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CHUBAROVITE, $KZn_2(BO_3)Cl_2$, A NEW MINERAL SPECIES FROM THE TOLBACHIK VOLCANO, KAMCHATKA, RUSSIA

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ABSTRACT

The new mineral chubarovite, $KZn_2(BO_3)Cl_2$, was found in the sublimates of active fumaroles at the Second and First scoria cones of the Northern Breakthrough of the Great Tolbachik Fissure Eruption, Tolbachik volcano, Kamchatka, Russia. At the Second scoria cone it occurs in the Arsenatnaya fumarole (the holotype) with fluoborite, krasheninnikovite, sylvite, halite, langbeinite, aphthitalite, orthoclase, fluorophlogopite, hematite, and tenorite. At the First scoria cone, chubarovite is closely associated with sellaite, fluorite, anhydrite, halite, cotunnite, challacolloite, sofiite, and flinteite. Chubarovite forms hexagonal or trigonal lamellar to tabular crystals up to 1.5 mm across and up to 0.5 mm thick, with aggregates and crystal crusts up to 1 cm across. The major crystal form is {001}, and lateral faces are {101}, {102}, {103}, {100}, and {110}; twins of two types are observed. Chubarovite is transparent, colorless, with vitreous luster. It is flexible but not elastic. The Mohs hardness is *ca.* 2. Cleavage is (001) perfect, mica-like. D(meas.) is 2.68(2), D(calc.) is 2.716 g cm^{-3}. Chubarovite is optically uniaxial (–), with ω 1.541(2), ε 1.539(2). The infrared spectrum is given. Chemical data (wt.%, determined by electron-microprobe, boron by ICP OES) are: K_2O 16.48, Rb_2O 0.46, ZnO 53.96, B_2O_3 10.98, Cl 24.48, $–O=Cl_2$ –5.53, total 100.83. The empirical formula, based on 5 (O+Cl) *apfu*, is: $(K_{1.05}Rb_{0.01})_{\Sigma 1.06}Zn_{2.00}B_{0.95}O_{2.92}Cl_{2.08}$. Chubarovite is trigonal, $R32$, a 4.9429(4), c 26.348(2) Å, V 557.50(8) Å^3, and $Z = 3$. The strongest reflections of the powder X-ray diffraction pattern

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[*d*,Å(*I*)(*hkl*)] are: 8.79(100)(003), 4.394(43)(006), 4.225(25)(101), 4.074(91)(012), 3.590(90)(104), 3.324(30)(015), 2.470(67)(110), and 2.245(25)(1.0.10). Chubarovite has a novel structure type. Its crystal structure, solved from single-crystal X-ray diffraction data ($R = 0.020$), is composed of layers of two types with an alternation along [001]. The anionic $\{Zn_2(BO_3)Cl_2\}^-$ layer consists of flat triangular BO_3 groups sharing all O vertices with bases of ZnO_3Cl tetrahedra. Each Cl atom is shared between one Zn-centered tetrahedron and three edge-connected KCl_6 octahedra belonging to the cationic layer formed by K^+ cations. The mineral is named in honor of the Russian mineralogist and physicist Valeriy M. Chubarov (born 1948).

Keywords: chubarovite, new mineral, chloride borate, crystal structure, fumarole sublimate, Tolbachik volcano, Kamchatka.

INTRODUCTION

Boron is considered in geochemistry as one of the most mobile elements that forms many simple and complex volatile compounds. This feature causes significant enrichment of volcanic exhalations with boron that, in particular, results in the formation of huge volcano-sedimentary borate deposits (Grew & Anovitz 1996). At the same time, the high volatility of boron prevents the formation of its minerals in high-temperature volcanic sublimates because of low pressures.

Boron minerals known in fumaroles at active volcanoes are not diverse and occur in small amounts, but the mineralogy of boron in this formation is very specific. In the first place, there are borofluorides, minerals with the tetrahedral anion $[BF_4]^-$, endemic for fumarole formation: avogadrite $(K,Cs)[BF_4]$, ferruccite $Na[BF_4]$ (Palache *et al.* 1951), barberiite $(NH_4)[BF_4]$ (Garavelli & Vurro 1994), and knasibfite $K_3Na_4[SiF_6]_3[BF_4]$ (Demartin *et al.* 2008). Another specific group includes natural boric acids, namely sassolite H_3BO_3 (Zambonini 1935, Basharina 1961, Serafimova 1979, Campostrini *et al.* 2011) and dimorphous metaborite and clinometaborite, HBO_2 (Demartin *et al.* 2011). These minerals are formed in fumaroles with temperatures not higher than 250–300 °C, and typically lower than 200 °C (Basharina 1961, Campostrini *et al.* 2011). In hotter fumaroles boron minerals are extremely rare; vonsenite $Fe^{2+}{}_2Fe^{3+}(BO_3)O_2$ found at Vesuvio, Campania (Russo & Punzo 2004), and Vulcano, Aeolian Archipelago (Demartin *et al.* 2011), both in Italy, is probably a product of relatively high-temperature (>300 °C) crystallization from fumarolic gas.

