

Weinebeneite, $\text{CaBe}_3(\text{PO}_4)_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, a new mineral species: mineral data and crystal structure.

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Abstract: *Weinebeneite* is a new mineral species from a spodumene pegmatite at *Weinebene* that occurs in the high-grade metamorphic rocks of *Koralpe*, *Carinthia*, *Austria*. It occurs in small fractures as a secondary mineral associated with *fairfieldite*, *roscherite* and *uralolite*. It forms clear, colorless, vitreous, platy crystals up to 0.1 x 0.3 x 0.5 mm surrounding rosettes of xenomorphic *weinebeneite* up to 20 mm in diameter. It is brittle with a splintery fracture. Mohs' hardness is 3 - 4; $d_{meas.} = 2.15(4) \text{ g/cm}^3$ and $d_{calc.} = 2.17 \text{ g/cm}^3$. Optically, *weinebeneite* is biaxial positive but nearly uniaxial with $2V_{\gamma}^{meas.} < 10^\circ$; $n_\alpha = 1.520$, $n_\beta = 1.520$, $n_\gamma = 1.530$ (589 nm); $Z : c = 42^\circ$ in acute angle β . *Weinebeneite* is monoclinic, $a = 11.897(2)$, $b = 9.707(1)$, $c = 9.633(1) \text{ \AA}$, $\beta = 95.76(1)^\circ$, $V = 1106.8(3) \text{ \AA}^3$ and $Z = 4$. The three strongest lines of the X-ray powder diffraction pattern are [d (Å), (hkl), I] : 2.513, (223), 100 ; 3.421, (221), 70 ; 5.92, (200), 60. The combined results of electron-microprobe, atomic absorption, electron energy-loss-spectroscopy analyses and structure refinement yield the formula $\text{Ca}_{0.99}\text{Be}_{3.02}\text{P}_{1.97}\text{O}_{7.88}(\text{OH})_{2.11} \cdot 4\text{H}_2\text{O}$ (based on O = 14) or, ideally, $\text{CaBe}_3(\text{PO}_4)_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}$. The name refers to the type locality.

The crystal structure of *weinebeneite* has been solved by direct methods and refined in space group *Cc* to $R = 0.043$ and $R_w = 0.044$ using 1341 independent reflections. *Weinebeneite* is a framework beryllophosphate with calcium and water molecules in the cavities of the structure. The beryllium- and phosphorus- tetrahedra share corners forming a layer consisting of 4- and 8-rings. Two superimposed 4.8^2 2D nets oriented parallel to (100) and related by translation in $b/2$ are connected by additional beryllium tetrahedra, giving rise to a framework with an unusual arrangement: five tetrahedra in two three-membered rings share a tetrahedron. *Weinebeneite* is the first reported example of a framework beryllophosphate containing three-membered rings. Calcium is located in channels parallel to [001], coordinated by three O atoms of the framework and four water molecules. One of the water molecules displays apparent positional disorder over two sites.

Key-words: *weinebeneite*, beryllophosphate, crystallography, crystal structure, framework.

Introduction

Weinebeneite was first found in a pegmatite vein from the spodumene deposit located in the *Carinthian* area of the *Koralpe*, *Austria*. The *Koralpe* is part of the *Austroalpine* crystalline basement and is predominantly composed of medium- to high-grade metamorphic rocks. *Göd*

(1989) summarized the exploration results for a lithium deposit that is the largest in Europe and showed that there are two different pegmatite types. Both types bear spodumene and occur as unzoned, dike-like bodies strictly concordant with the foliation of their host rocks. A coarse-grained type is hosted by amphibolites and eclogitic amphibolites, while the second type of

pegmatite is hosted by kyanite-bearing micaschists and has a fine-grained gneissic texture, caused by an extensive metamorphic overprint (Göd, 1989). The amphibolite-hosted pegmatites have a contact zone up to 0.5 m wide characterized by biotitization of amphibolites and by the occurrence of holmquistite. The crystallographic data and the description of the refined crystal structure of this holmquistite were reported by Walter & Walitzi (1985) and Walter *et al.* (1989). Petrographic and crystal chemical investigations of spodumene of the Weinebenepegmatites and other much smaller spodumene-bearing pegmatites in the Austroalpine basement of Styria and Carinthia were described by Koller *et al.* (1983), Heritsch (1984), Moser *et al.* (1987), Göd (1989) and Wenger & Armbruster (1990).

In addition to the common pegmatite minerals of the Weinebene deposit, numerous primary and secondary accessory minerals have been described (Niedermaier *et al.*, 1986, 1987, 1988, 1989, 1990; Černý *et al.*, 1989; Göd, 1989). The fine-grained pegmatites, especially, show many narrow fractures filled with the rare secondary phosphates fairfieldite, roscherite and uralolite, but also provided samples of a mineral which could not be identified, and that subsequently was shown to be the new mineral weinebeneite.

