

Uralolite, $\text{Ca}_2\text{Be}_4(\text{PO}_4)_3(\text{OH})_3 \cdot 5\text{H}_2\text{O}$: new data and crystal structure

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Abstract: Uralolite from the Weinebene, Koralpe, Carinthia, Austria, has been investigated with respect to morphology, crystal optics, chemical composition, X-ray powder pattern and crystal structure. Uralolite is monoclinic, space group $P2_1/n$, with $a = 6.550(1)$, $b = 16.005(3)$, $c = 15.969(4)$ Å, $\beta = 101.64(2)^\circ$, $V = 1639.6(8)$ Å³ and $Z = 4$. The structure refinement yielded $R = 0.058$ for 1651 reflections. The structure exhibits a novel type of corrugated tetrahedral layer parallel to (010). The layer has the composition $[\text{Be}_4(\text{PO}_4)_3(\text{OH})_3]^{4-}$ and contains S-shaped groups of four corner-sharing BeO_4 tetrahedra which link with PO_4 tetrahedra to form 3-, 4- and 8-membered rings, including the first occurrence of a BeBeBeP ring. Two Ca atoms in $\text{CaO}_5(\text{H}_2\text{O})_2$ coordination and a "free" water molecule complete the structure, which is pseudosymmetric and approximates space group $C2/c$.

Key-words: uralolite, berylllophosphate, crystallography, crystal structure.

Introduction

Uralolite, a rare hydrated calcium beryllium phosphate occurring in fibrous aggregates of minute acicular to lath-like crystals, has been described from three occurrences: the Ural Mountains type locality (Grigor'ev, 1964), the Dunton Gem mine near Newry, Maine, USA (Dunn & Gaines, 1978), and the Weinebene, a pass in the Koralpe linking Carinthia and Styria, Austria (Niedermayr *et al.*, 1988; Niedermayr & Göd, 1992; Taucher *et al.*, 1992). In the original description of uralolite, Grigor'ev (1964) determined the chemical formula to be $\text{CaBe}_3(\text{PO}_4)_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}$. This was corrected to $\text{Ca}_2\text{Be}_4(\text{PO}_4)_3(\text{OH})_3 \cdot 5\text{H}_2\text{O}$ by Dunn & Gaines (1978) on the basis of an analysis of material from the Dunton Gem mine. The original chemical formula of

uralolite, however, was recently shown to be valid for the new mineral weinebeneite, which was discovered at the Weinebene in small numbers of well-developed platy to block-like crystals partly associated with uralolite (Walter *et al.*, 1990; Walter, 1992). At the Weinebene uralolite occurs in appreciable amounts and occasionally in the form of crystals of unprecedented size, affording an opportunity to better characterize the mineral and to determine its crystal structure.

Occurrence and paragenesis

On the Carinthian side of the Weinebene pass ($14^\circ 59' 29''$ E, $46^\circ 50' 11''$ N), uralolite occurs in narrow fractures within spodumene pegmatites that are hosted by medium- to high-grade

metamorphic rocks of the Austroalpine crystalline basement. The fractures contain hydrothermal alteration products of the pegmatites and their host rocks, mica-schists and amphibolites. A variety of silicate, phosphate and sulfide minerals have been found in these fractures. The Be-bearing minerals are beryl, hydroxylherderite, roscherite, uralolite and weinebeneite. Other noteworthy minerals from this occurrence are fairfieldite/messelite, collinsite, montebrasite and large crystals of holmquistite (Walter *et al.*, 1989). For summaries on this spodumene deposit and its mineralization the reader is referred to Göd (1989), Niedermayr & Göd (1992), and Taucher *et al.* (1992). Hydrothermal alteration of Be-bearing pegmatites and/or rocks were obviously also the origin of the other two known occurrences of uralolite. At the Dunton gem mine uralolite was found in association with albite, elbaite, lepidolite, hydroxylherderite, beryllonite and roscherite (Dunn & Gaines, 1978). For the Ural mountains, uralolite was reported from a kaolin-hydromuscovite rock containing fluorite, beryl, apatite, crandallite, moraesite and glucine (Grigor'ev, 1964).

Physical and chemical properties

Crystals of uralolite from the Weinebene are transparent to translucent, colorless, with vitreous luster. They are brittle, show conchoidal fracture

and appear to have indistinct cleavages on {010} and {100}. The crystals are acicular to lath-like prismatic with elongation parallel to [100] and bladed development on {010} with striations parallel to [100]. Maximum dimensions are about 2 x 0.1 x 0.03 mm. A SEM photograph of a group of typical crystals is shown in Fig. 1. Optical goniometry revealed the forms {021}, {010}, {001} and {101}. Twinning, mentioned by Dunn & Gaines (1978) for material from the Dunton gem mine, was not found in our Weinebene specimens. However, intergrowth parallel to [100] was frequently observed in Weissenberg photographs (*cf.* structure determination).

