Belousovite, KZn(SO₄)Cl, a new sulfate mineral from the Tolbachik volcano with apophyllite sheet-topology.

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ABSTRACT

Belousovite, ideally $KZn(SO_4)Cl$, was found in a Yadovitava fumarole of the Second scoria cone of the North Breach of the Great Tolbachik Fissure Eruption (1975-1976), Tolbachik volcano, Kamchatka Peninsula, Russia. Belousovite occurs as irregularly-shaped grains and in the form of microcrystalline masses associated with kamchatkite, langbeinite, euchlorine, anglesite and zincite. Belousovite is monoclinic, $P2_1/c$, a = 6.8904(5), b = 9.6115(7), c = 8.2144(6) Å, $\beta = 96.582(2)$, V = 540.43(7) Å³ and Z = 10004 (from single-crystal diffraction data). The eight strongest lines of the powder X-ray diffraction pattern are $[d_{\text{meas}} Å(I)(hkl)]: 6.8451(100)(100), (3.6401)(71)(\overline{121}), (3.1592)(84)(1\overline{12}), (3.1218)(41)(\overline{211}), (3.1140)$ (52)(022), (2.9812)(41)(031), (2.9121)(44)(130) and $(2.0483)(19)(\overline{3}12)$. The chemical composition determined by the electron-microprobe analysis is (wt.%): K₂O 19.55, Rb₂O 0.58, ZnO 34.85, SO₃ 34.65, Cl 14.77, $-O = Cl_2$ 3.34, total 101.06. The empirical formula based on O + Cl = 5 apfu is K_{0.97}Rb_{0.01}Zn_{1.00}S_{1.01}O_{4.03}Cl_{0.97}. The simplified formula is KZn(SO₄)Cl. The crystal structure was solved by direct methods and refined to $R_1 = 0.029$ on the basis of 1965 independent observed reflections. The structure of belousovite consists of infinite $[ZnSO_4Cl]^-$ layers and K⁺ ions. $[ZnSO_4Cl]^-$ layers are formed by corner sharing mixed-ligand ZnO₃Cl tetrahedra and SO₄ tetrahedra. The topology of [ZnSO₄Cl]⁻ layers in belousovite is identical to [Si₄O₁₀]⁴⁻ layers in the minerals of the apophyllite group. A review of mixedligand ZnO_mCl_n coordination polyhedra in minerals and inorganic compounds is given.

Keywords: belousovite, new minerals, zinc; sulfates, tetrahedral structures, apophyllite, mixed-ligand coordination, Tolbachik volcano.

Introduction

THE volcanogenic exhalation sulfate mineralization from fumaroles of the Tolbachik volcano is renowned for its rich mineral diversity (Vergasova and Filatov, 2016; Siidra *et al.*, 2017*a*,*b*). Many fumarolic sulfate minerals contain alkali elements (K and/or Na) and chloride ions. Exhalative mineral

*E-mail: o.siidra@spbu.ru https://doi.org/10.1180/minmag.2017.081.084 assemblages from fumaroles of the First and Second scoria cones, Great Fissure Tolbachik eruption 1975–76 are well-known for their exceptional diversity of Cu-containing minerals. In addition to Cu, condensates of the 1975–76 eruption are also highly enriched in Zn (Menyailov *et al.*, 1980*a,b*). Zinc impurities are very common in the copper fumarolic minerals. A variety of zinc minerals *sensu stricto* (i.e. minerals with independent crystallographic positions of Zn) are known from fumaroles of the First and Second scoria cones: sofiite, Zn₂(SeO₃)Cl₂ (Semenova

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et al., 1992), prewittite, $\text{KPb}_{1.5}\text{ZnCu}_6(\text{SeO}_3)_2\text{O}_2$ Cl₁₀ (Shuvalov *et al.*, 2013), chubarovite, KZn₂(BO₃)Cl₂ (Pekov *et al.*, 2015*a*), mellizinkalite, K₃Zn₂Cl₇ (Pekov *et al.*, 2015*b*), flinteite, K₂ZnCl₄ (Pekov *et al.*, 2015*c*), cryobostryxite, KZnCl₃·2H₂O (Pekov *et al.*, 2015*d*), zincobradaczekite, NaZn₂Cu₂(AsO₄)₃ (Pekov *et al.*, 2016*a*), zincomenite, ZnSeO₃ (Pekov *et al.*, 2016*b*) and pharmazincite, KZnAsO₄ (Pekov *et al.*, 2017). The first sulfate Zn mineral hermannjahnite CuZn (SO₄)₂ was described only recently from the new fumaroles of the Fissure Tolbachik Eruption 2012– 13 and fumaroles of the Great Fissure Tolbachik Eruption 1975–76 (Siidra *et al.*, 2017*c*).

Herein we report on the chemical composition, structure and properties of belousovite, $KZn(SO_4)Cl$. The mineral is named in honour of Dr Alexander Borisovich Belousov (Александр Борисович Белоусов) (b. 1962), Institute of Volcanology, Russian Academy of Sciences, Petropavlovsk-Kamchatskiy, Kamchatka, Russia, in recognition of his contributions to volcanology (Belousov et al., 1999, 2013, 2015). Both the mineral and the mineral name were approved by International Mineralogical Association the Commission on New Minerals, Nomenclature and Classification (IMA2016-047, Siidra et al., 2016). Type material is deposited at the Mineralogical Museum, St. Petersburg State University, St. Petersburg, Russia (catalogue no. 1/19665).