The new mineral weinebeneite is named for the type locality. Both the new mineral and the name have been approved by the Commission on New Minerals and Mineral Names, IMA. Type specimens of weinebeneite are deposited in the Landesmuseum Joanneum, Graz/Styria; the Kärntner Landesmuseum, Klagenfurt/Carinthia; and the Naturhistorisches Museum, Vienna.

Occurrence and paragenesis

Weinebeneite is found about 2 km west of the Weinebene Pass, Koralpe, Carinthia / Austria, at the dump of the exploration adit (1:50.000 map, Österreichische Karte 188 Wolfsberg, 14° 59' 29'' E, 46° 50' 11'' N), 1575 m above sea level. Weinebeneite occurs in narrow fractures of the fine-grained pegmatites and is associated with uralolite, roscherite and fairfieldite. Weinebeneite occurs as platy colorless crystals up to 0.5 mm in length, surrounding rosettes of xenomorphic weinebeneite up to 20 mm in diameter. Paragenesis and morphological data of weinebeneite are described in Walter *et al.* (1990).

Physical and chemical properties

Crystals of weinebeneite are transparent to translucent, colorless, with vitreous luster, white streak and Mohs' hardness 3 - 4. The mineral is brittle and shows an irregular, splintery fracture; no cleavage was observed. It does not fluoresce in ultraviolet radiation. Density is 2.15(4) g/cm³, measured by pycnometer, compared to the calculated value of 2.17 g/cm³. Most observed crystals of weinebeneite have the same simple morphology: platy on {001} and elongated parallel to [100] with crystal sizes up to 0.1 x 0.3 x 0.5 mm; dominant forms (point group m) are {001}, {00 $\bar{1}$ }, {110}, { $\bar{1}$ 10} and {010}; rare forms are {100}, { $\bar{1}$ 00}, {111}, { $\bar{1}$ 11}, {113} and { $\bar{1}$ 13}; (Fig. 1). The stereographic projection is shown in Walter *et al.* (1990). No twinning was found. The a:b:c ratio calculated from measurements with an optical two-circle reflection goniometer is 1.227 : 1 : 0.994 compared with the ratio calculated from unit cell parameters of 1.2256 : 1 : 0.9924.

Optically, weinebeneite is biaxial positive, non-pleochroic, with a very small $2V_{\text{meas}}$ < 10°, and indices of refraction ($\lambda = 589$ nm) $n_{\alpha} = 1.520$, $n_{\beta} = 1.520$, $n_{\gamma} = 1.530$ (all +/- 0.001). The orientation is $Z : c = 42^{\circ}$ in acute angle β . Four crystals were measured on a spindle-stage using the $\lambda - t$ - variation method.

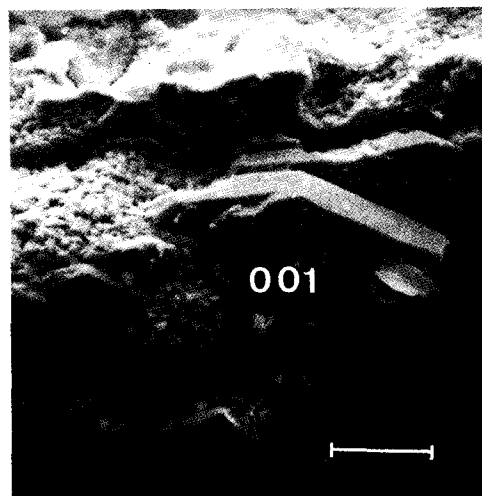


Fig. 1. SEM photograph of weinebeneite from Weinebene. Crystal platy on {001}, elongated parallel to [100], showing the dominant forms {001}, {110}, { $\bar{1}$ 10} and {010}; the rare forms {100} and {111} are represented by very small faces; scale bar : 40 μ m.

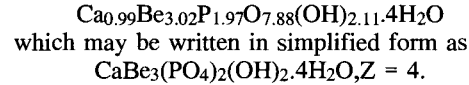
Table 1. Chemical data for weinebeneite from Weinebene.

