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Zincoberaunite, ZnFe³⁺₅(PO₄)₄(OH)₅·6H₂O, a new mineral from the Hagendorf South pegmatite, Germany

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Abstract The new mineral zincoberaunite, ideally $ZnFe^{3+}{}_{5}(PO_{4})_{4}(OH)_{5}{}_{6}GH_{2}O$, the Zn analogue of beraunite, is found in the Hagendorf South granitic pegmatite, Hagendorf, Bavaria, Germany, in two associations: (1) with potassium feld-spar, quartz, jungite, phosphophyllite and mitridatite (the holo-type) and (2) with flurlite, plimerite, Zn-bearing beraunite, schoonerite, parascholzite/scholzite, robertsite and altered phosphophyllite (the cotype). Zincoberaunite occurs as radial or randomly oriented aggregates of flexible fibers up to 1.5 mm long and up to 3 μ m thick. D_{calc} is 2.92 g/cm³ for the

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holotype and 2.94 g/cm³ for the cotype. Zincoberaunite is optically biaxial (-), $\alpha = 1.745(5)$, $\beta = 1.760(5)$, $\gamma = 1.770(5)$, $2V_{\text{meas}} = 80(5)^{\circ}$. Chemical composition of the holotype (electron probe microanalyser; H₂O by gas chromatography of ignition products) is: MgO 0.28 wt%, CaO 0.47 wt%, ZnO 7.36 wt%, Al2O3 0.88 wt%, Fe2O3 42.42 wt%, P2O5 31.63 wt%, H2O 16.2 wt%, total 101.1 wt%. The empirical formula calculated on the basis of 27 oxygen atoms per formula unit is $(Zn_{0.83}Ca_{0.08}Mg_{0.06})_{\Sigma 0.97}(Fe^{3+}_{4.88}Al_{0.16})_{\Sigma 5.04}(PO_4)_{4.09}(OH)_{4.78}$ 5.86H₂O. Zincoberaunite is monoclinic, space group C2/c; refined unit cell parameters (for the holotype at room temperature and the cotype at 100 K, respectively) are: a 20.837(2) and 20.836(4), b 5.1624(4) and 5.148(1), c 19.250(1) and 19.228(4) Å, ß 93.252(5) and 93.21(3)°, V 2067.3(3) and 2059.2(7) Å³, Z = 4. The crystal structure of the holotype specimen has been refined by the Rietveld method ($R_p = 0.30$ %; $R_{\rm B} = 0.18$ %) whereas the structure of the cotype has been solved from the single crystal data and refined to $R_1 = 0.056$ based on 1900 unique reflections with $I > 2\sigma(I)$. The strongest reflections of the powder X-ray diffraction pattern of the holotype specimen [(d, Å) (I, %) (hkl)] are: 10.37 (100) (200), 9.58 (32) (002), 7.24 (26) (20-2), 4.817 (22) (111), 4.409 (13) (112), 3.483 (14) (11-4, 600), 3.431 (14) (404), 3.194 (15) (006, 31–4), 3.079 (33) (314).

Keywords Zincoberaunite · New mineral · Beraunite group · Iron and zinc phosphate · Crystal structure · Granitic pegmatite · Hagendorf South · Bavaria

Introduction

This paper describes the new beraunite-group mineral zincoberaunite $ZnFe^{3+}{}_{5}(PO_4)_4(OH)_5 \cdot 6H_2O$ discovered in the abandoned Cornelia Mine Open Cut at the Hagendorf South granitic pegmatite, Hagendorf, 2.5 km NW of Waidhaus,

Upper Palatinate, Bavaria, Germany (49°39'1"N, 12°27'35"E). This mine was primarily operated for feldspar and quartz, together with minor lithium ore (with triphylite as the main source of Li), and is well-known for a wide variety of phosphate minerals (Mücke 1981; Kastning and Schlüter 1994). In particular, the Hagendorf South pegmatite is the type locality of 19 mineral species, mainly phosphates.

Zincoberaunite is named as the analogue of beraunite $Fe^{2+}Fe^{3+}_{5}(PO_4)_4(OH)_5 \cdot 6H_2O$ with Zn predominant among bivalent cations. The new mineral and its name were approved by the IMA CNMNC (IMA2015-117). The holotype material is deposited in the collections of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, Russia, with the registration number 4828/1. The cotype specimen is deposited in the Museum Victoria, Australia, with the registration number M53238.

General appearance and physical properties

Generalities

Two specimens have been investigated. In the holotype specimen zincoberaunite forms pale grey (with silky luster) radial aggregates up to 3 mm consisting of flexible fibers up to 1.5 mm long and up to 3 μ m thick (Fig. 1a). The associated minerals are potassium feldspar, quartz, jungite, phosphophyllite and mitridatite.

In the cotype specimen zincoberaunite occurs in close association with the new schoonerite-related mineral flurlite (Grey et al. 2015) as silvery white (with silky luster) mats of thin needles ranging from ~ 100 nm up to 2 μ m in diameter, with lengths up to 200 μ m (Figs. 1b, and 2). Aggregates of the mineral sit on mounds of densely packed needles of plimerite. The flurlite/plimerite/zincoberaunite assemblage occurs on mitridatite. Other associated minerals are Zn-bearing beraunite, schoonerite, parascholzite/scholzite, robertsite and altered phosphophyllite.

