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SANGUITE, $KCuCl_3$, A NEW MINERAL FROM THE TOLBACHIK VOLCANO, KAMCHATKA, RUSSIA

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Abstract

A new mineral sanguite, $KCuCl_3$, is found in the Glavnaya Tenoritovaya fumarole at the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption, Tolbachik volcano, Kamchatka, Russia. Associated minerals are belloite, avdoninite, eriochalcite, sylvite, halite, carnallite, mitscherlichite, chrysothallite, romanorlovite, mellizinkalite, gypsum, chlorothionite, kainite, sellaite, and earlier hematite, tenorite, and chalcocyanite. Sanguite forms prismatic crystals up to 1 mm long and up to 0.2 mm thick, typically combined in groups, dense clusters, or crusts up to several dozens of cm^2 in area. The major crystal forms are {011}, {100}, and {010}. The mineral is transparent, with vitreous luster. Its color is bright red, and slightly altered samples are dark red to brownish red. Sanguite is brittle. Its Mohs' hardness is *ca* 3. Cleavage is perfect on (010), fracture is stepped. $D_{meas} = 2.86(1)$, $D_{calc} = 2.88$ g cm^{-3}. Sanguite is optically biaxial (–), α 1.653(3), β 1.780(6), γ 1.900(8), $2V_{meas} = 85(5)°$. The Raman spectrum is reported. The chemical composition (wt.%, electron microprobe data) is: K 18.57, Cu 29.79, Cl 50.66, total 99.02. The empirical formula calculated on the sum of atoms = 5 *pfu* is: $K_{1.00}Cu_{0.99}Cl_{3.01}$. Sanguite is monoclinic, $P2_1/c$, a 4.0281(2), b 13.7906(5), c 8.7335(4) Å, β 97.137(4)°, V 481.38(3) Å^3, and $Z = 4$. The strongest reflections of the powder X-ray diffraction pattern [d,Å(I)(hkl)] are: 7.36(78)(011), 6.92(100)(020), 3.684(69)($11\bar{1}$), 3.146(64)(032, $10\bar{2}$), 3.068(63)($11\bar{2}$), 2.857(73)($12\bar{2}$), 2.709(82)(112, 042), and 2.574(56)(122). The crystal structure, solved from single-crystal X-ray diffraction data ($R = 0.0545$), contains almost planar, discrete dimers [$Cu^{2+}{}_2Cl_6$]. The KCl_9 polyhedra are connected *via* common faces to form interrupted layers. Neighboring layers are linked to each other by the common edges of the K-centered polyhedra. The mineral is named from the Latin *sanguis* (blood), alluding to its color.

Keywords: sanguite, new mineral, potassium copper chloride, crystal structure, fumarole, Tolbachik volcano, Kamchatka.

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INTRODUCTION

Chloride minerals are typical, sometimes major, components of fumarole deposits formed on many active volcanoes. However, copper chlorides are not common fumarolic products and are significantly distributed at only two volcanoes: Vesuvius in Campania, Italy (Russo & Punzo 2004), and Tolbachik in Kamchatka, Russia. At the latter, the greatest diversity of copper chlorides is known. They were formed mainly as a result of fumarolic activity related to the Great Tolbachik Fissure Eruption (GTFE) of 1975–1976 (Fedotov & Markhinin 1983). From fumaroles born by the GTFE, tolbachite $CuCl_2$ (Vergasova & Filatov 1983) and ponomarevite $K_4Cu_4OCl_{10}$ (Vergasova *et al.* 1988) were first described, the naturally occurring avdoninite $K_2Cu_5Cl_8(OH)_4 \cdot 2H_2O$ was first reported and completely studied (Chukanov *et al.* 2006, Pekov *et al.* 2015a), and melanothallite Cu_2OCl_2 was first crystal chemically characterized (Vergasova & Filatov 1982). Mitscherlichite $K_2CuCl_4 \cdot 2H_2O$, eriochalcite $CuCl_2 \cdot 2H_2O$, belloite CuCl(OH), and two modifications of $Cu_2Cl(OH)_3$, atacamite and paratacamite, were determined here (Vergasova & Filatov 1993, Chukanov *et al.* 2006, our data). Botallackite $Cu_2Cl(OH)_3$ and nantokite CuCl were also mentioned for Tolbachik (Fedotov & Markhinin 1983, Vergasova & Filatov 1993). In 2013–2014, three new copper and potassium chlorides were discovered by us at the second scoria cone of the Northern Breakthrough of the GTFE and approved by the IMA Commission on New Minerals, Nomenclature and Classification: sanguite $KCuCl_3$ (IMA No. 2013-002), chrysothallite $K_6Cu_6Tl^{3+}Cl_{17}(OH)_4 \cdot H_2O$ (IMA 2013–008), and romanorlovite $K_8Cu_6Cl_{17}(OH)_3$ (IMA 2014–011).