Occurrence and association

Belousovite occurs as a product of fumarolic activity. It was found in July, 2015 in the Yadovitaya fumarole, Second scoria cone, Northern Breakthrough (North Breach), Great Fissure eruption, Tolbachik volcano, Kamchatka, Russia. The Second scoria cone is located ~18 km SSW of the active shield volcano Ploskiy Tolbachik (Fedotov and Markhinin, 1983). Associated minerals are kamchatkite, langbeinite, euchlorine, anglesite and zincite (Fig. 1). Langbeinite forms intimate intergrowths with belousovite. Belousovite is a fumarolic mineral that is deposited directly from volcanic gas emissions as a sublimate. The temperature of gases at the sampling location was ~250°C. Belousovite is soluble in H₂O at room temperature and transforms slowly into hydrate in humid air. For this reason all the samples recovered were packed hermetically immediately after collecting and isolated to avoid any contact with the atmosphere.

Physical properties

Belousovite occurs as irregularly-shaped grains and in the form of microcrystalline masses up to 0.1 cm wide (Fig. 1). Belousovite is colourless; the streak is white; and the lustre is vitreous. The mineral is transparent in individual grains and translucent



FIG. 1. Belousovite (Bel, centre) in association with kamchatkite (Kam), langbeinite (Lan), euchlorine (Euc), anglesite (Ang) and Zincite (Zin).

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in aggregates. Belousovite is brittle with perfect cleavage on (100). The fracture is uneven. Hardness and density could not be measured due to the very small size of individual grains and the porosity of the aggregates. The calculated density based on the empirical formula of the holotype is 2.89 g cm^{-3} . Belousovite is optically biaxial (+), $\alpha = 1.532(2)$, $\beta = 1.544(2)$ and $\gamma = 1.570(2)$ (589 nm) with 2V (calc.) = 69.4°. Belousovite appears colourless and non-pleochroic under the microscope. The Gladstone-Dale compatibility index, $1 - (K_n/K_n) =$ 0.020, is excellent (Mandarino, 2007).

Chemical composition

Four crystals (65 \times 30, 30 \times 10, 15 \times 10 and 10 \times 10 µm) of belousovite checked previously by singlecrystal X-ray diffraction for quality were mounted in epoxy resin and polished without water and oil using a BUELHER CarbiMet P1000, MicroCut P2500 and ChemoMet I. The mineral was analysed using a Hitachi S-3400N scanning electron microscope equipped with an Oxford Instruments X-Max 20 Energy Dispersive Spectrometer (EDS) and INCA Wave 500 wavelength dispersive spectrometer (WDS). The conditions for EDS were: accelerating voltage of 20 kV, electron beam current of 1.0 nA and defocused beam (up to 15 µm). The current was measured using a Faraday cup. X-ray acquisition time was 30 s and X-ray processing time '5' for analysis. System calibration was performed on CoK α -K β . X-ray matrix correction was carried-out automatically by the Oxford Instruments AZtec Tru-Q including an exponential (XPP, Pouchou and Pichoir, 1991) and pile-up correction routine. The results of six spot analyses are reported in Table 1. The empirical formula based

TABLE 1. Chemical composition (wt.%) of belousovite.

on O + Cl = 5 atoms per formula units is $K_{0.97}Rb_{0.01}Zn_{1.00}S_{1.01}O_{4.03}Cl_{0.97}$. The ideal formula is KZn(SO₄)Cl.

The energy-dispersive spectrum shows that K, Zn, S, O and Cl are the major elements in the mineral, together with small amounts of Rb (Fig. S1, see supplementary material section below). We assumed that the mineral with potassium as a major element and minor rubidium may also contain sodium as a minor component, however, there is significant overlapping of $ZnL\alpha$ (12.254 Å, 1.0120 keV) and $L\beta$ (11.983 Å, 1.0120 keV)1.0350 keV) over NaKα (11.910 Å, 1.0410 keV) and $K\beta$ (11.617 Å, 1.0670 keV) so it is not feasible to measure low quantities of Na in the presence of Zn with the ED spectrometer. Instead we performed WD scanning in the range 11.500-12.500 Å and found only two lines belonging to Zn (TAP crystal, 10 nA beam current, scan speed = 0.25 Å per minute) (Fig. S2). Therefore, we are confident that the mineral does not contain Na. An attempt to use wavelength-dispersive analysis lead to strong damage of the mineral surface (Figs S3 and S4) so the mineral was only analysed by energy-dispersive analysis.

