New zinc and potassium chlorides from fumaroles of the Tolbachik volcano, Kamchatka, Russia: mineral data and crystal chemistry. III. Cryobostryxite, KZnCl₃·2H₂O

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Abstract: The new mineral cryobostryxite, KZnCl₃·2H₂O, is found in the Northern fumarole field at the First scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption, Tolbachik volcano, Kamchatka, Russia. Cryobostryxite is a secondary mineral formed in the upper, moderately hot (30-80 °C) zone of active fumaroles, probably as a product of the interactions between high-temperature volcanic sublimates and meteoric water. It is associated with gypsum, ralstonite and opal; earlier, primary minerals of the assemblage are sellaite, fluorite, halite, anhydrite, cotunnite, sofiite, flinteite, chubarovite, anglesite, challacolloite, zincomenite, saltonseaite, hollandite, hematite, jakobssonite, leonardsenite and olsacherite. Cryobostryxite occurs as anthodites (up to 0.5×2 mm), their aggregates (up to 4×5 mm), granular crusts (up to 2×2 mm) and, rarely, coarse prismatic to acicular crystals (up to 0.2×1 mm). The mineral is transparent, colourless, with vitreous lustre. It is brittle, cleavage is not observed. The Mohs hardness is *ca*. 2. $D_{\text{meas}} = 2.30(2)$, $D_{\text{calc}} = 2.300$ g cm⁻³. Cryobostryxite is optically biaxial (+), $\alpha = 1.522(2)$, $\beta = 1.530(2)$, $\gamma = 1.576(2)$ and $2V_{\text{meas}} = 30(15)^{\circ}$. The chemical composition (wt.%, electron-microprobe data, H₂O calculated for 2 molecules per formula unit, pfu) is: K 14.85, Tl 4.08, Zn 25.82, Cl 41.70, H₂O(calc.) 14.19, total 100.64. The empirical formula calculated on the basis of K + Tl + Zn + Cl = 5 *apfu* is $(K_{0.96}Tl^+_{0.05})_{\Sigma 1.01}Zn_{1.00}Cl_{2.99}$: 2H₂O. Cryobostryxite is monoclinic, $P2_1/c$, a = 6.2795(3), b = 10.1397(3), c = 12.0829(7) Å, $\beta = 107.732(5)^\circ$, V = 732.79(6) Å³ and Z = 4. The strongest reflections of the powder X-ray diffraction pattern [d, Å (I, %) (hkl)] are: 7.62 (30) (011), 5.986 (43) (100), 5.766 (35) (002), 3.907 (33) (-121), 3.466 (20) (121), 3.062 (100) (-202, 023), 2.996 (24) (-211, 200) and 2.853 (27) (-114). The crystal structure, solved from single-crystal X-ray diffraction data (R = 0.0654), contains isolated Zn-centred tetrahedra ZnCl₃(H₂O) connected via eight-coordinated K-centred polyhedra $KCl_7(H_2O)$ to form a pseudo-framework. Both Zn- and K-centred polyhedra involve only O(1) atoms of the $H_2O(1)$ molecules, whereas H₂O(2) molecules are located in holes of the K-Zn-Cl-H₂O(1) polyhedral pseudo-framework. The mineral name is based on two Greek words, $\kappa\rho\omega\sigma$, cold or ice, and $\beta\delta\sigma\tau\rho\nu\xi$, curl, reflecting the typical appearance: visually, anthodites of the mineral are very similar to ice curls. A novel chemical family of minerals including the potassium zinc chlorides flinteite K₂ZnCl₄, mellizinkalite K₃Zn₂Cl₇ and cryobostryxite is discussed in the light of crystal-chemical data and formation conditions.

Key-words: cryobostryxite; new mineral; potassium zinc chloride hydrate; crystal structure; fumarole sublimate; Tolbachik volcano; Kamchatka.