Boron mineralization in fumaroles related to active volcanoes of the Kamchatka peninsula, Russian Far East, is scarce and is represented mainly by sassolite reported for three volcanoes: Avachinsky (Naboko 1959), Klyuchevskoy (Basharina 1961), and Bezymyannyi (Serafimova 1979). Avogadrite and ferruccite were mentioned for fumarolic deposits of the Klyuchevskoy volcano (Piip 1956). For the Tolbachik volcano, the world record-holder in the diversity of fumarolic minerals (almost 200 mineral species: Vergasova & Filatov 2012; our data), boron mineralization was not reported before now, in spite of the relatively high content of B detected in both fumarolic gases (up to 143 mg/l: Fedotov & Markhinin 1983) and sublimate incrustations (up to 270 ppm: Meniaylov *et al.* 1980).

Two borates were found in the Arsenatnaya fumarole discovered in July 2012 (Pekov *et al.* 2014) at the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption of 1975–1976 (GTFE) located 18 km SSW of the Ploskiy Tolbachik volcano. In 2012, we found fluoborite very close chemically to its endmember, $Mg_3(BO_3)F_3$. During fieldwork in July 2013 we collected specimens with another borate mineral, a new species with the idealized formula $KZn_2(BO_3)Cl_2$ described in the present paper. It was named chubarovite (Russian Cyrillic: чубаровит) in honor of the Russian mineralogist and physicist Valeriy Mikhailovich Chubarov (born 1948), a specialist in electron microprobe analysis. He has worked in the Institute of Volcanology and Seismology of the Far Eastern Branch of the Russian Academy of Sciences in Petropavlovsk-Kamchatsky since 1983 and has made a great contribution to the mineralogy of Kamchatka, including studies of many minerals from the fumarolic exhalations of the Tolbachik volcano. Both the new mineral and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA 2014–018). The type specimen is deposited in the systematic collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow; the catalogue number is 94379.

OCCURRENCE AND GENERAL APPEARANCE

Arsenatnaya is an active fumarole located in the apical part of the Second scoria cone of the Northern Breakthrough of the GTFE, Tolbachik volcano, Kamchatka Peninsula, Far-Eastern Region, Russia (55° 41'N 160° 14'E, 1200 m asl). This scoria cone was formed in 1975. It is a monogenetic volcano about 300 m high and approximately 0.1 km^3 in volume (Fedotov & Markhinin 1983). Now, almost forty years later, its fumarole fields remain hot: up to 430 °C, according to our measurements performed in 2013–2014. The fumarolic gases at Arsenatnaya are now compositionally close to atmospheric air, with contents of <1 vol.% water vapor and <0.1 vol.% acid species, mainly CO_2, HF, and HCl (Zelenski *et al.* 2012). The Arsenatnaya fumarole is a system of numerous mineralized open pockets located between blocks of basalt scoria and volcanic bombs at depths of 0.3 to 1.0 m below the surface. The mineralization is very diverse: more than 60 minerals have been identified by us at Arsenatnaya (Pekov *et al.* 2014). Chubarovite was initially found in a fracture-like pocket about 5 × 20 × 40 cm in size in the northern part of the fumarole. The temperature in this pocket measured using a chromel-alumel thermocouple immediately after its uncovering (July 2013) was 350–360 °C.

Besides the holotype from the northern part of Arsenatnaya (all quantitative data of chubarovite given below were obtained for the holotype), the new mineral was also found later, in 2014, in the southern part of the same fumarole, and also at the First scoria cone of the Northern Breakthrough of the GTFE.

Chubarovite occurs as hexagonal or, less commonly, trigonal lamellar to tabular crystals typically formed by the pinacoidal and rhombohedral faces, sometimes with subordinate prismatic faces. The major form is the pinacoid {001}; lateral faces are represented by rhombohedra {101}, {102}, and {103} and prisms {100} and {110} (Figs. 1, 2 and 3a–f). Crystals are well-shaped (Figs. 1 and 2a–e,g) or crude (Fig. 2f,h), sometimes divergent, resembling flowers (Fig. 1b) or an open book. Simple twins of two types are observed: contact twins with the axis [001], rotation angle 180°, and single composition surface {001} (Figs. 1a, 2c,d and 3g,h) are common, whereas X-shaped penetration twins on (103) (Figs. 2a,b and 3i) are more rare. Commonly chubarovite crystals are combined in open-work groups, drusy aggregates (Figs. 1c and 2c–d), or more compact clusters (Fig. 2e). The mineral also forms dense or interrupted crystal crusts (Figs. 2f–h). Single crystals and twins are up to 1.5 mm across and up to 0.5 mm thick (typically not larger than 0.2 × 0.8 mm), and their aggregates and crystal crusts are up to 1 cm across. Areas “sprinkled” with separate crystals or aggregates of chubarovite are up to 20 cm^2.

In the northern part of Arsenatnaya, chubarovite overgrows basalt scoria and thin crusts or crystal clusters of the earliest fumarolic minerals, namely orthoclase, fluorophlogopite, hematite, and tenorite. An intimate association of chubarovite with another borate mineral, fluoborite, forming acicular to hair-like crystals, is typical (Figs. 2b,c,e). Fluoborite crystallized earlier than chubarovite and commonly forms inclusions in its crystals. Other minerals associated with the holotype chubarovite are krasheninnikovite, sylvite, halite, langbeinite, aphthitalite, arcanite, zincite, flinteite K_2ZnCl_4 (IMA 2014-009), wulffite $K_3NaCu_4O_2(SO_4)_4$ (IMA 2013-035), johillerite, urusovite, and pseudobrookite.

