



A crystal structure refinement of uralolite, $\text{Ca}_2\text{Be}_4(\text{PO}_4)_3(\text{OH})_3 \cdot 5\text{H}_2\text{O}$, from Weinebene, Austria

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Abstract

The crystal structure of uralolite, $\text{Ca}_2\text{Be}_4(\text{PO}_4)_3(\text{OH})_3 \cdot 5\text{H}_2\text{O}$, from the spodumene deposit of Weinebene, Carinthia, Austria, has been refined with X-ray single crystal data gathered on a CCD diffractometer. Uralolite is monoclinic, space group $P2_1/n$, $a = 6.553(1)$, $b = 16.005(3)$, $c = 15.979(3)$ Å, $\beta = 101.63(1)^\circ$, $V = 1641.5(5)$ Å³. While previously only isotropic displacement parameters and no hydrogen atom positions were reported for uralolite, now anisotropic displacement parameters were used for non-hydrogen atoms and hydrogen atoms were located and refined yielding $R_1 = 0.038$ for 3909 observed reflections. Uralolite is built up from corrugated layers $[\text{Be}_4(\text{PO}_4)_3(\text{OH})_3]^{4+}$ parallel to (010), which contain Z-shaped groups of four BeO_4 tetrahedra sharing corners via three OH groups and are further crosslinked by PO_4 tetrahedra. Two Ca atoms in $\text{Ca}(\text{O}_{\text{phosphate}})_5(\text{H}_2\text{O})_2$ coordination and an interstitial water molecule link these layers along [010]. The OH groups and the Ca-bonded H_2O molecules are all involved in hydrogen bonds with O...O distances of 2.780(2) – 3.063(2) Å and O-H...O angles of 150(1) – 179(1)° excluding a bifurcated bond. The interstitial water molecule displays a distorted tetrahedral environment of O atoms and accepts and donates each two hydrogen bonds. The crystal structure exhibits a $C2/c$ pseudosymmetry for the $[\text{Be}_4(\text{PO}_4)_3(\text{OH})_3]^{4+}$ layers and the Ca atoms. However, the disposition of the water molecules and an asymmetric hydrogen bond pattern involving OH groups as well as H_2O molecules are decisive for the lowering of the symmetry of the structure to the true space group $P2_1/n$.

Keywords Uralolite · Berylllophosphate · Structure refinement · Hydrogen bonding

Introduction

Uralolite is a rare hydrated calcium beryllium phosphate occurring in fibrous aggregates of minute acicular to lath-like crystals in fractures of the Weinebene spodumene pegmatites, Carinthia, Austria. A description of this deposit based on extensive pre-mining exploration was reported by Göd (1989). A rich variety of about 30 primary and more than 30 secondary minerals and their paragenetic relationships have been reported from this deposit

(Niedermayr and Göd 1992; Taucher et al. 1992, 1994). The presently known Be-bearing minerals of this deposit comprise primary beryl, $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{12}$, and secondary/tertiary uralolite, $\text{Ca}_2\text{Be}_4(\text{PO}_4)_3(\text{OH})_3 \cdot 5\text{H}_2\text{O}$, weinebeneite, $\text{CaBe}_3(\text{PO}_4)_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ (type locality; Walter 1992), roscherite $\text{Ca}_2\text{Mn}^{2+}_5\text{Be}_4(\text{PO}_4)_6(\text{OH})_4 \cdot 6\text{H}_2\text{O}$, hydroxylherderite, $\text{CaBe}(\text{PO}_4)(\text{OH})$, and bavenite, $\text{Ca}_4\text{Be}_2\text{Al}_2\text{Si}_9\text{O}_{26}(\text{OH})_2$ (Taucher et al. 1992; Niedermayr and Göd 1992). The deposit is currently of significant economic interest for the mining of spodumene ore and production of lithium ion battery grade Li_2CO_3 and $\text{LiOH} \cdot 2\text{H}_2\text{O}$ (European Lithium Ltd 2020). Only nine further occurrences of uralolite are known at present (Mindat.org 2022) and all of them with very small amounts in pegmatitic settings (Grigoriev 1964; Dunn and Gaines 1978). The properties and crystal structure of uralolite from Weinebene were previously reported by Mereiter et al. (1994). This work was based on single crystal diffraction data recorded with a Philips PW1100 four-circle diffractometer and a scintillation probe as point detector. With space group $P2_1/n$, $a = 6.550(1)$, $b = 16.005(3)$, $c = 15.969(3)$

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\AA , $\beta = 101.64(2)^\circ$, $Z = 4$ $\text{Ca}_2\text{Be}_4(\text{PO}_4)_3(\text{OH})_3 \cdot 5\text{H}_2\text{O}$, it yielded $R_1 = 0.058$ for 1651 observed out of 2878 independent reflections ($\theta_{\text{max}} = 25^\circ$, $\text{MoK}\alpha$ radiation, 117 refined parameters). Due to a pronounced pseudosymmetry of the crystal structure with space group $C2/c$ for a *zellengleiche* pseudostructure, hkl reflections with $h + k = 2n + 1$ were systematically weak. In order to overcome parameter correlation effects only isotropic displacement parameters were applied in this work and hydrogen atoms could not be located. With this situation in mind, it was considered worthwhile to refine the crystal structure of uralolite with CCD detector diffraction data using a larger data set with more $h + k = 2n + 1$ reflections in order to apply anisotropic displacement parameters for non-hydrogen atoms and to locate the hydrogen atoms.