The optical properties determined by spindle-stage methods using the λ -T-variation method were: biaxial negative, non-pleochroic, $n\alpha = 1.512$, $n\beta = 1.526$, $n\gamma = 1.533$ (all ± 0.002), $n\gamma - n\alpha = 0.021$, $2V_{\text{calc}} = 70^\circ$, $2V_{\text{obs}} = 66^\circ$, no observable dispersion; optical orientation $X // b$ and $Z : a = 9^\circ$ in the acute angle β . Grigor'ev (1964) reported $n\alpha = 1.510$, $n\beta = 1.525$, and $n\gamma = 1.536$, while Dunn & Gaines (1978) found $n\beta = 1.526$ and $n\gamma = 1.536$ (± 0.004).

A chemical analysis for Ca and P (no other elements detected) was carried out with an ARL-SEM electron microprobe at 15 kV accelerating voltage and ~ 15 nA sample current using natural apatite as standard. The data were corrected by the method of Bence & Albee (1968). Beryllium was determined by gravimetry, and the H₂O content by loss of ignition. The results in weight%

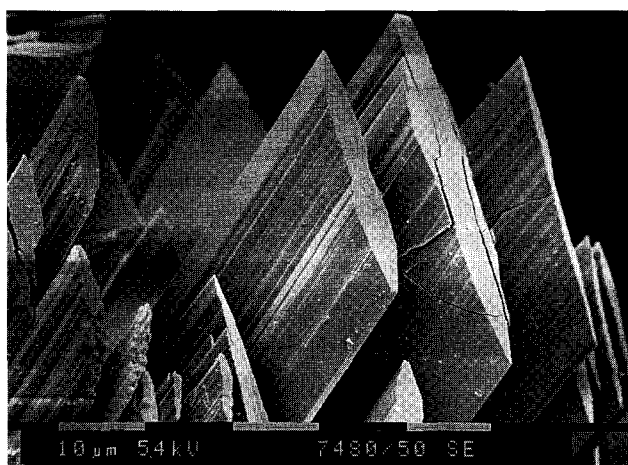


Fig. 1. SEM photograph of a group of uralolite crystals from the Weinebene. The crystals are platy on {010} with striations parallel to [100] caused by alternation of dominant {021} and subordinate {010} faces. Narrow {001} faces complete the [100] prism zone, and {101} faces with lens-like cross sections terminate the crystals. Scale bar: 10 μm .

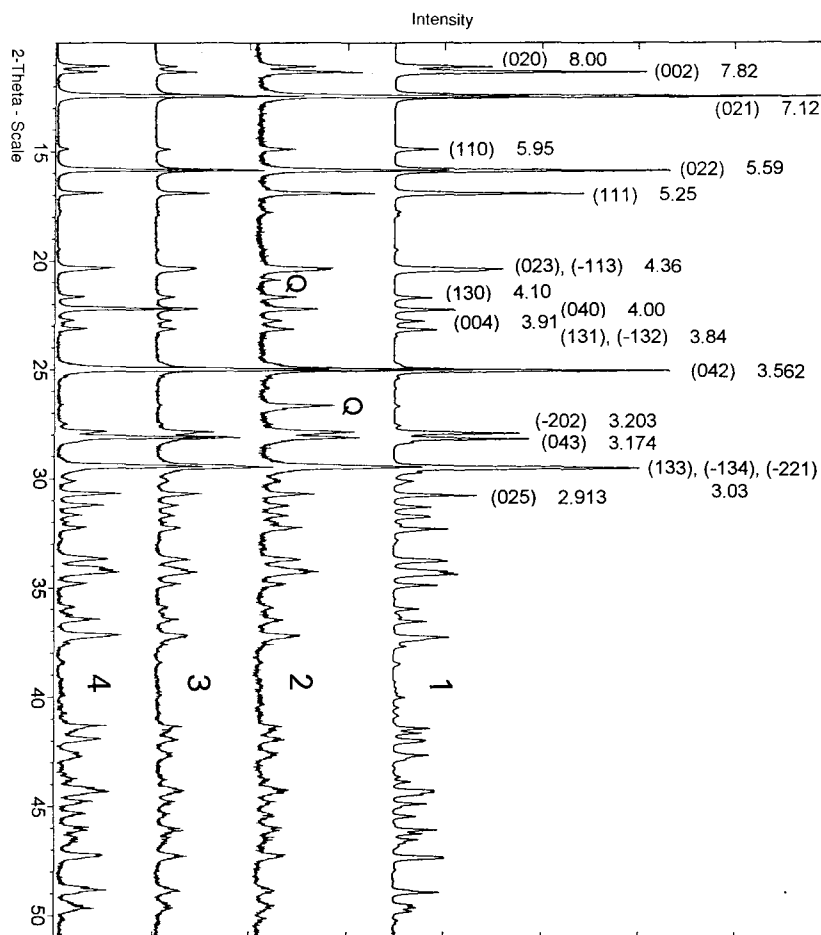


Fig. 2. Powder patterns of uralolite: 1 = calculated with indexing and d -values (\AA) of the most significant peaks, 2 = Weinebene, Austria, 3 = Ural Mountains, Russia, 4 = Dunton gem mine, USA. Q = quartz admixture; diffractometer, $\text{CuK}\alpha$ radiation, graphite monochromator.

were $\text{CaO} = 21.2$ [20.69], $\text{BeO} = 17.5$ [18.45], $\text{P}_2\text{O}_5 = 40.1$ [39.27] and $\text{H}_2\text{O} = 21.0$ [21.59], sum 99.8 [100], where the figures in square brackets represent the theoretical values for the formula $\text{Ca}_2\text{Be}_4(\text{PO}_4)_3(\text{OH})_3 \cdot 5\text{H}_2\text{O}$.