In the southern part of Arsenatnaya, small (up to 0.1 mm) crystals of chubarovite overgrow langbeinite and halite crusts and are associated with aphthitalite, vanthoffite, fluoborite, calciolangbeinite, sylvite, flinteite, zincite, svabite, and hematite.

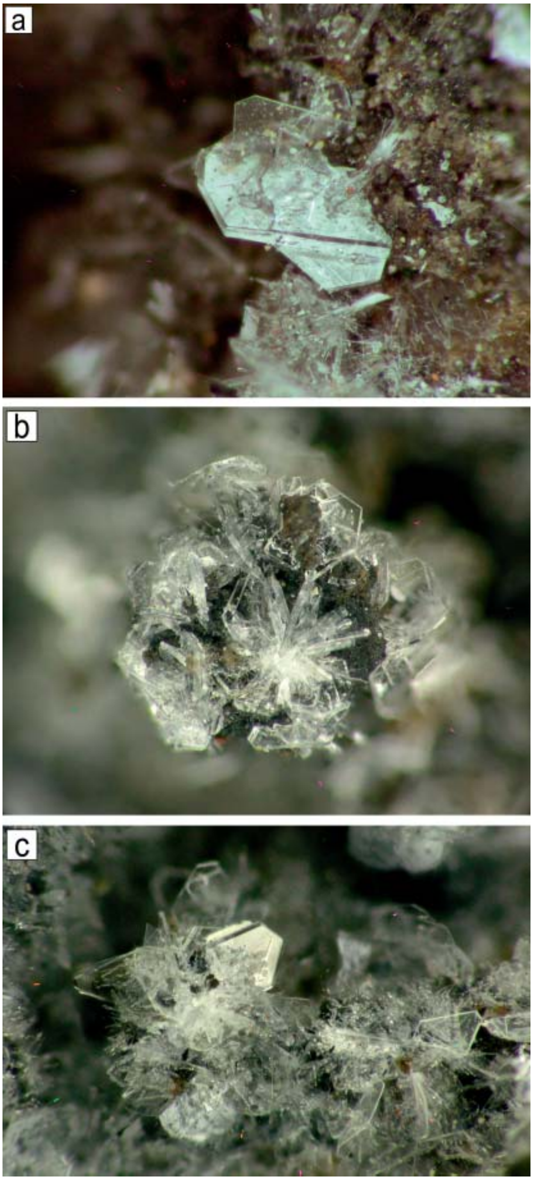

FIG. 1. Morphology of chubarovite: (a) contact twin with the single composition surface {001}; (b) strongly divergent crystal (in the center) and single crystals; (c) typical drusy aggregate. FOV 2 mm for each photograph.

The First scoria cone, a monogenetic volcano formed in 1975 before the Second scoria cone (Fedotov & Markhinin 1983), is joined with the latter from South and has a similar size. Active fumarole fields are situated in the walls of its crater.

