $V = 360.02(4)$ Å³ (Table 3).

Neutron-intensity data were collected at 293 K on the diffractometer VIVALDI at the Institut Laue-Langevin in Grenoble (France). VIVALDI operates in Laue geometry, with the crystal illuminated by a broad and continuous part of the incident thermal neutron spectrum; this increases the detected diffracted intensity by one to two orders of magnitude compared with a conventional monochromatic experiment. The diffractometer is equipped with a large solid-angle (8 sterad) cylindrical image-plate detector that encircles the crystal (McIntyre *et al.*, 2006). The larger crystal of hydroxylherderite was mounted with the two-fold axis well away from the single instrument rotation axis, in order to avoid bias in the final refined anisotropic displacement parameters due to the blind region in reciprocal space around the rotation axis. A total of 11 Laue diffraction patterns, each

accumulated over 25 min on average, were collected at an average of 17° intervals in rotation of the crystal perpendicular to the incident neutron beam. The diffraction patterns were then indexed using the program LAUEGEN, Daresbury Laboratory Laue Suite (Campbell, 1995; Campbell *et al.*, 1998), over a wavelength range of 0.78–5.2 Å and to a minimum d spacing of 0.46 Å. The intensities were then integrated using the program INTEGRATE+, which uses a two-dimensional version of the minimum $\sigma(I)/I$ algorithm (Wilkinson *et al.*, 1988). Correction for absorption was deemed unnecessary in view of the small fraction of absorbing elements. The intensities were normalized to the intensity of a common incident wavelength, using a curve derived by comparing equivalent reflections and corrected for the different angles of incidence via the program LAUE4 (Piltz, 2011). Only reflections with wavelengths between 0.85 Å and 1.70 Å were accepted for scaling, as those reflections outside this range were either considerably weaker (<0.85 Å) or likely to suffer large extinction (>1.70 Å). A total of 15,475 reflections were observed, of which 7369 were with

wavelengths between 0.85 Å and 1.70 Å, yielding 1761 unique reflections in the Laue class $2/m$ (Table 3). The reflection conditions suggested the space group $P2_1/a$.

Polarized Raman spectroscopy

Polarized Raman spectra of hydroxylherderite were collected using a 458 nm excitation laser focused through an Olympus-BX microscope with 100× objective lens and 18 mW power at the sample. Spectra were collected through a confocal

aperture into a 0.3 m Andor Shamrock-303 spectrograph with a holographic 1800 lines per mm diffraction grating, giving about 1 cm^{-1} spectral resolution. The CCD camera, Andor Newton DU970, was set to collect each spectrum for 30 s, with four accumulations each. A polarizer was placed before and after the sample to compare spectra using three different polarized angles, 0, 45 and 90° from an arbitrary reference plane. Peak deconvolution and fitting was carried out using the software package, *PeakFit*® (Systat Software Inc.).

TABLE 3. Details of neutron-data collection and refinement of hydroxylherderite.

Crystal shape	Rectangular prism
Crystal size (mm)	$3.1 \times 2.8 \times 1.8$
Crystal colour	Translucent white
Unit-cell parameters	$a = 9.7856(5)\text{ Å}$ $b = 7.6607(5)\text{ Å}$ $c = 4.8025(3)\text{ Å}$ $\beta = 90.02(3)^\circ$ $V = 360.02(4)\text{ Å}^3$
Chemical formula	$\text{CaBePO}_4(\text{OH}_{0.83}\text{F}_{0.17})$
Space group	$P2_1/a$
Z	4
ρ (g/cm ³)	2.972
T (K)	293
Radiation	Polychromatic, neutron
Diffractometer	VIVALDI, Laue diffractometer
$\lambda_{\text{min}}/\lambda_{\text{max}}$ (Å)	0.78/5.2
d_{min} (Å)	0.46 $-18 \leq h \leq 18$ $-15 \leq k \leq 13$ $-9 \leq l \leq 7$
No. measured reflections	15,475
No. measured reflections (between 0.85 Å and 1.70 Å)	7369
No. unique reflections	1761
No. unique refl. with $F_o > 4\sigma(F_o)$	1614
No. refined parameters	85
R_{int}	0.0644
R_σ	0.0448
R_1 (F) with $F_o > 4\sigma(F_o)$	0.0363
R_1 (F) for all the unique reflections	0.0427
wR_2 (F^2)	0.0663
GoF	1.814
Weighting Scheme: a, b	0.01, 0
Residuals (fm/Å ³)	± 0.8