X-ray crystallography

Powder X-ray diffraction data were collected using a Rigaku R-AXIS Rapid II single-crystal diffractometer equipped with cylindrical image plate detector using Debye-Scherrer geometry (CoKa radiation, d = 127.4 mm). Data (in Å) are given in Table 2. Unit-cell parameters refined from the powder data (Britvin et al. 2017) are as follows: monoclinic, space group $P2_1/c$, a=6.90(1) Å,

Constituent	Mean	Range	S.D.	Probe standard
K ₂ O	19.55	19.46–19.76	0.12	KCl
Rb ₂ O	0.58	0.48-0.64	0.06	RbCl
ZnÔ	34.85	34.53-35.59	0.39	Zn
SO ₂	34.65	34.33-34.80	0.18	CaSO ₄
Cl	14.77	14.50-14.85	0.18	KCl
$-O = Cl_2$	3.34			
Total	101.06			

S.D. - standard deviation.

Ι	$d_{\rm meas}$	$d_{\rm calc}$	h k l
100	6.8451	6.8450	1 0 0
7	6.2134	6.2207	0 1 1
10	5.5826	5.5756	1 1 0
9	4.8182	4.8179	$\overline{1}$ 1 1
4	3.9901	3.9332	1 2 0
71	3.6401	3.6381	$\bar{1}$ 2 1
11	3.4377	3.4225	2 0 0
5	3.3408	3.3404	1 0 2
84	3.1592	3.1553	1 1 2
41	3.1218	3.1158	$\bar{2}$ 1 1
52	3.1140	3.1103	0 2 2
41	2.9812	2.9822	0 3 1
44	2.9121	2.9017	1 3 0
15	2.9041	2.8937	2 1 1
17	2.6217	2.6173	0 1 3
9	2.2208	2.2200	3 1 0
6	2.1983	2.1994	$\bar{2}$ 1 3
3	2.1544	2.1713	1 2 3
8	2.1625	2.1634	1 4 1
19	2.0681	2.0483	<u>3</u> 1 2
12	1.9521	1.9510	3 2 1
11	1.8744	1.8711	0 5 1
10	1.8649	1.8647	3 1 2
8	1.8421	1.8606	1 1 4
14	1.8241	1.8464	<u>2</u> 3 3
6	1.8029	1.8171	$\overline{1}$ 5 1

TABLE 2. Powder X-ray diffraction data for belousovite.

TABLE 3. Crystallographic data and refinement parameters for belousovite.

Cravetal size (mm)	0.20 × 0.20 × 0.24
Crystal size (IIIII)	$0.20 \times 0.20 \times 0.24$
space group	$F Z_1 / C$
$a(\mathbf{A})$	6.8904(5)
b (A)	9.6115(7)
<i>c</i> (A)	8.2144(6)
β (°)	96.582(2)
$V(Å^3)$	540.43(7)
$\mu (mm^{-1})$	6.106
D_{calc} (g/cm ³)	2.900
Radiation wavelength (Å)	0.71073 (MoKα)
θ-range (°)	2.976-39.369
Total reflections.	3017
Unique reflections	2169
Unique $ Fo \ge 4s_F$	1965
R _{int}	0.015
R_1^{m}	0.029
R_1 (all data)	0.033
GoF	1.140
$\rho_{\max,\min} (e^{-\cdot} \text{\AA}^{-3})$	+0.914/-0.976

X-ray diffraction analysis using a Bruker APEX II DUO X-ray diffractometer with a micro-focus X-ray tube operated with MoK α radiation at 50 kV and 40 mA. The data were integrated and corrected for absorption using a multiscan type model implemented in the Bruker programs *APEX* and *SADABS* (Bruker-AXS, 2014). More than a hemisphere of X-ray diffraction data was collected. The refinement in the *P*2₁/*c* space group converged to *R*₁ = 0.029 (Table 3). The final model included anisotropic displacement parameters for all atoms. The final atomic coordinates and anisotropic

The eight strongest lines are shown in bold.

b = 9.65(2) Å, c = 8.18(2) Å, $\beta = 96.5(2)^{\circ}$, V = 541(1) Å³ and Z = 4.

A transparent isometric crystal fragment of belousovite was mounted on a thin glass fibre for

TABLE 4. Coordinates and isotropic displacement parameters $(Å^2)$ of atoms and bond-valence sums* (BVS) in belous ovite.

Atom	BVS	x	У	Z	$U_{ m eq}$
Zn(1)	1.97	0.09754(3)	0.19709(3)	0.03886(3)	0.00642(8)
S(1)	5.96	-0.10809(7)	0.06725(6)	-0.27242(7)	0.00607(10)
K(1)	1.11	0.36115(6)	-0.08093(5)	-0.30380(6)	0.00973(10)
Cl(1)	1.02	0.39194(7)	0.17706(6)	-0.03603(7)	0.01064(11)
O(1)	2.02	0.0362(2)	0.11943(18)	-0.3795(2)	0.0085(3)
O(2)	1.99	-0.1223(2)	0.16742(19)	-0.1364(2)	0.0090(3)
O(3)	2.01	-0.0219(2)	-0.06554(19)	-0.2039(2)	0.0105(3)
O(4)	2.00	-0.2983(2)	0.0473(2)	-0.3622(2)	0.0119(3)

* Expressed in valence units (vu) and calculated using the parameters from Brese and O'Keeffe (1991).