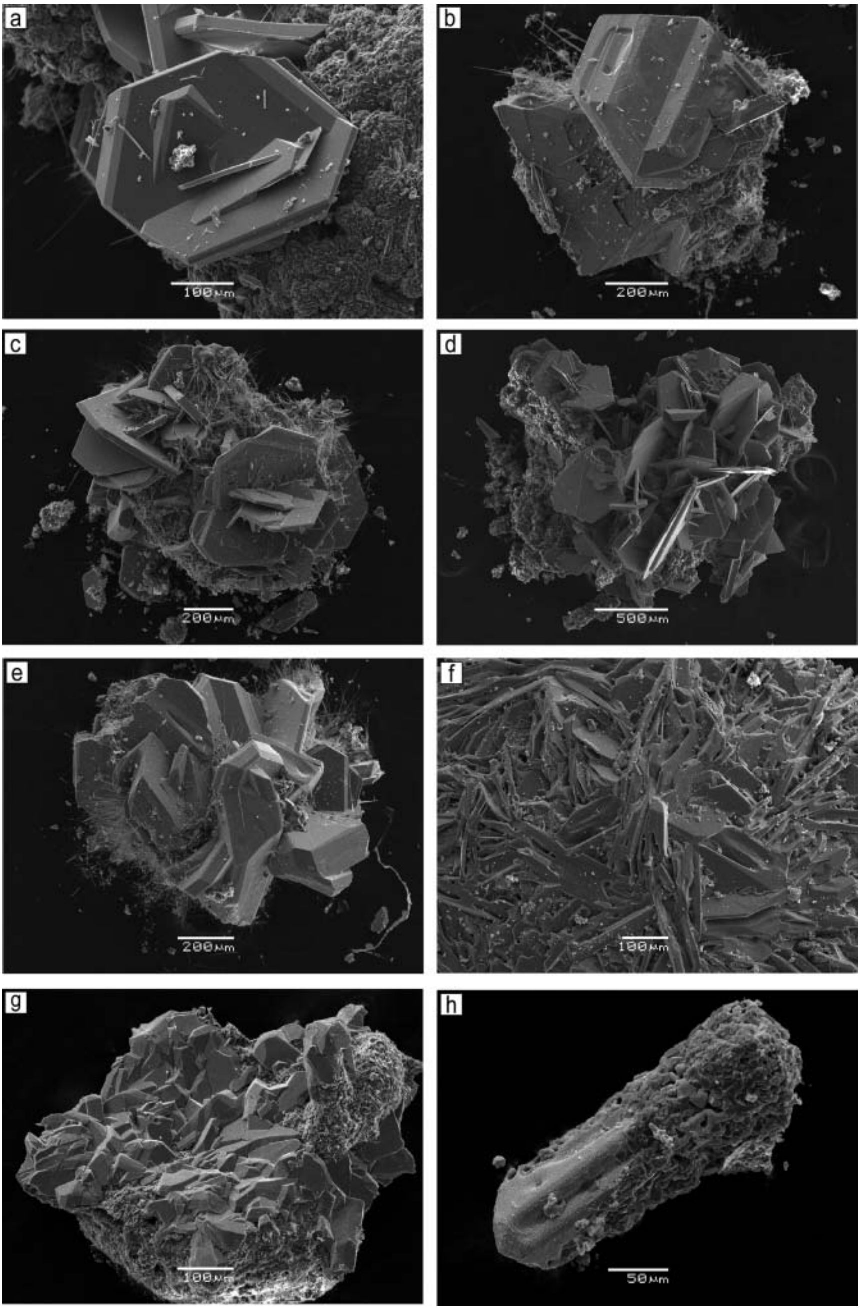

FIG. 2. Morphology of chubarovite (a–f: from the Arsenatnaya fumarole, g–h: from the First scoria cone): (a, b) X-shaped penetration twins on (103); (c, d) crystal groups containing contact twins with the single composition surface {001}; (e) crystal cluster with a tabular crystal of complicated shape (in the center) and X-shaped penetration twin on (103) (in the upper part); (f) dense monomineralic crust formed by crude crystals; (g) crystals on sellaite crust; (h) crust of crude crystals overgrowing prismatic crystal of challacolloite. Acicular, hair-like crystals of fluoborite intimately associated with chubarovite are observed in (b), (c), and (e). SEM (SE) images.

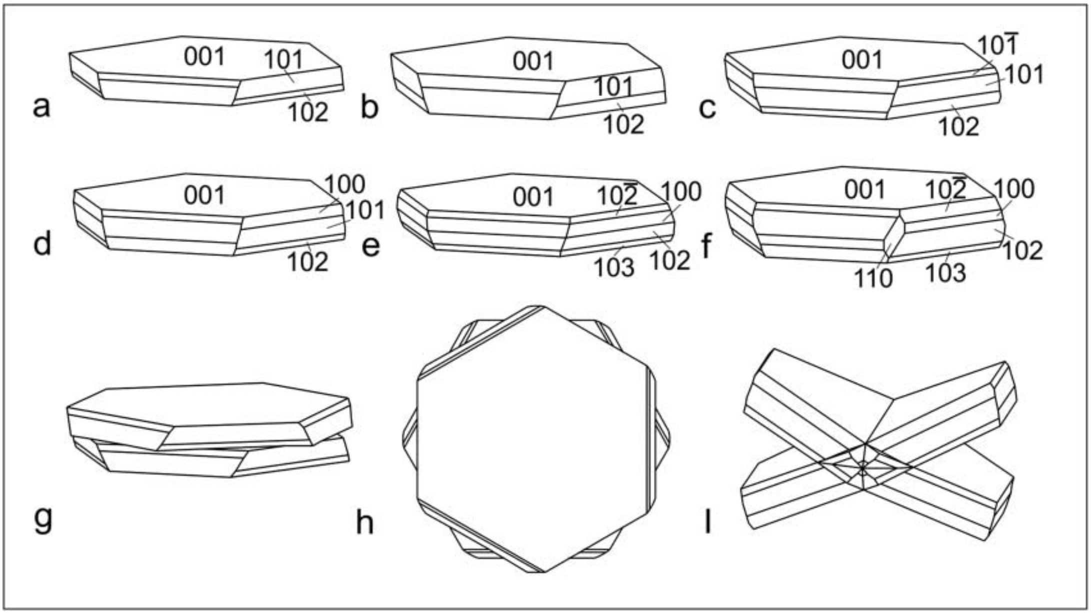

FIG. 3. Crystals (a–f) and twins (g–i) of chubarovite; (g, h) contact twin with axis [001], rotation angle 180°, and single composition surface {001} (in two projections); (i) penetration twin on (103).

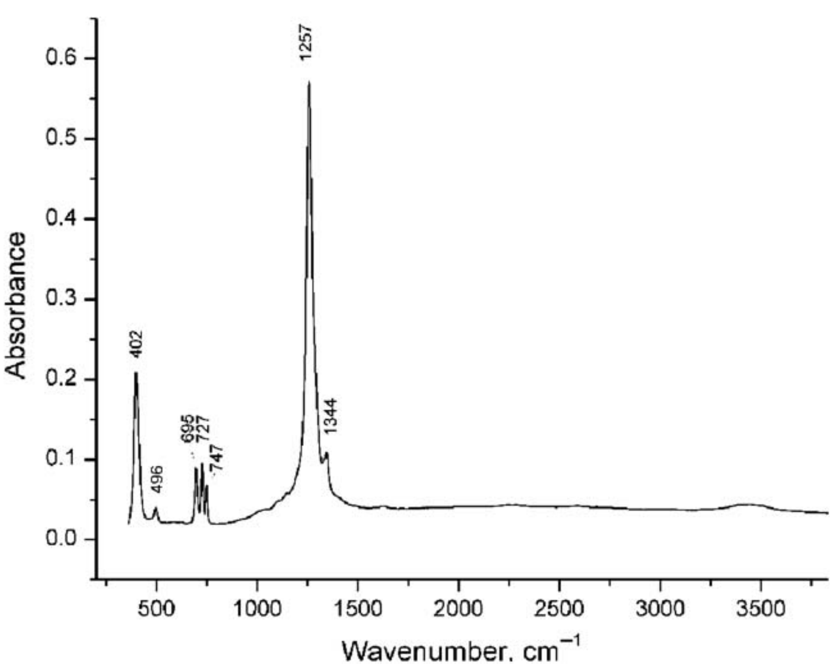

FIG. 4. The IR spectrum of chubarovite.