	1	2	3	4
BeO	21.1	-	3.02	20.66
CaO	15.5	15.1 - 15.9	0.99	15.44
P ₂ O ₅	39.2	38.1 - 40.3	1.97	39.09
H ₂ O	25.5	-	10.11	24.81
Σ	101.3			100.00

1. mean analytical results for weinebeneite wt.%
 2. electron microprobe ranges
 3. cations based on O = 14
 4. theoretical wt.% for the ideal formula
 Ca Be₃ (PO₄)₂ (OH)₂ · 4H₂O

The chemical analysis was carried out with an ARL-SEMQ electron microprobe using a wavelength dispersive system and the data reduction method of Bence & Albee (1968). Operating conditions were 15 kV accelerating voltage and 20 nA sample current, measured on brass. Apatite was used as a standard. Except for Ca and P, no detectable amounts of elements with an atomic number greater than 8 were found. One analysis by electron energy-loss-spectroscopy

(EELS) detected a significant amount of beryllium, subsequently quantified by AAS analysis with BeO as standard. H₂O was determined by loss on ignition. The results of the chemical analyses are listed in Table 1 and yield the empirical formula, based on O = 14 :



Calculations using the Gladstone - Dale relationship with the constants of Mandarino (1981) indicate superior compatibility (Mandarino, 1979):
 $1-(Kp/Kc) = -0.012.$

Structure determination

Single-crystal rotation and Weissenberg photographs showed weinebeneite to be monoclinic and the systematic absences indicate C2/c and Cc as possible space groups. Unit-cell dimensions (Table 3) were obtained by least-squares fitting of data for 33 reflections (internal standard: quartz) obtained using a Siemens D-5000 X-ray powder diffractometer with CuKα radiation. The X-ray powder pattern of weinebeneite is reported in Table 2. Further work was done with a STOE four-circle diffractometer and graphite-monochromatized MoKα radiation (λ = 0.71069 Å). Intensity data were obtained at room temperature from one single crystal; experimental details are presented in Table 3. Data reduction including corrections for background and Lorentz-polarization was done. An absorption correction was not applied because of the small crystal dimensions and the low linear absorption coefficient. Scattering functions with anomalous dispersion terms

Table 2. Powder diffraction pattern of weinebeneite (diffractometer, CuKα - radiation, internal standard quartz).

h k l	d _{obs}	d _{calc}	I _{obs}	I _{calc}	h k l	d _{obs}	d _{calc}	I _{obs}	I _{calc}
1 1 0	7.49	7.51	13	17	0 0 4	2.3947	2.3961	14	6
1 1 1	6.10	6.10	12	20	3 3 1	2.3839	2.3840	5	3
2 0 0	5.92	5.92	60	100	2 2 3	2.3595	2.3597	16	11
1 1 1	5.74	5.73	42	62	1 1 4	2.3261	2.3260	7	5
0 2 0	4.85	4.85	44	32	3 1 3	2.3015	2.3017	11	4
0 0 2	4.79	4.79	32	31	5 1 1	2.2867	2.2876	5	2
0 2 1	4.33	4.33	49	50	2 4 0		2.2453		4
1 1 2	4.16	4.16	35	34	1 1 4	2.2433	2.2417	15	7
1 1 2	3.92	3.93	25	7	2 4 1	2.2042	2.2048	13	5
2 0 2	3.92	3.92	25	8	2 4 1	2.1666	2.1678	8	4
3 1 0	3.66	3.66	8	7	4 2 2	2.1615	2.1599	13	3
2 2 1	3.57	3.57	15	11	0 2 4	2.1482	2.1486	6	2
2 0 2	3.554	3.554	10	11	3 1 4	2.0962	2.0953	4	2
3 1 1	3.524	3.526	7	7	4 2 3	2.0699	2.0700	8	5
2 2 1	3.421	3.421	70	56	2 4 2	2.0642	2.0636	14	8
3 1 1	3.313	3.314	9	8	6 0 0	1.9731	1.9728	13	8
1 3 0	3.123	3.121	10	4	4 0 4	1.9608	1.9609	12	5
3 1 2	3.046	3.046	31	27	0 4 3	1.9323	1.9325	4	3
1 1 3	3.008	3.009	18	13	3 1 4	1.9243	1.9236	5	6
1 3 1	2.991	2.991	29	17	3 3 3	1.9115	1.9116	15	6
4 0 0	2.959	2.959	60	33	4 2 3		1.9040		4
1 3 1	2.945	2.945	45	30	5 3 1	1.9039	1.9035	33	23
1 1 3	2.874	2.874	34	24	2 4 3	1.8713	1.8708	15	10
3 1 2	2.7840	2.7841	36	29	6 2 0	1.8278	1.8276	6	3
4 0 2	2.6388	2.6390	6	3	4 4 2		1.7863		3
3 1 3	2.5245	2.5246	4	3	5 1 3	1.7860	1.7858	13	7
2 2 3	2.5130	2.5129	100	58	0 2 5	1.7831	1.7829	14	7
3 3 0	2.5014	2.5020	10	8	6 2 1	1.7661	1.7653	4	3
3 3 1	2.4598	2.4594	24	19	3 5 0	1.7419	1.7419	4	2
0 4 0	2.4265	2.4267	18	13	0 4 4	1.7054	1.7050	13	10

Table 3. Experimental details and unit cell parameters.

