

Kaliochalcite, $\text{KCu}_2(\text{SO}_4)_2[(\text{OH})(\text{H}_2\text{O})]$, a new tsumcorite-group mineral from the Tolbachik volcano, Kamchatka, Russia

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Abstract: The new tsumcorite-group mineral kaliochalcite, $\text{KCu}_2(\text{SO}_4)_2[(\text{OH})(\text{H}_2\text{O})]$ (IMA 2013–037), is found in several fumaroles at the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption, Tolbachik volcano, Kamchatka, Russia. Two fumaroles, Yadovitaya and Arsenatnaya, are considered as its type localities. The mineral seems to be a product of the interactions involving the high-temperature, sublimate KCu-sulphates and atmospheric water vapour at temperatures not higher than 100–150°C. Kaliochalcite mostly occurs in polymineralic crusts (up to several dozens cm^2 in area and up to 0.5 cm thick), where it is typically the major component. The mineral forms fine-grained pseudomorphs after anhydrous KCu-sulphates, mainly euchlorine, fedotovite or piypite, usually with their relics. Other associated minerals are hematite, tenorite, langbeinite, apthitalite, steklite, lammerite, chlorothionite, gypsum, etc. Pseudo-rhombohedral or more complicated crystals of kaliochalcite (commonly up to 0.02×0.04 mm, rarely up to 0.03×0.1 mm) are observed in cavities. The mineral is light green, bright grass-green or almost colourless. Kaliochalcite is transparent in individuals and translucent in aggregates, with vitreous lustre. It is brittle, the Mohs' hardness is 4. No cleavage was observed, the fracture is uneven. The calculated density, D_{calc} , is 3.49 g cm^{-3} . Kaliochalcite is optically biaxial (+), $\alpha 1.630(3)$, $\beta 1.650(3)$, $\gamma 1.714(3)$, $2V_{\text{meas}} 55(10)^\circ$. The IR spectrum is given. The chemical composition (wt%, electron-microprobe data, H_2O by selective sorption from the gaseous products of heating) is: Na_2O 0.04, K_2O 11.01, CaO 0.27, FeO 0.15, CuO 40.28, ZnO 0.39, SO_3 40.97, H_2O 5.84, total 98.95. The empirical formula, calculated on the basis of 10 O *apfu*, is: $(\text{K}_{0.94}\text{Ca}_{0.02}\text{Na}_{0.01})_{\Sigma 0.97}(\text{Cu}_{2.03}\text{Zn}_{0.02}\text{Fe}_{0.01})_{\Sigma 2.06}\text{S}_{2.05}\text{O}_{8.20}(\text{OH})_{1.01}(\text{H}_2\text{O})_{0.79}$. Kaliochalcite is monoclinic, space group $C2/m$, a 8.935(2), b 6.252(2), c 7.602(2) Å, β 117.318(5)°, V 377.3(2) Å³ and $Z = 2$. The strongest reflections of the X-ray powder pattern [$d, \text{Å}(hkl)$] are: 6.78(100)(001), 3.484(70)(20–2), 3.249(63)(11–2), 2.892(77)(201), 2.852(83)(02–1), 2.554(72)(31–2, 22–1), 2.326(44)(22–2) and 1.693(37)(42–3, 22–4). The crystal structure was solved from single-crystal X-ray diffraction data, $R = 0.100$. The structure is built up from chains of edge-sharing Cu^{2+}O_6 Jahn-Teller distorted octahedra connected by SO_4 tetrahedra and H-bonds to form $\{\text{Cu}_2(\text{SO}_4)_2[(\text{OH})(\text{H}_2\text{O})]\}^-$ layers. The linkage between these layers is provided by K^+ cations and H-bonds. Kaliochalcite is named as the potassium analogue of natrochalcite.

Key-words: kaliochalcite; new mineral; natrochalcite; tsumcorite group; potassium copper sulphate; crystal structure; fumarole; Tolbachik volcano; Kamchatka.

Introduction

Copper sulphates are numerous and abundant in deposits of fumaroles related to the Tolbachik volcano in the Kamchatka peninsula (Far-Eastern Region, Russia). The major occurrences of the exhalation copper minerals are located at the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption

(55°41'N 160°14'E, 1200 m asl), a monogenetic volcano 300 m high and about 0.1 km^3 in volume, formed in 1975 (Fedotov & Markhinin, 1983). This mineralization, mainly represented by tenorite and Cu^{2+} sulphates, is so rich in some areas that these occurrences were evaluated for their potential copper mining interest (Naboko & Glavatskikh, 1983; Vergasova & Filatov, 1993). Twenty one sulphate minerals with species-defining Cu^{2+} were reliably

identified there. Ten of them were first discovered at Tolbachik: alumoklyuchevskite, atlasovite, fedotovite, kamchatkite, klyuchevskite, nabokoite, piypite, vergasovaite (Vergasova & Filatov, 2012) and the recently described wulffite and parawulffite (Pekov *et al.*, 2014). All these minerals, as well as chalcocyanite, dolerophanite, and euchlorine, are H-free and were found in active, hot fumaroles. Seven other copper sulphates found in the deposits of Tolbachik fumaroles contain OH groups or H₂O molecules (antlerite, bonattite, chalcantite, cyanochroite, kröhnkite, linarite and natrochalcite). All these minerals, as well as the H-free species chlorothionite closely associated with hydrous sulphates and chlorides, are considered as secondary minerals, the products of low-temperature alteration of the primary, sublimate mineralization.