Introduction

This paper is the third one in a series of coupled articles on the mineralogy and crystal chemistry of new zinc and potassium chlorides from active fumaroles located at the scoria cones of the Northern Breakthrough of the Great Tolbachik Fissure Eruption of 1975–76 (NB GTFE), Tolbachik volcano, Kamchatka Peninsula, Far-Eastern Region, Russia. General data on zinc mineralization in these fumaroles are reported in the first paper of the series devoted to mellizinkalite, $K_3Zn_2Cl_7$ (Pekov *et al.*, 2015a). Flinteite, K_2ZnCl_4 , is described in the second article (Pekov *et al.*, 2015b).

The present paper provides the mineralogical and structural data on the new species cryobostryxite, KZnCl₃·2H₂O, and contains the discussion on comparative crystal chemistry and genetic features of these three natural potassium zinc chlorides forming a novel chemical family of minerals. Cryobostryxite (Cyrillic: криобостриксит) is named on the basis of two Greek words, κρύος, cold or ice, and βόστρυξ, curl, reflecting the typical appearance of the mineral: visually, its lustrous, water-clear, colourless curled anthodites are very similar to ice curls. Both the new mineral and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA2014–058). The type specimen is deposited in the systematic collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, with the registration number 94995.

Occurrence and general appearance

Specimens of the new mineral were collected by us in July 2013 in active fumaroles belonging to the Northern fumarole field at the northern slope of the crater of the First scoria cone of the NB GTFE. This scoria cone, situated 18 km SSW of the active volcano Ploskiy Tolbachik, was formed in 1975. It is 300 m high and approximately 0.1 km³ in volume (Fedotov & Markhinin, 1983). Several fumarolic fields active to present day are located on its summit and in the walls of a crater.

The Northern fumarole field, the most interesting in mineralogical aspect, occupies an area over 100 m^2 . According to our measurements using chromel-alumel thermocouple during the 2012-2014 fieldworks, numerous gas vents had temperatures up to 300 °C. Volcanic gas is here enriched with HCl and HF (Zelenski & Taran, 2012). The richest mineralization occurs at depths from 10 to 30 cm below the surface and is mainly represented by sellaite, fluorite, halite and anhydrite forming white or grey crusts on basalt scoria and partially replacing it. Cotunnite, sofiite and flinteite are subordinate minerals. Chubarovite KZn₂(BO₃)Cl₂ (IMA2014–018), anglesite, challacolloite, zincomenite ZnSeO₃ (IMA2014–014), saltonseaite, hollandite, hematite, jakobssonite, leonardsenite and olsacherite were found in minor amounts. All the above-mentioned minerals are hydrogen-free; they were collected by us from pockets with temperatures in the range 140-300 °C. Unlike this, in the upper, moderately hot (30-80 °C) zone located not deeper that 10-15 cm below the surface, hydrous minerals occur, namely gypsum, ralstonite, opal, and cryobostryxite associated with secondary halite and, sporadically, with vernadite replacing saltonseaite.





Fig. 1. Morphology of cryobostryxite: (a) near-parallel aggregate of anthodites in a crack in basalt scoria; (b) both curled anthodites and granular, sugar-like crusts on basalt scoria. Field of view: (a) 3.0 mm, (b) 2.8 mm. Photo: I.V. Pekov & A.V. Kasatkin.

Cryobostryxite was found on the surface of basalt scoria or on incrustations consisting of sellaite, fluorite, halite and/or anhydrite. Most typically the new mineral occurs as anthodites: curled, slightly twisted or, less commonly, relatively straight, up to 2 mm long and 0.5 mm thick (Figs. 1 and Fig. 2a). They form near-parallel columnar (Fig. 1a) or chaotic open-work aggregates up to 4×5 mm in area. Occasionally cryobostryxite anthodites are combined in clusters looking like well-known "gypsum flowers". Another morphological variety of the mineral forms granular, sugar-like crusts (Fig. 1b) up to 2×2 mm in area and up to 0.3 mm thick. The grains composing such crusts have a microspherulitic structure (Fig. 2b). Rarely, coarse prismatic to acicular or spear-like crystals (up to 1 mm long and up to 0.2 mm thick) of cryobostryxite were observed.