unit cell parameters	a = 11.897(2) Å b = 9.707(1) Å c = 9.633(1) Å β = 95.76(1)° V = 1106.8(8) Å ³
space group	Cc
Z	4
calculated density	2.17 gcm ⁻³
crystal size	0.08 x 0.13 x 0.24 mm
μMoKα	9.08 cm ⁻¹
data collection limits	3° ≤ 2θ ≤ 70° -19 ≤ h ≤ 19, 0 ≤ k ≤ 15, 0 ≤ l ≤ 15
scan mode	ω-scan, Δω = 1.25°
number/frequency of standard reflections	3/100
unique reflections	2504
reflections > 5σ(F _o)	1341
refined parameters	158
R	0.043
R _w	0.044
w = 1/[σ(F _o)] ²	

Table 4. Atomic coordinates, equivalent isotropic (B_{eq}) and anisotropic thermal parameters (U_{ij}) of weinebeneite.

Atom	x	y	z	B_{eq}	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P1	0.2785(1)	0.0985(2)	0.1409(2)	0.54(3)	71(6)	57(8)	76(7)	17(7)	15(6)	1(7)
P2	-0.2780(1)	0.0992(2)	0.3606(2)	0.71(3)	81(6)	94(9)	95(7)	9(7)	14(5)	-6(8)
Be1	-0.3006(8)	0.8817(9)	0.1613(10)	0.65(17)	83(31)	91(45)	73(35)	-8(27)	-24(29)	-73(31)
Be2	-0.1925(8)	0.3821(9)	0.3460(10)	0.78(17)	136(35)	36(42)	125(41)	-7(27)	89(32)	-22(31)
Be3	0.0014(9)	0.5184(7)	0.2517(12)	0.66(10)	59(21)	120(28)	72(25)	-19(40)	2(19)	9(46)
Ca	0.1124(2)	0.0853(2)	0.3718(2)	1.32(2)	144(5)	197(7)	160(6)	41(6)	49(4)	19(6)
O1	-0.0939(4)	0.6163(5)	0.1650(5)	0.87(10)	103(21)	109(27)	117(23)	12(17)	-24(18)	44(18)
O2	0.2150(4)	0.7795(5)	0.6971(6)	0.97(10)	135(22)	68(23)	166(26)	-21(20)	43(20)	-6(21)
O3	0.2388(4)	0.9725(5)	0.2213(5)	0.71(9)	107(21)	79(23)	83(21)	-29(17)	11(18)	43(18)
O4	0.2431(4)	0.9230(6)	0.4847(5)	0.89(9)	123(19)	114(23)	100(20)	55(20)	25(17)	27(22)
O5	0.2853(5)	0.7213(6)	0.3029(6)	1.02(10)	163(24)	96(24)	128(24)	-29(21)	71(20)	10(21)
O6	0.2573(4)	0.5836(6)	0.5177(5)	0.91(9)	144(19)	167(24)	35(18)	-6(23)	5(16)	9(23)
O7	0.0943(4)	0.6210(6)	0.3323(6)	1.25(11)	49(20)	178(31)	249(29)	19(17)	11(19)	-82(22)
O8	0.2597(4)	0.4676(5)	0.2905(6)	0.99(11)	84(19)	123(27)	169(27)	-4(18)	-35(19)	-41(21)
O9(OH)	0.0638(4)	0.4212(6)	0.1442(6)	1.08(9)	116(19)	143(26)	150(24)	10(23)	29(18)	-35(25)
O10(OH)	-0.0622(4)	0.4263(6)	0.3603(6)	1.04(9)	84(20)	182(26)	129(22)	-5(21)	38(19)	51(25)
W1	-0.5254(5)	0.6453(6)	0.1881(6)	1.85(11)	234(25)					
W2	0.4918(5)	0.3807(6)	0.3780(7)	2.20(13)	278(33)					
W3	0.4905(5)	0.3629(7)	0.0437(7)	2.09(13)	265(32)					
W4(1) ¹	0.2250(9)	0.7474(15)	0.0035(15)	2.19(32)	277(76)					
W4(2) ²	0.1950(11)	0.7323(16)	0.0061(17)	1.74(30)	221(72)					

Site occupancies are 1.0, only ¹W4(1) occupancy = 0.55 and ²W4(2) occupancy = 0.45. The starred atoms are refined isotropically. $B_{eq} = 8/3 \cdot (U_{11} + U_{22} + U_{33})$; anisotropic temperature factors are in the form $\exp[-2\pi^2(h^2a^2U_{11} + \dots + 2kbc^*U_{23})]$; U_{ij} are multiplied by 10^4 .

for neutral atoms were taken from the International Tables for X-ray Crystallography, vol. IV (1974).