U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
0.00853(10)	0.00514(15)	0.00587(14)	-0.00027(7)	0.00206(7)	0.00029(7)
0.00721(16)	0.0055(3)	0.0056(2)	0.00045(15)	0.00084(13)	0.00004(13)
0.00870(15)	0.0118(2)	0.0088(2)	-0.00100(15)	0.00135(12)	-0.00008(12)
0.00897(17)	0.0114(3)	0.0121(3)	-0.00007(17)	0.00363(15)	0.00011(14)
0.0152(6)	0.0046(8)	0.0067(8)	0.0016(5)	0.0054(5)	-0.0008(5)
0.0101(5)	0.0098(8)	0.0071(8)	-0.0047(5)	0.0015(4)	0.0004(5)
0.0140(6)	0.0079(8)	0.0105(9)	0.0056(6)	0.0049(5)	0.0036(5)
0.0098(5)	0.0159(9)	0.0093(8)	-0.0010(6)	-0.0023(5)	-0.0015(5)
	0.00853(10) 0.00721(16) 0.00870(15) 0.00897(17) 0.0152(6) 0.0101(5) 0.0140(6) 0.0098(5)	0.00853(10) 0.00514(15) 0.00721(16) 0.0055(3) 0.00870(15) 0.0118(2) 0.00897(17) 0.0114(3) 0.0152(6) 0.0046(8) 0.0101(5) 0.0098(8) 0.0140(6) 0.0079(8) 0.0098(5) 0.0159(9)	$\begin{array}{c ccccc} 0 & 0 & 0 \\ 0.00853(10) & 0.00514(15) & 0.00587(14) \\ 0.00721(16) & 0.0055(3) & 0.0056(2) \\ 0.00870(15) & 0.0118(2) & 0.0088(2) \\ 0.00897(17) & 0.0114(3) & 0.0121(3) \\ 0.0152(6) & 0.0046(8) & 0.0067(8) \\ 0.0101(5) & 0.0098(8) & 0.0071(8) \\ 0.0140(6) & 0.0079(8) & 0.0105(9) \\ 0.0098(5) & 0.0159(9) & 0.0093(8) \\ \end{array}$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

TABLE 5. Anisotropic displacement parameters (Å²) of atoms in belousovite.

TABLE 6. Selected interatomic distances (in Å) in belousovite.

Zn(1)–O(1)	1.9502(17)	K(1)–O(4)	2.7412(17)
Zn(1) - O(3)	1.9676(17)	K(1) - O(4)	2.747(2)
Zn(1)-O(2)	1.9871(17)	K(1) - O(3)	2.8559(16)
Zn(1)-Cl(1)	2.1947(5)	K(1) - O(2)	2.9352(18)
		K(1)–O(1)	2.9647(17)
S(1)–O(4)	1.4411(17)	K(1) - Cl(1)	3.2329(8)
S(1)–O(2)	1.4865(18)	K(1) - Cl(1)	3.2480(7)
S(1) - O(1)	1.4881(15)	K(1) - Cl(1)	3.3053(8)
S(1)–O(3)	1.4905(18)		

displacement parameters are given in Tables 4, 5 and selected interatomic distances in Table 6. Lists of observed and calculated structure factors have been deposited with the Principal Editor of *Mineralogical Magazine* and are available as Supplementary material (see below).

The structure of belousovite contains one K^+ , one Zn^{2+} and one S^{6+} site (Fig. 2, Table 4).

Each of the K⁺ cations forms four K–O bonds with the K–O bond lengths in the range of 2.747(2)–2.9647(17) Å and three K–Cl bonds with the K–Cl bond lengths in the range of 3.2329(8)– 3.3053(8) Å. The Zn²⁺ cation is in a tetrahedral environment. It is coordinated by three oxygens and a chloride anion. The Zn–Cl distance of 2.1947(5) Å is significantly longer than those of the Zn–O bonds (1.9502(17)–1.9871(17) Å). One symmetrically independent S⁶⁺ cation forms rather symmetrical SO₄ tetrahedra. The individual S–O distances are in the range of 1.4411(17)–1.4905(18) Å, which is in good agreement for well-refined sulfate structures (1.394–1.578 Å; Hawthorne *et al.*, 2000).

The structure of belousovite consists of infinite $[ZnSO_4Cl]^-$ layers and K^+ ions (Fig. 3). $[ZnSO_4Cl]^-$ layers (Fig. 4*a*) are parallel to the *bc* plane and are interconnected via K^+ cations.

Discussion

The crystal structure of belousovite is isotypic with previously reported synthetic RbZnSO4Cl and TlZnSO₄Cl (Bosson, 1976). In order to investigate whether the topological structure of the layers in belousovite has any similarities with other minerals and synthetic compounds one has to examine their nodal representations (Fig. 4c), where each black node represents tetrahedron (SO₄ or ZnO₃Cl). Two nodes are connected by an edge if the corresponding polyhedra share one common anion. This type of topology (linkage of 4-membered rings creating 8-membered rings) is known in silicate crystal chemistry as the topology of the $[Si_4O_{10}]^{4-}$ layers (Fig. 4b) in the minerals of the apophyllite group (Dunn et al. 1978; Dunn and Wilson, 1978; Liebau, 1985). The '...up-down...' orientations of the Si- O_t (O_t = terminal oxygen atom in a silicate group) bonds relative to the plane of the layer in apophyllite are different from Zn-Cl and S-Ot bond orientations in belousovite. All silicate tetrahedra in each 4-membered ring are oriented in the same direction in apophyllite whereas in belousovite each 4-membered ring consists of two pairs of tetrahedra oriented in opposite directions. Observed '...up-down...' orientations of tetrahedral groups in 4-membered rings in belousovite are similar to those in the $[Si_4O_{10}]^{4-}$ layer in cavansite (Fig. 4d) (Zubkova et al. 2009).