Physical properties and optical characteristics

Cryobostryxite is aqua-transparent, colourless, with white streak and vitreous lustre. Visually it resembles ice. The mineral is brittle. Its Mohs hardness is *ca.* 2. Cleavage or parting is not observed and the fracture is uneven. The





Fig. 2. Morphology of cryobostryxite: (a) separate anthodite; (b) microspherulitic crust. SEM (SE) images.

density measured by flotation in heavy liquids (bromoform + dimethylformamide) is 2.30(2) g cm⁻³. The density calculated using the empirical formula is 2.300 g cm⁻³.

Cryobostryxite is optically biaxial (+), with $\alpha = 1.522(2)$, $\beta = 1.530(2)$, $\gamma = 1.576(2)$ (589 nm), $2V_{\text{meas}} = 30(15)^{\circ}$ and $2V_{\text{calc}} = 46^{\circ}$. No dispersion of the optical axes was observed. Under the microscope cryobostryxite is colourless and non-pleochroic. Süsse & Brehler (1964) reported for the synthetic analogue of the mineral that the plane of optical axes is (010) and $Z \wedge c = 26^{\circ}$.

IR spectroscopy

The infrared absorption spectrum of cryobostryxite (Fig. 3) was obtained from a powdered sample mixed with anhydrous KBr and pelletized. The pellet was analyzed using an ALPHA FTIR spectrometer (Bruker Optics) at the resolution of 4 cm⁻¹. Sampling scan number was 16. The IR spectrum of a pure KBr disc was subtracted from the overall spectrum.



Fig. 3. Powder infrared spectrum of cryobostryxite.

The strongest bands in the IR spectrum of cryobostryxite correspond to O–H stretching ($3200-3600 \text{ cm}^{-1}$) and H–O–H bending (1607 cm^{-1}) vibrations of H₂O molecules, as well as to vibrations of H₂O molecule as a whole (508 cm^{-1}). The band at 3590 cm^{-1} and the doublet $3533 + 3520 \text{ cm}^{-1}$ conform with weak hydrogen bonds formed by the atoms H3 and H4 (see below); the splitting $3533 + 3520 \text{ cm}^{-1}$ probably is of dynamic nature due to thermal excitation of low-frequency lattice modes. Bands at 3372 and 3210 cm^{-1} conform with strong hydrogen bonds formed by the atoms H1 and H2. Weak bands in the range $600-1200 \text{ cm}^{-1}$ correspond to overtones and combination modes. Absorptions corresponding to B–O, C–O, N–O and N–H bonds are absent.

Chemical data

Chemical data for cryobostryxite were obtained using a Jeol JSM-6480LV scanning electron microscope equipped with an INCA-Wave 500 wavelength-dispersive spectrometer (Laboratory of local methods of matter investigation, Faculty of Geology, Moscow State University). The WDS mode was used, with an acceleration voltage of 20 kV, a beam current of 10 nA, and a 5 μ m beam diameter. The following standards were used: microcline (K), TlAsS₂ (Tl), ZnSe (Zn), and NaCl (Cl). H₂O was not analysed because of the paucity of pure material. Its content calculated by total difference is compatible with the crystal-structure data (see below).

The average over four spot analyses of cryobostryxite (wt.%, ranges/standard deviations are in parentheses, H₂O calculated for 2 molecules *pfu*) is: K 14.85 (14.12–15.58/0.72), Tl 4.08 (3.61–4.68/0.45), Zn 25.82 (24.83–27.11/0.97), Cl 41.70 (41.18–42.24/0.51), H₂O(calc.) 14.19, total 100.64. Contents of other elements with atomic number higher than 8 are below detection limits. The empirical formula calculated on the basis of K + Tl + Zn + Cl = 5 *apfu* is (K_{0.96}Tl_{0.05})_{Σ 1.01}Zn_{1.00}Cl_{2.99}·2H₂O. The idealized formula KZnCl₃·2H₂O requires K 15.84, Zn 26.48, Cl 43.08, H₂O 14.60, total 100.00 wt.%.