Experimental

Using a crystal preserved from the previous study (Mereiter et al. 1994), X-ray diffraction data were collected with a Bruker Smart CCD diffractometer and graphite monochromatized $\text{MoK}\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$, from a sealed tube. A crystal measuring $0.28 \times 0.08 \times 0.02 \text{ mm}$ was applied to collect six ω -scan frame sets covering a full sphere of the reciprocal space up to $\theta_{\text{max}} = 30.1^\circ$. The raw data were integrated and processed with the program *SAINTE* (Bruker 1999) and were then corrected for absorption with the multi-scan method using program *SADABS* (Bruker 1999). The resulting 38377 data were then merged to 4823 unique reflections ($R_{\text{merge}} = 0.050$). Structure refinement was carried out with program *SHELXL* (Sheldrick 2015). Anisotropic temperature factors for non-hydrogen atoms were applied before a difference Fourier synthesis revealed clearly 12 of the 13 expected hydrogen atoms. The missing hydrogen atom, belonging to the interstitial water molecule of O5w, was obscured by relatively large anisotropic displacement effects of this oxygen atom, but could be reasonably inferred by geometric considerations (distorted tetrahedral environment of O5w by two H-bond donors and two adequate H-bond acceptors). All hydrogen atoms were then included in the refinement, at first unrestrained (O-H = 0.78(4) to 1.00(6) \AA , mean value 0.86 \AA ; $U_{\text{iso}} = 0.03\text{--}0.15 \text{ \AA}^2$), and then with geometric restraints: The O-H distances were fixed at 0.85 \AA and H-O-H angles at 108° using hard DFIX restraints. The isotropic displacement parameters of the H atoms were divided into three groups – hydroxyl groups, water molecules of O1w to O4w, and water molecule of O5w – and each group was refined with a common U_{iso} . These procedures were considered as useful in obtaining the most reliable and consistent information on hydrogen bonding. A check of the occupancy of the interstitial water molecule of O5w gave a population factor of 0.99(1) indicating that there is no

deficiency. The final refinement converged at $R_1 = 0.0380$ for 3909 $F_o > 4\sigma(F_o)$. Crystallographic data are summarized in Table 1, atomic parameters are given in Tables 2 and 3. Selected bond lengths and bond angles are presented in Table 4, and hydrogen bond data are reported in Table 5. A crystallographic information file (CIF) with structure factors is available as electronic supplementary material. Structural graphics was generated with programs *MERCURY* (Macrae et al. 2006) and *DIAMOND* (Brandenburg 2012).

Discussion

The present study confirms the previous structure determination of Mereiter et al. (1994) but provides now very satisfactory anisotropic displacement parameters for non-hydrogen atoms, hydrogen atom positions, and an improvement in the precision of atomic positions and bond lengths. Although the e.s.d.s for bond lengths to Ca, Be, and P are reduced to about one third of their former values (Mereiter et al. 1994), the changes in geometric parameters

Table 1 Crystal data and structure refinement for uralolite

Chemical formula	$\text{Ca}_2\text{Be}_4(\text{PO}_4)_3(\text{OH})_3 \cdot 5\text{H}_2\text{O}$
Formula weight	542.21
Temperature	297(2) K
Wavelength	0.71073 \AA
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 6.553(1) \text{ \AA}$ $\alpha = 90^\circ$ $b = 16.005(3) \text{ \AA}$ $\beta = 101.63(1)^\circ$ $c = 15.979(3) \text{ \AA}$ $\gamma = 90^\circ$ $V = 1641.5(5) \text{ \AA}^3$
Z	4
Density (calculated)	2.194 Mg/m^3
Absorption coefficient	1.093 mm^{-1}
$F(000)$	1096
Crystal size	$0.28 \times 0.08 \times 0.02 \text{ mm}^3$
θ range for data collection	1.82 to 30.09°
Index ranges	$-9 \leq h \leq 9$, $-22 \leq k \leq 22$, $-22 \leq l \leq 22$
Reflections collected	38377
Independent reflections	4823 [$R_{\text{int}} = 0.050$]
Absorption correction	Semi-empirical from equivalents
Transmission	0.82 - 0.96
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4823 (3909 with $I > 2\sigma(I)$) / 22 / 304
Goodness-of-fit on F^2	1.116
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0380$, $wR_2 = 0.0782$
R indices (all data)	$R_1 = 0.0538$, $wR_2 = 0.0839$
Largest difference peak and hole	0.59 and -0.49 e \AA^{-3}

Table 2 Atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2) for uralolite

Atom	x	y	z	$U_{\text{eq}}/U_{\text{iso}}$
Ca1	0.87841(7)	0.08287(3)	0.06763(3)	0.01074(9)
Ca2	0.11495(7)	0.08369(3)	0.43884(3)	0.01155(10)
Be1	0.2398(4)	0.26152(18)	0.12751(17)	0.0093(5)
Be2	0.5923(4)	0.16560(18)	0.17784(17)	0.0097(5)
Be3	0.4162(4)	0.16208(18)	0.33176(17)	0.0105(5)
Be4	0.7637(4)	0.26486(18)	0.38608(17)	0.0093(5)
P1	0.31246(8)	0.11545(3)	0.03228(3)	0.00735(11)
P2	0.68992(8)	0.12317(3)	0.48463(3)	0.00780(11)
P3	0.00586(9)	0.21818(3)	0.25743(3)	0.00776(10)
O1	0.1775(2)	0.17157(10)	0.07859(10)	0.0120(3)
O2	0.5352(2)	0.11183(10)	0.08707(9)	0.0109(3)
O3	0.3180(3)	0.14937(10)	-0.05699(10)	0.0125(3)
O4	0.2093(2)	0.03011(10)	0.02492(10)	0.0127(3)
O5	0.8296(2)	0.18080(10)	0.44152(10)	0.0111(3)
O6	0.4767(2)	0.11259(10)	0.42332(10)	0.0121(3)
O7	0.6522(3)	0.16129(11)	0.56729(10)	0.0159(3)
O8	0.8080(3)	0.04204(10)	0.50107(11)	0.0154(3)
O9	0.1251(2)	0.27449(10)	0.20707(10)	0.0117(3)
O10	-0.1533(2)	0.16443(10)	0.19580(10)	0.0114(3)
O11	0.1614(2)	0.15929(10)	0.31561(10)	0.0118(3)
O12	-0.1014(2)	0.27411(10)	0.31295(10)	0.0123(3)
O1h	0.4911(2)	0.25844(9)	0.16316(10)	0.0111(3)
O2h	0.5145(2)	0.25675(10)	0.34449(9)	0.0109(3)
O3h	0.5043(2)	0.11826(9)	0.25425(9)	0.0120(3)
O1w	0.7724(2)	0.17108(15)	-0.05040(13)	0.0381(6)
O2w	0.9397(3)	-0.03259(11)	0.16825(11)	0.0288(5)
O3w	0.2411(2)	0.13029(10)	0.58450(11)	0.0213(4)
O4w	-0.1435(3)	0.01218(11)	0.32615(10)	0.0250(4)
O5w	0.1310(3)	0.44476(14)	0.28778(14)	0.0687(10)
H1h	0.5623(7)	0.2932(3)	0.1408(4)	0.061(8)
H2h	0.500(3)	0.2762(5)	0.29412(18)	0.061(8)
H3h	0.4639(15)	0.0684(2)	0.2427(7)	0.061(8)
H1a	0.8381(4)	0.1938(4)	-0.0852(2)	0.070(5)
H1b	0.6432(2)	0.1723(7)	-0.0727(4)	0.070(5)
H2a	0.8707(5)	-0.0726(2)	0.1412(4)	0.070(5)
H2b	1.0646(3)	-0.0490(3)	0.1851(5)	0.070(5)
H3a	0.3680(3)	0.1444(3)	0.5892(5)	0.070(5)
H3b	0.2375(7)	0.08461(17)	0.6113(3)	0.070(5)
H4a	-0.2471(4)	0.0442(2)	0.3094(3)	0.070(5)
H4b	-0.1091(6)	-0.0091(3)	0.28226(16)	0.070(5)
H5a	0.0383(4)	0.4251(3)	0.31265(19)	0.32(5)
H5b	0.1619(4)	0.4072(2)	0.25488(13)	0.32(5)