One of the interesting structural features of belousovite is the presence of mixed-ligand



FIG. 2. Coordination of atoms in belousovite.



FIG. 3. General projection of the crystal structure of belousovite along the b axis ($ZnO_3Cl = green$, $SO_4 = yellow$).



FIG. 4. (a) General projection of the [Zn(SO₄)Cl]⁻ layer formed by SO₄ (yellow) and ZnO₃Cl (green) tetrahedra in belousovite. (b) [Si₄O₁₀]⁴ layer formed by the linkage of 4-membered rings resulting in 8-membered rings in the crystal structure of apophyllite. (c) Nodal representation, identical for [Zn(SO₄)Cl]⁻ layers in belousovite and [Si₄O₁₀]⁴ layers in apophyllite. (d) The [Si₄O₁₀]⁴⁻ layer in cavansite has the '...up-down...' orientations of the Si–O_t bonds in 4-membered rings similar to Zn–Cl and S–O_t bonds orientations in belousovite. See the text for details.

ZnO₃Cl coordination polyhedra. Table 7 gives a review of observed Zn–O–Cl stereochemistries in minerals and synthetic materials. There are in total six stereochemically different mixed-ligand coordinations. The ZnO₃Cl tetrahedra, as in belousovite, are the most common, whereas ZnO₄Cl tetragonal pyramids are very rare. Tetrahedra of ZnO₃Cl were reported recently in the structure of another exhalative mineral, chubarovite, KZn₂(BO₃) Cl₂ (Pekov *et al.*, 2015*a*), also found in the sublimates of active fumaroles at the Second and First scoria cones of the Northern Breakthrough of the Great Fissure Tolbachik eruption. The topology of layers in chubarovite is completely different from that of belousovite. The crystal structure of the fumarolic selenite–chloride sofiite, $Zn_2(SeO_3)Cl_2$ (Semenova *et al.*, 1992) contains two different mixed-ligand coordinations of Zn: octahedron ZnO_4Cl_2 and tetrahedron ZnO_2Cl_2 . Protonated Zn (OH)₃Cl tetrahedra were described previously in the structures of gordaite NaZn₄(SO₄)(OH)₆Cl(H₂O)₆ (Adiwidjaja *et al.*, 1997) and simonkolleite Zn₅(OH)₈Cl₂(H₂O) (Hawthorne and Sokolova, 2002).

Prewittite, $\text{KPb}_{1.5}\text{Cu}_6\text{Zn}(\text{SeO}_3)_2O_2\text{Cl}_{10}$ (Shuvalov *et al.*, 2013), has a chemical composition somewhat

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Coordination number	Communication of the second se	Example			
	bond-lengths	Site	Formula/mineral	Ref.	
[4] = [(3)+(1)]	Tetrahedron, ZnO ₃ Cl	Zn2	$Zn_{5}(OH)_{8}Cl_{2}(H_{2}O)$, simonkolleite	1	
	<Zn $-$ O $> = 1.95 Å$	Zn1	$KZn_2(BO_3)Cl_2$ chubarovite	2	
	<Zn $-$ Cl $> = 2.26$ Å	Zn1	$NaZn_4(SO_4)(OH)_6Cl(H_2O)_6$, gordaite	3,4	
		Zn2	$CaZn_8(SO_4)_2(OH)_{12}Cl_2(H_2O)_9$	5	
		Zn1	$TlZn(SO_4)Cl$	6	
		Zn1	$RbZn(SO_4)Cl$	6	
		Zn1	$KZn(SO_4)Cl$, belousovite	this work	
		Zn1	BaZn(TeO ₃)Cl ₂	7	
[4] = [(2)+(2)]	Tetrahedron, ZnO_2Cl_2	Zn1	$Zn_2(SeO_3)Cl_2$, sofiite	8	
	<Zn $-$ O $> = 2.01 Å$	Zn1	$Zn_2(TeO_3)Cl_2$	9	
	< Zn - Cl > = 2.24 Å	Zn1	β -Zn ₂ (SeO ₃)Cl ₂	10	
		Zn2	BaZn(TeO ₃)Cl ₂	7	
		Zn1	$CuZn(TeO_3)Cl_2$	11	
		Zn1	Sb ₂ ZnO ₃ Cl ₂	12	
[4] = [(1)+(3)]	Tetrahedron, ZnOCl ₃	Zn1	$KZnCl_3(H_2O)_2$	13	
	<zn–o>= 2.00 Å <zn–cl> = 2.26 Å</zn–cl></zn–o>	Zn1	$KZnCl_3(H_2O)$	14	
[5]=[(4)+(1)]	Tetragonal pyramid, ZnO ₄ Cl <zn–o> = 2.06 Å <zn–cl> = 2.39 Å</zn–cl></zn–o>	Zn2	Zn ₂ (TeO ₃)Cl ₂	9	
[6] = [(4)+(2)]	Octahedron, ZnO ₄ Cl ₂	Zn2	$Zn_2(SeO_2)Cl_2$, Sofiite	8	
	$<$ Zn $-$ O $> = 2.06 Å^{-2}$	Zn2	β - $Zn_2(SeO_3)Cl_2$	10	
	< Zn - Cl > = 2.60 Å	Zn1	$ZnCl_{2}(H_{2}O)_{1,33}$	15	
[6] = [(2)+(4)]	Octahedron, ZnO_2Cl_4 <zn-o>= 2.03 Å <zn-cl>= 2.50 Å</zn-cl></zn-o>	Zn1	$Zn(AuCl_4)_2(H_2O)_2$	16	