The crystal structure was solved by direct methods in space group Cc , using the SHELXS-86 system (Sheldrick, 1986). A first E-map gave reliable P-O and T-O-T distances, which correspond to the features of the tetrahedral framework. Fourier syntheses were used to locate other atoms in the tetrahedral framework and showed additional peaks for the extraframework positions. The values of $|E^2 - 1|$ are intermediate to those of centrosymmetric and non-centrosymmetric structures. The subsequent structure refinement, using the program SHELX-76 (Sheldrick, 1976), was carried out twice, first using space group $C2/c$ and then space group Cc .

In space group $C2/c$, the extraframework cation (calcium) and the water molecules occupy general positions. These sites, when fully occupied, give 8 Ca and 32 H₂O per unit-cell. Least-squares refinement of isotropic displacement factors of calcium and water resulted in extremely high values. This indicates that the assumed site occupation factors were wrong. As implied by the chemical analyses, only 4 Ca and 16 H₂O are required. The site occupancies for space group $C2/c$ were thus set to 0.5 for Ca and water and refinement continued with isotropic displacement factors, giving $R = 0.18$ ($2\sigma(F_o)$ cut-off).

The refinement converged to $R = 0.09$ in space group Cc with fully occupied Ca and H₂O posi-

tions. Pairs of atoms of the framework are nearly centrosymmetrically related in space group Cc , but the extraframework atoms do not form such pairs. Therefore the structure was subsequently refined in non-centrosymmetric space group Cc .

Final anisotropic refinement (the displacement factors of water were refined isotropically, the H atoms were not located) converged with $R = 0.043$ and $R_w = 0.044$. The last difference-Fourier map showed residual electron density of -0.6 to 1.0 e \AA^{-3} .

The final positional and thermal parameters are given in Table 4. Lists of structure factors are available from the author upon request.

Description of the structure

The details of the crystal structure of weinebeneite are best seen in projections along $[100]$ (Fig.3) and $[001]$ (Fig.4). Weinebeneite is a framework beryllphosphate with calcium and water molecules in cavities. Selected interatomic distances and angles are given in Tables 5 and 6.

The tetrahedral framework

All P- and Be-tetrahedra share vertices forming a framework, which consists of 3-, 4- and 8-membered rings. Two phosphorous and two beryllium tetrahedra are connected in 4-rings with the sequence of up (U) and down (D) linkage:

Table 5. Interatomic distances (Å) and angles (°) of the framework.

P1 - O1	1.522(6)	P2 - O5	1.539(6)	Be1 - O2	1.609(10)	Be2 - O3	1.638(10)	Be3 - O1	1.642(11)
- O2	1.532(6)	- O6	1.537(5)	- O6	1.642(10)	- O4	1.654(10)	- O7	1.625(11)
- O3	1.547(5)	- O7	1.531(6)	- O8	1.606(11)	- O5	1.630(10)	- O9	1.634(11)
- O4	<u>1.536(5)</u>	- O8	<u>1.533(6)</u>	- O9	<u>1.649(10)</u>	- O10	<u>1.601(10)</u>	- O10	<u>1.621(11)</u>
P1 - O	1.534	P2 - O	1.535	Be1 - O	1.627	Be2 - O	1.631	Be3 - O	1.631
O1 - O2	2.535(7)	O5 - O6	2.513(8)	O2 - O6	2.651(8)	O3 - O4	2.578(7)	O1 - O7	2.625(8)
O1 - O3	2.534(7)	O5 - O7	2.514(8)	O2 - O8	2.598(7)	O3 - O5	2.604(8)	O1 - O9	2.687(7)
O1 - O4	2.500(7)	O5 - O8	2.483(8)	O2 - O9	2.666(7)	O3 - O10	2.640(7)	O1 - O10	2.635(8)
O2 - O3	2.432(7)	O6 - O7	2.527(8)	O6 - O8	2.672(8)	O4 - O5	2.707(8)	O7 - O9	2.654(9)
O2 - O4	2.525(7)	O6 - O8	2.464(8)	O6 - O9	2.711(7)	O4 - O10	2.715(7)	O7 - O10	2.685(8)
O3 - O4	<u>2.500(7)</u>	O7 - O8	<u>2.532(8)</u>	O8 - O9	<u>2.638(8)</u>	O5 - O10	<u>2.713(8)</u>	O9 - O10	<u>2.684(8)</u>
O - O	2.504	O - O	2.505	O - O	2.656	O - O	2.659	O - O	2.662
P1		P2		Be1		Be2		Be3	
O1 - O2	112.2(3)	O5 - O6	109.7(3)	O2 - O6	109.4(6)	O3 - O4	103.1(6)	O1 - O7	106.9(5)
O1 - O3	111.3(3)	O5 - O7	110.0(3)	O2 - O8	107.7(6)	O3 - O5	105.7(6)	O1 - O9	110.1(6)
O1 - O4	109.7(3)	O5 - O8	107.9(3)	O2 - O9	109.7(6)	O3 - O10	109.1(6)	O1 - O10	107.8(7)
O2 - O3	104.4(3)	O6 - O7	111.0(3)	O6 - O8	110.8(6)	O4 - O5	111.0(6)	O7 - O9	109.0(7)
O2 - O4	110.8(3)	O6 - O8	106.8(3)	O6 - O9	111.0(6)	O4 - O10	112.9(6)	O7 - O10	111.8(6)
O3 - O4	<u>108.4(3)</u>	O7 - O8	<u>111.4(3)</u>	O8 - O9	<u>108.1(6)</u>	O5 - O10	<u>114.1(6)</u>	O9 - O10	<u>111.2(5)</u>
O-P1-O	109.5	O-P2-O	109.5	O-Be1-O	109.5	O-Be2-O	109.3	O-Be3-O	109.5
ring P1-Be3-Be2		ring P2-Be3-Be1		ring P1-Be1-P2-Be2					
P1-O3-Be2	129.5(5)	P2-O8-Be1	130.3(5)	P1-O2-Be1	136.5(5)				
P1-O1-Be3	129.7(5)	P2-O7-Be3	128.0(5)	P1-O4-Be2	130.9(5)				
Be2-O10-Be3	127.1(6)	Be1-O9-Be3	125.0(6)	P2-O5-Be2	135.9(5)				
				P2-O6-Be1	135.5(5)				