are small and do not warrant a detailed comparison with the earlier values (Table 4). An important result is the clarification of the hydrogen bonds in uralolite, which play a distinctive role in the structure and its symmetry.

$[\text{Be}_4(\text{PO}_4)_3(\text{OH})_3]^{4-}$ layers

The structure of uralolite is based on corrugated layers of composition $[\text{Be}_4(\text{PO}_4)_3(\text{OH})_3]^{4-}$ which extend parallel to (010) at $y = \frac{1}{4}$ and $\frac{3}{4}$ of the monoclinic unit cell, and which are mutually linked via two $\text{Ca}(\text{H}_2\text{O})_2^{2+}$ fragments and an additional interstitial water molecule (Fig. 1). As shown in Fig. 2 the $[\text{Be}_4(\text{PO}_4)_3(\text{OH})_3]^{4-}$ layer contains a unique Z-shaped group of four BeO_4 tetrahedra crosslinked by PO_4 groups. The four independent Be atoms are linked via three OH groups. Be2 and Be3 are each bonded to two OH groups and two PO_4 oxygen atoms. Be1 and Be4 in turn are each bonded to one OH group and three PO_4 oxygen atoms. Of the three independent PO_4 groups, those of P1 and P2 link three Be and have each one oxygen atom (O4, O8) in terminal position while those of P3 link four Be. Thus, in terms of the links between tetrahedra, all four BeO_4 and one PO_4 tetrahedra are four-connected and two PO_4 are three-connected. The $[\text{Be}_4(\text{PO}_4)_3(\text{OH})_3]^{4-}$ layer (Fig. 1a) contains following tetrahedral rings: Three-membered BeBeP, four-membered BeBeBeP, four-membered $(\text{BeP})_2$, six-membered $(\text{BeBeP})_2$ and eight-membered $(\text{BeP})_4$ rings. As pointed out previously (Mereiter et al. 1994), and remaining unchanged ever since, the four-membered rings BeBeBeP in uralolite are unique among berylllophosphates, arsenates and silicates as well as the tetrahedral architecture of the layer among silicates (Liebau 1985; Hawthorne and Huminicki 2002). For a comparison of sheet topologies in beryllium minerals including uralolite, see Huminicki and Hawthorne (2002). Bond lengths and bond angles in the BeO_4 and PO_4 tetrahedra show usual variations with Be-O ranging from 1.600(3) to 1.663(3) Å, mean value 1.632 Å, and P-O ranging from 1.5071(17) to 1.5548(16) Å, mean value 1.535 Å. In their review on the crystal chemistry of beryllium, Hawthorne and Huminicki (2002) give Be-O = 1.633 Å as grand mean tetrahedral Be-O bond distance. Bond angles O-Be-O are in the range 100.53(17)-116.62(19)°, and O-P-O angles 105.13(9)-112.50(10)°, where in both cases the lowest values represent shared edges between the Ca polyhedra and BeO_4 as well as PO_4 tetrahedra (Fig. 3). The Be-O-Be bond angles of O1h and O2h (115.60(17) and 117.20(17)°) are both involved in tetrahedral BeBeP rings. They are notably smaller than that of O3h (126.90(16)°), which bridges the two inner BeO_4 tetrahedra and is part of two BeBeBeP rings (Fig. 2).

Ca coordination

The coordination of the two independent Ca atoms and how they connect the $[\text{Be}_4(\text{PO}_4)_3(\text{OH})_3]^{4-}$ layers in detail is shown in Fig. 3. Both Ca atoms are seven coordinated and form $\text{CaO}_5(\text{H}_2\text{O})_2$ polyhedra, where the five phosphate oxygen atoms adopt a roughly equatorial arrangement about Ca and the two water molecules are in approximately axial