TABLE 7. Mixed-ligand ZnO_mCl_n coordination polyhedra in minerals and inorganic compounds.

References: (1) Hawthorne and Sokolova (2002); (2) Pekov *et al.* (2015*a*); (3) Adiwidjaja *et al.* (1997); (4) Zhu *et al.* (1997); (5) Burns *et al.* (1998); (6) Bosson (1976); (7) Jiang *et al.* (2006); (8) Semenova *et al.* (1992); (9) Johnsson and Törnroos (2003*a*); (10) Johnsson and Törnroos (2007); (11) Johnsson and Törnroos (2003*b*); (12) Jo *et al.* (2010); (13) Suesse and Brehler (1964); (14) Brehler and König (1969); (15) Follner and Brehler (1970); (16) Jones *et al.* (1988).

similar to belous ovite. But Zn^{2+} cations form pure chloride $ZnCl_4$ tetrahedra in the structure of prewittite.

Belousovite, $KZn(SO_4)Cl$, reported herein is a new and unique mineral species, and the first sulfate compound and mineral containing K, Zn and Cl in the one mineral. The discovery of belousovite expands our knowledge on mineralogy and geochemistry of zinc mixed-ligand species in volcanic fumarolic environments.

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Supplementary material

To view supplementary material for this article, please visit https://doi.org/10.1180/minmag.2017. 081.084

References

Adiwidjaja, G., Friese, K., Klaska, K.H. and Schlueter, J. (1997) The crystal structure of gordaite NaZn₄SO₄(OH)₆Cl₆(H₂O). Zeitschrift für Kristallographie – Crystalline Materials, **212**, 704–707.

- Belousov, A., Belousova, M. and Voight, B. (1999) Multiple edifice failures, debris avalanches and associated eruptions in the Holocene history of Shiveluch volcano, Kamchatka, Russia. *Bulletin of Volcanology*, 61, 324–342.
- Belousov, A., Belousova, M. and Nechayev, A. (2013) Video observations inside conduits of erupting geysers in Kamchatka, Russia, and their geological framework: Implications for the geyser mechanism. *Geology*, **41**, 387–390.
- Belousov, A., Belousova, M., Edwards, B., Volynets, A. and Melnikov, D. (2015). Overview of the precursors and dynamics of the 2012-13 basaltic fissure eruption of Tolbachik Volcano, Kamchatka, Russia. *Journal of Volcanology and Geothermal Research*, **307**, 22–37.
- Bosson, B. (1976) The crystal structures of RbZnSO₄Cl and TlZnSO₄Cl. *Acta Crystallographica*, **B32**, 2044–2047.
- Brehler, B. and König, B. (1969) Kristallstruktur von Kaliumtrichlorozincatmonohydrat. *Naturwissenschaften*, 56, 279–279.
- Brese, N.E. and O'Keeffe, M. (1991) Bond-valence parameters for solids. *Acta Crystallographica*. B47, 192–197.
- Britvin, S.N., Dolivo-Dobrovolsky, D.V. and Krzhizhanovskaya, M.G. (2017) Software for processing the X-ray powder diffraction data obtained from the curved image plate detector of Rigaku RAXIS Rapid II diffractometer. *Proceedings of the Russian Mineralogical Society*, **146**, 104–107.
- Bruker-AXS (2014) APEX2. Version 2014.11-0. Madison, Wisconsin, USA.
- Burns, P.C., Roberts, A.C. and Nikischer, A.J. (1998) The crystal structure of $Ca(Zn_8(SO_4)_2(OH)_{12}Cl_2)(H_2O)_9$, a new phase from slag dumps at Val Varenna, Italy. *European Journal of Mineralogy*, **10**, 923–930.
- Dunn, P.J. and Wilson, W.E. (1978) Nomenclature revisions in the apophyllite group: hydroxyapophyllite, apophyllite, fluoroapophyllite. *Mineralogical Record*, 9, 95–98.
- Dunn, P.J., Rouse, R.C., Norberg, J.A. and Peacor, D.R. (1978) Hydroxyapophyllite, a new mineral, and a redefinition of the apophyllite group. I. Description, occurences, and nomenclature. II. Crystal structure. *American Mineralogist*, **63**, 196–202.
- Fedotov, S.A. and Markhinin, Ye.K. (1983) The Great Tolbachik Fissure Eruption. Cambridge University Press, New York.
- Follner, H. and Brehler, B. (1970) Die Kristallstruktur des ZnCl₂(H₂O)_{1.333}. *Acta Crystallographica*, **B26**, 1679–1682.
- Hawthorne, F.C., Krivovichev, S.V. and Burns, P.C. (2000) The crystal chemistry of sulfate minerals. Pp. 1–112 in: Sulfate Minerals: Crystallography,

Geochemistry, and Environmental Significance (C.N. Alpers, J.L. Jambor and D.K. Nordstrom, editors). Reviews in Mineralogy and Geochemistry, **40**. The Mineralogical Society of America and the Geochemical Society, Chantilly, Virginia, USA.