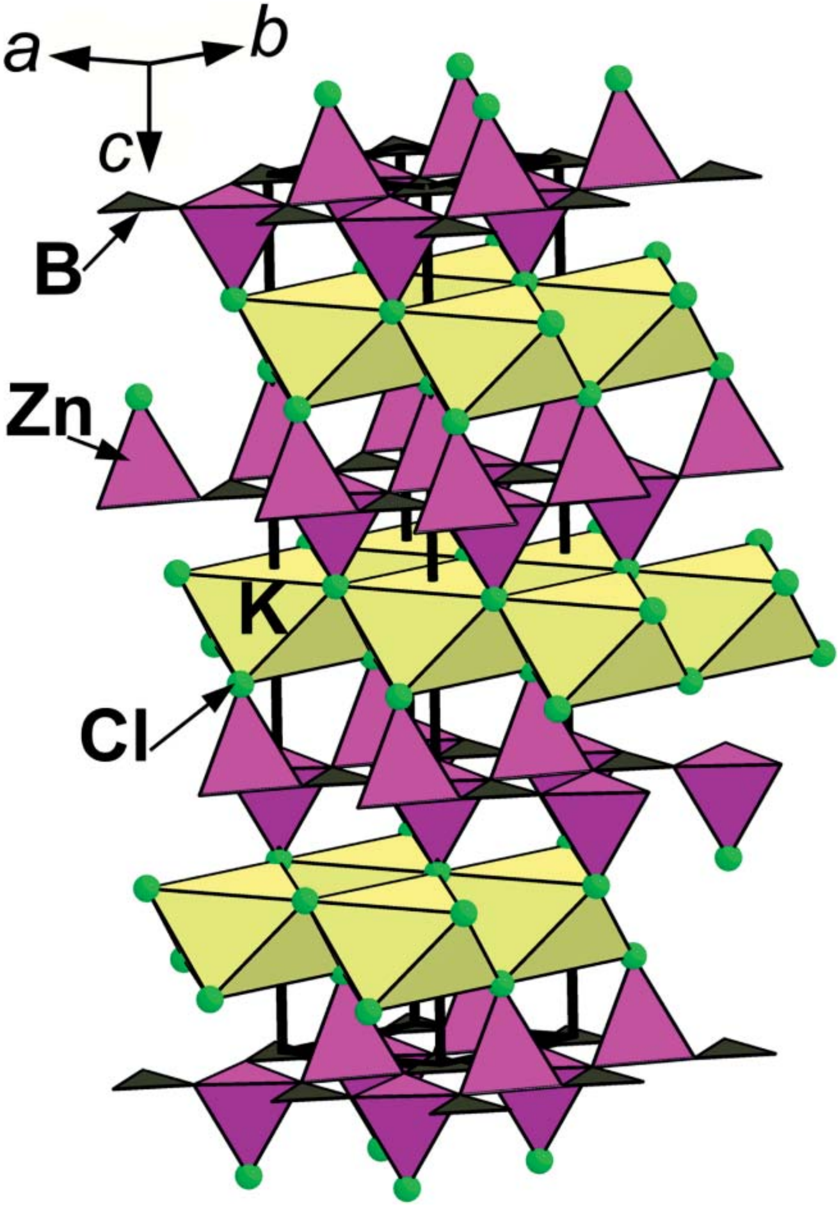

FIG. 5. The crystal structure of chubarovite.

Chubarovite was found in several small fumaroles belonging to the Northern fumarole field. It occurs in open pockets located at depths of 0.1 to 0.2 m below the surface. The temperatures measured inside these pockets immediately after their uncovering (July 2014) were 270–290 ºC. Here chubarovite typically forms tabular crystals up to 0.3 mm, well-shaped or crude, with clusters and crusts (Fig. 2g) up to 2 mm across overgrowing crusts mainly consisting of sellaite and fluorite. Other associated minerals are anhydrite, halite, cotunnite, challacolloite, sofiite, flinteite, zincomenite $ZnSeO_3$ (IMA 2014-014), anglesite, saltonseaite, hollandite, and secondary ralstonite and gypsum. In one of these fumaroles, crusts of chubarovite overgrow challacolloite crystals (Fig. 2h).

PHYSICAL PROPERTIES AND OPTICAL DATA

Chubarovite is transparent and colorless. The streak is white and the luster is vitreous. The mineral is non-fluorescent under ultraviolet rays or an electron beam. It is flexible but not elastic, like gypsum; lamellae can be easily bent. The Mohs hardness is *ca.* 2. Cleavage is (001) perfect, mica-like, and the fracture is laminated. The density measured by flotation in heavy liquids (bromoform + dimethylformamide) is 2.68(2) g cm^{-3}, and the density calculated from the empirical formula is 2.716 g cm^{-3}.