The needles of zincoberaunite are elongated along [010] and somewhat flattened on $\{100\}$. Cleavage is good on $\{100\}$, the fracture is splintery. Density of the new mineral could not be measured because of the fibrous character of aggregates. Density calculated using the empirical formula is

Fig. 1 Images of zincoberaunite. a Radial aggregates of zincoberaunite on potassium feldspar (holotype specimen). b White needles of zincoberaunite (cotype specimen) associated with orange to dark red flurlite platelets



Fig. 2 Secondary electrons image showing needles of zincoberaunite (the cotype specimen) overgrowing mounds of plimerite and associated with stacked platelets of flurlite

equal to 2.92 g/cm^3 (for the holotype) and 2.94 g/cm^3 (for the cotype). The new mineral is non-fluorescent under the UV radiation.

Zincoberaunite is optically biaxial (-), $\alpha = 1.745(5)$, $\beta = 1.760(5)$, $\gamma = 1.770(5)$ (white light); $2V_{\text{meas}} = 80(5)^{\circ}$, $2V_{\text{calc}} = 78^{\circ}$. Dispersion of optical axes is distinct, $r < \nu$. The orientation is: Y = b, $Z \approx c$. The pleochroism is distinct. The absorption scheme is: X = Y (pale beige) < Z(light orange-brown).

Infrared spectroscopy

In order to obtain infrared (IR) absorption spectra (Fig. 3), powdered samples of zincoberaunite and other beraunitegroup minerals were mixed with dried KBr, pelletized, and analyzed using a Bruker ALPHA FTIR spectrometer with a resolution of 4 cm⁻¹ and 16 scans. The IR spectrum of a pellet of pure KBr was used as a reference.

Absorption bands in the IR spectrum of zincoberaunite and their assignments are (cm⁻¹; s – strong band, sh – shoulder): 3562, 3515w, 3276, 2990sh (O–H stretching vibrations of





Fig. 3 Powder IR absorption spectra of (a) zincoberaunite, (b) deep blue beraunite $(Fe^{3+}, Fe^{2+})_{5.26}Al_{0.74}(PO_4)_4(OH,O)_5 \cdot nH_2O$ from the Leveäniemi mine, Svappavaara, Sweden, and (c) eleonorite

OH⁻ anions and H₂O molecules), 1645sh, 1625 (bending vibrations of H₂O molecules), 1140sh, 1070s, 1032s, 990 s, 970sh [$\nu_3(F_2)$ – asymmetric P–O stretching vibrations of PO₄^{3–} anions], 940sh [$\nu_1(A_1)$ – symmetric P–O stretching vibrations of PO₄^{3–} anions], 885sh, 798w (Fe^{3+…}O–H and Zn[…]O–H bending vibrations), 665sh, 603, 580 (triply degenerate $\nu_4(F_2)$ O–P–O bending mode of PO₄^{3–} anions), 466, 440, 405sh, 368 (lattice modes involving Fe³⁺–O stretching and $\nu_2(E)$ O–P–O bending vibrations, possibly combined with libration modes of H₂O molecules).

The presence of the nondegenerate $v_1(A_1)$ band of symmetric P–O stretching vibrations in PO₄^{3–} anions and the splitting of the degenerate $v_3(F_2)$ band of the asymmetric stretching modes of PO₄^{3–} anions reflect the distortion of the tetrahedron P1O₄ (see below). The IR spectrum of zincoberaunite is similar to those of other beraunite-group minerals.

Chemical data

Five electron probe micro-analyser (EPMA) measurements of the holotype sample and seven analyses of the cotype sample were carried out using an Oxford INCA Wave 700 (20 kV, 20 nA, 3 μ m beam diameter) and a JEOL JXA 8500 F Hyperprobe (12 kV, 2 nA, the beam diameter 1 μ m) instruments, respectively. The H₂O content in the holotype sample was analyzed by chromatography of products of ignition at 1200 °C. The content of CO₂ was not analyzed because of the absence of absorption bands corresponding to vibrations of

 $(Fe^{3+}_{5.76}Al_{0.18}Mn^{3+}_{0.09})_{\Sigma 6.03}(PO_4)_{3.92}O(OH)_{4.34}\cdot 5.98H_2O$ from the Rotläufchen mine, Hesse, Germany. The spectra have been offset for comparison

C–O bonds in the IR spectrum. Contents of other elements with atomic numbers greater than 6 are below detection limits. Analytical data are given in Table 1.

The empirical formula of the holotype sample based on 27 oxygen atoms per formula unit (apfu) is $(Zn_{0.83}Ca_{0.08}Mg_{0.06})_{\Sigma 0.97}(Fe^{3+}_{4.88}Al_{0.16})_{\Sigma 5.04}(PO_4)_{4.09}(O-H)4.78\cdot5.86H_2O$. The empirical formula of the cotype, $(Zn_{0.73}Mn^{2+}_{0.04}Fe^{3+}_{0.16})_{\Sigma 0.93}Fe^{3+}_{5}(PO_4)_4(OH)_{5.02}\cdot5.98H_2O$, was calculated on 4 P atoms in view of the fact that for this sample H₂O was not determined by direct methods. The trivalent state of iron in zincoberaunite was concluded from structural data (see below).