In the present paper we describe a new hydrous sulphate of copper and potassium from Tolbachik. This mineral belonging to the tsumcorite group was named *kaliocalcite* (Cyrillic:) as the potassium (*kalium*, in Latin) analogue of natrochalcite, with K dominant instead of Na (Table 1). Both the mineral and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA 2013–037). 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 94121.

Occurrence and general appearance

Kaliocalcite occurs in significant amounts in several active fumaroles located in the apical part of the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption. It is one of the most common copper minerals in polyphase incrustations formed in the upper (moderately hot) parts of the mineralized zones of the fumaroles and mainly consisting of sulphates. We consider two fumaroles, Yadovitaya (“Poisonous”) and Arsenatnaya, as the type localities of kaliocalcite. The new mineral was also identified in Glavnaya Tenoritovaya, Zelenaya and two unnamed fumaroles.

Specimens bearing this mineral were collected by one of the authors (MNM) and M.E. Zelenski in the 1990s – 2000s but the title compound was initially misidentified as natrochalcite, on the basis of powder X-ray diffraction data. Later the electron-probe examination showed the presence of the potassium analogue of natrochalcite, but further studies were strongly hampered by the fine-grained nature and polyminerale character of the aggregates, which were in all cases significantly polluted (20–50 vol%) by euchlorine, fedotovite, piypite, langbeinite, apthitalite and unidentified phases. Abundant micro-inclusions of these impurities together gave many extra reflections in the X-ray powder diagrams

Table 1. Comparative data for kaliocalcite and natrochalcite.

Mineral	Kaliocalcite	Natrochalcite
Formula	KCu ₂ (SO ₄) ₂ [(OH)(H ₂ O)]	NaCu ₂ (SO ₄) ₂ [(OH)(H ₂ O)]
Crystal system	Monoclinic	Monoclinic
Space group	<i>C2/m</i>	<i>C2/m</i>
Unit-cell data		
<i>a</i> , Å	8.935	8.75–8.81
<i>b</i> , Å	6.252	6.16–6.19
<i>c</i> , Å	7.602	7.44–7.51
β, °	117.32	118.7
<i>V</i> , Å ³	377	352–359
<i>Z</i>	2	2
Strongest reflections of the X-ray powder pattern:	6.78–100	6.57–80
<i>d</i> , Å – <i>I</i>	4.432–35	4.82–60
	3.484–70	3.44–80
	3.249–74	3.20–70
	2.892–77	2.797–100
	2.852–83	2.522–80
	2.554–72	2.302–60
	2.326–44	
	1.693–37	
Optical data		
α	1.630	1.649
β	1.650	1.655
γ	1.714	1.714
optical sign, 2 <i>V</i>	(+) 55°	(+) 37°
<i>D</i> , g cm ^{−3}	3.49 (calc)	3.49 (meas), 3.54 (calc)
Sources	this work	Palache <i>et al.</i> (1951); Rumanova & Volodina, (1958); Chevrier <i>et al.</i> (1993); Anthony <i>et al.</i> (2003)

and extra bands in the IR spectra and they prevented correct determination of H₂O content. In July 2012 one specimen with pure aggregates of the new mineral, including single crystals suitable for structure analysis, was found by the authors (IVP and DIB) in the Yadovitaya fumarole. The majority of the analytical data given in this paper were obtained for this specimen, considered as the holotype of kaliocalcite. Other studies are carried out mainly on the material collected by us in 2008–2013.

In July 2013, temperatures of 90–110°C were measured by us with chromel-alumel thermocouple inside fumarole chambers, in the kaliocalcite-bearing areas. In the inner zones of the same fumaroles, where temperature reached 270–430°C, only anhydrous sulphates were observed.