Table 3 Atomic displacement parameters (\AA^2) for uralolite

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ca1	0.0089(2)	0.0120(2)	0.0118(2)	-0.0020(2)	0.0033(2)	-0.0013(2)
Ca2	0.0099(2)	0.0119(2)	0.0135(2)	0.0044(2)	0.0038(2)	0.0015(2)
Be1	0.0074(12)	0.0116(13)	0.0088(12)	0.0010(9)	0.0012(9)	0.0004(10)
Be2	0.0073(12)	0.0118(12)	0.0098(12)	-0.0014(10)	0.0012(9)	0.0004(10)
Be3	0.0093(13)	0.0148(13)	0.0069(11)	0.0007(10)	0.0009(9)	0.0004(10)
Be4	0.0082(12)	0.0108(13)	0.0090(11)	-0.0005(9)	0.0020(9)	-0.0015(10)
P1	0.0063(2)	0.0088(2)	0.0069(2)	-0.0008(2)	0.0011(2)	-0.0006(2)
P2	0.0071(2)	0.0083(2)	0.0078(2)	0.0004(2)	0.0010(2)	0.0003(2)
P3	0.0067(2)	0.0104(2)	0.0063(2)	-0.0003(2)	0.0014(2)	-0.0003(2)
O1	0.0082(7)	0.0140(8)	0.0142(7)	-0.0045(6)	0.0034(6)	-0.0003(6)
O2	0.0073(7)	0.0156(8)	0.0094(7)	-0.0031(6)	0.0009(5)	0.0006(6)
O3	0.0151(8)	0.0137(8)	0.0090(7)	0.0019(6)	0.0034(6)	0.0022(6)
O4	0.0136(8)	0.0116(7)	0.0133(7)	-0.0019(6)	0.0033(6)	-0.0037(6)
O5	0.0088(7)	0.0116(7)	0.0132(7)	0.0038(6)	0.0029(6)	0.0000(6)
O6	0.0094(7)	0.0168(8)	0.0092(7)	0.0029(6)	-0.0005(5)	-0.0024(6)
O7	0.0176(8)	0.0190(8)	0.0123(7)	-0.0068(6)	0.0058(6)	-0.0064(7)
O8	0.0129(8)	0.0112(8)	0.0229(8)	0.0050(6)	0.0052(6)	0.0032(6)
O9	0.0141(8)	0.0125(7)	0.0099(7)	-0.0009(6)	0.0056(6)	-0.0005(6)
O10	0.0073(7)	0.0146(8)	0.0118(7)	-0.0034(6)	0.0008(5)	-0.0010(6)
O11	0.0072(7)	0.0157(8)	0.0115(7)	0.0038(6)	-0.0002(5)	-0.0004(6)
O12	0.0133(8)	0.0142(8)	0.0113(7)	-0.0015(6)	0.0066(6)	0.0000(6)
O1h	0.0084(7)	0.0109(7)	0.0138(7)	0.0000(6)	0.0018(6)	0.0002(6)
O2h	0.0100(7)	0.0116(7)	0.0104(7)	0.0010(6)	0.0007(5)	-0.0001(6)
O3h	0.0136(7)	0.0134(7)	0.0103(7)	-0.0011(6)	0.0056(6)	-0.0016(6)
O1w	0.0148(10)	0.0562(15)	0.0426(13)	0.0320(11)	0.0045(9)	0.0026(10)
O2w	0.0463(13)	0.0197(9)	0.0184(9)	-0.0007(7)	0.0021(9)	-0.0023(9)
O3w	0.0157(8)	0.0237(9)	0.0246(9)	-0.0036(7)	0.0042(7)	-0.0020(7)
O4w	0.0294(11)	0.0274(10)	0.0175(9)	0.0006(7)	0.0029(8)	0.0004(8)
O5w	0.063(2)	0.0318(14)	0.099(3)	0.0178(15)	-0.0129(18)	-0.0006(14)

trans-disposition. Each $\text{CaO}_5(\text{H}_2\text{O})_2$ polyhedron shares edges with one BeO_4 and one PO_4 tetrahedron and one edge with its centrosymmetric counterpart. The Ca-O bond distances vary from 2.2431(17) to 2.5448(17) \AA and have mean values of 2.414 and 2.423 \AA for Ca1 and Ca2, respectively. A mean bond length of 2.448(133) \AA was reported for 7-coordinated Ca (Gagné and Hawthorne 2016). In each polyhedron the shortest and longest Ca-O bonds are to the two oxygen atoms that are shared by two Ca, O4 and O4' in case of Ca1, and O8 and O8' in case of Ca2 (Fig. 3; atoms with primed labels are used to distinguish them from their inversion related equivalents). Despite the apparent similarity of the environments of Ca1 and Ca2, their water molecules show significant differences in their positions relative to Ca, in H_2O orientations, and in hydrogen bonding. At comparable distances between Ca1-Ca1' = 3.954(1) \AA and Ca2-Ca2' = 3.802(1) \AA , the separation between O1w and O2w' is 3.668(2) \AA , a value much larger than between O3w and O4w', 2.831(2) \AA , which represents a hydrogen bond (Fig. 3) addressed below.

OH groups, H_2O molecules and hydrogen bonding

The hydrogen bond scheme discussed previously (Mereiter et al. 1994) was found to be largely correct except for two bonds involving O1w and O5w. The hydrogen bonds found in the present investigation are listed in Table 5. A graphic representation of the entire hydrogen bond system is included in Fig. 1b. The three OH groups of the $[\text{Be}_4(\text{PO}_4)_3(\text{OH})_3]^{4-}$ layer adopt distorted tetrahedral coordination figures by two Be, one donated hydrogen bond and one accepted hydrogen bond. Most intriguing is the hydrogen bond O2h-H2h...O1h (O2h...O1h = 2.871(2) \AA) within the Be_4 cluster shown in Fig. 2. It leads to an asymmetry in the Be_4 cluster because it forces O1h-H1h to adopt a hydrogen bond with an external acceptor O3w (O1h...O3w = 2.875(2) \AA), whereas O2h in turn becomes acceptor of a hydrogen from water molecule O1w (O1w...O2h = 2.784(2) \AA). The third OH group of O3h is donor and acceptor of hydrogen bonds to the interstitial water molecule of O5w and from the Ca1-bonded water