Cryobostryxite dissolves readily in H₂O at room temperature.

X-ray crystallography and crystal structure

Ther powder X-ray diffraction study of cryobostryxite was carried out on a Rigaku R-AXIS Rapid II single-crystal diffractometer equipped with cylindrical image plate detector using Debye-Scherrer geometry (d = 127.4 mm; $CoK\alpha$ -radiation). Powder X-ray diffraction data are given in Table 1. The unit-cell parameters refined from the powder data are: a = 6.280(2), b = 10.141(2), c = 12.087(5) Å, $\beta = 107.67(3)^{\circ}$ and $V = 733.5(6) \text{ Å}^3$.

Single-crystal X-ray diffraction studies were carried out using an Xcalibur S CCD diffractometer. A full sphere of three-dimensional data was collected. Crystal data, data collection information and structure

Table 1. Powder X-ray diffraction data for cryobostryxite.

lobs	$d_{\rm obs}$	$I_{\rm calc}*$	$d_{\rm calc}^{**}$	h k l
30	7.62	31	7.608	011
43	5.986	34	5.981	100
35	5.766	40	5.754	002
18	5.155	16	5.152	110
16	4.978	12	4.972	-102
22	4.643	20	4.640	021
12	4.468	13	4.464	-112
33	3.907	39	3.906	-121
4	3.857	3	3.867	120
19	3.590	16	3.588	013
16	3.563	12	3.556	-113
20	3.466	15	3.466	121
4	3.423	3	3.418	112
1	3.243	0.5	3.243	031
100	3.062	39, 100	3.063, 3.059	-202,023
24	2.996	25, 4	2.996, 2.991	-211,200
13	2.937	6, 6	2.943, 2.932	130, -212
8	2.917	9	2.914	032
10	2.879	7	2.877	004
27	2.853	39	2.850	-114
15	2.754	18	2.754	131
3	2.705	1	2.708	-213
3	2.668	3	2.667	-221
11	2.611	14	2.610	211
2	2.570	1	2.576	220
18	2.535	2, 29	2.536, 2.535	033, 040
6	2.486	7	2.486	-204
6	2.459	9	2.458	-223
19	2.384	37	2.384	221
2	2.342	3	2.343	-115
7	2.319	10	2.320	042
2	2.300	1	2.299	-231
3	2.271	2	2.271	114
5	2.233	0.5, 0.5, 3	2.236, 2.232,	141, -224,
			2.231	-134
6	2.190	4, 2	2.191, 2.182	034, 133
7	2.124	5	2.123	-215
9	2.111	8	2.110	231