In the Yadovitaya fumarole, the major high-temperature sublimate minerals are euchlorine, fedotovite, piypite, chalcocyanite, alumoklyuchevskite, langbeinite, steklite, hematite, tenorite, tolbachite, with subordinate apthitalite, kamchatkite, anhydrite, lyonsite, pseudolyonsite, lammerite, lammerite-β, orthoclase (As-bearing variety), rutile (Fe- and Sb-bearing variety), pseudobrookite, vergasovaite, cupromolybdate, *etc.* In the relatively

low-temperature, outer zone, hydrous minerals are observed: kaliocalcite, cyanochroite, chlorothionite, gypsum, belloite, avdoninite, eriochalcite, kröhnkite, *etc.* In the Arsenatnaya fumarole tenorite, hematite, euchlorine, wulfite, apthitalite, langbeinite, sylvite, halite, anhydrite, chalcocyanite, dolerophanite, krashennikovite, lammerite, johillerite, bradaczekite, urusovite, ericlxmanite ($\text{Cu}_4\text{O}(\text{AsO}_4)_2$, IMA 2013–022), As-bearing orthoclase, and fluorophlogopite are the common primary, sublimate minerals; the secondary mineralization is mainly represented by gypsum, kaliocalcite, opal and unidentified Al sulphates.

In all above-mentioned fumaroles, kaliocalcite mostly occurs in massive, porcelain-like or, more commonly, porous polymineralic green crusts up to several dozens cm^2 in area and up to 0.5 cm thick. They cover basalt scoria or cement loose scoria material in the upper part of the fumaroles. Fine-grained kaliocalcite (with individual crystals typically less than 5 μm in size) is typically the major component of the crusts. These aggregates are commonly partial pseudomorphs after primary, anhydrous KCu-sulphates, mainly euchlorine $\text{KNaCu}_3\text{O}(\text{SO}_4)_3$, fedotovite $\text{K}_2\text{Cu}_3\text{O}(\text{SO}_4)_3$ or piypite $\text{K}_8\text{Cu}_9\text{O}_4(\text{SO}_4)_8\text{Cl}_2$, in some cases after kamchatkite $\text{KCu}_3\text{O}(\text{SO}_4)_2\text{Cl}$, alumoklyuchevskite $\text{K}_3\text{Cu}_3\text{AlO}_2(\text{SO}_4)_4$, or wulfite $\text{K}_3\text{NaCu}_4\text{O}_2(\text{SO}_4)_4$. This is clearly confirmed by well-preserved crystal shapes and typical crystal clusters (Figs. 1–3), as well as by the presence of abundant relics of these minerals in the pseudomorphs. In small cavities of granular kaliocalcite aggregates, tiny crystals and their crusts were observed (Figs. 3 and 4). In the holotype specimen, kaliocalcite occurs as light green complete pseudomorphs after groups (up to 2 mm across) of spear-like piypite crystals (Figs. 2 and 3) and as clusters and crusts formed by its own pale green to almost colourless crystals on basalt scoria near these pseudomorphs.

Crystals of kaliocalcite are typically tiny, not larger than 0.02×0.04 mm, rarely up to 0.03×0.1 mm. The



Fig. 1. Partial pseudomorphs of kaliocalcite after well-shaped fedotovite crystals. Yadovitaya fumarole. Field of view (FOV): 4.3 mm. Photo: I.V. Pekov & A.V. Kasatkin. (Online version in colour)

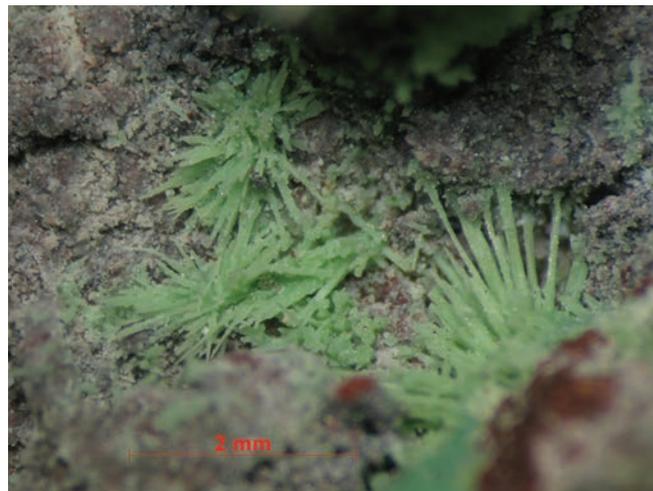


Fig. 2. Complete pseudomorphs of kaliocalcite after bush-like groups of piypite crystals. The holotype specimen, Yadovitaya fumarole. FOV: 2.9 mm. Photo: I.V. Pekov & A.V. Kasatkin. (Online version in colour)

largest individuals are imperfect. The crystals are pseudo-rhombohedral or more complicated, sometimes elongated along [001] or flattened on [100] and in some cases curved. Based on images obtained under the scanning electron microscope (Figs. 3 and 4), we assume, by analogy with natrochalcite crystal drawings (Palache *et al.*, 1951), that the main forms of kaliocalcite crystals (class $2/m$) are {111} and {100}. Subordinate faces are {001} and, presumably, {110} and {221} in some cases. For instance, the crystals shown on Fig. 3b seem shaped by the prismatic {111} and pinacoidal {100} faces (forming an elongated pseudo-rhombohedron) with minor triangular pinacoidal {001} faces on the terminations.