X-ray powder diagrams

The first recognition of uralolite from the Weinebene (Niedermayr *et al.*, 1988) was difficult owing to the poor X-ray powder diffraction data given by Grigor'ev (1964) and included as pattern 16-718 in the JCPDS-ICDD X-ray powder diffraction file. New X-ray powder pat-

terns of uralolite from the Weinebene, the Ural mountains and the Dunton gem mine were therefore recorded and are compared in Fig. 2. In order to reduce preferred orientation effects, the samples were suspended in ethanol on silicon single-crystal sample holders and were then dried. The patterns confirm the identity of the mineral from the three occurrences. Taking into account a quartz admixture (Q) for the Weinebene sample and some remaining preferred orientation effects (*i.e.* the first two peaks of pattern 4 in Fig. 2), the experimental patterns fit well the theoretical pattern calculated from the crystal structure data reported below. Note that the

powder patterns show significant net intensities only for reflections with $h + k = 2n$, a feature that will be outlined below.

Structure determination

Uralolite from the Weinebene is monoclinic, space group $P2_1/n$, with $a = 6.550(1)$, $b = 16.005(3)$, $c = 15.969(4)$ Å, $\beta = 101.64(2)^\circ$, $V = 1639.6(8)$ Å³, $Z = 4$ Ca₂Be₄(PO₄)₃(OH)₃·5H₂O, formula mass 542.22, and a calculated specific gravity of 2.197 g cm⁻³. Rotation and Weissenberg photographs of several crystals showed that reflections with $h + k = 2n$ were systematically stronger than those with $h + k = 2n + 1$, on the average by a factor of eight. This indicated that the structure exhibits a pronounced pseudo-symmetry with $C2/c$ as pseudo-space group, of which $P2_1/n$ is a zellengleiche subgroup. Most of the examined crystals consisted of subindividuals intergrown parallel to the needle axis [100] with varying misorientation angles that caused either broadened and/or splitted reflections on $0kl$ -Weissenberg photographs. A very small crystal (0.012 x 0.042 x 0.35 mm) not showing this effect was used for the determination of accurate cell dimensions on a Philips PW1100 four-circle diffractometer (MoK α radiation, graphite monochromator). A larger crystal (0.024 x 0.077 x 0.70 mm), which showed somewhat broader reflection scan profiles, was then used to measure 3256 reflections with $\theta = 2$ to 25° , $h = -7$ to 7 , $k = 0$ to 19 , $l = 0$ to 18 , recorded by 1.4° ω -scans at a scan rate of $1^\circ/\text{min}$. Data reduction included corrections for background, LP and an effect caused by the length of the crystal, which was larger than the approximately elliptical region of homogeneous intensity of the primary X-ray beam. After stepwise optimization, this effect was finally corrected by $I_{\text{corr}} = I_{\text{meas}} \cdot (1 - 0.15 \cdot \sin \chi)$. Absorption ($\mu = 10.67$ cm⁻¹) was small and therefore neglected. The data were then merged to 2878 symmetry-independent non-extinguished reflections of which 1651 had $F_o > 4\sigma(F_o)$. The structure was solved by direct methods, followed by difference Fourier syntheses and least-squares refinements. The use of anisotropic temperature factors offered no sufficient advantage in R values and brought about larger parameter correlation effects caused by the $C2/c$ pseudosymmetry of the structure. Therefore, in the final refinement, isotropic temperature factors were applied to all atoms. With 1651 reflections weighted by $w = 1/[\sigma^2(F_o) + 0.0002 \cdot F_o^2]$ and

with 117 varied parameters this refinement converged at $R = 0.058$, $R_w = 0.054$ and $S = 1.6$. In the final cycle all shifts/ σ were smaller than 0.01, and the residual electron density varied between -0.75 and 1.08 e Å⁻³. Attempts to locate the hydrogen atoms from difference maps did not provide results that justified their introduction into the structure refinement. The calculations were carried out with program SHELX76 (Sheldrick, 1976), using scattering functions for neutral atoms from the International Tables for X-ray Crystallography, vol. IV (1974).

Final atomic parameters are given in Table 1. A list of structure factors and X-ray powder diffraction data may be obtained from the authors or through the E.J.M. Editorial Office.

Description of the structure

Uralolite is a beryllophosphate built up of infinite layers of corner-sharing BeO₄ and PO₄ tetrahedra. These layers have the composition

Table 1. Atomic coordinates and isotropic thermal parameters [Å²] for uralolite.