Note: $R_{\text{int}} = \sum |F_{\text{obs}}^2 - F_{\text{obs}}^2(\text{mean})| / \sum [F_{\text{obs}}^2]$; $R_\sigma = \sum [\sigma(F_{\text{obs}}^2)] / \sum [F_{\text{obs}}^2]$; $R_1 = \sum |F_{\text{obs}} - |F_{\text{calc}}|| / \sum |F_{\text{obs}}|$; $wR_2 = [\sum [w(F_{\text{obs}}^2 - F_{\text{calc}}^2)^2] / \sum [w(F_{\text{obs}}^2)^2]]^{0.5}$, $w = 1 / [\sigma^2(F_{\text{obs}}^2) + (a*P)^2 + b*P]$, $P = (\text{Max}(F_{\text{obs}}^2, 0) + 2*F_{\text{calc}}^2) / 3$.
Unit-cell parameters from the X-ray study (see text for details).

Results

Neutron structure refinement of hydroxylherderite

The neutron-intensity data of hydroxylherderite were processed to calculate the normalized structure factors (E) and their statistical distributions using the program *E-STATISTICS*, implemented in the *WinGX* package (Farrugia, 1999). The structure was found to be centrosymmetric with 81.4% likelihood. A similar finding was obtained by the Sheldrick $|E^2-1|$ criterion (Sheldrick, 1997), which indicated that the structure is centrosymmetric ($|E^2-1| = 0.923$). The structure refinement was then performed in the space group $P2_1/a$ using the *SHELX-97* software (Sheldrick 1997, 2008), starting from the H-free structure model of Harlow and Hawthorne (2008). The neutron scattering lengths of Ca, Be, P, O, F and H have been used according to Sears (1986). As the Laue method does not allow precise estimation of the absolute volume of the unit cell, the refinement was conducted with the unit-cell parameters based on single-crystal XRD (Table 3). The effects of secondary isotropic extinction were corrected adequately by Larson's formalism (Larsen, 1967), implemented in *SHELXL-97*. The O5 site was first modeled with a mixed (O + F) scattering length and the fraction of O + F was refined. However, the use of F and O neutron scattering lengths to model the occupancy of the O5 site did not allow the refinement of the F/O fraction, due to the very similar F/O scattering lengths (i.e. 5.805 fm for O and 5.654 fm for F). Further cycles of the refinement were thus conducted modelling the O5 site with the scattering length of O alone, with an unconstrained site occupancy factor (s.o.f., Table 4). When convergence was achieved, the largest negative residual peak was found at $x \approx 0.419$, $y \approx 0.457$, $z \approx 0.130$ in the final difference-Fourier map of the nuclear density. The final cycles of anisotropic refinement were then conducted assigning H to this residual peak (as H has a negative neutron scattering length). Convergence was achieved rapidly with: (1) all the principal mean-square atomic displacement parameters defined positively (H included); (2) no significant correlation among the refined parameters in the variance-covariance matrix; (3) no peak larger than $\pm 0.8 \text{ fm}\cdot\text{\AA}^3$ in the final difference-Fourier map of the nuclear density (Table 3); (4) the final agreement index $R_1 = 0.0363$ for 85 refined parameters and 1614 unique

TABLE 4. Site coordinates, site occupancy factor (s.o.f.) and anisotropic displacement parameters ($\text{\AA}^2$) of hydroxylherderite. The anisotropic displacement factor exponent takes the form: $-2\pi^2[(ha*)^2U^{11} + \dots + 2hka*b*U^{12}]$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Site	s.o.f.	x	y	z	U_{eq}	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ca	1.0	0.33105(6)	0.11140(7)	0.99740(11)	0.0088(1)	0.0084(3)	0.0089(2)	0.0091(2)	-0.0009(1)	0.0014(2)	-0.0014(1)
Be	1.0	0.33893(4)	0.41390(4)	0.53513(6)	0.00790(7)	0.0075(2)	0.0076(1)	0.0086(1)	-0.0001(1)	0.0011(1)	0.0000(1)
P	1.0	0.08136(5)	0.27109(5)	0.47045(10)	0.00606(9)	0.0053(2)	0.0059(2)	0.0069(2)	-0.0001(1)	0.0009(2)	0.0000(1)
O1	1.0	0.03960(5)	0.39878(5)	0.24679(9)	0.00935(9)	0.0094(2)	0.0084(2)	0.0102(2)	0.0005(1)	0.0003(2)	0.0024(1)
O2	1.0	0.45868(5)	0.28353(5)	0.65239(9)	0.00862(9)	0.0072(2)	0.0091(2)	0.0096(2)	0.0022(1)	0.0025(1)	0.0011(1)
O3	1.0	0.19329(5)	0.34467(6)	0.66626(9)	0.00902(9)	0.0069(2)	0.0114(2)	0.0088(2)	-0.0023(1)	0.0006(2)	-0.0009(1)
O4	1.0	0.14216(5)	0.10671(5)	0.32955(9)	0.00935(9)	0.0109(2)	0.0065(2)	0.0107(2)	0.0016(1)	0.0033(2)	-0.0001(1)
O5	0.998(4)	0.33381(6)	0.41306(6)	0.20330(9)	0.0103(2)	0.0104(3)	0.0120(2)	0.0083(2)	0.0006(1)	0.0002(2)	0.0003(1)
H	0.835(9)	0.41950(15)	0.45665(21)	0.13028(29)	0.0286(5)	0.0196(8)	0.0374(8)	0.0288(7)	-0.0073(5)	0.0078(5)	0.0041(5)