Iobs	$d_{\rm obs}$	$I_{\rm calc}^{*}$	$d_{\rm calc}^{**}$	h k l
7	2.095	5, 2	2.096, 2.091	025, -302
10	2.080	11	2.079	142
6	2.048	2	2.048	-312
4	2.033	1	2.032	-311
9	1.997	1, 6, 3	1.997, 1.996,	051, -225,
~	1.077	2	1.994	300
2	1.977	3	1.9/5	-116
/	1.953	0 1	1.953	-242
10	1.943	9,4	1.943, 1.938	232, -304
11	1.921	5, 2, 5, 5	1.922, 1.921,	-321, 134
9	1.895	10	1.894	-323
6	1.882	5, 0.5, 4	1.885, 1.882,	016, -243,
			1.878	-152
3	1.866	1	1.865	151
3	1.841	1	1.840	311
3	1.827	1	1.826	125
3	1.816	2	1.815	204
7	1.789	3, 4, 5	1.793, 1.789,	053, -153,
-			1.787	214
3	1.777	2, 1	1.775, 1.775	-315, -244
2	1.755	2	1.755	321
2	1.750	3	1.748	-333
4	1.731	7,3	1.730, 1.728	-136, 302
2	1.719	4	1.717	330
5	1.702	1, 4, 4, 5	1.704, 1.703,	045, -251,
0	1 672	660	1.701, 1.099	-117, -323
0	1.072	0, 0, 9	1.075, 1.072,	-134, 001,
4	1 637	3	1.636	-316
6	1.630	11	1.629	-161
3	1.615	4	1.613	-342
4	1.601	1.4	1.600, 1.599	-162,234
3	1.588	3	1.588	-227
8	1.568	1.7	1.568, 1.567	-402,340
5	1.551	2, 1	1.551, 1.550	-155, -412
7	1.539	2,7	1.539, 1.537	332, -137
6	1.531	1, 2	1.531, 1.530	-404, 154
3	1.496	2	1.494	-423
3	1.482	3	1.482	-255
3	1.456	2, 1	1.456, 1.455	-352, 163
2	1.449	0.5	1.448	-263
2	1.435	1	1.433	333
2	1.432	1	1.431	314
1	1.417	1	1.415	216
2	1.406	2	1.405	-406
2	1.395	1, 1	1.395, 1.394	-434,056
2	1.387	2	1.387	-346
1	1.370	1	1.371	-318
2	1.354	1	1.355	073
1	1.315	1	1.315	-2/1
2	1.303	0.5, 4, 1	1.302, 1.302,	-1/4, -303,
1	1 277	0.5	1.300	271
1	1.277	0.5	1.277	082
2	1.237	1 4	1.230	-365
ے۔ 1	1.235	3	1.233	182
1	1.17/	5	1.121	102

*Only reflections with $I_{\rm calc} \ge 0.5$ are given. **For unit-cell parameters calculated from single-crystal data; d_{calc} and I_{calc} were calculated using the STOE WinX^{Pow} software package (STOE WinX^{Pow}, 2002).

Formula	$(K_{0.95}Tl_{0.05})ZnCl_3 \cdot 2H_2O$
Formula weight	255.12
Temperature, K	293(2)
Radiation and wavelength, Å	ΜοΚα; 0.71073
Crystal system, space group, Z	Monoclinic, $P2_1/c$; 4
Unit-cell dimensions, Å, °	a = 6.2795(3)
	b = 10.1397(3)
	c = 12.0829(7)
	$\beta = 107.732(5)$
$V, Å^3$	732.79(6)
Absorption coefficient μ , mm ⁻¹	5.985
F ₀₀₀	492
Crystal size, mm	$0.06 \times 0.16 \times 0.25$
Diffractometer	Xcalibur S CCD
θ range for data collection, °	2.68-28.28
Index ranges	$-8 \le h \le 8, -13 \le k \le 13,$
	$-16 \le l \le 16$
Reflections collected	11166
Independent reflections	1819 ($R_{\rm int} = 0.0735$)
Independent reflections with $I > 2\sigma(I)$	1569
Structure solution	direct methods
Refinement method	full-matrix least-squares on F^2
Number of refined parameters	77
Final <i>R</i> indices $[I \ge 2\sigma(I)]$	R1 = 0.0654, wR2 = 0.0878
<i>R</i> indices (all data)	R1 = 0.0820, wR2 = 0.0928
GoF	1.289
Largest diff. peak and hole, $e/Å^3$	0.503 and -0.542

Table 2. Crystal data, data collection information and structure refinement details for cryobostryxite.

refinement details are given in Table 2. Data reduction was performed using CrysAlisPro Version 1.171.35.21 (Agilent, 2012). The data were corrected for Lorentz and polarization effects. An empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm, was applied. The structure was solved by direct methods and refined with the use of the SHELX software package (Sheldrick, 2008) on the basis of 1569 independent reflections with $I > 2\sigma(I)$. Atom coordinates and displacement parameters are given in Table 3, selected interatomic distances in Table 4 and bond valence calculations in Table 5.