Atom	x	y	z	B _{iso}
Ca1	0.8791(3)	0.0829(1)	0.0676(1)	0.95(3)
Ca2	0.1154(3)	0.0830(1)	0.4378(1)	1.11(3)
Be1	0.2408(17)	0.2623(7)	0.1268(6)	0.8(2)
Be2	0.5904(18)	0.1664(7)	0.1766(6)	0.8(2)
Be3	0.4163(19)	0.1628(8)	0.3315(7)	1.0(2)
Be4	0.7678(17)	0.2647(8)	0.3855(6)	1.0(2)
P1	0.3128(3)	0.1152(1)	0.0320(1)	0.76(4)
P2	0.6904(3)	0.1235(1)	0.4836(1)	0.79(4)
P3	0.0062(4)	0.2184(1)	0.2570(1)	0.77(3)
O1	0.1778(8)	0.1714(4)	0.0785(3)	1.0(1)
O2	0.5351(8)	0.1120(4)	0.0867(3)	1.0(1)
O3	0.3183(9)	0.1491(4)	-0.0572(3)	1.1(1)
O4	0.2103(8)	0.0302(4)	0.0247(3)	1.2(1)
O5	0.8303(8)	0.1809(4)	0.4400(3)	0.9(1)
O6	0.4773(8)	0.1133(4)	0.4227(3)	1.0(1)
O7	0.6524(9)	0.1612(4)	0.5667(3)	1.3(1)
O8	0.8073(9)	0.0421(4)	0.4993(3)	1.2(1)
O9	0.1274(8)	0.2747(4)	0.2065(3)	1.1(1)
O10	-0.1531(9)	0.1647(4)	0.1958(3)	1.1(1)
O11	0.1605(9)	0.1605(4)	0.3149(3)	1.0(1)
O12	-0.0995(8)	0.2739(4)	0.3124(3)	1.0(1)
O1h	0.4921(9)	0.2588(4)	0.1621(3)	1.0(1)
O2h	0.5142(9)	0.2575(4)	0.3435(3)	1.1(1)
O3h	0.5038(10)	0.1187(3)	0.2537(4)	1.2(1)
O1w	0.7727(10)	0.1717(4)	-0.0507(4)	2.6(1)
O2w	0.9404(10)	-0.0333(4)	0.1684(4)	2.5(1)
O3w	0.2414(9)	0.1299(4)	0.5838(3)	1.7(1)
O4w	-0.1463(10)	0.0122(4)	0.3254(4)	2.7(1)
O5w	0.1241(14)	0.4449(6)	0.2900(6)	5.7(2)

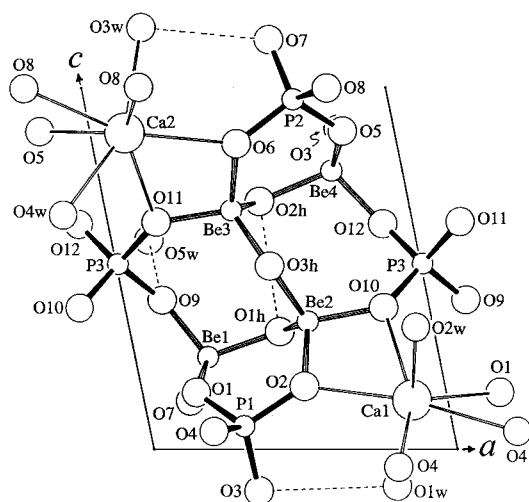


Fig. 3. Asymmetric unit of uralolite in a view along [010] with completed coordination spheres for Ca, Be and P. Dotted lines are postulated hydrogen bonds. Only half of the unit cell in the *c*-direction is shown.

$[\text{Be}_4(\text{PO}_4)_3(\text{OH})_3]^{4-}$ and exhibit an interesting new architecture. They extend at $y \sim 1/4$ and $y \sim 3/4$ parallel to (010) and are linked via two kinds of $\text{CaO}_5(\text{H}_2\text{O})_2$ polyhedra and a "free" water molecule O5w. Fig. 3 shows the bonding between the atoms in one asymmetric unit.

Tetrahedral layer

Bond lengths and angles within the $[\text{Be}_4(\text{PO}_4)_3(\text{OH})_3]^{4-}$ layer are listed in Table 2. P-O and Be-O bond lengths are within the normal range, and their overall average values are $\langle \text{P-O} \rangle = 1.532 \text{ \AA}$ and $\langle \text{Be-O} \rangle = 1.632 \text{ \AA}$. The nucleus of the $[\text{Be}_4(\text{PO}_4)_3(\text{OH})_3]^{4-}$ layer is an S-shaped short chain of four BeO_4 tetrahedra in which the tetrahedra are linked by sharing OH vertices (Fig. 3). This central $\text{Be}_4(\text{OH})_3$ unit is reinforced by four adjacent PO_4 tetrahedra, which bridge pairs of Be tetrahedra. Repeated two-dimensional condensation of this basic unit leads to a complex corrugated layer that exhibits 3-, 4- and 8-membered rings of tetrahedra (Fig. 3, 4 and 5). BeBeP, BePBeP- and $(\text{BeP})_4$ -rings as present in uralolite are now well known from a

Table 2. Bond lengths (\AA) and angles ($^\circ$) of the $[\text{Be}_4(\text{PO}_4)_3(\text{OH})_3]^{4-}$ layer.