Note: O9 and O10 are (OH)-groups

Table 6. Interatomic distances (Å) and angles (°) of the extraframework sites and O..O distances (Å) of the hydrogen bond system.

Ca - O2	2.541(6)	O2 - O3	2.432(7)	Ca	O2 - O3	58.3(2)
- O3	2.449(5)	O2 - W1	2.945(8)	O2 - W1	73.7(2)	
- O4	2.396(6)	O2 - W4(1)*	2.960(20)	O2 - W4(1)*	73.8(5)	
- W1	2.362(6)	O3 - O4	2.578(7)	O3 - O4	64.3(2)	
- W2	2.453(6)	O3 - W2	3.549(8)	O3 - W2	92.4(2)	
- W3	2.362(7)	O4 - W2	3.089(8)	O4 - W2	79.1(2)	
- W4(1)*	<u>2.388(14)</u>	O4 - W4(1)*	3.220(20)	O4 - W4(1)*	84.4(4)	
Ca - O	2.422	W1 - W2	3.148(8)	W1 - W2	81.6(2)	
		W1 - W3	3.413(9)	W1 - W3	92.5(2)	
		W2 - W3	2.958(9)	W2 - W3	75.7(2)	
		W3 - W4(1)*	<u>3.070(10)</u>	W3 - W4(1)*	<u>80.4(4)</u>	
		O - O	3.033	O-Ca-O	77.8	
Ca - W4(2)*	2.349(16)	O2 - W4(2)*	3.040(20)	O2 - W4(2)*	76.9(5)	
		O4 - W4(2)*	3.410(20)	O4 - W4(2)*	91.7(4)	
		W3 - W4(2)*	2.800(10)	W3 - W4(2)*	72.9(4)	
O9 - O7	3.090(9)	W3 - O1	2.888(8)			
O10 - O1	3.025(8)	W3 - O6	2.809(8)			
W1 - O9	2.927(8)	W4(1)* - O5	2.910(20)			
W1 - O5	2.709(8)	W4(1)* - O8	2.980(20)			
W2 - O7	2.854(8)	W4(2)* - O5	2.950(20)			
W2 - O8	2.929(8)	W4(2)* - O8	3.000(20)			
W4(1)* - W4(2)*	0.389(18)					

Note: * indicates the disordered water molecule.

UUDD - (P1-Be2-P2-Be1). This kind of ring contributes to a two-dimensional net consisting only of 8-rings that connect 4-rings. The layer contains crankshaft chains with an orientation of tetrahedra corresponding to the 4.8² 2D net no. 23 in the classification of Smith (1978). In silicates, this type of net is represented by the structures of gismondine, garronite and zeolite P1 (Liebau, 1985; Smith, 1978). In the structure of

weinebeneite, two such layers are oriented parallel (100). They are shifted one relative to the other through the translation $b/2$ and connected by beryllium tetrahedra Be3, which are located between the layers. The Be3-tetrahedra are found at positions where a pair of upwards pointing tetrahedra of the lower net cross a pair of downwards pointing tetrahedra of the upper net (Fig. 2). The layer-connecting Be3-tetrahedron is