TABLE 5. Principal root-mean-square components (R1, R2 and R3, $\times 10^2$ Å) of the atomic displacement parameters.

Site	R1	R2	R3	R1/R3
<i>Ca</i>	10.63(9)	8.8(1)	8.5(1)	1.24
<i>Be</i>	9.59(5)	8.72(6)	8.2(1)	1.16
<i>P</i>	8.5(1)	7.68(7)	7.0(1)	1.22
<i>O1</i>	10.95(5)	9.7(1)	8.2(1)	1.34
<i>O2</i>	11.22(9)	9.06(6)	7.1(1)	1.57
<i>O3</i>	11.22(9)	9.2(1)	7.7(1)	1.45
<i>O4</i>	11.96(8)	9.1(1)	7.48(7)	1.60
<i>O5</i>	11.04(9)	10.1(1)	9.1(1)	1.21
<i>H</i>	20.0(2)	18.2(2)	11.1(4)	1.80

reflections with $F_o > 4\sigma(F_o)$ (Table 3). Atomic coordinates and their displacement parameters are listed in Tables 4 and 5, bond lengths and angles in Table 6. A crystallographic information file (CIF) has been deposited with the Principal Editor of *Mineralogical Magazine* and is available from www.minersoc.org/pages/e_journals/dep_mat_mm.html.

Raman spectrum of hydroxylherderite

An unpolarized Raman spectrum of hydroxylherderite from 0–3800 cm^{-1} is shown in Fig. 2. For the purpose of this discussion, the Raman spectra

will be broken down into three spectral regions: a low-wavenumber region 0–500 cm^{-1} (Fig. 3), where external (lattice) mode vibrations dominate, a mid-wavenumber region at 500–1200 cm^{-1} (Fig. 4), where phosphate vibrational modes are present and a high-wavenumber region at 3400–3800 cm^{-1} where O–H vibrational modes are observed (Figs 5 and 6). No Raman peaks were observed between 1200 and 3400 cm^{-1} and the absence of H–O–H bending modes at 1500–1700 cm^{-1} confirms that there is no molecular H_2O in the structure. A table of observed Raman modes and band assignments after Frost *et al.* (2014) are presented in Table 7.

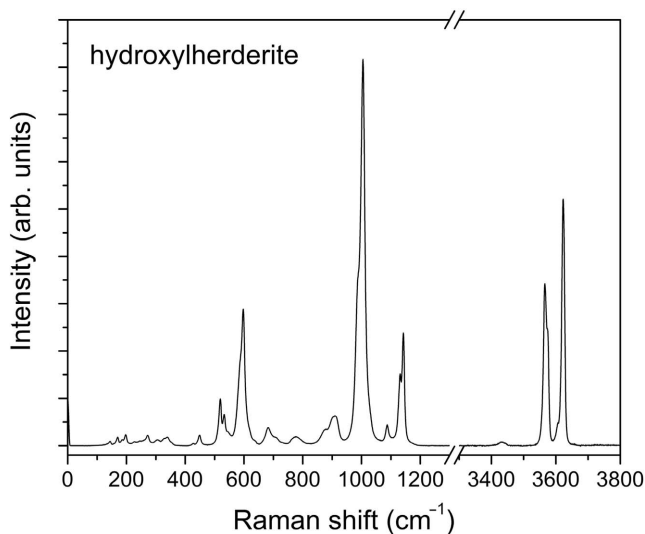


FIG. 2. Unpolarized Raman spectrum of hydroxylherderite.