Table 4 Selected bond lengths and angles for uralolite

Bond lengths [Å]			
Ca1-O4#1	2.3333(16)	Ca2-O8#3	2.2431(17)
Ca1-O1w	2.3462(18)	Ca2-O11	2.3823(16)
Ca1-O2	2.3773(16)	Ca2-O3w	2.4252(18)
Ca1-O1#2	2.3976(17)	Ca2-O5#4	2.4385(16)
Ca1-O2w	2.4292(19)	Ca2-O6	2.4763(16)
Ca1-O10#2	2.4725(16)	Ca2-O4w	2.4880(18)
Ca1-O4#2	2.5448(17)	Ca2-O8#4	2.5072(17)
<Ca1-O>	2.414	<Ca2-O>	2.423
Be1-O7#5	1.600(3)	Be3-O3h	1.627(3)
Be1-O9	1.615(3)	Be3-O11	1.638(3)
Be1-O1h	1.631(3)	Be3-O6	1.641(3)
Be1-O1	1.650(3)	Be3-O2h	1.643(3)
<Be1-O>	1.624	<Be3-O>	1.637
Be2-O1h	1.625(3)	Be4-O12#2	1.608(3)
Be2-O10#2	1.633(3)	Be4-O5	1.621(3)
Be2-O3h	1.637(3)	Be4-O2h	1.639(3)
Be2-O2	1.663(3)	Be4-O3#6	1.646(3)
<Be2-O>	1.640	<Be4-O>	1.629
P1-O4	1.5180(17)	P2-O8	1.5071(17)
P1-O3	1.5336(16)	P2-O7	1.5197(17)
P1-O2	1.5444(16)	P2-O6	1.5455(16)
P1-O1	1.5494(16)	P2-O5	1.5548(16)
<P1-O>	1.5364	<P2-O>	1.5318
P3-O9	1.5243(16)		
P3-O12	1.5276(16)		
P3-O10	1.5440(16)		
P3-O11	1.5525(16)		
<P3-O>	1.5371		
Bond angles (°)			
O7#5-Be1-O9	101.93(18)	O3h-Be3-O11	112.04(18)
O7#5-Be1-O1h	116.62(19)	O3h-Be3-O6	114.31(19)
O9-Be1-O1h	109.05(17)	O11-Be3-O6	100.53(17)
O7#5-Be1-O1	111.36(18)	O3h-Be3-O2h	107.53(18)
O9-Be1-O1	112.02(18)	O11-Be3-O2h	113.99(19)
O1h-Be1-O1	105.97(18)	O6-Be3-O2h	108.46(17)
O1h-Be2-O10#2	114.09(18)	O12#2-Be4-O5	110.41(18)
O1h-Be2-O3h	109.63(18)	O12#2-Be4-O2h	111.17(17)
O10#2-Be2-O3h	111.35(18)	O5-Be4-O2h	106.84(17)
O1h-Be2-O2	109.50(17)	O12#2-Be4-O3#6	103.63(17)
O10#2-Be2-O2	100.93(16)	O5-Be4-O3#6	112.71(18)
O3h-Be2-O2	111.08(18)	O2h-Be4-O3#6	112.15(18)
O4-P1-O3	109.88(9)	O8-P2-O7	111.23(10)
O4-P1-O2	111.44(9)	O8-P2-O6	112.50(10)
O3-P1-O2	110.10(9)	O7-P2-O6	108.07(9)
O4-P1-O1	105.68(9)	O8-P2-O5	105.13(9)
O3-P1-O1	111.21(9)	O7-P2-O5	111.12(9)
O2-P1-O1	108.44(9)	O6-P2-O5	108.78(9)
O9-P3-O12	107.76(9)		
O9-P3-O10	110.17(9)		

Table 4 (continued)

O12-P3-O10	111.47(9)		
O9-P3-O11	109.30(9)		
O12-P3-O11	109.37(9)		
O10-P3-O11	108.75(9)		
P1-O1-Be1	128.43(14)	P2-O7-Be1#6	136.99(15)
P1-O2-Be2	119.73(14)	P3-O9-Be1	135.15(15)
P1-O3-Be4#5	140.04(14)	P3-O10-Be2#4	129.79(14)
P2-O5-Be4	128.23(14)	P3-O11-Be3	127.11(14)
P2-O6-Be3	122.51(14)	P3-O12-Be4#4	138.84(15)
Be2-O1h-Be1	115.60(17)	Be3-O3h-Be2	126.90(16)
Be4-O2h-Be3	117.20(17)		

Symmetry transformations used to generate equivalent atoms: #1 $-x+1, -y, -z$; #2 $x+1, y, z$; #3 $-x+1, -y, -z+1$; #4 $x-1, y, z$; #5 $x-1/2, -y+1/2, -z-1/2$; #6 $x+1/2, -y+1/2, z+1/2$

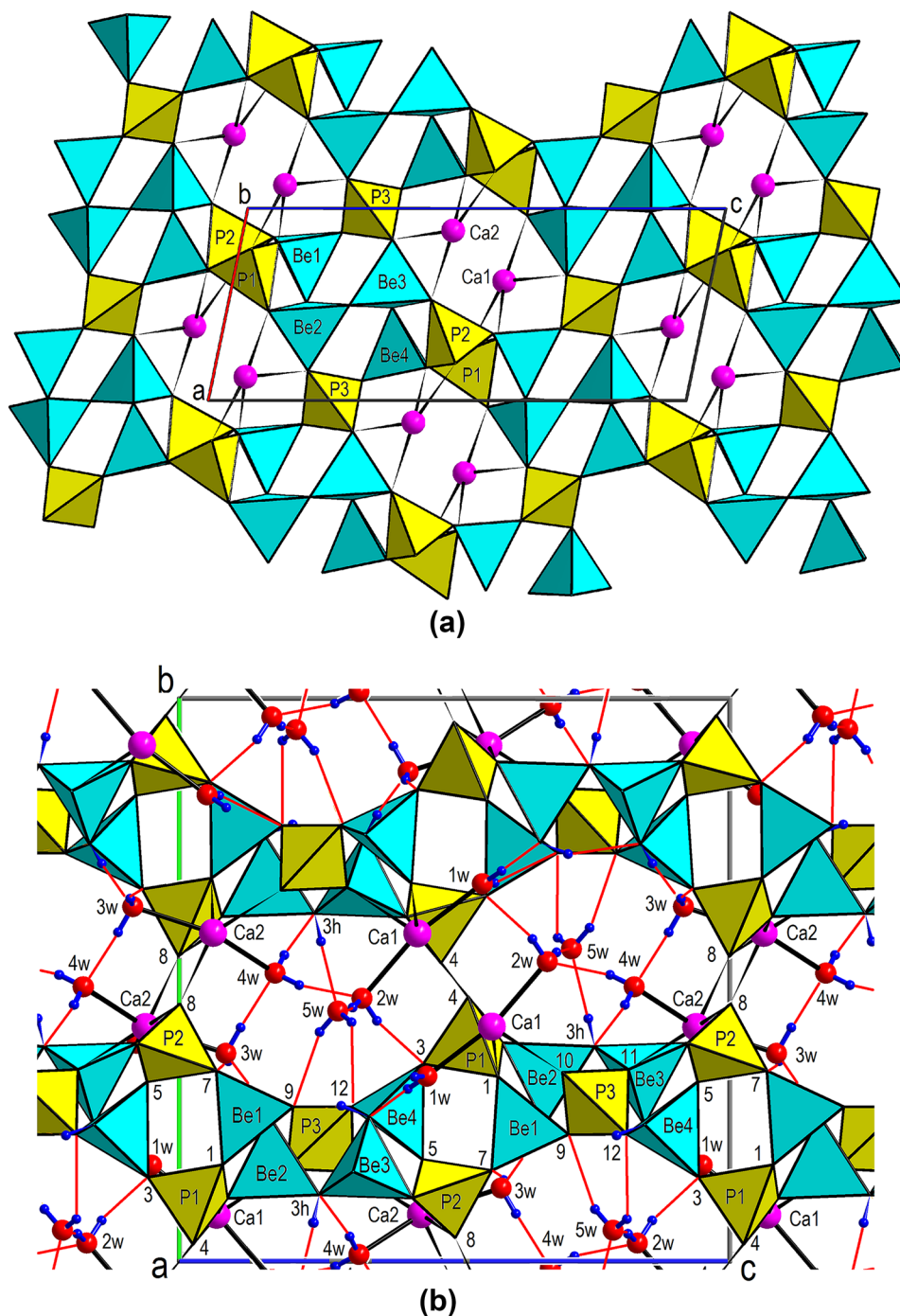
molecule of O1w, respectively. Of the four Ca-bonded water molecules O1w stands out by having the shortest Ca-Ow bond (Ca1-O1w by ~ 0.1 Å shorter than the remaining three Ca-Ow bonds), by being no hydrogen bond acceptor, and by having an approximately planar coordination by Ca1 and three hydrogen bond acceptors, with O2h forming a linear and with O3 and O12 a bifurcated hydrogen bond. The remaining three Ca-bonded water molecules have longer Ca-Ow bonds (≈ 2.45 Å) and show tetrahedral environments by one Ca, one hydrogen bond donor ($\text{O}\cdots\text{O} \approx 2.8$ Å) and two hydrogen bond acceptors ($\text{O}\cdots\text{O} \approx 2.78\text{--}2.91$ Å). The interstitial water molecule O5w accepts two clearcut hydrogen bonds from O3h and O2w ($\text{O}\cdots\text{O} \approx 2.95$ and 2.78 Å) but has troubles with