Chubarovite is optically uniaxial (–), $\omega = 1.541(2)$, $\varepsilon = 1.539(2)$. Under the microscope, the mineral is colorless and nonpleochroic.

Infrared spectroscopy

An infrared (IR) absorption spectrum was obtained from a powdered sample of chubarovite that was mixed with anhydrous KBr and pelletized. The pellet was analyzed using an ALPHA FTIR spectrometer (Bruker Optics) at a resolution of 4 cm^{-1}. The sampling scan number was 16. The IR spectrum of an analogous pellet of pure KBr was used as a reference.

Absorption bands in the IR spectrum of chubarovite (Fig. 4) are (cm^{-1}, s – strong band, w – weak band): 1344w, 1257s, 747, 727, 695, 496w, 402s. Despite the fact that BO_3^{3-} is triangular, the band at 1257 cm^{-1} (*i.e.*, situated in the range corresponding to the degenerate stretching mode of the orthoborate group) has a satellite at 1344 cm^{-1}. The observed splitting indicates that the BO_3^{3-} groups are involved in collective vibrations of the 2D system $[Zn_2(BO_3)]$ in the anionic layers of composition $\{Zn_2(BO_3)Cl_2\}^-$ (see text below and Figs. 5 and 6). This assumption is in agreement with the absence of strong bands in the range of Zn–O stretching vibrations of isolated ZnO_4 tetrahedra (475–540 cm^{-1}: Tarte & Preudhomme 1963, Rao *et al.* 2012) or isolated groups of ZnO_4 tetrahedra (578–581 cm^{-1}: Sava & Vişan 2007). Instead, a series of bands is observed from 600 to 800 cm^{-1}, corresponding to combinations of degenerate and non-degenerate modes of BO_3^{3-} groups (Li *et al.* 1994). Bands below 500 cm^{-1} correspond to lattice modes involving Zn–O stretching vibrations and both translational and librational vibrations of BO_3 groups. Bands corresponding to H_2O, OH^-, and covalent C–O bonds are absent in the IR spectrum of chubarovite (very weak absorptions above 1500 cm^{-1} are due to water absorbed by the KBr pellet).

The IR spectrum of chubarovite is unique and can be used as its reliable diagnostic tool.

Chemical Composition

The contents of metals and chlorine in chubarovite were determined 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 20 nA, and a 3 μm beam diameter.

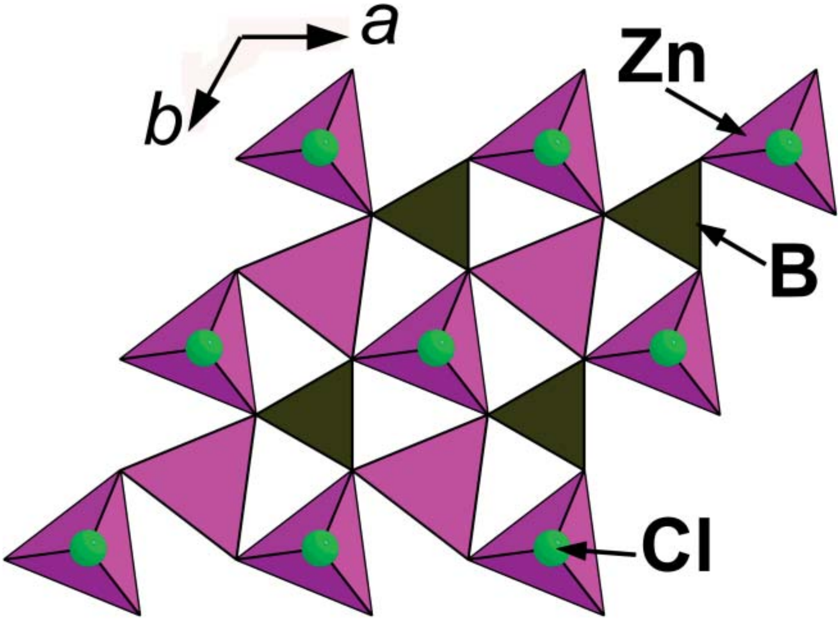

FIG. 6. The anionic $\{Zn_2(BO_3)Cl_2\}^-$ layer formed by triangular BO_3 groups and ZnO_3Cl tetrahedra, connected *via* common O vertices, in the structure of chubarovite.

TABLE 1. POWDER X-RAY DIFFRACTION DATA FOR CHUBAROVITE

I_{obs}	d_{obs}, Å	I_{calc}	d_{calc}, Å	*h k l*
100	8.79	100	8.783	003
43	4.394	43	4.391	006
25	4.225	17	4.225	101
91	4.074	68	4.071	012
90	3.590	79	3.589	104
30	3.324	29	3.323	015
7	2.929	6	2.928	009
5	2.612	7	2.610	018
67	2.470	79	2.471	110
5	2.379	7	2.379	113
25	2.245	43	2.244	1.0.10
8	2.154	11	2.154	116
5	2.133	6	2.133	021
11	2.112	16	2.113	202
14	2.091	22	2.090	0.1.11
5	2.036	8	2.036	024
7	1.983	12	1.983	205
2	1.889	2	1.889	119
9	1.833	13	1.832	1.0.13
4	1.795	5	1.795	208
3	1.758	2	1.757	0.0.15
3	1.724	3	1.723	0.1.14
4	1.663	13	1.661	0.2.10
3	1.643	7	1.642	1.1.12
2	1.615	4	1.615	211
5	1.606	13	1.606	122
5	1.598	11	1.596	2.0.11
3	1.572	7	1.571	2.1.4
5	1.547	11	1.547	1.2.5
3	1.538	2	1.537	1.0.16
2	1.486	0.5	1.486	217
3	1.473	5	1.472	0.2.13
3	1.453	5	1.452	128
11	1.431	15, 18	1.432, 1.427	1.1.15, 030
2	1.411	1, 5	1.413, 1.408	2.0.14, 303
5	1.380	14	1.379	2.1.10
1	1.359	6	1.357	306
3	1.342	12	1.341	1.2.11
1	1.320	1	1.319	1.0.19
1	1.307	1	1.305	0.2.16
0.5	1.284	1	1.283	309