Physical properties and optical characteristics

Kaliocalcite is light green to bright grass-green, more rarely light bluish-green to very pale greenish, almost colourless. Its streak is pale green to white. The mineral is transparent in individuals and translucent in aggregates. Crystals show vitreous lustre whereas fine-grained, porcelain-like aggregates are dull. The mineral is brittle. The Mohs' hardness is 4. Cleavage or parting were not observed, the fracture is uneven. Density could not be measured because of paucity of pure and massive material: particles more than 0.05 mm in size, even monomineralic, are porous. The calculated density is 3.49 g cm^{-3} .

Kaliocalcite is optically biaxial (+), $\alpha = 1.630(3)$, $\beta = 1.650(3)$, $\gamma = 1.714(3)$ (589 nm), $2V_{\text{meas}} = 55(10)^\circ$, $2V_{\text{calc}} = 60^\circ$. Dispersion of optical axes is strong, $r < v$. Under the microscope, kaliocalcite is colourless to pale green, non-pleochroic or with very weak pleochroism.

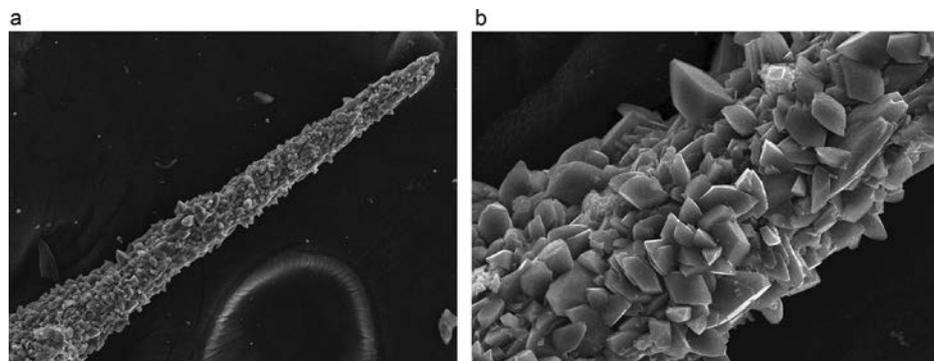


Fig. 3. Complete pseudomorph of kaliochalcite after spear-shaped piypite crystal (a) and its magnified fragment (b). The holotype specimen, Yadovitaya fumarole. FOV: *a* – 0.48 mm, *b* – 0.12 mm. Scanning electron microscope (SEM) secondary-electron (SE) images.

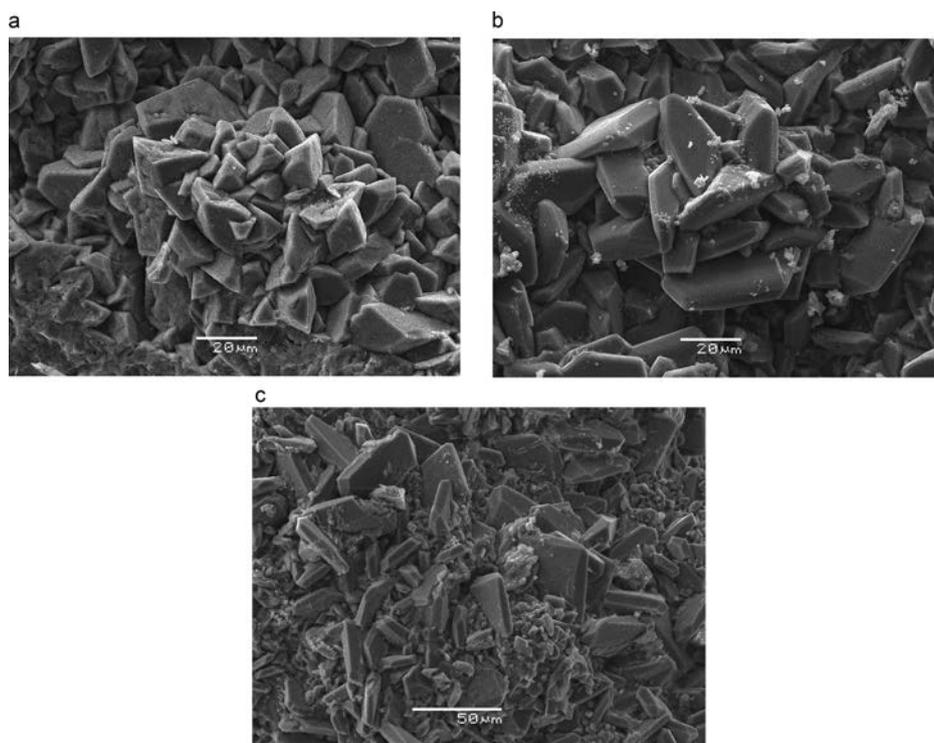


Fig. 4. Crystal crusts of kaliochalcite: *a*, *b* – Yadovitaya fumarole, *c* – Arsenatnaya fumarole. SEM (SE) images.