CRYSTAL CHEMISTRY OF HYDROXYLHERDERITE

TABLE 6. Relevant interatomic distances (Å) and angles (°) in the hydroxylherderite structure.

<i>Ca</i> — <i>O</i> 1	2.3731(8)	<i>P</i> — <i>O</i> 1	1.5091(7)
<i>Ca</i> — <i>O</i> 1'	2.3672(11)	<i>P</i> — <i>O</i> 2	1.5429(7)
<i>Ca</i> — <i>O</i> 2	2.4588(8)	<i>P</i> — <i>O</i> 3	1.5495(8)
<i>Ca</i> — <i>O</i> 3	2.7456(9)	<i>P</i> — <i>O</i> 4	1.5485(6)
<i>Ca</i> — <i>O</i> 3'	2.6157(7)	< <i>P</i> — <i>O</i> >	
<i>Ca</i> — <i>O</i> 4	2.4422(9)	<i>O</i> 1— <i>P</i> — <i>O</i> 2	111.61(4)
<i>Ca</i> — <i>O</i> 5	2.5137(7)	<i>O</i> 1— <i>P</i> — <i>O</i> 3	112.79(4)
<i>Ca</i> — <i>O</i> 5'	2.4165(9)	<i>O</i> 1— <i>P</i> — <i>O</i> 4	108.67(4)
< <i>Ca</i> — <i>O</i> >		<i>O</i> 2— <i>P</i> — <i>O</i> 3	107.74(4)
		<i>O</i> 2— <i>P</i> — <i>O</i> 4	109.03(4)
<i>Be</i> — <i>O</i> 2	1.6393(7)	<i>O</i> 3— <i>P</i> — <i>O</i> 4	106.82(4)
<i>Be</i> — <i>O</i> 3	1.6461(6)	<i>O</i> 1— <i>O</i> 2	2.5245(6)
<i>Be</i> — <i>O</i> 4	1.6242(5)	<i>O</i> 1— <i>O</i> 3	2.5475(9)
<i>Be</i> — <i>O</i> 5	1.5944(6)	<i>O</i> 1— <i>O</i> 4	2.4842(6)
< <i>Be</i> — <i>O</i> >		<i>O</i> 2— <i>O</i> 3	2.4978(7)
<i>O</i> 2— <i>Be</i> — <i>O</i> 3	106.93(3)	<i>O</i> 2— <i>O</i> 4	2.5172(8)
<i>O</i> 2— <i>Be</i> — <i>O</i> 4	109.59(4)	<i>O</i> 3— <i>O</i> 4	2.4875(7)
<i>O</i> 2— <i>Be</i> — <i>O</i> 5	111.29(3)		
<i>O</i> 3— <i>Be</i> — <i>O</i> 4	103.80(3)	<i>O</i> 5— <i>H</i>	0.968(2)
<i>O</i> 3— <i>Be</i> — <i>O</i> 5	110.74(4)	<i>O</i> 5— <i>H</i> *	0.996(2)
<i>O</i> 4— <i>Be</i> — <i>O</i> 5	114.02(3)		
<i>O</i> 2— <i>O</i> 3	2.6398(7)	<i>O</i> 5... <i>O</i> 2	3.163(1)
<i>O</i> 2— <i>O</i> 4	2.6666(6)	<i>H</i> ... <i>O</i> 2	2.544(2)
<i>O</i> 2— <i>O</i> 5	2.6697(9)	<i>O</i> 5— <i>H</i> ... <i>O</i> 2	121.8(1)
<i>O</i> 3— <i>O</i> 4	2.5735(6)		
<i>O</i> 3— <i>O</i> 5	2.6666(8)	<i>O</i> 5... <i>O</i> 4	3.081(1)
<i>O</i> 4— <i>O</i> 5	2.6998(6)	<i>H</i> ... <i>O</i> 4	2.428(2)
		<i>O</i> 5— <i>H</i> ... <i>O</i> 4	124.4(1)

Interatomic distance corrected for “riding motion” following Busing and Levy (1964).