The ideal formula is $ZnFe^{3+}{}_{5}(PO_4)_4(OH)_5 \cdot 6H_2O$, which indicates an ideal chemical composition of 8.87 wt% ZnO, 43.50 wt% Fe₂O₃, 30.94 wt% P₂O₅, and 16.69 wt% H₂O. The Gladstone-Dale compatibility index (Mandarino 1981) is: $1 - (K_p/K_c) = -0.016$, superior.

X-ray diffraction data and crystal structure

Powder X-ray diffraction data for the holotype sample (Table 2) were collected at room temperature with a Rigaku R-AXIS Rapid II diffractometer equipped with rotating anode (Co $K\alpha$, 40 kV, 15 mA), microfocus optics and cylindrical image plate detector (d = 127.4 mm). The crystal structure was refined by the Rietveld method using the program package Topas 4.2 (Bruker 2009) – Table 3. The background was modeled using Chebyshev polynomial approximation. The peak profile was described using the fundamental parameter

 Table 1
 Chemical composition

 of zincoberaunite as determined
 by EPMA (in wt%)

Constituent	Holotype sample			Cotype sample		
	Mean	Range	Standard	Mean	Range	Standard
MgO	0.28	0.00 - 0.58	Diopside	(bdl)	(bdl)	(bdl)
CaO	0.47	0.24 - 0.78	Wollastonite	(bdl)	(bdl)	(bdl)
MnO	(bdl)	(bdl)	(bdl)	0.28	0.12 - 0.44	Rhodonite
ZnO	7.36	6.58 - 7.83	Zn	6.3	4.30 - 8.88	Phosphophyllite
Al_2O_3	0.88	0.42 - 1.23	Albite	(bdl)	(bdl)	(bdl)
Fe ₂ O ₃ *	42.42	41.84 - 43.48	Fe ₂ O ₃	43.7	39.6 - 47.8	Hematite
P_2O_5	31.63	30.47 - 32.70	LaPO ₄	30.2	28.0 - 31.7	Berlinite
H ₂ O	16.2(5)			16.5**		
Total	99.24			97.0		

bdl, content measured was below the respective detection limit

* Iron is assumed to be trivalent, from crystal-chemical considerations and by analogy with other beraunite-group minerals

** The H₂O content was calculated assuming that 5 OH⁻ and 6 H₂O are present in the structure

approach. Atomic positions of metal and oxygen atoms of beraunite (Moore and Kampf 1992) were used as initial model. At the first stage, the octahedral sites M1 - M4 were refined as fully occupied by iron. The refinement of isotropic thermal parameters of the M1 - M4 sites has clearly indicated a considerable deficit at M1 and an excess at M2. The further distribution of metal atoms over octahedral positions has been done according to the EPMA chemical data and occupancy analysis. Neutral scattering factors were used for all atoms. Soft distance restraints were applied to stabilize the refinement process. The restraints for T-O (tetrahedral) and R-O (octahedral) distances were realized using Topas 4.2 Launch mode with the weighting factor for penalties K = 2. Most resulting interatomic values differ from the initial distances no more than by 0.02 - 0.03 Å. Among O–P–O angles, only O4-P1-O1 was restrained. The final Rietveld refinement plot is given in Fig. 4.

A needle measuring 2 μ m in diameter by 40 μ m long was used for a single crystal data set of the cotype sample collected on the macromolecular beam line MX2 of the Australian Synchrotron. Data were collected at 100 K using an ADSC Quantum 315r detector and monochromatic radiation with a wavelength of 0.7100 Å. A φ -scan was employed with framewidths of 1° and a counting time per frame of 1 s. The intensity data sets were processed to produce data files which were refined using SHELXL-97 (Sheldrick 2008). Refined single crystal parameters are: a = 20.836(4), b = 5.148(1), c = 19.228(4) Å, $\beta = 93.21(3)^\circ$, V = 2059.2(7) Å³.

The published atomic coordinates for metal and oxygen atoms in beraunite (Moore and Kampf 1992) were used to start the refinement, with the scattering curve for zinc replacing iron in the M1 site. The H atoms associated with the hydroxyl ions and water molecules were located in a difference Fourier map. Soft restraints were used for the O-H distances (0.90(2) Å and for the H - H distances of the watermolecules (1.45(3) Å). The refined site scattering at the M1site was lowered from 30 to 27.4(2) electrons per formula unit (epfu), and a bond valence calculation (Brown and Altermatt 1985) gave a valence sum of 2.32, consistent with the presence of trivalent iron in M1, as reported for the oxidized beraunite mineral, eleonorite (Chukanov et al. 2016). With assignment of $Zn_{0,7}Fe^{3+}$ to M1, the structure refined to $R_1 = 0.0565$ for 1473 observed reflections to a resolution of 0.80 A, using anisotropic displacement parameters for all nonhydrogen atoms and a single isotropic displacement for the H atoms. This was further lowered to 0.0561 by allowing vacancies at M1 while retaining the same ratio of Zn to Fe. This gave 0.675(6)Zn + 0.289(2)Fe + 0.036, corresponding to 27.8 epfu. The vacancy concentration is of similar magnitude to that determined from the EMP analyses. The resulting structural formula, with OH⁻ adjusted for charge balance is $(Zn_{0.67}Fe^{3+}_{0.29})_{\Sigma 0.96}Fe^{3+}_{5}(PO_4)_4(OH)_{5.21}(H_2O)_{3.79}\cdot 2H_2O.$ This gives 6.0 wt% ZnO, 46.3 wt% Fe₂O₃ and 31.1 wt% P_2O_5 .