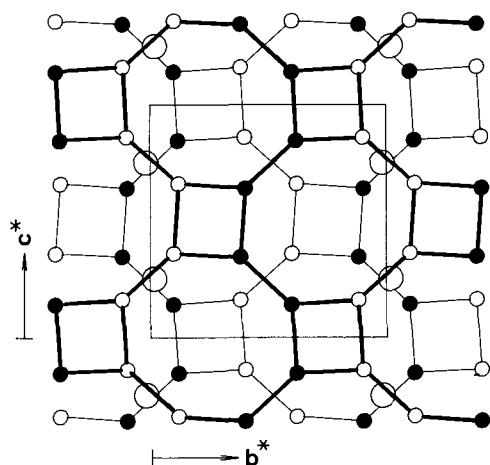


Fig. 2. A pair of superimposed 2D nets plotted with the refined atomic parameters of the P- and Be-sites of the weinebeneite structure. The two layers are shifted through the translation $b/2$. Filled circles indicate upward- and open circles downward-pointing tetrahedra. The layers are connected through additional tetrahedra at positions indicated by large open circles. The unit cell of weinebeneite is given by solid lines.

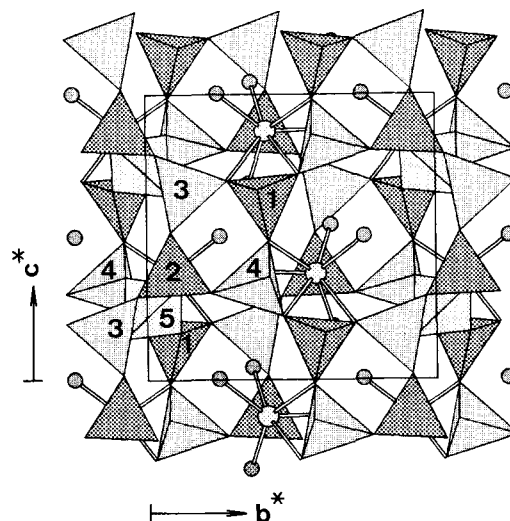


Fig. 3. Projection along [100] of the crystal structure of weinebeneite showing a slice between $x=0.05$ and $x=0.95$. The tetrahedra are numbered: 1 = P1, 2 = P2, 3 = Be1, 4 = Be2, 5 = Be3. Bonds (sticks) are shown between Calcium (large open circles) and water molecules (filled circles) and between Calcium and framework oxygens (tetrahedra corners).

an important structural element, which is shared between two three-membered rings (P1-Be3-Be2 and P2-Be3-Be1, Fig.3). Such an unusual arrangement of five tetrahedra composed of two three-membered rings, and sharing a tetrahedron, is also found in the lovdarite structure, which is the first recorded example of a framework beryllosilicate containing three-membered rings (Merlino, 1981,1990). However, in the lovdarite structure the 2D-net-tetrahedra are oriented differently than in the weinebeneite structure.

The two unique P-tetrahedra in the weinebeneite structure have a typical range of bond lengths and angles. P is coordinated only by O atoms and has the shortest (P1-O1 = 1.522 Å) and the longest (P1-O3 = 1.547 Å) P-O bond lengths. The mean P-O distances in both tetrahedra are nearly equal and the variation in bond lengths is in good agreement with local bond-valence requirements (Table 7), calculated according to data of Brown & Altermatt (1985). The three unique Be tetrahedra are also tetrahedrally coordinated by four O atoms, with a range of bond distances and angles typical of Be tetrahedra also found in the structures of the framework beryllophosphates tiptopite (Peacor *et al.*, 1987) and pahasapaite (Rouse *et al.*, 1989). The

Be2 tetrahedron has the shortest (Be2-O10 = 1.601 Å) and the longest (Be2-O4 = 1.654 Å) Be-O distances in the structure. The variation in Be-O bond lengths can be rationalized in terms of the local anion bond-valence requirements of this structure (Table 7). O9 and O10 belong to (OH)-groups, bonded only to Be tetrahedra and H atoms (not located in the structure refinement), and are involved in a hydrogen bond system, as confirmed by the bond-valence requirements (Table 7). Channels along [001] with approximate free dimensions of 4.4 x 6.3 Å are an important feature of the weinebeneite framework (Fig. 4).

Extraframework sites

Ca atoms and water molecules are located in channels of the structure. Calcium is coordinated by three O atoms of the framework and four water molecules with bond lengths of 2.349 Å to 2.541 Å. The water molecules W1, W2 and W3 are located in channels (Fig. 4), whereas W4 is positioned in the layers of the framework near the centers of 8-membered rings. Only the water

Table 7. Empirical bond-valences (v.u.) in weinebeneite calculated following Brown & Altermatt (1985) and Ferraris & Ivaldi (1988).