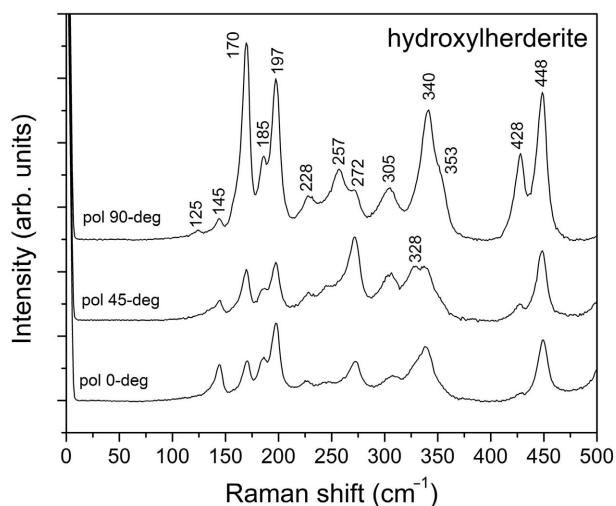


FIG. 3. Raman spectra of hydroxylherderite in the low-wavenumber region using three different polarizations of the incident laser.

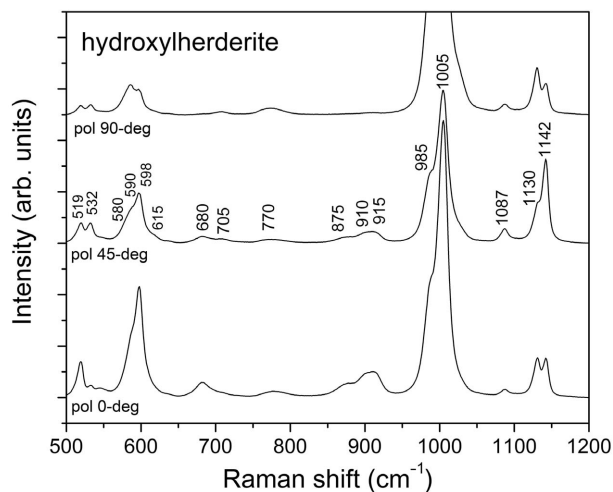


FIG. 4. Raman spectra of hydroxylherderite in the mid-wavenumber region using three different polarizations of the incident laser.

Discussion

The EPMA-WDS and ICP-AES results of this study are mutually consistent (Tables 1 and 2), showing that the chemical composition of the hydroxylherderite from the Bennett pegmatite is close to $\text{CaBePO}_4(\text{OH}_{0.67}\text{F}_{0.33})$. Ca can be replaced by a small amount of Na ($<0.003\text{--}0.008$ a.p.f.u., Tables 1 and 2) and P by Si ($<0.01\text{--}0.03$ a.p.f.u., Tables 1 and 2). These experimental findings agree with the previous

results of Leavens *et al.* (1978) and Harlow and Hawthorne (2008). The unit-cell parameters of the hydroxylherderite in this study, measured by single-crystal XRD, confirm the general trend between cell parameters and OH content reported by Lager and Gibbs (1974), Leavens *et al.* (1978), Harlow and Hawthorne (2008) and in the RRUFF database (Downs and Hall-Wallace, 2003; <http://rruff.info>): the β angle and the b -cell parameter tend to decrease with increasing the OH content,

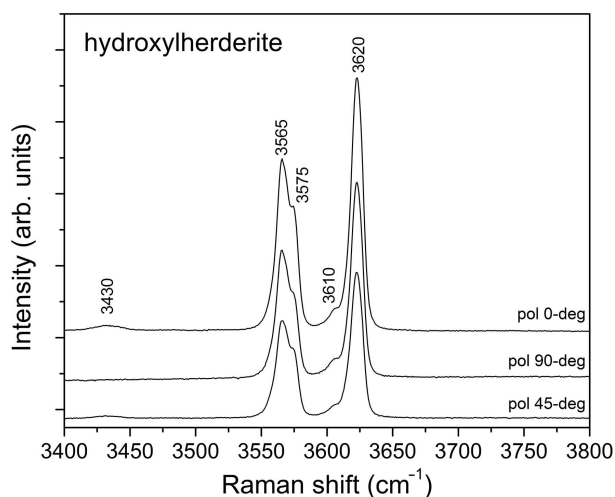


FIG. 5. Raman spectra of hydroxylherderite in the high-wavenumber region using three different polarizations of the incident laser.