The crystal structure of cryobostryxite (Fig. 4a and b), as well as its isostructural Tl-free synthetic analogue $KZnCl_3 \cdot 2H_2O$ (Süsse & Brehler, 1964), contains isolated Zn-centred tetrahedra $ZnCl_3(H_2O)$ with three Zn–Cl bonds ranging from 2.246 to 2.262 Å and one Zn–O bond of 2.005 Å (Table 4). The tetrahedra are connected *via* eight-coordinated K-centred polyhedra $KCl_7(H_2O)$ to form a pseudo-framework. Both Zn- and K-centred polyhedra involve only O(1) atoms of the H₂O(1) molecules whereas $H_2O(2)$ molecules are located in holes of the K-Zn-Cl-H₂O(1) polyhedral pseudo-framework (Fig. 4b) and form hydrogen bonds (Table 5). Admixed Tl in the K site (Tables 3 and 5) is monovalent.

Discussion

The presence of H₂O molecules in cryobostryxite and the minerals associated with it (gypsum, ralstonite and opal) indicates that this assemblage was probably formed not as the result of direct deposition from hot volcanic gas, but during a secondary stage, as a product of the interactions between earlier, high-temperature sublimates (primary phases) and meteoric water or water vapour (and, possibly, involving HCl-bearing fumarolic gas) at relatively low temperatures, presumably not higher than 100 °C. We cannot exclude the involvement of volcanic water or water vapour in this process but consider this hardly probable because of the low content of H₂O (about 1 %) in fumarolic gases of the NB GTFE at present day (Zelenski et al., 2011). Another argument for the secondary, supergene origin of cryobostryxite, deposition from aqueous solution rather than from volcanic gas, is its typical appearance as anthodites (Figs. 1 and Fig. 2a), which are formed as a result of crystallization from solutions on a porous or cracked surface involving capillary action.

Table 3. Atom fractional coordinates, isotropic displacement parameters (U_{eq} , Å²) and site occupancies for cryobostryxite.

Atom	x	у	Z	$U_{ m eq}$	s.o.f.
K	0.33616(16)	0.85944(9)	0.12225(8)	0.0319(4)	$K_{0.9456(12)}Tl_{0.0544(12)}$
Zn	0.03941(10)	0.61783(6)	0.29203(5)	0.02769(19)	1
Cl(1)	0.1836(2)	0.44015(13)	0.39981(12)	0.0327(3)	1
Cl(2)	0.2138(2)	0.80189(13)	0.38086(11)	0.0330(3)	1
Cl(3)	0.6656(2)	0.63225(13)	0.25397(12)	0.0357(3)	1
O(1)	0.0901(6)	0.6122(4)	0.1361(3)	0.0305(8)	1
H(1)	-0.032(5)	0.621(5)	0.082(3)	0.037	1
H(2)	0.162(7)	0.550(4)	0.117(4)	0.037	1
O(2)	0.7340(6)	0.8877(4)	0.4337(4)	0.0385(10)	1
H(3)	0.754(8)	0.824(4)	0.392(4)	0.046	1
H(4)	0.609(5)	0.875(5)	0.445(5)	0.046	1

Table 4. Selected interatomic distances (Å) in	n the structure	of cr	yobostry	xite.
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K – O(1) 2.977(4) - Cl(3) 3.146(2) - Cl(3) 3.180(2) - Cl(1) 3.213(2)	Zn – O(1) 2.005(4 - Cl(1) 2.246(1) - Cl(3) 2.255(1) - Cl(2) 2.262(1)	\$)))		
- Cl(2) 3.226(2) - Cl(1) 3.272(2) - Cl(1) 3.296(2) - Cl(2) 3.487(2) Hydrogen bonds*				
D-H	d(<i>D</i> –H)	$D-\mathrm{H}\cdot\cdot\cdot A$	d(<i>D</i> – <i>A</i>)	$\angle (D-\mathrm{H}\cdot\cdot\cdot A)^{\mathrm{o}}$
O(1) - H(1)	0.85(1)	$O(1)-H(1)\cdot\cdot\cdot O(2)$	2.766(5)	163(4)
O(1) - H(2)	0.85(1)	$O(1)-H(2) \cdot \cdot \cdot O(2)$	2.771(5)	168(5)
O(2) - H(3)	0.85(1)	$O(2)-H(3) \cdot \cdot \cdot Cl(3)$	3.323(4)	160(4)
O(2) – H(4)	0.85(1)	$O(2)-H(4)\cdot\cdot\cdot Cl(2)$	3.250(4)	152(5)

*H atoms were located in a difference Fourier map and refined with O–H and H–H distances restrained to 0.85(1) and 1.37(2) Å, respectively, to hold near-optimal geometry (Nardelli, 1999) and U_{iso} (H) = 1.2 U_{eq} (O).