P1 - O1	1.552(5)	P2 - O5	1.557(5)	P3 - O9	1.533(6)	Be1 - O1	1.659(12)	Be2 - O2	1.655(12)
- O2	1.540(5)	- O6	1.541(6)	- O10	1.540(6)	- O7	1.591(12)	- O10	1.646(12)
- O3	1.532(6)	- O7	1.523(6)	- O11	1.536(6)	- O9	1.610(12)	- O1h	1.611(12)
- O4	<u>1.511(6)</u>	- O8	<u>1.507(6)</u>	- O12	<u>1.516(6)</u>	- O1h	<u>1.630(12)</u>	- O3h	<u>1.644(12)</u>
P1 - O	1.534	P2 - O	1.532	P3 - O	1.531	Be1 - O	1.623	Be2 - O	1.639
P1		P2		P3		Be1		Be2	
O1 - O2	108.2(3)	O5 - O6	108.7(3)	O9 - O10	110.5(3)	O1 - O7	111.6(7)	O2 - O10	100.9(7)
O1 - O3	111.2(3)	O5 - O7	111.8(3)	O9 - O11	108.9(3)	O1 - O9	111.4(7)	O2 - O1h	110.3(7)
O1 - O4	105.8(3)	O5 - O8	105.0(3)	O9 - O12	108.0(3)	O1 - O1h	105.6(7)	O2 - O3h	110.9(7)
O2 - O3	110.0(3)	O6 - O7	107.8(3)	O10 - O11	108.9(3)	O7 - O9	102.3(7)	O10 - O1h	113.9(7)
O2 - O4	111.7(3)	O6 - O8	112.2(3)	O10 - O12	111.5(3)	O7 - O1h	117.0(7)	O10 - O3h	110.3(7)
O3 - O4	<u>109.9(3)</u>	O7 - O8	<u>111.4(3)</u>	O11 - O12	<u>108.9(3)</u>	O9 - O1h	<u>109.0(7)</u>	O1h - O3h	<u>110.2(7)</u>
O-P1-O	109.5	O-P2-O	109.5	O-P3-O	109.5	O-Be1-O	109.5	O-Be2-O	109.4
ring Be1-P1-Be4-P2		ring Be1-Be2-Be3-P3		ring Be2-Be3-Be4-P3		Be3 - O6	1.635(13)	Be4 - O3	1.652(13)
Be1-O1-P1	128.2(5)	Be1-O9-P3	135.5(5)	Be2-O10-P3	130.1(6)	- O11	1.643(13)	- O5	1.606(13)
Be1-O7-P2	136.6(6)	Be1-O1h-Be2	115.3(6)	Be2-O3h-Be3	126.7(7)	- O2h	1.642(14)	- O12	1.597(13)
Be4-O3-P1	140.5(6)	Be2-O3h-Be3	126.7(7)	Be3-O2h-Be4	116.4(7)	- O3h	<u>1.630(13)</u>	- O2h	<u>1.665(13)</u>
Be4-O5-P2	128.8(5)	Be3-O11-P3	127.5(6)	Be4-O12-P3	138.8(6)	Be3 - O	1.638	Be4 - O	1.630
ring Be1-Be2-P1		ring Be3-Be4-P2				Be3		Be4	
Be1-O1-P1	128.2(5)	Be3-O6-P2	122.6(6)			O6 - O11	101.0(7)	O3 - O5	113.4(7)
Be1-O1h-Be2	115.3(6)	Be3-O2h-Be4	116.4(7)			O6 - O2h	108.9(8)	O3 - O12	104.5(7)
Be2-O2-P1	119.4(5)	Be4-O5-P2	128.8(5)			O6 - O3h	114.1(8)	O3 - O2h	110.7(7)
						O11 - O2h	113.6(8)	O5 - O12	110.9(7)
						O11 - O3h	111.8(8)	O5 - O2h	106.6(7)
						O2h - O3h	<u>107.4(8)</u>	O12 - O2h	<u>111.0(7)</u>
						O-Be3-O	109.5	O-Be4-O	109.5

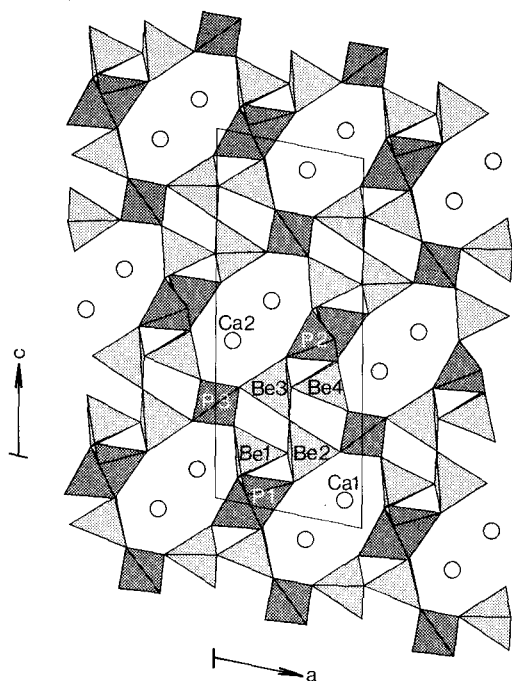


Fig. 4. View of a $[\text{Be}_4(\text{PO}_4)_3(\text{OH})_3]^{4+}$ tetrahedral layer in uralolite with calcium atoms as shaded circles.