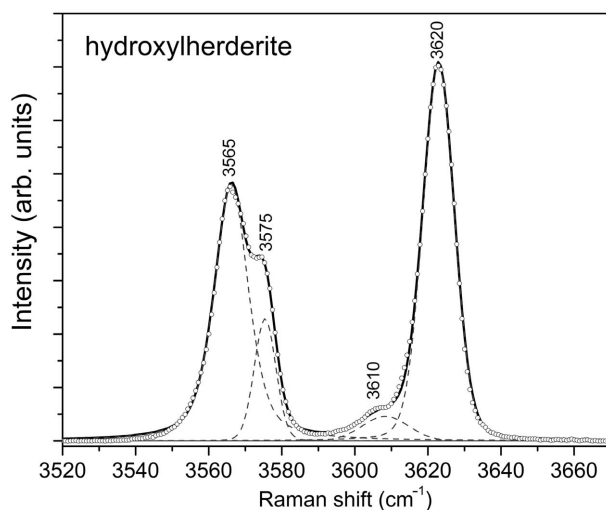


FIG. 6. Deconvolution of Raman modes in the O–H stretching region of hydroxylherderite.

whereas a and c increase, which results in a positive correlation between unit-cell volume and OH content. However, the low number and the scattering of data available in the literature are not sufficient to derive a reliable function which correlates unit-cell parameters vs. F content.

The neutron-structure refinement of the present study confirms the general structure model of hydroxylherderite refined previously by XRD (e.g. Lager and Gibbs, 1974; Harlow and Hawthorne, 2008). The Be and P tetrahedra are distorted significantly, as the differences between the longest and the shortest bond length ($\Delta_{\max}$) are: $\Delta_{\max}(\text{Be}) \approx 0.052 \text{ \AA}$ and $\Delta_{\max}(\text{P}) \approx 0.039 \text{ \AA}$ (Table 6). Even the differences between the maximum and the minimum intra-tetrahedral $O\text{--}T\text{--}O$ angle of the Be- and P-tetrahedra

reflect a significant distortion, being $\sim 7.1^\circ$ and $\sim 6.0^\circ$, respectively. More pronounced is the Ca-polyhedron distortion, with bond-distances ranging between ~ 2.37 and $\sim 2.74 \text{ \AA}$ (i.e. $\Delta_{\max}(\text{Ca}) \approx 0.4 \text{ \AA}$, Table 6). Similar findings can be deduced on the basis of the data reported by Lager and Gibbs (1974) and Harlow and Hawthorne (2008), based on X-ray structure refinements.

The neutron structure refinement shows that in hydroxylherderite only one independent H site occurs, bonded to $O5$ and with $O5\text{--}H$ distance, corrected for “riding motion” (Busing and Levy, 1964), of $0.996(2) \text{ \AA}$ (Table 6). The principal root-mean-square components of the H -site displacement parameters are fairly anisotropic due to bifurcation of the H bond (Table 5). The

TABLE 7. Frequencies of Raman bands of hydroxylherderite observed in this study.

Assignment*	Frequency (cm^{-1})
Lattice vibrations	125, 145, 170, 185, 197, 228, 257, 272
CaO and BaO stretching modes	305, 328, 340, 353
PO_4^{3-} ν_2 symmetric bending	428, 448, 519, 532
PO_4^{3-} ν_4 out-of-plane bending	580, 590, 598, 615
Unassigned	680, 705, 770, 875, 910, 915
PO_4^{3-} ν_1 symmetric stretching	985, 1005
PO_4^{3-} ν_3 antisymmetric stretching	1087, 1130, 1142
O–H stretching bands	3565, 3575, 3610, 3620

* Band assignments after Frost *et al.* (2014).

refinement conducted with unconstrained *H*-site occupancy leads to a refined s.o.f. of 83(1)% (Table 4), with a resulting chemical formula of $\text{CaBePO}_4(\text{OH}_{0.83}\text{F}_{0.17})$. There is a significant difference between the analytical chemical formula (i.e. $\text{CaBePO}_4(\text{OH}_{0.67}\text{F}_{0.33})$; Tables 1 and 2) and that deduced by the structure refinement. The neutron structure refinement cannot provide unambiguously the F/O fraction at *O5*. Fixing the F/O fraction on the basis of the EPMA-WDS and ICP-AES findings, the refinement converges, though a slightly worse agreement is observed with the fraction of H fixed to 67%. As the fragments used for the EPMA-WDS, ICP-AES and neutron diffraction experiments come from the same large crystal, which appears to be chemically homogeneous on the basis of the EPMA-WDS data, it is unclear why the OH content estimated by EPMA-WDS and ICP-AES are different from the neutron structure refinement. However, a variation of the F content in such a large crystal as that used for this multi-methodological study cannot be excluded.