The standards used are as follows: microcline (K), $Rb_2Nb_4O_{11}$ (Rb), ZnSe (Zn), and NaCl (Cl). Contents of other elements with atomic numbers higher than 6 are below detection limits in all studied samples. The presence of significant amounts of chlorine in chubarovite prevents the quantitative determination of boron by electron microprobe due to the overlap of X-ray emission lines of the *K* series of B with *L* lines of Cl. Boron was determined in the holotype specimen by ICP OES using a Varian 720-ES instrument. The sample for analysis was dissolved in HNO_3.

The average chemical composition of the holotype specimen of chubarovite (wt.%, ranges for four electron microprobe analyses are in parentheses) is: K_2O 16.48 (16.27–16.69), Rb_2O 0.46 (0.44–0.48), ZnO 53.96 (53.63–54.16), B_2O_3 10.98, Cl 24.48 (24.16–24.79), $-O=Cl_2$ –5.53, total 100.83.

The empirical formula of chubarovite, calculated on the basis of 5 anions (O+Cl) *pfu*, is:

TABLE 2. CRYSTAL DATA, DATA COLLECTION INFORMATION, AND STRUCTURE REFINEMENT DETAILS FOR CHUBAROVITE

Formula	$KZn_2(BO_3)Cl_2$
Formula weight	299.55
Crystal system, space group	Trigonal, $R32$ (no. 155)
Z	3
a, c (Å)	4.9429(4), 26.348(2)
V (Å^3)	557.50(8)
$F(000)$	426
Absorption coefficient μ (mm^{-1})	7.657
Crystal dimensions (mm)	0.14 × 0.16 × 0.45
Diffractometer	Xcalibur S CCD
λ (Mo$K\alpha$) (Å), T (K)	0.71073, 293(2)
Collection mode	(full) sphere
θ range for data collection(°)	4.82–32.62
h, k, l ranges	$-7 \le h \le 7$, $-7 \le k \le 7$, $-39 \le l \le 38$
Reflections collected	3886
Unique reflections	450 (R_{int} = 0.0595)
Reflections with $I > 2\sigma(I)$	439
Structure solution	direct methods
Refinement method	full-matrix least-squares *on* F^2
No. of refined parameters	17
Extinction coefficient	0.0030(7)
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0201, $wR2$ = 0.0491
R indices (all data)	$R1$ = 0.0208, $wR2$ = 0.0496
GoF	1.169
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e/Å^3)	–0.516, 0.591

$(K_{1.05}Rb_{0.01})_{\Sigma 1.06}Zn_{2.00}B_{0.95}O_{2.92}Cl_{2.08}$. The idealized formula is $KZn_2(BO_3)Cl_2$, which requires K_2O 15.72, ZnO 54.33, B_2O_3 11.62, Cl 23.67, $-O{=}Cl_2$ –5.34, total 100.00 wt.%.

TABLE 3A. ATOM COORDINATES AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS (Å^2) FOR CHUBAROVITE

Atom	x/a	y/b	z/c	U_{eq}
K	0	0	1/2	0.0406(3)
Zn	2/3	1/3	0.027896(11)	0.01453(13)
Cl	2/3	1/3	0.11350(3)	0.0366(2)
O	0	0.7224(4)	0	0.0196(5)
B	0	0	0	0.0137(7)

X-RAY CRYSTALLOGRAPHY AND CRYSTAL STRUCTURE

Powder X-ray diffraction data for chubarovite (Table 1) were collected with a Rigaku R-AXIS Rapid II single-crystal diffractometer equipped with a cylindrical image plate detector using Debye-Sherrer geometry (d = 127.4 mm; Mo$K\alpha$ radiation). Unit-cell parameters refined from the powder data are: a 4.9425(3), c 26.374(3) Å, V 558.0(1) Å^3, Z = 3.

Single-crystal X-ray studies were carried out using an Xcalibur S CCD diffractometer. The data were corrected for Lorentz factor and polarization effects. An absorption correction was applied according to the shape of the crystal. Crystal data, data collection information, and structure refinement details are given

TABLE 3B. ANISOTROPIC DISPLACEMENT PARAMETERS (IN Å^2) FOR CHUBAROVITE

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
K	0.0342(4)	0.0342(4)	0.0533(7)	0.000	0.000	0.01711(18)
Zn	0.00981(14)	0.00981(14)	0.02397(19)	0.000	0.000	0.00491(7)
Cl	0.0435(3)	0.0435(3)	0.0227(4)	0.000	0.000	0.02174(16)
O	0.0094(9)	0.0081(6)	0.0416(13)	0.0027(4)	0.0054(7)	0.0047(4)
B	0.0087(9)	0.0087(9)	0.0238(18)	0.000	0.000	0.0044(4)

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å) IN THE STRUCTURE OF CHUBAROVITE

Zn–O	1.9455(12) ×3
–Cl	2.2556(9)
B–O	1.372(2) ×3
K–Cl	3.1790(4) ×6

in Table 2. The structure model was obtained by direct methods and refined with the use of the SHELX-97 software package (Sheldrick 2008) on the basis of 439 independent reflections with $I > 2\sigma(I)$ to $R = 0.0201$. Atom coordinates and equivalent isotropic displacement parameters for chubarovite are given in Table 3a, anisotropic displacement parameters in Table 3b, selected interatomic distances in Table 4, and bond valence calculations in Table 5.