Table 5 Hydrogen bonds for uralolite

D-H...A	d(D-H) [Å]	d(H...A) [Å]	d(D...A) [Å]	<(D-H...A) [°]
O1h-H1h...O3w#1	0.85	2.026(2)	2.875(2)	176.2(6)
O2h-H2h...O1h	0.85	2.101(5)	2.871(2)	150.3(10)
O3h-H3h...O5w#2	0.85	2.101(3)	2.951(3)	178.6(12)
O1w-H1a...O2h#1	0.85	1.937(2)	2.784(2)	173.9(3)
O1w-H1b...O3	0.85	2.226(3)	2.978(2)	147.6(3)
O1w-H1b...O12#1	0.85	2.338(4)	3.063(2)	143.5(4)
O2w-H2a...O3#3	0.85	2.044(3)	2.880(2)	167.6(6)
O2w-H2b...O5w#4	0.85	1.956(3)	2.783(3)	163.7(7)
O3w-H3a...O7	0.85	1.982(3)	2.807(2)	163.3(8)
O3w-H3b...O4w#5	0.85	2.007(3)	2.831(2)	163.2(4)
O4w-H4a...O3h#6	0.85	2.063(2)	2.909(2)	173.3(4)
O4w-H4b...O2w#6	0.85	1.949(3)	2.780(2)	165.8(4)
O5w-H5a...O12	0.85	2.585(5)	3.192(3)	129.3(4)
O5w-H5b...O9	0.85	2.253(4)	3.012(3)	148.7(4)

X-ray hydrogen atom positions have been refined with hard restraints $\text{O-H} = 0.85$ Å for O-H and H_2O , and $\text{H-O-H} = 108^\circ$ for H_2O . Symmetry transformations used to generate equivalent atoms are: #1 $x+1/2, -y+1/2, -z-1/2$; #2 $-x+1/2, y-1/2, z+1/2$; #3 $-x+1, -y, -z$; #4 $-x+1/2, y-1/2, -z+1/2$; #5 $-x, -y, -z+1$; #6 $x-1, y, z$

Fig. 1 The $[\text{Be}_4(\text{PO}_4)_3(\text{OH})_3]^{4-}$ tetrahedral layer in uralolite. **(a)** Projection of a single layer at $y \approx 1/4$ along $[010]$ with Ca atoms attached to it. **(b)** Stacking of two consecutive layers viewed along $[100]$ with Ca atoms, water molecules, and hydrogen bonds (red lines); numbers denote oxygen atoms



a pair of suitable acceptor atoms. According to the structure refinement the acceptors are O9 and O12 forming an edge of the PO_4 tetrahedron of P3, but the H-bonds are strongly bent and weak (Table 5). This water molecule has the notably largest displacement parameters of the structure (Table 2) and appears to rattle around modestly in a closed structural cavity. It was proven that this water molecule position is fully occupied, but its hydrogen bond parameters $d(\text{H}\cdots\text{A})$ and $\langle\text{DHA}\rangle$ (Table 5) are certainly inaccurate. Nevertheless a

hydrogen bond interaction with O1w ($\text{O5w}\cdots\text{O1w} = 3.15 \text{ \AA}$) can be ruled out, particularly by taking the bonding situation of O1w into account, especially the short Ca1-O1w bond.