Infrared spectroscopy

The infrared (IR) absorption spectrum of kaliochalcite was obtained for 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} and an accumulation of 16 scans. The IR spectrum of an analogous pellet of pure KBr was used as a reference.

The IR spectra of kaliochalcite and its Na-analogue natrochalcite are given in Fig. 5. The assignment of bands in the IR spectrum of kaliochalcite was made in accordance with IR spectroscopic data for the synthetic analogues of natrochalcite and kaliochalcite, their deuterated counterparts and synthetic $(\text{Na}_{0.5}\text{K}_{0.5})\text{Cu}_2(\text{SO}_4)_2[(\text{OH})(\text{H}_2\text{O})]$, an intermediate member

of the natrochalcite–kaliochalcite solid-solution series (Beran *et al.*, 1997). Absorption bands in the IR spectrum of kaliochalcite (cm^{-1} ; s – strong band, w – weak band, sh – shoulder) and their assignments are: 3370sh, 3334 (O–H-stretching vibrations of OH^- groups and H_2O molecules), 2044w (O–H-stretching vibrations of trace amounts of HSO_4^- groups), 1623 (bending vibrations of H_2O molecules), 1224s, 1061s [$\nu_3(F_2)$ – asymmetric stretching vibrations of SO_4^{2-} anions], 998s [$\nu_1(A_1)$ – symmetric stretching vibrations of SO_4^{2-} anions], 914 (bending vibrations of $\text{Cu} \cdots \text{OH}$), 830w (possibly a combination mode), 655, 621, 599 [$\nu_4(F_2)$ – bending vibrations of SO_4^{2-} anions], 492w, 439w, 374 [lattice modes involving Cu–O stretching vibrations and $\nu_2(E)$ bending mode of SO_4^{2-} anions]. The relatively strong intensity of

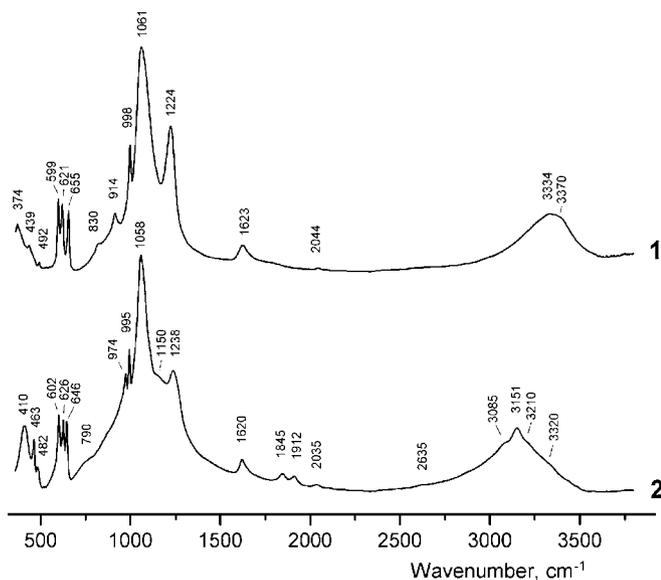


Fig. 5. Infrared (IR) spectra of holotype kaliocalcite (1) and natrochalcite from its type locality, Chuquicamata Mine, Calama, Antofagasta Region, Chile (2).

the non-degenerate $\nu_1(A_1)$ band reflects rather strong distortions of SO_4 tetrahedra (see below), and the absence of splitting of this band indicates the presence of the only kind of distorted SO_4^{2-} group. As compared with natrochalcite, kaliocalcite is characterized by higher frequencies of O–H stretching vibrations (in the range 3000 to 3400 cm^{-1}) and by higher frequencies of $\text{Cu} \cdots \text{OH}$ bending vibrations (914 and 974 cm^{-1} , respectively).

Consequently, kaliocalcite is characterized by much weaker hydrogen bonds than natrochalcite. As a result, partial protonation of SO_4^{2-} groups by the mechanism $\text{H}_2\text{O} + \text{SO}_4^{2-} \rightarrow \text{OH}^- + \text{HSO}_4^-$ (resulting in the appearance of absorption bands of HSO_4^- groups at 1845, 1912 and 2035 cm^{-1} in the IR spectrum of natrochalcite) is much less pronounced in kaliocalcite.

Characteristic bands of BO_3^{3-} , CO_3^{2-} , NO_3^- and organic groups are absent in the IR spectrum of kaliocalcite. The IR spectrum of the new mineral is unique and can be used as a good diagnostic tool.

Chemical data

Chemical data for kaliocalcite 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 20 nA, and a 3 μm beam diameter. H_2O was determined in the holotype sample by selective sorption of H_2O on $\text{Mg}(\text{ClO}_4)_2$ from the gaseous products obtained by heating the mineral at 1100°C in an oxygen stream at ambient pressure. Analytical data are given in Table 2.

Table 2. Chemical composition (wt%) of kaliocalcite.