- Hawthorne, F.C. and Sokolova, E. (2002) Simonkolleite, $Zn_5(OH)_8Cl_2(H_2O)$, a decorated interrupted-sheet structure of the form $[M_{\Phi 2}]_4$. *Canadian Mineralogist*, **40**, 939–946.
- Jiang, H., Feng, M.L. and Mao, J.G. (2006) Synthesis, crystal structures and characterizations of BaZn (SeO₃)₂ and BaZn(TeO₃)Cl₂. Journal of Solid State Chemistry, **179**, 1911–1917.
- Jo, V., Kim, M.K., Lee, D.W., Shim, I.W. and Ok, K.M. (2010) Lone pairs as chemical scissors in new antimony oxychlorides, Sb₂ZnO₃Cl₂ and Sb₁₆Cd₈O₂₅ Cl₁₄. *Inorganic Chemistry*, **49**, 2990–2995.
- Johnsson, M. and Törnroos, K.W. (2003*a*) A synthetic zinc tellurium oxochloride, Zn₂(TeO₃)Cl₂. Acta Crystallographica, C 59, i53–i54.
- Johnsson, M. and Törnroos, K.W. (2003b) Synthesis and crystal structure of the layered compound CuZn(TeO₃) Cl₂. Solid State Sciences, **5**, 263–266.
- Johnsson, M. and Törnroos, K.W. (2007) Zinc selenium oxochloride, beta-Zn₂(SeO₃)Cl₂, a synthetic polymorph of the mineral sophiite. *Acta Crystallographica*, C63, i34–i36.
- Jones, P.G., Schelbach, R., Schwarzmann, E. and Thoene, C. (1988) Diaquabis(tetrachloroaurate(III)-Cl1,Cl2)zinc(II). Acta Crystallographica, C44, 1162–1164.
- Liebau, F. (1985) *Structural Chemistry of Silicates. Structure, Bonding and Classification.* Berlin Heidelberg New York Tokyo, Springer.
- Mandarino, J.A. (2007) The Gladstone–Dale compatibility of minerals and its use in selecting mineral species for further study. *Canadian Mineralogist*, 45, 1307–1324.
- Menyailov, I.A. and Nikitina, L.P. (1980a) Chemistry and metal contents of magmatic gases: the new Tolbachik volcanoes case (Kamchatka). *Bulletin of Volcanology*, 43, 197–205.
- Menyailov, I.A., Nikitina, L.P. and Shapar, V.N. (1980b) Geochemical Features of Exhalations of Great Tolbachik Fissure Eruption. Nauka, Moscow 235 p. [in Russian].
- Pekov, I.V., Zubkova, N.V., Pautov, L.A., Yapaskurt, V.O., Chukanov, N.V., Lykova, I.S., Britvin, S.N., Sidorov, E.G. and Pushcharovsky, D.Y. (2015*a*) Chubarovite, KZn₂(BO₃)Cl₂, a new mineral species from the Tolbachik volcano, Kamchatka, Russia. *Canadian Mineralogist*, **53**, 273–284.
- Pekov, I.V., Zubkova, N.V., Yapaskurt, V.O., Lykova, I.S., Belakovskiy, D.I., Vigasina, M.F., Sidorov, E.G., Britvin, S.N. and Pushscharovsky, D.Yu. (2015b) New zinc and potassium chlorides from fumaroles of the Tolbachik volcano, Kamchatka, Russia: mineral

data and crystal chemistry. I. Mellizinkalite, K₃Zn₂Cl₇. *European Journal of Mineralogy*, **27**, 247–253.