variety of beryllophosphates, *e.g.* from moraesite, $\text{Be}_2(\text{PO}_4)(\text{OH})\cdot 4\text{H}_2\text{O}$ (3- and 4-rings within a chain; Merlini & Pasero, 1992), from herderite, $\text{CaBe}(\text{PO}_4)(\text{F},\text{OH})$ (4- and 8-rings within a layer; Lager & Gibbs, 1974), or from weinebeneite, $\text{CaBe}_3(\text{PO}_4)_2(\text{OH})_2\cdot 4\text{H}_2\text{O}$ (3-, 4-, 6- and 8-rings within a framework; Walter, 1992). In addition to these known structural elements, uralolite contains a new one, namely a 4-membered BeBeBeP-ring (Fig. 3 and 4). In addition, the whole architecture of the tetrahedral layer in uralolite is new for beryllophosphates as well as for silicates (Liebau, 1985). Among the 15 different oxygen atoms of the tetrahedral layer, 13 are shared between two tetrahedra. The remaining two are PO_4 oxygen atoms at unshared tetrahedral vertices (O4, O8). Thus the ratio between the number of oxygen atoms and the number of tetrahedra is $15 : 7 = 2.14$, close to ratios found for double-layer and framework silicates (Liebau, 1985). However in contrast with this relation, the tetrahedral layer of uralolite lacks much of the character of a typical silicate double layer, as may be seen from the well-resolved (010) projection shown in Fig. 4. A feature that distinguishes

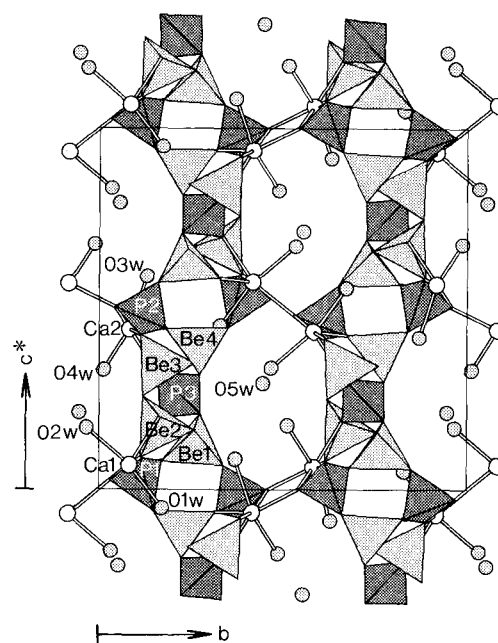


Fig. 5. Structure of uralolite in a projection along [100], *i.e.* parallel to the $[\text{Be}_4(\text{PO}_4)_3(\text{OH})_3]^{4+}$ layers and showing their corrugation.

the $[\text{Be}_4(\text{PO}_4)_3(\text{OH})_3]^{4+}$ layer from silicates is the comparatively small T-O-T angle (T = tetrahedral centre). These angles range from 115° to 141° for uralolite and thus are low in comparison to silicate TOT angles, which have their highest frequency at 139° and very few examples in the $115\text{--}120^\circ$ range (Liebau, 1985).

Ca coordination

The two independent Ca atoms of uralolite exhibit irregular seven-fold coordinations $\text{CaO}_5(\text{H}_2\text{O})_2$, both being similar in shape (Fig. 3, Table 3). Ca1 is bonded to four phosphate oxygen atoms of one tetrahedral layer and to only one phosphate oxygen of another layer. The polyhedron shares edges with a Be2 and a P1 tetrahedron (*via* O2-O10 and O1-O4, respectively), while a third edge (O4-O4') is shared with a second Ca1 polyhedron related with the first one by inversion. The water molecules (O1w and O2w) are bonded only to Ca1. An analogous situation is found for Ca2, which is also bonded to four phosphate oxygens of one tetrahedral

Table 3. Bond lengths (Å) for the $\text{CaO}_5(\text{H}_2\text{O})_2$ polyhedra and postulated hydrogen bonds.

Ca1 - O1	2.393(5)	Ca2 - O5	2.443(5)
- O2	2.380(5)	- O6	2.478(6)
- O4	2.547(6)	- O8	2.503(6)
- O4	2.333(6)	- O8	2.251(6)
- O10	2.475(6)	- O11	2.390(6)
- O1w	2.355(7)	- O3w	2.429(6)
- O2w	<u>2.439(7)</u>	- O4w	<u>2.491(7)</u>
Ca1 - O	2.417	Ca2 - O	2.426
Postulated Hydrogen Bonds			
O1h - O3w	2.868(8)	O3w - O7	2.805(8)
O2h - O1h	2.871(8)	O3w - O4w	2.833(9)
O3h - O5w	2.948(11)	O4w - O3h	2.900(9)
O1w - O3	2.979(8)	O4w - O2w	2.777(9)
O1w - O2h	2.778(9)	O5w - O9	3.035(11)
O2w - O3	2.872(8)	O5w - O1w	3.147(11)
O2w - O5w	2.817(11)		

layer and to one of another layer (O8'). It shares edges with a Be3 tetrahedron (O6-O11), a P2 tetrahedron (O5-O8), and a second Ca2 polyhedron (O8-O8'), and bonds to two unshared water molecules (O3w and O4w). Both Ca atoms reside within the eight-membered rings of the tetra-

dral layers and are mainly anchored there. However, they contribute much to the coherence of the structure perpendicular to (010) by participating in comparatively short Ca-O bonds (Ca1-O4', Ca2-O8')