Constituent	Sample			Probe standard
	1	2	3	
Na_2O	0.04 (0.00–0.14)	bdl		NaCl
K_2O	11.01 (10.43–11.29)	11.59	11.97	orthoclase
CaO	0.27 (0.00–0.67)	bdl		CaWO_4
FeO	0.15 (0.08–0.28)	bdl		CuFeS_2
CuO	40.28 (39.35–40.61)	38.09	40.45	CuFeS_2
ZnO	0.39 (0.00–1.49)	1.70		ZnS
SO_3	40.97 (40.06–42.28)	42.84	40.71	ZnS
H_2O	5.84	(7.08)*	6.87	
Total	98.95	101.30	100.00	

1—the holotype sample from the Yadovitaya fumarole (averaged from 5 spot analyses, ranges are in parentheses); 2—sample from the Arsenatnaya fumarole; 3—calculated for the idealized formula $\text{KCu}_2(\text{SO}_4)_2[(\text{OH})(\text{H}_2\text{O})]$. Contents of other elements with atomic numbers higher than carbon are below detection limits (bdl).

* H_2O content calculated for the $\text{O}_8(\text{OH})_1(\text{H}_2\text{O})_1$ composition of the anionic part of the formula.

The empirical formulae of kaliocalcite calculated on the basis on 10 O *apfu* are:

- $(\text{K}_{0.94}\text{Ca}_{0.02}\text{Na}_{0.01})_{\Sigma 0.97}(\text{Cu}_{2.03}\text{Zn}_{0.02}\text{Fe}_{0.01})_{\Sigma 2.06}\text{S}_{2.05}\text{O}_{8.20}(\text{OH})_{1.01}(\text{H}_2\text{O})_{0.79}$ for the holotype sample from the Yadovitaya fumarole (with the OH: H_2O ratio calculated by charge balance);
- $\text{K}_{0.94}(\text{Cu}_{1.83}\text{Zn}_{0.08})_{\Sigma 1.91}\text{S}_{2.04}\text{O}_8(\text{OH})(\text{H}_2\text{O})$ for the sample from the Arsenatnaya fumarole (calculated data for H_2O , see Table 2).

Kaliocalcite hydrolyses and further slowly dissolves in H_2O at room temperature.

X-ray crystallography and crystal structure

X-ray powder diffraction data (Table 3) for kaliocalcite were collected using a STOE IPDS II diffractometer equipped with Image Plate area detector, using the Gandolfi method (MoK α -radiation; detector-to-sample distance: 200 mm). The parameters of the monoclinic unit cell refined from the powder data are: $a = 8.933(3)$, $b = 6.255(1)$, $c = 7.607(3)$ Å, $\beta = 117.29(3)^\circ$ and $V = 377.8(3)$ Å³.

Single-crystal X-ray studies were carried out using a Bruker Smart Apex II DUO diffractometer with a micro-focus X-ray tube. Crystal data, data collection information and structure refinement details are given in Table 4. The atom coordinates published for synthetic $\text{KCu}_2(\text{SO}_4)_2[(\text{OH})(\text{H}_2\text{O})]$ by Giester & Zemann (1987) were used initially and the structure was successfully refined with the use of SHELX software package (Sheldrick, 2008) on the basis of F^2 for 389 unique observed reflections with $F^2 \geq 4\sigma(F^2)$ to $R_1 = 0.100$. The studied crystals are very tiny and diffract rather poor. Larger crystals are

unacceptable for single-crystal X-ray studies due to the low quality. The reported data were obtained from the best acicular crystal fragment with a size of $0.005 \times 0.005 \times 0.09$ mm. This is the reason for the low quality of obtained single-crystal data. Hydrogen atoms were not located but all other structural features obtained for kaliochalcite are in good agreement with those of its synthetic analogue for which good X-ray diffraction data were published (Tardy & Brégeault, 1974; Giester & Zemmann, 1987). Atom coordinates and displacement parameters are given in Table 5 and selected interatomic distances in Table 6. Measured and calculated X-ray powder

diffraction patterns are in good agreement one with each other (Table 3).

The structure of kaliochalcite is identical to that of synthetic $\text{KCu}_2(\text{SO}_4)_2[(\text{OH})(\text{H}_2\text{O})]$ (Tardy & Brégeault, 1974; Giester & Zemmann, 1987; Chevrier *et al.*, 1990). It is based on chains of edge-sharing Cu^{2+}O_6 Jahn-Teller distorted octahedra interconnected by SO_4 tetrahedra and hydrogen bonds to form layers of $\{\text{Cu}_2(\text{SO}_4)_2[(\text{OH})(\text{H}_2\text{O})]\}^-$ composition. The linkage between these layers is provided by K^+ cations and hydrogen bonds (Fig. 6). Oxygen atoms belonging to H_2O molecules and OH groups statistically occupy the O(3) site.

Table 3. X-ray powder diffraction data for the holotype kaliochalcite.