Pseudosymmetry

The pseudosymmetry of the crystal structure of uralolite has been pointed out previously (Mereiter et al. 1994). In Fig. 1a it can be noted that in addition to the symmetry elements

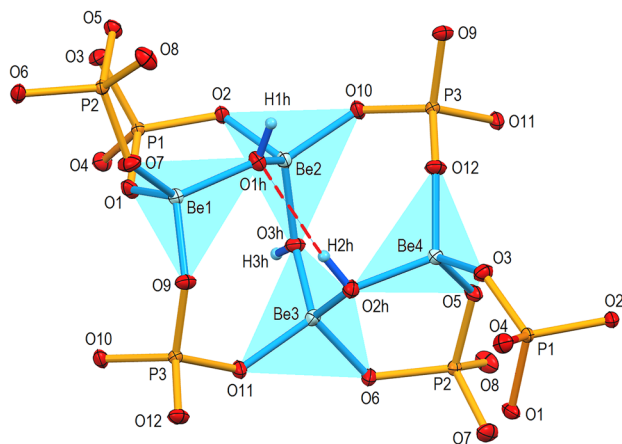


Fig. 2 A fragment of the $[\text{Be}_4(\text{PO}_4)_3(\text{OH})_3]^{4+}$ layer in uralolite showing the four independent BeO_4 tetrahedra and their connection by PO_4 groups. Displacement ellipsoids are drawn at 50% probability. Red broken line denotes hydrogen bond $\text{O2h}\cdots\text{H2h}\cdots\text{O1h}$

of space group $P2_1/n$, there are twofold pseudo-rotations parallel to $[010]$ at $x, z = 0, 1/4$ (passing near P3) and $1/2, 1/4$ (passing near O3h, the corner shared between Be2 and Be3 tetrahedra), and pseudo-inversions at $x, y, z = 1/4, 1/4, 0$ (relating approximately for instance adjacent P1 and P2) and $x, y, z = 3/4, 1/4, 0$ (relating approximately adjacent Ca1 and Ca2 for instance). By modest shifts of their atoms the $P2_1/n$ structure can thus be transformed into a *zellengleiche* structure with pseudo-space group $C2/c$. Whereas deviations from space group symmetry $C2/c$ are small for Ca atoms and $[\text{Be}_4(\text{PO}_4)_3(\text{OH})_3]^{4+}$ layers disregarding hydrogen atoms (0.06–0.22 Å), they are significant for all water molecules, hydrogen atoms, and hydrogen bonds (0.42–0.92 Å for O1w through O5w). A good example for the latter deviations can be seen in Fig. 1b for the water molecules of O2w and O4w near $y, z = 1/2, 1/4$ which differ in height by 0.72 Å along $[010]$, and much more so with regard of the positions of their hydrogen atoms and hydrogen bonds. Qualitatively, the same is valid for the pair O1w and O3w (corresponding height difference 0.65 Å). These features lead to the differences in Ca coordination outlined above and in Fig. 3. A simple proof for the pseudosymmetry is that the crystal structure can be refined in space group $C2/c$ using only reflections with $h+k=2n$, and with one Ca (Ca1), two Be (Be1, Be2), one Oh (O1h), one PO_4 tetrahedron (P1, O1 through O4) and O9, O10 of P3 in general positions ($Z=8$ in $C2/c$, $Z=4$ in $P2_1/n$), whereas P3 and O3h adopt special positions on twofold axes. The water molecules O1w through O4w show up in half occupied split position pairs, and O5w near a twofold axis and also in a half-occupied general position. Using anisotropic displacement parameters for all atoms except water oxygen atoms and neglecting H atoms the structure can be refined in space group $C2/c$ to $R_1=0.0403$

for $2128 F_o > 4\sigma(F_o)$ ($h+k=2n$ only). The outlined features show that the entire system of hydrogen bonds starting with the asymmetry of the three Be-bonded OH groups and ending with all water molecules are decisive for the true space group symmetry $P2_1/n$ of uralolite and its deviation from $C2/c$ pseudosymmetry.

Structural relationships

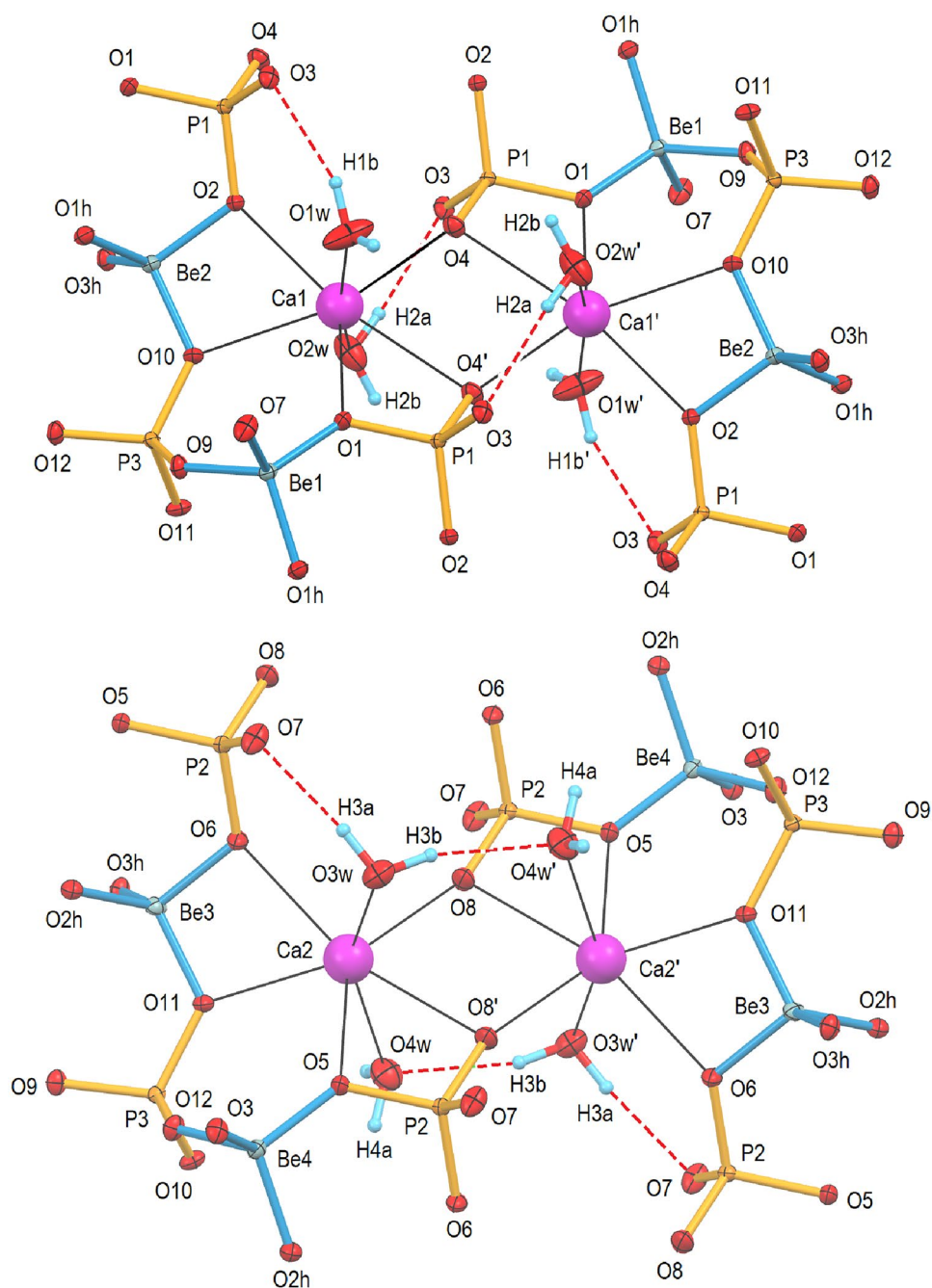
Overviews on beryllium in earth sciences including beryllium minerals and their crystal chemistry have been given in the review volume 50 of the Mineralogical Society of America (Hawthorne and Huminicki 2002). Therefore, the subsequent discussion is restricted only to calcium beryllium phosphate minerals without further cations, namely hurlbutite, $\text{CaBe}_2(\text{PO}_4)_2$, hydroxylherderite, $\text{CaBe}(\text{PO}_4)(\text{OH})$, weinebeneite, $\text{CaBe}_3(\text{PO}_4)_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, uralolite, $\text{Ca}_2\text{Be}_4(\text{PO}_4)_3(\text{OH})_3 \cdot 5\text{H}_2\text{O}$, and fransoletite / parafransoletite, $\text{Ca}_3\text{Be}_2(\text{PO}_4)_2(\text{PO}_3\text{OH})_2 \cdot 4\text{H}_2\text{O}$.