- Pekov, I.V., Zubkova, N.V., Yapaskurt, V.O., Britvin, S.N., Vigasina, M.F., Sidorov, E.G. and Pushcharovsky, D.Y. (2015c) New zinc and potassium chlorides from fumaroles of the Tolbachik volcano, Kamchatka, Russia: mineral data and crystal chemistry. II. Flinteite, K₂ZnCl₄. European Journal of Mineralogy, 27, 581–588.
- Pekov, I.V., Zubkova, N.V., Britvin, S.N., Yapaskurt, V.O., Chukanov, N.V., Lykova, I.S., Sidorov, E.G. and Pushcharovsky, D.Y. (2015d) New zinc and potassium chlorides from fumaroles of the Tolbachik volcano, Kamchatka, Russia: mineral data and crystal chemistry. III. Cryobostryxite, KZnCl₃·2H₂O. European Journal of Mineralogy, 27, 805–812.
- Pekov, I.V., Lykova, I.S., Koshlyakova, N.N., Belakovskiy, D.I., Vigasina, M.F., Turchkova, A.G., Britvin, S.N., Sidorov, E.G. and Scheidl, K.S. (2016*a*) Zincobradaczekite, IMA 2016-041. CNMNC Newsletter No. 33, October 2016, page 1137; *Mineralogical Magazine*, 80, 1135–1144.
- Pekov, I.V., Zubkova, N.V., Yapaskurt, V.O., Britvin, S.N., Chukanov, N.V., Lykova, I.S., Sidorov, E.G. and Pushcharovsky, D.Y. (2016b) Zincomenite, ZnSeO₃, a new mineral from the Tolbachik volcano, Kamchatka, Russia. *European Journal of Mineralogy*, 28, 997–1004.
- Pekov, I.V., Yapaskurt, V.O., Belakovskiy, D.I., Vigasina, M.F., Zubkova, N.V. and Sidorov, E.G. (2017) New arsenate minerals from the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka, Russia. VII. Pharmazincite, KZnAsO₄. *Mineralogical Magazine*, **81**, 1001–1008.
- Pouchou, J.L. and Pichoir, F. (1991) Quantitative analysis of homogeneous or stratified microvolumes applying the model "PAP". Pp. 31–75 in: *Electron Probe Quantitation* (K.F.J. Heinrich and D.E. Newbury, editors). Plenum Press, New York.
- Semenova, T.F., Rozhdestvenskaya, I.V., Filatov, S.K. and Vergasova, L.P. (1992) Crystal structure and physical properties of sophiite, Zn₂(SeO₃)Cl₂, a new mineral. *Mineralogical Magazine*, **56**, 241–245.
- Shuvalov, R.R., Vergasova, L.P., Semenova, T.F., Filatov, S. K., Krivovichev, S.V., Siidra, O.I. and Rudashevsky, N. S. (2013) Prewittite KPb_{1.5}Cu₆Zn(SeO₃)₂O₂Cl₁₀, a new mineral from Tolbachik fumaroles, Kamchatka

peninsula, Russia: Description and crystal structure. *American Mineralogist*, **98**, 463–469.

- Siidra, O.I., Nazarchuk, E.V., Zaitsev, A.N., Lukina, E.A., Kayukov, R.A., Vergasova, L.P., Filatov, S.K., Karpov, G.A. and Shilovskikh, V.V. (2016) Belousovite, IMA 2016-047. CNMNC Newsletter No. 33, October 2016, page 1139; *Mineralogical Magazine*, 80, 1135–1144.
- Siidra, O.I., Nazarchuk, E.V., Zaitsev, A.N., Lukina, E.A., Avdontseva, E.Y., Vergasova, L.P., Vlasenko, N.S., Filatov, S.K., Turner, R. and Karpov, G.A. (2017*a*) Copper oxosulfates from fumaroles of Tolbachik vulcano: puninite, Na₂Cu₃O(SO₄)₃ – a new mineral species and structure refinements of kamchatkite and alumoklyuchevskite. *European Journal of Mineralogy*, **29**, 499–510.
- Siidra, O.I., Lukina, E.A., Nazarchuk, E.V., Depmeier, W., Bubnova, R.S., Agakhanov, A.A., Avdontseva, E.Y., Filatov, S.K. and Kovrugin, V.M. (2017b) Saranchinaite, Na₂Cu(SO₄)₂, a new exhalative mineral from Tolbachik volcano, Kamchatka, Russia, and a product of the reversible dehydration of kröhnkite, Na₂Cu(SO₄)₂(H₂O)₂. *Mineralogical Magazine*, **82**, 257–274.
- Siidra, O.I., Nazarchuk, E.V., Agakhanov, A.A., Lukina, E.A., Zaitsev, A.N., Turner, R., Filatov, S. K., Pekov, I.V., Karpov, G.A. and Yapaskurt, V.O. (2017c) Hermannjahnite, CuZn(SO₄)₂, a new mineral with chalcocyanite derivative structure from the Naboko scoria cone of the 2012–2013 fissure eruption at Tolbachik volcano, Kamchatka, Russia. *Mineralogy* and Petrology, **112**, 123–134.
- Suesse, P. and Brehler, B. (1964) Die Kristallstruktur des KZnCl₃(H₂O)₂. Beiträge zur Mineralogie und Petrographie, **10**, 132–140.
- Vergasova, L.P. and Filatov, S.K. (2016) A study of volcanogenic exhalation mineralization. *Journal of Volcanology and Seismology*, **10**, 71–85.
- Zhu, L., Seff, K., Witzke, T. and Nasdala, L. (1997) Crystal structure of Zn₄Na(OH)₆SO₄Cl×6(H₂O). *Journal of Chemical Crystallography*, 27, 325–329.
- Zubkova, N.V., Pekov, I.V., Pushcharovsky, D.Yu. and Chukanov, N.V. (2009) The crystal structure and refined formula of mountainite, KNa₂Ca₂[Si₈O₁₉(OH)]·6H₂O. *Zeitschrift für Kristallographie – Crystalline Materials*, **224**, 389–396.