I_{obs}	d_{obs}	I_{calc}^*	d_{calc}^{**}	hkl
100	6.78	100	6.754	001
28	4.926	29	4.911	110
20	4.662	23	4.650	11-1
35	4.432	42	4.421	20-1
9	3.978	10	3.969	200
70	3.484	86	3.478	20-2
15	3.380	14	3.377	002
63	3.249	74	3.246	11-2
77	2.892	83	2.891	201
83	2.852	99	2.837	02-1
29	2.686	36	2.683	31-1
72	2.554	19, 74	2.554, 2.553	31-2, 22-1
25	2.472	19, 21	2.474, 2.456	112, 220
44	2.326	58	2.325	22-2
4	2.198	3, 3	2.211, 2.196	40-2, 40-1
18	2.136	25	2.134	202
4	2.031	2	2.034	311
13	1.988	2, 13	1.996, 1.985	13-1, 400
15	1.967	18	1.960	22-3
5	1.860	7	1.857	113
14	1.827	2, 21	1.827, 1.827	13-2, 02-3
14	1.803	8, 13	1.805, 1.797	42-2, 42-1
10	1.763	16	1.762	222
15	1.741	23	1.739	40-4
37	1.693	36, 22	1.695, 1.689	42-3, 004
9	1.626	5, 18	1.637, 1.623	330, 22-4
12	1.564	26	1.563	040
5	1.523	4, 3	1.523, 1.520	04-1, 42-4
12	1.497	19	1.496	421
14	1.471	9, 3, 15	1.474, 1.474, 1.465	60-3, 24-1, 223
6	1.448	4, 8	1.454, 1.446	240, 402
8	1.425	4, 7, 5	1.428, 1.426, 1.422	60-1, 24-2, 133
8	1.377	17	1.375	241
10	1.341	16	1.341	62-2
3	1.300	5	1.299	62-1
4	1.278	2, 2, 1, 3, 3	1.285, 1.284, 1.277, 1.276, 1.274	60-5, 04-3, 62-4, 44-2, 44-1
3	1.264	1, 5	1.263, 1.261	530, 242
10	1.240	4, 6, 14	1.243, 1.241, 1.240	20-6, 31-6, 02-5
3	1.221	3, 3, 2	1.228, 1.218, 1.218	440, 620, 71-4
2	1.189	3, 3	1.188, 1.188	62-5, 15-2
3	1.177	4, 2	1.175, 1.175	333, 314
3	1.166	2, 6	1.167, 1.162	42-6, 44-4
4	1.151	2, 1, 1, 1, 2, 7	1.155, 1.153, 1.152, 1.152, 1.148, 1.147	22-6, 71-5, 35-1, 441, 423, 04-4
1	1.129	2, 2	1.130, 1.126	205, 006
2	1.119	1, 2	1.119, 1.117	621, 80-3

*Only reflections with intensities ≥ 1 are given. **Calculated from single-crystal data.

Table 4. Crystallographic data and refinement parameters for kaliocalcite.

<i>Crystal data</i>	
Temperature	293 K
Radiation, wavelength	MoK α , 0.71073 Å
Crystal system	monoclinic
Space group	<i>C2/m</i>
Unit-cell dimensions (Å)	8.935(2), 6.2520(18), 7.602(2)
Unit-cell volume (Å ³)	377.29(18) Å ³
Z	2
Calculated density (g/cm ³)	3.436
Absorption coefficient (mm ⁻¹)	6.785
<i>Data collection</i>	
θ range	3.02–27.99°
<i>h, k, l</i> ranges	–11→11, –7→8, –10→9
Total reflections collected	478
Unique reflections $F > 4\sigma(F)$	389
<i>Structure refinement</i>	
Refinement method	Full-matrix least-squares on F^2
Weighting coefficients <i>a, b</i>	0.16280, 0.0
Extinction coefficient	0.013(11)
Data/restraints/parameters	478/0/52
$R_1 [F > 4\sigma(F)]$, $wR_2 [F > 4\sigma(F)]$	0.101, 0.226
R_1 all, wR_2 all	0.109, 0.236
Goodness-of-fit on F^2	1.011
Largest diff. peak and hole	2.19, –2.18 e Å ⁻³

Discussion

Kaliocalcite, $\text{KCu}_2(\text{SO}_4)_2[(\text{OH})(\text{H}_2\text{O})]$, is the potassium analogue of natrochalcite, $\text{NaCu}_2(\text{SO}_4)_2[(\text{OH})(\text{H}_2\text{O})]$ (Rumanova & Volodina, 1958; Giester & Zemann, 1987; Chevrier *et al.*, 1993: Table 1), and a new member of the tsumcorite group. Both of these minerals are found in fumarolic deposits of Tolbachik. In all studied samples

kaliocalcite is almost Na-free, whereas natrochalcite contains no K in considerable amounts. However, the intermediate sulphate $(\text{K}_{0.5}\text{Na}_{0.5})\text{Cu}_2(\text{SO}_4)_2[(\text{OH})(\text{H}_2\text{O})]$ could be synthesized (Beran *et al.*, 1997), thus revealing the possibility of existence of a solid-solution series between natrochalcite and kaliocalcite.