The H-bonding scheme in hydroxylherderite is now well defined: only two significantly weak (long) H bonds, energetically favourable, have been found with *O2* and *O4* as ‘acceptors’ and with *O5*...*O2* = 3.163(1) Å, *H*...*O2* = 2.544(2) Å and H-bond angle *O5*–*H*...*O2* = 121.8(1)°; *O5*...*O4* = 3.081(1) Å, *H*...*O4* = 2.428(2) Å and H-bond angle *O5*–*H*...*O4* = 124.4(1)° (Table 6). The bifurcated configuration of the H-bonding scheme is shown in Fig. 7. The H-bonding geometry in hydroxylherderite is similar to that of datolite [ideally $\text{CaBSiO}_4(\text{OH})$], which shares the same framework topology (Rinaldi *et al.*, 2010). In datolite, only one independent *H* site occurs and its refined position (by single-crystal X-ray refinement, Rinaldi *et al.*, 2010) suggests a bifurcated H-bonding scheme with *O5* as ‘donor’ and *O4* and *O2* as ‘acceptors’ (with *O5*–*H* ≈ 0.8 Å and (1) *O5*...*O4* ≈ 2.99 Å, *H*...*O4* ≈ 2.33 Å and *O5*–*H*...*O4* ≈ 140° and (2) *O5*...*O2* ≈ 2.96 Å, *H*...*O2* ≈ 2.36 Å and *O5*–*H*...*O2* ≈ 131°).

Figure 3 shows a detail of the Raman low-wavenumber region collected on the same point of an un-oriented crystal using three different polarizations, labelled ‘pol 0-deg’, ‘pol 45-deg’ and ‘pol 90-deg’ relative to an arbitrary reference polarization. Below 300 cm^{-1} , eight bands can be observed with variable intensity depending on the polarization at 125, 145, 170, 185, 197, 228, 257 and 272 cm^{-1} . Except for the newly observed band at 125 cm^{-1} , which only occurs in the

90-deg polarized spectrum, these bands also correspond to peaks reported by Frost *et al.* (2014), though band assignments were not made. Four strongly polarizable peaks are observed between 300–350 cm^{-1} , at 305, 328, 340 and 353 cm^{-1} , which are attributed to BeO and CaO stretching vibrations (Frost *et al.*, 2014).

A comparison with a number of different phosphate minerals (Frezzotti *et al.*, 2012) suggests that the bands observed in Fig. 3 at 428 and 448 cm^{-1} , as well as possibly those at 519 and 532 cm^{-1} shown in Fig. 4, are attributed to ν_2 in-plane bending vibrations of the phosphate (PO_4)^{3−} and H phosphate $\text{H}\cdots\text{OPO}_3^{3−}$ units with reduced symmetry (Frost *et al.*, 2014). However, main bands are also in the 520–550 cm^{-1} region of many borates (Frezzotti *et al.*, 2012), so the assignment of 519 and 532 cm^{-1} to ν_2 of phosphate groups is tentative. In the measured plane, the 428 cm^{-1} band is considerably more polarizable than the 448 cm^{-1} band (Fig. 3). In the 580–650 cm^{-1} range (Fig. 4), four bands were deconvolved at 580, 590, 598 and 615 cm^{-1} , which are attributed to the ν_4 out-of-plane bending vibrations of the phosphate and H-phosphate units with reduced symmetry (Frost *et al.*, 2014).

Figure 4 shows that the most intense and sharp band in the mid-wavenumber region occurs at 1005 cm^{-1} , with a strong shoulder centred at

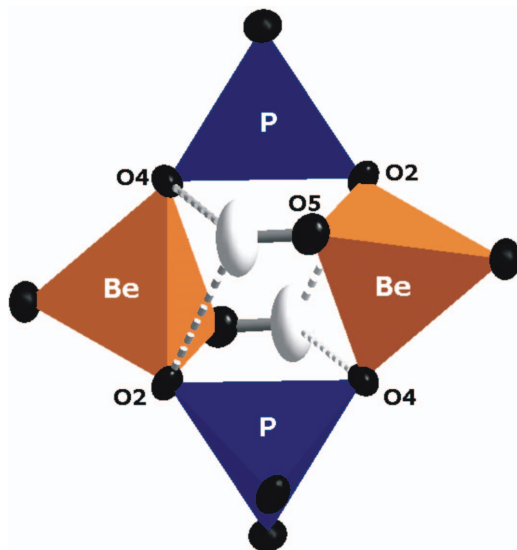


FIG. 7. Hydrogen-bonding scheme in hydroxylherderite based on the neutron structure refinement of this study. Displacement ellipsoid probability factor: 90%.