Further details of the data collection and refinement are given in Table 3. The refined atomic coordinates, site multiplicities, site occupancies, isotropic displacement parameters and bond valence sums are given in Table 4. Selected bond distances are reported in Table 5. A general view of the zincoberaunite structure is given in Fig. 5.

Discussion

Crystal structure

The structure of zincoberaunite is shown in projection along the 5 Å axis (*b*) in Fig. 4. The key feature of the structure is a

Table 2Powder X-raydiffraction data (d in Å) ofzincoberaunite (holotypematerial) and beraunite

Zincoberaunite		Beraunite	,*	h k l	
I _{obs}	$d_{\rm obs}$	d_{calc}	Icalc	d _{calc}	
100	10.37	10.448	100	10.459	200
32	9.58	9.596	39	9.617	002
26	7.24	7.282	31	7.294	20 - 2
5	6.86	6.871	1	6.882	202
4	5.187	5.224	3	5.229	400
22	4.817	4.830	29	4.841	111
13	4.409	4.415	13	4.425	112
5	4.123	4.146	2	4.153	310
4	4.067	4.081	4	4.089	31 - 1
10	3.749	3.758	10	3.766	312
3	3.622	3.641	0.5	3.647	40 - 4
7	3.525	3.535	4	3.542	31-3
14	3.483	3.489, 3.483	12, 16	3.497, 3.486	11-4,600
14	3.431	3.435	12	3.432	404
7	3.318	3.337	3	3.340	60-2
9	3.233	3.247, 3.226, 3.214	4, 3, 7	3.252, 3.231, 3.218	510, 51 - 1, 602
15	3.194	3.199, 3.192	12, 10	3.205, 3.198	006, 31 – 4
10	3.164	3.178	11	3.182	511
33	3.079	3.084	28	3.090	314
4	2.884	2.900, 2.867	2, 2	2.904, 2.872	60-4, 31-5
4	2.858	2.844	4	2.849	513
5	2.833	2.802	1	2.807	40-6
9	2.737	2.748	8	2.752	51-4
8	2.712	2.713	8	2.719	11-6
5	2.601	2.612	5	2.615	800
11	2.577	2.584, 2.578	7,6	2.587, 2.581	710, 71 – 1
4	2.527	2.536, 2.527	2, 1	2.541, 2.531	51-5,71-2
5	2.487	2.491, 2.488, 2.484	2, 2, 2	2.493, 2.493, 2.484	316, 22 - 1, 802
4	2.432	2.432, 2.427	2, 1	2.437, 2.430	22 - 2, 60 - 6
4	2.422	2.419	2	2.420	11-7
4	2.310	2.313, 2.309	4, 2	2.318, 2.314	420, 208
3	2.229	2.230, 2.228	4, 4	2.234, 2.234	40-8,714
2	2.201	2.195	0.5	2.199	71-5
3	2.154	2.157, 2.154	1, 1	2.162, 2.157	423, 118
7	2.107	2.105	5	2.109	42-4
3	2.080	2.091, 2.089	3, 3	2.092, 2.092	91-2, 10.0.0
3	2.061	2.063, 2.061, 2.050	2, 2, 1	2.067, 2.067, 2.054	424, 71 - 6, 517
6	2.008	2.012, 2.008, 1.992	5, 4, 1	2.015, 2.012, 1.996	622, 026, 62 - 3
1	1.970	1.973, 1.972, 1.968	2, 2, 1	1.976, 1.976, 1.971	51-8, 11-9, 806
4	1.922	1.924, 1.919	5, 3	1.928, 1.923	31-9, 0.0.10
2	1.888	1.889	1	1.893	518
3	1.869	1.870	3	1.874	319
3	1.833	1.835, 1.835	2,2	1.838, 1.838	820, 717
1	1.818	1.814	2	1.816	915
3	1.807	1.810	1	1.813	91-6
3	1.784	1.784, 1.784	1, 1	1.788, 1.788	1.1.10, 11.1. – 1
2	1.744	1.745, 1.745, 1.742	2, 2, 2	1.748, 1.748, 1.744	22-8, 823, 11.13
2	1.719	1.721, 1.719	3, 3	1.723, 1.723	91-7, 3.1.10

Table 2 (continued)

Zincoł	peraunite		Beraunite	*	h k l
I _{obs} 4	d _{obs} 1.713	d _{calc} 1.713	I _{calc} 3	d _{calc} 1.716	626
2	1.693	1.696, 1.691	2, 2	1.698, 1.694	12.0.2, 824
3	1.686	1.683	1	1.685	82-5
3	1.657	1.655, 1.652	1, 0.5	1.658, 1.654	1.1 11, 11.1 5
2	1.641	1.642, 1.641	1, 1	1.644, 1.644	11.1.4, 6.0.10
7	1.617	1.621, 1.612, 1.612	6, 1, 1	1.626, 1.615, 1.615	33-3, 134, 10.2.1