Table 5. Bond valence calculations for cryobostryxite.

	K*	Zn	\sum	H-bonding	\sum
Cl(1)	0.15				
	0.13	0.53	0.93		0.93
	0.12				
Cl(2)	0.15	0.51	0.73	+0.11(O(2))	0.84
	0.07				
Cl(3)	0.18	0.51	0.86	+0.11(O(2))	0.97
	0.17				
$O(1) = H_2O(1)$	0.10	0.44	0.54	-0.19 (O(2))	0.16
				-0.19 (O(2))	
$O(2) = H_2O(2)$			0.00	+0.19 (O(1))	
				+0.19(O(1))	0.16
				-0.11 (Cl(2))	
				-0.11 (Cl(3))	
\sum	1.07	1.99			

*Calculated for the site fully occupied by K. Bond-valence parameters for K–O, K–Cl, Zn–O and Zn–Cl were taken from Brese & O'Keeffe (1991) and for H-bonding from Ferraris & Ivaldi (1988) and from Malcherek & Schlüter (2007).

Thus, cryobostryxite is considered as a secondary, supergene mineral. Flinteite, which is very soluble in water and unstable in moist air, appears as the most probable source of cations and presumably of chlorine for its formation.

The K-Zn chlorides discovered in deposits of active fumaroles related to the Tolbachik volcano form a novel chemical family of minerals. It includes the structurally different flinteite K₂ZnCl₄, mellizinkalite K₃Zn₂Cl₇ and cryobostryxite KZnCl₃·2H₂O. Taking into account that flinteite was probably formed in hot fumaroles as a result of a phase transition from its hypothetic high-temperature protophase belonging to the β -K₂SO₄ structure type (Pekov *et al.*, 2015b), we believe this family is represented by four members at Tolbachik (Table 6). The K-Zn chlorides are not uncommon there: a significant portion of zinc in deposits of fumaroles belonging to the Northern fumarole field at the First scoria cone of the NB GTFE is concentrated in them.

We observe a correlation between the measured temperature and the presence of a mineral of this family. Only flinteite was collected from fumaroles with temperatures over 270 °C at both the First and the Second scoria cones of the NB GTFE, in agreement with data on conditions of crystallization and phase transitions for synthetic K₂ZnCl₄: its high-temperature modification (Fig. 4c) is stable above 280 °C, an incommensurate phase exists in the range 280-130 °C and, below 130 °C, a flinteite-type low-temperature K₂ZnCl₄ phase (Fig. 4d) is stable (Kucharczyk et al., 1982; Quilichini et al., 1990; Kusz et al., 1997; Ferrari et al., 2001). Mellizinkalite was found only in the Glavnaya Tenoritovaya fumarole at the Second scoria cone, in association with hydrous chlorides and sulphates inside cameras at temperatures near 110 °C (Pekov et al., 2015a), which is in agreement with the thermodynamic calculations showing that K₃Zn₂Cl₇ is stable below 230-250 (Baxter & Heikinheimo. °C 2005). Mellizinkalite is intimately associated with flinteite for which in this case direct crystallization is assumed, based on data by Takai et al. (1995) who reported the precipitation of a low-temperature K₂ZnCl₄ modification from aqueous solution at 35 °C. Cryobostryxite, a hydrous mineral, occurs in the lowermost-temperature assemblage (<80 °C during collecting); its synthetic analogue was prepared from an aqueous solution at 25 °C (D'Ans & Kaufmann, 1957). Thus, we suggest the following general evolution series of K-Zn chlorides in the Tolbachik fumaroles with decreasing temperature: high-temperature $K_2ZnCl_4 \rightarrow$ flinteite + mellizinkalite \rightarrow cryobostryxite. In members of this series the (K +