Water molecules and hydrogen bonds

The assignment of the different kinds of oxygen atoms to the species O^{2-} , OH^- and H_2O is obvious from their bonding situations as well as from the bond valence calculation presented in Table 4. The OH groups are each bonded to two Be, while the water molecules are Ca-bonded or "free" (O5w). Although H atoms could not be located from the X-ray data, it was possible to work out a hydrogen bond scheme from stereochemical and bond valence considerations (Tables 3 and 4). According to this scheme all OH groups and H_2O molecules adopt distorted tetrahedral coordination figures: the three Be-bonded OH groups accept and donate one hydrogen bond each, the Ca-bonded water molecules O1w through O4w donate two hydrogen bonds and accept one each, and the "free" O5w donates and accepts two hydrogen bonds within a coordination by five oxygen atoms with O-O distances

Table 4. Empirical bond-valences ν and bond valence sums $\Sigma\nu$ for uralolite calculated according to Brown & Altermatt (1985) and Ferraris & Ivaldi (1988). $\Sigma\nu'$ are bond valence sums without hydrogen bonds.

	P1	P2	P3	Be1	Be2	Be3	Be4	Ca1	Ca2	$\Sigma\nu'$	H - bonds	$\Sigma\nu$
O1	1.19			0.47				0.32		1.98		1.98
O2	1.23				0.48			0.33		2.04		2.04
O3	1.26						0.48			1.74	+0.16 +0.13	2.03
O4	1.33							0.37, 0.21		1.91		1.91
O5		1.18						0.54	0.28	2.00		2.00
O6		1.23				0.50			0.25	1.98		1.98
O7		1.29		0.57						1.86	+0.18	2.04
O8		1.35							0.46, 0.23	2.04		2.04
O9			1.25	0.54						1.79	+0.12	1.91
O10			1.23		0.49			0.25		1.97		1.97
O11			1.24			0.49			0.32	2.05		2.05
O12			1.31				0.56			1.87		1.87
O1h				0.51	0.54					1.05	-0.16 +0.16	1.05
O2h						0.49	0.46			0.95	-0.16 +0.19	0.98
O3h					0.49	0.51				1.00	-0.14 +0.15	1.01
O1w								0.35		0.35	-0.13 -0.19 +0.11	0.14
O2w								0.28		0.28	-0.16 -0.18 +0.19	0.13
O3w									0.29	0.29	-0.18 -0.17 +0.16	0.10
O4w									0.24	0.24	-0.15 -0.19 +0.17	0.07
O5w											-0.11 -0.12 +0.14 +0.18	0.09
$\Sigma\nu$	5.01	5.05	5.03	2.09	2.00	1.99	2.04	2.11	2.07			

Table 5. Berylllophosphate minerals with known crystal structures. The column "ring type" gives the number of BeO₄ and PO₄ tetrahedra forming rings. For uralolite "4a,b" indicates the presence of two different kinds of rings (see text). For references on minerals marked with an asterisk the reader is referred to the paper of Kampf (1992).

framework structures		ring type
hurlbutite *	Ca ^[7-9] Be ₂ (PO ₄) ₂	- 4 6 8
beryllonite *	Na ^[6-9] Be(PO ₄)	- 4 6 -
babefphite *	Ba ^[9] Be(PO ₄)(F,O)	- - 6 -
weinebeneite	Ca ^[7] Be ₃ (PO ₄) ₂ (OH) ₂ ·4H ₂ O	3 4 6 8
pahasapaite *	(Ca,Li,K) _{10,5} ^[7] Li ₈ ^[4] Be ₂₄ (PO ₄) ₂₄ ·38H ₂ O	- 4 6 8
tiptopite *	K ₂ ^[12] (Li,Na,Ca) ₆ ^[8] Be ₆ (PO ₄) ₆ (OH) ₂ ·1.3H ₂ O	- 4 6 -
layer structures		
herderite	Ca ^[8] Be(PO ₄)(F,OH)	- 4 - 8
hydroxylherderite	Ca ^[8] Be(PO ₄)(OH)	- 4 - 8
uralolite	Ca ₂ ^[7] Be ₄ (PO ₄) ₃ (OH) ₃ ·5H ₂ O	3 4a,b - 8
chain structures		
väyrynenite	(Mn,Fe) ^[6] Be(PO ₄)(OH,F)	3 - - -
moraesite	Be ₂ (PO ₄)(OH)·4H ₂ O	3 4 - -
roscherite *	Ca ₂ ^[7] (Fe,Mg) ₅ ^[6] Be ₄ (PO ₄) ₆ (OH) ₄ ·6H ₂ O	- 4 - -
zanazziite *	Ca ₂ ^[7] (Mg,Fe) ₅ ^[6] Be ₄ (PO ₄) ₆ (OH) ₄ ·6H ₂ O	- 4 - -
fransoletite	Ca ₃ ^[6,7] Be ₂ (PO ₄) ₂ (PO ₃ OH) ₂ ·4H ₂ O	- 4 - -
parafraoletite	Ca ₃ ^[6,7] Be ₂ (PO ₄) ₂ (PO ₃ OH) ₂ ·4H ₂ O	- 4 - -
ehrlite	Ca ₂ ^[7,8] Zn ^[4] Be(PO ₄) ₂ (PO ₃ OH)·4H ₂ O	- 4 - -
groups		
gainesite *	Na ₂ ^[6,12] (Zr,Zn) ₂ ^[6] (Be,Li)(PO ₄) ₄	[P ₄ BeO ₁₆] - cluster