985 cm^{-1} in the deconvolved fit. In herderite, bands at 983 and 1005 cm^{-1} observed by Rickers *et al.* (2006) were assigned to phosphate ν_1 (symmetric stretching vibration) and ν_3 (antisymmetric stretching vibration) modes, respectively, by Frezzotti *et al.* (2012). In contrast, Frost *et al.* (2014) assigned the $\sim 1000 \text{ cm}^{-1}$ peak, which varied from 998 to 1006 cm^{-1} between three samples, to the ν_1 symmetric stretch of PO_4^{3-} units, with the 985 cm^{-1} band being assigned to the stretching mode of HOPO_3^{3-} units. Whether or not the 985 and 1005 cm^{-1} bands correspond to the ν_1 and ν_3 vibrations of PO_4^{3-} (Rickers *et al.*, 2006) or two ν_1 modes (phosphate and H phosphate; Frost *et al.*, 2014) is thus uncertain. There are three additional bands at 1087, 1130 and 1142 cm^{-1} (Fig. 4), corresponding to bands at 1085, 1128 and 1138 cm^{-1} in Frost *et al.* (2014), which are attributed to ν_3 antisymmetric stretching modes of phosphate and hydrogen-phosphate units by Frost *et al.* (2014).

Figure 5 shows Raman spectra of hydroxylherderite for three different polarizations in the O–H stretching region. Unlike many bands in the low or mid-wavenumber region, major differences of intensity in the O–H bands with varying polarization are not observed. Two main features are in the O–H region, with one sharp band at 3620 cm^{-1} and a split band with peaks at 3565 and 3575 cm^{-1} . A weak shoulder of the 3620 cm^{-1} band occurs at 3610 cm^{-1} and an additional band is at 3430 cm^{-1} , which does vary with polarization. In general, these bands are in agreement with modes observed by Frost *et al.* (2014) at 3623 cm^{-1} , shoulder at 3609 cm^{-1} and a split peak at 3568 and 3587 cm^{-1} ; however Frost *et al.* (2014) did not report seeing the 3430 cm^{-1} band. The deconvolved fitting of O–H stretching modes is shown in Fig. 6.

The modes observed in the O–H stretching region suggest at least four distinct H-bonding environments. The findings in the neutron-structure refinement were: (1) only one independent proton site with two different H bonds (with O2 and O4 as ‘acceptors’); (2) no evidence of Be/P disorder between the tetrahedral sites. However, the EPMA-WDS and ICP-AES data show a small, but significant, amount of Si that probably replaces P at the tetrahedral site (Si/P a.p.f.u. = 0.01–0.03, Tables 1 and 2). Though in small quantities, Si appears to be a common element in herderite–hydroxylherderite (e.g. Harlow and Hawthorne, 2008). Where Si replaces P, the two O atoms O2 and O4 of the

tetrahedron, i.e. both ‘acceptors’ of the H bond, will be displaced from their average position, as $\text{Si}-\text{O} > \text{P}-\text{O}$. On this basis, at least four different environments for the H bonding can be predicted. A substitution of 1–3% cannot be detected unambiguously by a structure refinement of diffraction data. In contrast, the effects of such a substitution can be detected clearly by Raman spectroscopy. In addition, there is a weak band at a significantly lower wavenumber at $\sim 3430 \text{ cm}^{-1}$ (Fig. 6, Table 7), which might be ascribed to a Si–OH group (silanol).

Concluding remarks

This paper contributes to a series on H bonding in Be silicates (Gatta *et al.*, 2008, 2012, 2014), showing that neutron diffraction is an effective tool for determining the H positions in mineral structures. In hydroxylherderite, the H position has been located and a single H site found with a very weak (long) and bifurcated H bond, which allows significant substitution of F along the solid solution herderite–hydroxylherderite, although no natural samples of pure herderite have been reported. Hydroxylherderite contains highly non-linear H bonding, which prohibits easy correlation of H-bonding geometry with spectroscopy (Libowitzky, 1999; Libowitzky and Beran, 2006). By combining single-crystal neutron-diffraction data with Raman spectroscopy, this work contributes further data for correlating non-linear H-bonding geometry to OH-stretching frequencies.

If the experimental findings of this study on hydroxylherderite are compared to the structural data reported recently on the isotypic datolite by Rinaldi *et al.* (2010), the highly non-linear O–H...O angles found in hydroxylherderite and datolite appear to be governed by the structure topology, irrespective of their crystal chemistry.

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