Hurlbutite, $\text{CaBe}_2(\text{PO}_4)_2$, has a framework structure built up from alternating 4-connected BeO_4 and PO_4 tetrahedra forming $(\text{BeP})_2$, $(\text{BeP})_3$, and $(\text{BeP})_4$ tetrahedral rings with an architecture analogous to danburite, $\text{CaB}_2\text{Si}_2\text{O}_8$, and related to feldspars like anorthite, $\text{CaAl}_2\text{Si}_2\text{O}_8$ (Lindbloom et al. 1974). Ca is 7-coordinated with mean Ca-O = 2.469 Å disregarding a further oxygen at 3.09 Å. The CaO_7 polyhedron shares edges with a BeO_4 and a PO_4 tetrahedron (not adjacent edges). The O-T-O angles (T = Be, P) corresponding to the shared edges are the smallest in this structure (102.8 and 103.9°), just like in uralolite.

Hydroxylherderite, $\text{CaBe}(\text{PO}_4)(\text{OH})$, has a layer structure built up from alternating 3-connected $\text{BeO}_3(\text{OH})$ and PO_4 tetrahedra forming $(\text{BeP})_2$ and $(\text{BeP})_4$ tetrahedral rings where the Be-bonded OH group and a phosphate oxygen atom are in terminal positions. All hydroxylherderites investigated so far have a significant OH by F substitution leading to ideal herderite $\text{CaBe}(\text{PO}_4)\text{F}$ (Harlow and Hawthorne 2008). Ca is 8-coordinated in the shape of a square antiprism with a mean bond length of $\text{Ca-O} \approx 2.50$ Å, where four of the ligands are two Be-bonded OH-groups and two terminal PO_4 oxygen atoms. The polyhedron shares edges with two BeO_4 tetrahedra, but not with PO_4 , and the corresponding O-Be-O bond angles are small (103–106°). Each CaO_8 polyhedron shares edges with three adjacent Ca polyhedra.

Weinebeneite, $\text{CaBe}_3(\text{PO}_4)_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, at present still only known from the namesake occurrence (Walter 1992) and occurring there in paragenesis with uralolite (Taucher et al. 1992), bears some close relationships to the latter. It has a framework structure being built up from 4-connected $\text{BeO}_3(\text{OH})$, $\text{BeO}_2(\text{OH})_2$, and PO_4 tetrahedra and contains BeBeP , $(\text{BeP})_2$, $(\text{BeBeP})_2$, and $(\text{BeP})_4$ tetrahedral rings. BeBeP rings are presently known only from uralolite,

Fig. 3 Comparison of two independent Ca atoms in uralolite and their coordination. Both assemblies are centrosymmetric; a few atoms were labeled with primes to distinguish them from their equivalents. Note the difference in H₂O orientations and internal hydrogen bond patterns of the two assemblies



weinebeneite, moraesite, $\text{Be}_2(\text{PO}_4)(\text{OH})\cdot 4\text{H}_2\text{O}$ (Merlino and Pasero 1992), and väyrynenite, $(\text{Mn,Fe})\text{Be}(\text{PO}_4)(\text{OH,F})$ (Mrose and Appleman 1962; Huminicki and Hawthorne 2000). A most distinctive feature of weinebeneite is a quasi-linear group of three BeO_4 tetrahedra linked by sharing vertices via two OH groups, i.e. $\text{Op}_3\text{Be}(\text{OH})\text{BeOp}_2(\text{OH})\text{BeOp}_3$ where Op denote phosphate O atoms (Walter 1992). This unique trimer relates weinebeneite to the Z-shaped tetramer of BeO_4 tetrahedra in uralolite. An infinite extension of the OH mediated link of BeO_4 tetrahedra is present in the

$\text{Be}(\text{PO}_4)(\text{OH,F})$ chains of väyrynenite. The tetrahedral framework of weinebeneite contains large zeolite-like infinite pores extending along the *a*-axis, and these pores are occupied by Ca and four Ca-bonded water molecules.

Finally, fransoletite and its dimorph parafransoletite, $\text{Ca}_3\text{Be}_2(\text{PO}_4)_2(\text{PO}_3\text{OH})_2\cdot 4\text{H}_2\text{O}$ (Kampf 1992), stand out by bearing OH groups not on BeO_4 but on PO_4 tetrahedra. Here 4-connected BeO_4 and 3-connected PO_4 tetrahedra (half of them bearing OH) form infinite chains of $(\text{BeP})_2$ rings crosslinked by $\text{CaO}_4(\text{H}_2\text{O})_2$ and $\text{CaO}_5(\text{H}_2\text{O})_2$ polyhedra.

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