*Calculated from the structure data reported by Moore and Kampf (1992): JCPDS-ICDD #76-2087.

cluster of three face-sharing octahedra, Fe4-M1-Fe4, referred to as the h-cluster by Moore (1970). These clusters are connected by corner-sharing to the $P1O_4$ and $P2O_4$ tetrahedra and to pairs of corner-shared Fe3-centred octahedra to form

Table 3 Data collection and refinement details for zincoberaunite		Rietveld refinement (for the holotype sample)	Refinement based on single-crystal data (for the cotype sample)
	Formula	$(Zn_{0.7}Fe^{3+}_{0.2}Ca_{0.1})(Fe^{3+}_{0.6}Al_{0.3}Mg_{0.1})$ $(Fe^{3+}_{1.9}Zn_{0.1})Fe^{3+}_{2.0}(PO_4)_4$ $(OH)_{2}(H_{2}O)_{2}:2H_{2}O$	$\begin{array}{l}(Zn_{0.67}Fe^{3+}{}_{0.29})_{\Sigma 0.96}Fe^{3+}{}_{5}(PO_{4})_{4}\\(OH)_{5.21}(H_{2}O)_{3.79}\cdot 2H_{2}O*\end{array}$
	Formula weight	902.55	911.9
	Temperature	100 K	300 K
	Equipment used for the data collection	Rigaku R-Axis II (cylindrical image plate detector, $d = 127.4$ mm)	Macromolecular beam line MX2 of the Australian Synchrotron
	Radiation	CoKα, 1.79021 Å	0.7100 Å
	Crystal system	Monoclinic	Monoclinic
	Space group	C2/c	C2/c
	a (Å)	20.837(2)	20.836(4)
	<i>b</i> (Å)	5.1624(4)	5.148(1)
	<i>c</i> (Å)	19.250(1)	19.228(4)
	eta (°)	93.252(5)	93.21(3)
	$V(\text{\AA}^3)$	2067.3(3)	2059.2(7)
	Ζ	4	4
	$D_{\text{calc}}, \text{g/cm}^3$	2.90	2.94
	Range	2θ from 7 to 110°	$-21 \le h \le 26, -6 \le k \le 5, -24 \le l \le 24$
	R factors	$R_{\rm exp} = 0.0047, R_{\rm wp} = 0.0041,$ $R_{\rm p} = 0.0030, R_{\rm B} = 0.0018$	$R_1 = 0.0561, wR_2 = 0.1202$ [$I > 2$ sigma(I)];
		P / B	$R_1 = 0.0797, wR_2 = 0.1279$ (all data)
	GooF	0.87	1.166
	Other data		Crystal size: 0.003 x 0.003 x 0.04 mm
			Reflections collected / unique 4658 / $1900 [R_{int} = 0.0641].$
			Refinement method: Full-matrix least squares on F^2 .
			Absorption coefficient 4.852 mm^{-1} .
			Absorption correction SADABS.
			Min/Max transmission 0.58/0.75.
			Data resolution 0.80 Å.
			Extinction coefficient 0.0022(3).
			Largest diff. peak and hole: 0.90 and -0.77 e A^{-3} .

*The excess of OH is due to the presence of subordinate Fe^{3+} in M1.

range 7-80°



heteropolyhedral slabs coplanar to (100). The slabs are interconnected via corner-sharing with Fe₂O₂(OH)₂(H₂O)₂ octahedra to form a 3D framework containing large 10-sided channels along [010]. The water molecules Ow3 are located in the channels and are held by H-bonding to the framework atoms O6 and Ow2. The H-bonding scheme in zincoberaunite is given in Table 6. The bonds involve O - O distances in the range 2.69 to 3.29 Å, corresponding to weak to medium bond strengths. The bonding scheme is the same as reported for tvrdýite, a beraunite-group member with $Al > Fe^{3+}$ (Sejkora et al. 2016).

Bond valence sums (Table 4) are the strong evidence that all the Fe in zincoberaunite is trivalent. The BV value of 2.35 for the nominally divalent M1 site is due to the presence of subordinate Fe³⁺.

Origin of zincoberaunite

Different kinds of granitic pegmatites are characterized by different forms of zinc concentration. In rare-metal pegmatites, a substantial part of zinc occurs in silicates and oxides. The contents of Zn in muscovite from Li- and Be-rich pegmatites may reach 0.09 and 0.14 wt%, respectively (Wise and Brown 2010). Elbaite from Li-rich pegmatites may contain up to 0.35 apfu Zn (Soares et al. 2009). Gahnite is typical for Lirich pegmatites, whereas in Li-poor pegmatites the main spinel is hercynite (Heimann 2014). Under mild hydrothermal conditions Zn can easily be mobilized by aqueous fluids (Telus et al. 2012).