Fig. 4. The crystal structures of K-Zn chlorides (for crystal data see Table 6): (a), (b) cryobostryxite KZnCl₃·2H₂O, (c) high-temperature K₂ZnCl₄ (drawn after Ferrari *et al.*, 2001), (d) flinteite K₂ZnCl₄ (Pekov *et al.*, 2015b) and (e) mellizinkalite K₃Zn₂Cl₇ (Pekov *et al.*, 2015a). The unit cells are outlined.

Zn):Cl ratio decreases in the same sequence: 0.75 [high-temperature K_2ZnCl_4 and flinteite] $\rightarrow 0.71$ [mellizinkalite] $\rightarrow 0.67$ [cryobostryxite]. This trend could be caused by the decrease of general activity of metals in fumarolic mineral-forming systems with decreasing temperature.

The crystal structures of all the discussed K-Zn chlorides (Table 6) are characterized by the presence of isolated Zncentred tetrahedra: $ZnCl_4$ in synthetic high-temperature K_2ZnCl_4 , flinteite, and mellizinkalite and $ZnCl_3(H_2O)$ in cryobostryxite (Fig. 4). In the structure of mellizinkalite, the Zn cations form, besides $Zn(2)Cl_4$ tetrahedra, also $Zn(1)Cl_4$ flat squares connected in pairs *via* common Cl–Cl edges to form Zn_2Cl_6 dimers (Fig. 4e). These polyhedra could also be described as significantly distorted octahedra with four short Zn(1)–Cl bonds, with distances in the range 2.243(3)–2.336(3) Å, and two strongly elongated Zn(1)–Cl bonds, with the distances 2.99 and 3.12 Å. In this case also discrete Zn-Cl complexes are formed: groups isolated from each other and built by two edge-sharing octahedra connected with two Zn-centred tetrahedra *via* common vertices.

Mineral/Compound	Synthetic*	Flinteite	Mellizinkalite	Cryobostryxite
Formula	K_2ZnCl_4	K_2ZnCl_4	$K_3Zn_2Cl_7$	KZnCl ₃ ·2H ₂ O
Crystal system	Orthorhombic	Orthorhombic	Triclinic	Monoclinic
Space group	Pnam	$Pna2_1$	<i>P</i> -1	$P2_1/c$
a, Å	9.046	26.8090(10)	6.7737(4)	6.2795(3)
b, Å	12.579	12.4085(6)	10.5715(13)	10.1397(3)
<i>c</i> , Å	6.882	7.2512(3)	11.0730(9)	12.0829(7)
α, °			117.930(10)	
β, °			106.909(5)	107.732(5)
γ, °			90.389(8)	
$V, Å^3$	783.1	2412.18(18)	660.61(10)	732.79(6)
Ζ	4	12	2	4
$D_{\rm meas}$, g cm ⁻³	not determined	not determined	2.46(2)	2.30(2)
$D_{\rm calc}, {\rm g} {\rm cm}^{-3}$	2.42	2.49	2.49	2.30
Optical data	not determined			
α		1.573	1.556	1.522
β		1.574	1.612	1.530
Ŷ		1.576	1.663	1.576
optical sign, $2V_{\text{meas}}$		$+40^{\circ}$	-85°	$+30^{\circ}$
Source	Ferrari et al. (2001)	Pekov et al. (2015b)	Pekov et al. (2015a)	this work

Table 6. Comparative data for natural potassium zinc chlorides and the synthetic high-temperature modification of K₂ZnCl₄.

*A hypothetic natural analogue of this compound belonging to the β -K₂SO₄ structure type and stable above 280°C is assumed to be a protophase of flinteite in fumaroles related to the Tolbachik volcano.

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