Kaliocalcite occurs only in moderately hot, outer parts of the fumaroles where it replaces hydrogen-free KCu-sulphates formed as sublimates under temperatures not lower than 360–380°C (Pekov *et al.*, 2014). The new mineral contains OH groups and H₂O molecules and is associated with other hydrous sulphates and OH- and/or H₂O-bearing chlorides. The last observation indicates that kaliocalcite was formed not as a result of direct deposition from gaseous phase (gases in the fumaroles of the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption contain no more than 1 % water vapour: Zelenski *et al.*, 2012), but as a product of the interactions involving earlier, high-temperature sublimate sulphate minerals and atmospheric water vapour at relatively low temperatures, presumably not higher than 100–150°C. The fumarolic gas can be the third component in this mineral-forming system which can be considered as a “mixed” one, *i.e.* combining features of fumarolic and supergene processes.

Table 6. Selected interatomic distances (Å) in the structure of kaliocalcite.

Cu(1)–O(4)	1.978(6) × 2	S(1)–O(2)	1.453(10)
Cu(1)–O(3)	1.984(5) × 2	S(1)–O(1)	1.473(9)
Cu(1)–O(1)	2.342(7) × 2	S(1)–O(4)	1.496(6) × 2
K(1)–O(1)	2.727(9) × 2		
K(1)–O(4)	2.738(6) × 4		
K(1)–O(2)	2.798(10) × 2		

Table 5. Atom coordinates and displacement parameters (Å²) for kaliocalcite.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}		
Cu(1)	¼	¼	0	0.0104(8)		
K(1)	0	½	½	0.0165(14)		
S(1)	0.0814(3)	0	0.2886(4)	0.0089(11)		
O(1)	0.1860(11)	0	0.1850(14)	0.017(3)		
O(2)	0.1875(12)	0	0.5017(14)	0.018(3)		
O(3)	0.1560(10)	½	0.0765(13)	0.021(3)		
O(4)	–0.0276(8)	0.1951(9)	0.2281(9)	0.018(2)		
Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu(1)	0.0152(11)	0.0070(11)	0.0070(11)	–0.0017(4)	0.0035(8)	0.0004(4)
K(1)	0.018(2)	0.022(2)	0.006(2)	0	0.0029(16)	0
S(1)	0.0140(16)	0.0066(14)	0.0048(16)	0	0.0032(12)	0
O(1)	0.019(5)	0.017(4)	0.010(5)	0	0.004(4)	0
O(2)	0.021(5)	0.017(4)	0.010(5)	0	0.002(4)	0
O(3)	0.029(4)	0.016(3)	0.019(5)	0	0.011(4)	0
O(4)	0.023(3)	0.014(3)	0.015(4)	0.000(2)	0.006(3)	0.004(2)

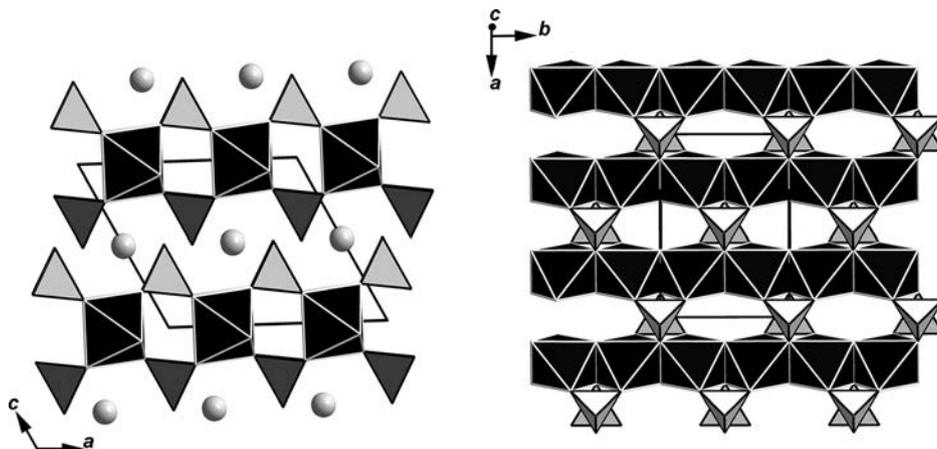


Fig. 6. General projection of the crystal structure of kaliochalcite along b (SO_4 tetrahedra = grey; CuO_6 octahedra = black; K atoms = grey balls) (left) and general view of the natrochalcite-type $\{\text{Cu}_2(\text{SO}_4)_2[(\text{OH})(\text{H}_2\text{O})]\}^-$ layers in kaliochalcite (right).

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