The Hagendorf South granitic pegmatite belongs to a group of pegmatites situated on the northern part of the Oberpfälzer Wald Mts. and characterized by high contents of phosphorus distributed between feldspar and phosphate minerals (Strunz et al. 1975; Kastning and Schlüter 1994). A specific feature of the Hagendorf South pegmatite is abundance of sphalerite, which is the main form of Zn concentration in primary

parageneses (Kastning and Schlüter 1994). On the lowtemperature hydrothermal stage sphalerite partly decomposed (Dill 2009).

In both associations described above, zincoberaunite is one of the latest minerals. Hypothetically, it crystallized at the low-temperature hydrothermal or supergene stage. Znand P-rich solutions coming from alteration reactions of sphalerite and primary phosphates (triphylite and/or zwieselite) were the most probable source of zinc and phosphorus for zincoberaunite. Trivalent state of iron in zincoberaunite (which follows from the bond valence sums for octahedral sites) and its close association with mitridatite indicate oxidizing conditions of mineral formation at the latest stages, most probably, as a result of supergene alteration reactions.

Relationship with other beraunite-group minerals

Beraunite was described as a new mineral by Breithaupt (1841), and up to 2014 it was the only valid mineral representing this structure type. Based on crystallochemical considerations and a chemical analysis, Fanfani and Zanazzi (1967) suggested the following idealized formula of this mineral: $Fe^{2+}_{0.5}Fe^{3+}_{2.5}(PO_4)_2(OH)_{2.5}$ · $3H_2O$ [in the current IMA list of minerals (http://pubsites.uws.edu.au/imacnmnc/imalist.htm) the idealized formula of beraunite is given as $Fe^{2+}Fe^{3+}{}_{5}[PO_{4}]_{4}(OH)_{5}\cdot 6H_{2}O]$. Later it was shown (Moore and Kampf 1992) that in beraunite from Mullica Hill, New Jersey, USA, 83 % Fe^{2+} resides in the central M(1)site with mean M(1)-O distance 2.11 Å, whereas the other octahedral cation sites M(2), M(3), and M(4) (with mean M-O distances 2.01 to 2.02 Å) are occupied by Fe³⁺.

Moore and Kampf (1992) suggested the following endmember formulae for beraunite-type minerals with only iron as species-defining metal: Fe²⁺Fe³⁺₅(OH)₅(H₂O)₄(PO₄)₄· $2H_2O$ and $Fe^{3+}{}_6O(OH)_4(H_2O)_4(PO_4)_4 \cdot 2H_2O$. The latter **Table 4** Fractional atomiccoordinates, site multiplicities,site occupancies and isotropicdisplacement parameters $[B_{eq}$ (Rietveld), U_{eq} (single crystal)]and bond valences (BV) forzincoberaunite

Site	Mult.	x	у	Z	Occupancy	$B_{ m eq}$ $U_{ m eq}$	BV
<i>M</i> 1	4	0	0	0	Zn _{0.7} Fe _{0.2} Ca _{0.1}	2.2(3)	2.26
		0	0	0	Zn _{0.675(6)} Fe _{0.289(2)}	0.012(1)	2.35
М2	4	0.25	0.25	0	Fe _{0.6} Al _{0.3} Mg _{0.1}	2.8(6)	2.50
		0.25	0.25	0	Fe	0.012(1)	3.07
МЗ	8	0.0432(2)	0.284(1)	0.1721(3)	Fe _{0.95} Zn _{0.05}	0.7(3)	3.18
		0.0439(1)	0.2748(2)	0.1728(1)	Fe	0.012(1)	3.03
<i>M</i> 4	8	0.1075(2)	0.033(1)	0.4132(3)	Fe	0.9(3)	2.89
		0.1082(1)	0.0368(2)	0.4137(1)	Fe	0.012(1)	2.98
P1	8	0.1047(2)	0.475(1)	0.0233(3)	Р	0.7(2)	5.01
		0.1047(1)	0.4772(4)	0.0249(1)	Р	0.011(1)	4.99
P2	8	0.4085(3)	0.053(1)	0.1848(3)	Р	0.7(2)	5.03
		0.4074(1)	0.0441(4)	0.1821(1)	Р	0.011(1)	4.95
01	8	0.1770(3)	0.476(2)	0.0135(5)	0	2.4(2)	
		0.1772(3)	0.4869(11)	0.0148(3)	0	0.013(1)	1.80
02	8	0.4257(4)	0.248(2)	0.0219(5)	0	2.4(2)	
		0.4265(3)	0.2502(11)	0.0183(3)	0	0.014(1)	1.95
03	8	0.4275(4)	0.218(2)	0.5086(5)	0	2.4(2)	
O4	8	0.4243(3) 0.0891(4)	0.2358(11) 0.438(3)	0.5018(3) 0.0982(3)	0 0	0.014(1) 2.4(2)	1.95
		0.0918(3)	0.4442(12)	0.1011(3)	0	0.018(1)	1.92
05	8	0.4777(3)	0.043(2)	0.1631(8)	0	2.4(2)	
0.6	0	0.4794(3)	0.4442(12)	0.1680(3)	0	0.015(1)	1.83
06	8	0.1002(6)	0.482(3)	0.2398(4)	0	2.4(2)	1 70
07	8	0.1018(3) 0.3745(9)	0.4842(12) 0.307(2)	0.2410(3) 0.1623(5)	0	0.018(1) 2 4(2)	1.72
0,	0	0.3788(3)	0.307(2) 0.3141(11)	0.1654(3)	0	0.014(1)	1.85
08	8	0.1286(9)	0.341(2)	0.3565(7)	0	2.4(2)	1.00
		0.1303(3)	0.3463(11)	0.3640(3)	0	0.014(1)	1.88
OH1	8	0.0053(4)	0.041(3)	0.3917(4)	0	2.4(2)	
		0.0071(3)	0.0393(11)	0.3953(3)	0	0.015(1)	1.26
OH2	8	0.1938(4)	0.024(2)	0.4607(7)	0	2.4(2)	
0112	4	0.1919(3)	0.0225(11)	0.4626(3)	0	0.015(1)	1.19
OHS	4	0	0.102(4)	0.25	0	2.4(2)	1.00
OW1	8	0.3892(5)	0.1077(17) 0.476(2)	0.23 0.323(1)	0	2.4(2)	1.09
0.111	0	0.3847(3)	0.4764(12)	0.3213(3)	0	0.021(1)	0.36
OW2	8	0.269(1)	0.057(3)	0.0940(5)	0	2.4(2)	0.00
		0.2471(3)	0.0840(12)	0.0989(3)	0	0.016(1)	0.41
OW3	8	0.238(1)	0.390(5)	0.220(1)	0	2.4(2)	
		0.2299(4)	0.3520(13)	0.2168(3)	0	0.026(2)	0
H1	8	-0.017(8)	-0.08(3)	0.370(8)	Н	0.10(2)	
H2	8	0.206(8)	0.16(3)	0.489(7)	H	0.10(2)	
H3	4	0	-0.067(4)	0.25	H	0.10(2)	
H4	8	0.416(8)	0.58(2)	0.307(8)	H	0.10(2)	
H5	8	0.376(9)	0.36(2)	0.287(6)	H	0.10(2)	
H6	8	0.278(6)	-0.03(3)	0.109(8)	H	0.10(2)	
H7	8	0.247(8)	0.20(2)	0.133(0)	H	0.10(2)	
H8	8	0.259(6)	0.46(3)	0.240(8)	Н	0.10(2)	
H9	8	0.193(4)	0.35(3)	0.238(8)	Н	0.10(2)	