The crystal structure of chubarovite (Fig. 5) is unique. It is composed of layers of two types with an alternation along [001]. The anionic $\{Zn_2(BO_3)Cl_2\}^-$ layer (Fig. 6) consists of flat triangular BO_3 groups sharing all O vertices with bases of ZnO_3Cl tetrahedra characterized by opposite orientation of their apical vertices, which are represented by Cl atoms. Each BO_3 triangle is connected to six Zn-centered tetrahedra. Each Cl atom is shared between one Zn-centered tetrahedron and three edge-connected KCl_6 octahedra (Fig. 5) belonging to the cationic layer formed by K^+ cations (Fig. 7). Thus, chubarovite has a distinctly layered structure that is responsible for its (001) perfect, mica-like cleavage.

TABLE 5. BOND VALENCE CALCULATIONS FOR CHUBAROVITE*

	K	Zn	B	Σ
O		$0.52^{\times3\downarrow\ \times2\rightarrow}$	$1.00^{\times3\downarrow}$	2.04
Cl	$0.17^{\times6\downarrow\ \times3\rightarrow}$	0.51		1.02
Σ	1.02	2.07	3.00	

*Parameters are taken from Brese & O'Keeffe (1991).

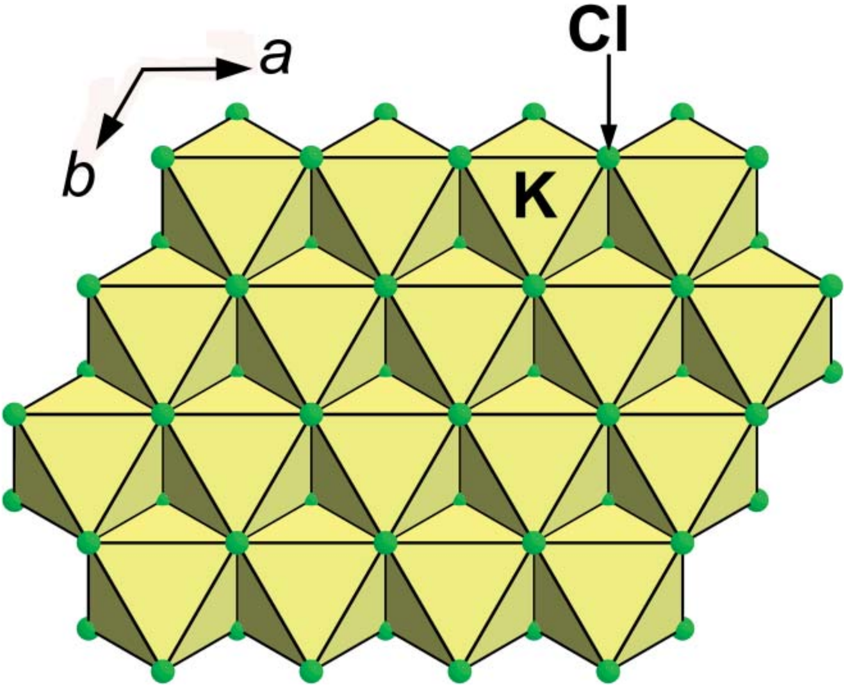

FIG. 7. The cationic layer consisting of edge-connected KCl_6 octahedra in the structure of chubarovite.

DISCUSSION

Chubarovite is the first borate mineral with species-defining zinc. No natural or synthetic compound related to chubarovite in terms of both chemistry and structure is found in the literature and databases. However, the tetrahedral layers $\{Zn_2O_3Cl_2\}^{4-}$ in the structure of chubarovite are very similar to the $\{Zn_2O_5\}^{6-}$ layers found in the synthetic silicate $K_2Mn_2Zn_4Si_4O_{15}$ (Pushcharovsky *et al.* 1969). As was mentioned above, in chubarovite the boron triangles are located in the centers of six-membered rings of these layers, whereas in the latter compound they are substituted with SiO_4 tetrahedra.

The borate mineralization in active fumaroles of the Tolbachik volcano, represented by chubarovite $KZn_2(BO_3)Cl_2$ and the earlier-formed OH-free fluoborite $Mg_3(BO_3)F_3$ and intimately associated with one another in the Arsenatnaya fumarole, formed at a temperature not lower than 360 ºC. We believe that chubarovite was deposited directly from the gas phase (an obvious source of all its constituents: B, O, Cl, Zn, K, and admixed Rb) as a volcanic sublimate. Taking into account the very low volatility of Mg in fumarolic gases at temperatures up to 400–500 °C (Symonds & Reed 1993), we assume that this element could be extracted from host basalt, *i.e.*, fluoborite was probably formed as a result of gas-rock interaction.

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