below 3.3 Å. Apart from the four postulated hydrogen bonds, which are directed toward phosphate oxygen atoms (Table 3), the sense of direction of the remaining H-bonds remains open to question. Based on the fact that the H-bonds in uralolite form a 2-dimensional conjugated system, three different models of O-H vector sense can be deduced.

Pseudosymmetry

Fig. 4 shows that the [Be₄(PO₄)₃(OH)₃]⁴⁻ layer is distinctly pseudosymmetric: to a good approximation, twofold axes pass through the atoms P3 and O3h parallel to *y*, and centres of inversion are present in the midst of the eight-membered tetrahedral rings, e.g. at *x*, *y*, *z* = 3/4, 1/4, 0, and also between P1 and P2, e.g. at 1/4, 1/4, 0. This means that by moderate shifts of the atoms the uralolite structure can be enhanced in symmetry from space group *P2₁/n* to space group *C2/c* without altering the unit cell in origin or in base

vectors. After applying *C2/c* symmetry operations to the real structure of uralolite, the following pairs of atoms become equivalent and are then, after suitable transformations, shifted by the given distances: Ca1/Ca2 - 0.10 Å, Be1/Be4 - 0.20 Å, Be2/Be3 - 0.14 Å, P1/P2 - 0.28 Å, P3/P3 - 0.22 Å, O1/O5 - 0.33 Å, O2/O6 - 0.16 Å, O3/O7 - 0.33 Å, O4/O8 - 0.42 Å, O9/O12 - 0.32 Å, O10/O11 - 0.18 Å, O1h/O2h - 0.09 Å, O3h/O3h - 0.12 Å, O1w/O3w - 0.85 Å, O2w/O4w - 1.52 Å, and O5w/O5w - 1.85 Å. The listed distances show that the water molecules are most responsible for deviations from *C2/c* symmetry, because of packing effects and/or hydrogen bonds. When the [Be₄(PO₄)₃(OH)₃]⁴⁻ layers at *y* ~ 1/4 and *y* ~ 3/4 in the actual structure of uralolite are compared with those in an averaged *C2/c* structure, they are seen to have shifted relative to each other by about 0.1 Å approximately parallel to [101]. The *C2/c*-pseudosymmetry is also evident from the diffraction data. It is possible to refine an averaged structure using only the *h* + *k* = 2*n* reflections in space group

C2/c. One obtains $R = 0.070$ for 1078 reflections and a largely reasonable structure model in which only the water molecules reside in half-occupied "disordered" sites.

Discussion

Uralolite belongs to a group of about 20 mineralic and a larger number of non-mineralic berylllophosphates. Table 5 lists the 17 berylllophosphate minerals for which the crystal structures are known. In all of these minerals beryllium is present in the form of BeO_4 tetrahedra which combine with PO_4 tetrahedra to form various corner-sharing tetrahedral edifices subdividable into groups, chains, layers and frameworks (Kampf, 1992). Within these structures 3-, 4-, 6- and 8-membered rings of tetrahedra are present (Table 5). By far most frequent are 4-membered rings of alternating BeO_4 and PO_4 tetrahedra which are found in chain, layer and framework structures. As outlined by Kampf (1992), they contain only Be-O-P links with a favourable Pauling bond valence sum of $2/4 + 5/4 = 1.75$ valence units (*vu*) for the bridging oxygen atom, at variance with bond valence sums of 1 *vu* and 2.5 *vu* for oxygen in Be-O-Be and P-O-P links, respectively. Extensions of this building principle are the even-numbered 6- and 8-membered rings of alternating BeO_4 and PO_4 tetrahedra. They are restricted in occurrence to layer and framework berylllophosphates. The only exception to the principle of BeO_4/PO_4 alternation in even-numbered rings are the Be-Be-Be-P-rings of uralolite, where the oxygen atoms forming the Be-O-Be links represent OH groups. Tetrahedral rings composed of an odd number of tetrahedra necessarily contain connections between two BeO_4 tetrahedra (disregarding condensed phosphates unknown among minerals), and these must have OH groups in their Be-O-Be links. Only 3-membered rings (Be-Be-P) are presently known and are found in the four minerals moraesite (Merlino & Pasero, 1992), weinebeneite (Walter, 1992), uralolite (reported here) and värynenite (Mrose & Appleman, 1962). The given sequence of the four minerals reflects also the increasing number of continuously OH-linked BeO_4 tetrahedra in their structures: two in moraesite, three in weinebeneite, four in uralolite and infinite in värynenite. Considering that 3-membered tetrahedral rings are rare among sili-

cate structures (Liebau, 1985), their relative abundance in berylllophosphates is noteworthy.

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