	P1	P2	Be1	Be2	Be3	Ca	H9	H10	W		W		W		W		Σ
									1 ¹	1 ²	2 ¹	2 ²	3 ¹	3 ²	4 ¹	4 ²	
O1	1.29				0.49			0.13					0.16				2.07
O2	1.26		0.54			0.21											2.01
O3	1.21			0.50		0.27											1.98
O4	1.25			0.48		0.31											2.04
O5		1.24		0.51					0.22						0.14*		2.11
O6		1.24	0.49												0.18		1.91
O7		1.26			0.52		0.12				0.17						2.07
O8		1.26	0.54										0.15			0.13*	2.08
O9(OH)			0.49		0.51		0.88		0.15								2.03
O10(OH)				0.55	0.52			0.87									1.94
W1						0.34			0.78	0.85							1.97
W2						0.27					0.83	0.85					1.95
W3						0.34							0.84	0.82			2.00
W4						0.34*									0.86*	0.87*	2.07
Σ	5.01	5.00	2.06	2.04	2.04	2.08	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	

Note: * indicates calculated sum for W4(1) and W4(2).

molecule W4 displays disorder over two distinct positions. During refinement, a single position for W4 gave very high isotropic displacement factors for this site. A subsequent difference-Fourier map resulted in two distinct positions W4(1) and W4(2). Variation in Ca-O and Ca-water bond lengths are in good agreement with the local anion bond-valence requirements of the

weinebeneite structure. Table 7 presents bond-valence balance calculated according to Brown & Altermatt (1985) for cation-oxygen bonds and hydrogen bond strengths using the O...O distances (Table 6) calculated according to Ferraris & Ivaldi (1988). Bond-valence requirements confirm that W1 to W4 correspond to water molecules, all involved in a hydrogen sys-

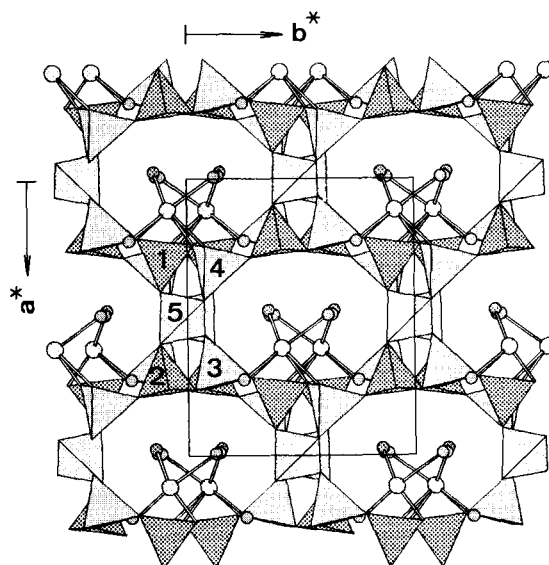


Fig. 4. Projection along [001] of the crystal structure of weinebeneite showing a slice between $z = 0$ and $z = 1.05$. The tetrahedra are numbered as in Fig. 3. Calcium (large open circles), W1, W2, and W3 (filled circles) are located in channels of the framework. The disordered water molecule W4 (filled circles) is located within the layers of the framework near the centers of 8-membered rings.

tem. The bond-valence sums around the donor anions were set to the ideal values 2.0 for water molecules and 1.0 for OH groups.

Conclusions

The results of the structure refinement of weinebeneite confirm the formula calculated from the chemical analyses. Isotypes of weinebeneite were not found. However, some specific features of the framework of the lovdarite structure are similar to those of the weinebeneite structure. According to lovdarite, which is named a zeolite-like mineral (Merlino, 1981, 1990) and reported as a new structure type in the zeolite atlas of Meier & Olson (1987), weinebeneite could be named a beryllphosphate with a zeolite-like structure.

The weinebeneite formula is identical to the original formula for uralolite, $\text{CaBe}_3(\text{PO}_4)_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, proposed by Grigor'ev (1964). However, Dunn & Gaines (1978) found that uralolite from the Dunton gem mine, Newry, Maine, has the formula $\text{Ca}_2\text{Be}_4(\text{PO}_4)_3(\text{OH})_3 \cdot 5\text{H}_2\text{O}$ and that the X-ray powder pattern is identical to that of uralolite from the Ural Mountains. Chemical and single crystal work with uralolite from the Weinebene pegmatites verify the chemical formula given by Dunn & Gaines (1978; Mereiter, personal communication). The X-ray powder data and chemical formulae of weinebeneite and uralolite are distinctly different. Therefore uralolite and weinebeneite are two different mineral species.

Weinebeneite is also different from glucine, $\text{CaBe}_4(\text{PO}_4)_2(\text{OH})_4 \cdot 0.5\text{H}_2\text{O}$, reported by Grigor'ev (1963) and different from fransoletite, $\text{H}_2\text{Ca}_3\text{Be}_2(\text{PO}_4)_4 \cdot 4\text{H}_2\text{O}$, reported by Peacor *et al.* (1983).

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