Upper values correspond to the holotype sample; lower values and data for H atoms correspond to the cotype sample

Table 5Selected bond lengthsfor zincoberaunite (upper valuescorrespond to the holotypesample; lower values and data forH atoms correspond to the cotypesample)

<i>M</i> 1 – O2	2.081(9) x2 2.045(5) x2	<i>M</i> 2 – OH2	1.958(10) x2 1.963(6) x2
-OH1	2.104(7) x2	-O1	1.946(9) x2
-03	2.037(5) x2 2.111(9) x2	-OW2	1.979(6) x2 2.085(12) x2
Average	2.084(6) x2 2.099		2.089(5) x2 1.996
<i>M</i> 3 – O4	2.055 1.930(11)	<i>M</i> 4 – O(8)	2.010 1.988(14)
-05	1.952(5) 1.911(10)	-OH2	1.927(6) 1.972(10)
-OH3	1.949(6) 2.024(11)	-07	1.936(6) 1.918(12)
-06	1.983(4) 1.996(12)	-02	1.933(5) 2.075(11)
-OH1	2.041(6) 1.990(11)	-03	2.126(5) 2.146(10)
-OW1	2.039(6) 2.127(11)	-OH1	2.144(5) 2.138(11)
Average	2.138(7) 1.996		2.115(6) 2.039
P1-O4	2.017 1.51(1)	P2-08	2.030 1.54(2)
-01	1.513(5) 1.53(1)	-07	1.537(6) 1.54(1)
-03	1.536(6) 1.54(1)	-06	1.542(6) 1.52(1)
-02	1.538(6) 1.56(1)	-05	1.533(5) 1.53(1)
Average	1.556(6) 1.535		1.540(6) 1.532
c	1.536		1.538

Fig. 5 Projection of the zincoberaunite structure along [010]. The unit cell is outlined



Table (

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Table 0 11-boliding in the cotype sample of zincoberautine					
D-HA	d(D-H)	<i>d</i> (HA)	<i>d</i> (DA)	<(DHA)	
OH1 – H(1)O5	0.91(3)	2.22(15)	2.821(8)	123(16)	
OH1-H(1)Ow1	0.91(3)	2.22(17)	2.870(9)	128(15)	
OH2-H(2)O1	0.91(4)	1.99(16)	2.741(8)	139(17)	
OH3-H(3)O5	0.90(2)	2.547(19)	3.295(9)	140.8(3)	
Ow1-H(4)O6	0.90(4)	2.29(15)	2.895(9)	125(17)	
Ow1-H(5)O7	0.90(3)	2.36(10)	3.107(8)	141(12)	
Ow2-H(6)O8	0.90(3)	2.04(7)	2.886(9)	155(16)	
Ow2-H(7)Ow3	0.90(2)	1.84(6)	2.695(8)	158(16)	
Ow3-H(8)Ow3	0.91(4)	2.20(8)	2.972(7)	142(15)	
Ow3-H(9)O6	0.90(3)	2.01(11)	2.818(9)	148(17)	

II handing in the actions commute of the

formula corresponds to eleonorite, a mineral validated by the IMA CNMNC in 2015 (IMA 2015-003; Chukanov et al. 2016).

One more beraunite-type mineral tvrdýite $Fe^{2+}Fe_2^{3+}Al_3(PO_4)_4(OH)_5\cdot 6H_2O$ has been approved by the IMA CNMNC recently (IMA 2014-082; Sejkora et al. 2016). Thus, zincoberaunite is the fourth member of the beraunite group.

The general crystal-chemical formula of beraunite-group minerals may be written as follows: $M1M2M3_2M4_2(PO_4)_4(OH,O)(OH)_4 \cdot 6H_2O$ where $M1 = Fe^{2+}$, Fe^{3+} , Mn^{2+} , Zn, Mg; M2, M3 and $M4 = Fe^{3+}$, Al, and minor Cr. The sites M3 and M4 can contain minor amounts of Zn (Sejkora et al. 2016). Oxidative supergene conditions

 Table 7
 Comparative data for beraunite-group minerals

Mineral	Zincoberaunite	Beraunite	Eleonorite	Tvrdýite
Formula	$ZnFe^{3+}{}_{5}(PO_{4})_{4} (OH)_{5} \cdot 6H_{2}O$	$\begin{array}{c} Fe^{2+}Fe^{3+}{}_{5}(PO_{4})_{4}\\ (OH)_{5}\cdot 6H_{2}O\end{array}$	Fe ³⁺ ₆ (PO ₄) ₄ O (OH) ₄ · 6H ₂ O	Fe ²⁺ Fe ₂ ³⁺ Al ₃ (PO ₄) ₄ (OH) ₅ ·6H ₂ O
Crystal system	Monoclinic C2/c	Monoclinic C2/c	Monoclinic C2/c	Monoclinic C2/c
a, Å	20.931	20.630 - 20.953	20.679	20.564
<i>b</i> , Å	5.159	5.164 - 5.171	5.148	5.101
<i>c</i> , Å	19.225	19.22 - 19.266	19.223	18.883
β.°	93.34	93.30 - 93.61	93.574	93.68
VÅ ³	2072	2044 - 2084	2042.5	1976.7
Z	4	4	4	4
Strong lines	10.37 (100)	10.295 (100)	10.41 (100)	10.227 (100)
of the powder	9.58 (32)	7.250 (17)	9.67 (38)	9,400 (6)
X-ray	7.24 (26)	5.147 (12)	7.30 (20)	7.156 (14)
diffraction	4.817 (22)	3.438 (29)	4.816 (31)	5.120 (7)
nattern:	4.409 (13)	3.298 (15)	3.432 (18)	3.416 (11)
d. Å (L. %)	3.483 (14)	3.150 (16)	3.197 (18)	3.278 (6)
	3.431 (14)	2.575 (15)	3.071 (34)	2.562 (5)
	3.194 (15)			2.051 (3)
	3.079 (33)			
Optical data	Biaxial (-)	Biaxial (+) or (-)	Biaxial (+)	Biaxial (-)
1	$\alpha = 1.745$	$\alpha = 1.69 - 1.707$	$\alpha = 1.765$	$\alpha = 1.650$
	$\beta = 1.760$	$\beta = 1.73 - 1.735$	$\beta = 1.780$	$\beta = 1.671$
	$\gamma = 1.770$	$\gamma = 1.73 - 1.738$	$\gamma = 1.812$	v = 1.677
	$2 V = 80^{\circ}$	$2V = 20^{\circ}$ (for optically negative sample)	$2 V = 75^{\circ}$	$2 V = 56^{\circ}$
Strong and	3562	3572	3553	3610
characteristic	3276	3286	3506	3394
bands in the IR	1070	3192	3265	3255
spectrum	1032	1031	1032	1058
-P	990	991	988	1017
	603	604	588	994
	580	590	500	613
	466	456	482	485
Density, $g \cdot cm^{-3}$	2.919 (calc.)	2.894 (calc.)	2.92 (meas.)2.931 (calc.)	2.834 (calc.)
References	This work	Blanchard and Denahan 1968; Moore and Kampf 1992; Sejkora et al. 2006, our data for the IR spectrum	Chukanov et al. 2016	Sejkora et al. 2016

Note: the reflections of the powder X-ray diffraction pattern of beraunite are given for a Zn- and Al-rich variety (Sejkora et al. 2006).

result in the coupled substitution of Fe^{2+} for Fe^{3+} (at the *M*1 site) and OH^- for O^{2-} (Chukanov et al. 2016). Beraunitegroup minerals show a rather wide compositional diversity. In particular, a Mn-rich mineral of this group with the approximate formula $Mn_{0.5}Fe^{3+}{}_{5.5}(PO_4)_4(OH,O)_6 \cdot nH_2O$ has been described by Marzoni Fecia di Cossato et al. (1989) in a phosphatic nodule from a granite at Mangualde, Portugal. Comparative data for beraunite-group minerals are given in Table 7.

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