In this paper we present the mineralogical description and the crystal structure data of sanguite (Cyrillic: сангвит). The new mineral is named from the Latin *sanguis* (blood), alluding to its color: fresh crystals have a bright red color like arterial blood, whereas slightly altered samples are dark red to brownish red, similar in color to coagulated blood. The type specimens are deposited in the systematic collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, with the catalogue numbers 94128 (the holotype) and 94139.

OCCURRENCE AND GENERAL APPEARANCE

The type specimens of the new mineral were found in July 2012 in the Glavnaya Tenoritovaya ("Major Tenorite") fumarole at the apical part of the Second scoria cone of the Northern Breakthrough of the GTFE (55°41′N, 160°14′E, 1200 m asl). In July 2013, additional material was collected at the same place and the temperatures were measured, using a chromel-alumel thermocouple, in different parts of the fumarole.

The Second scoria cone is a monogenetic volcano about 300 m high and approximately 0.1 km^3 in volume, formed in 1975. It is situated 18 km SSW of the active Ploskiy Tolbachik volcano (Fedotov & Markhinin 1983). The Glavnaya Tenoritovaya fumarole is located in the western wall of a large contraction fracture cross-cutting the top of the scoria cone in the near-meridional direction. Gas vents belonging to this fumarole occupy an area of 1.7 × 4.2 m. In the main part of this area, temperatures of 350–360 °C were measured at a depth of approximately 20 cm below the surface. Major minerals formed in this oxide-sulfate zone are hematite, tenorite, euchlorine, dolerophanite, chalcocyanite, anglesite, krasheninnikovite, and anhydrite (listed in order of distribution). The rich chloride

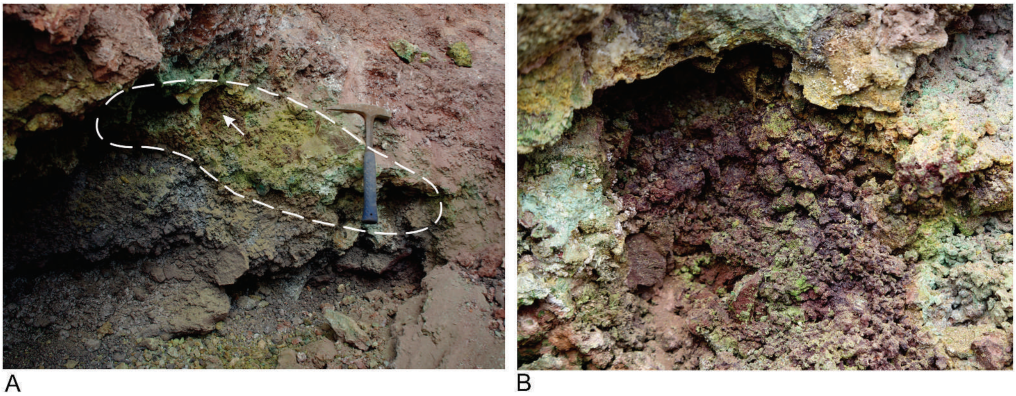

FIG. 1. Occurrence of sanguite *in situ*. (a) The uncovered northern part of the Glavnaya Tenoritovaya fumarole with the outlined sulfate-chloride zone in which the sanguite-richest area is marked with an arrow; (b) its enlarged fragment, the area strongly enriched by dark-red sanguite, with subordinate green avdoninite and belloite and bluish chlorothionite (FOV width: 25 cm). Photo: L.A. Pautov, July 2013.

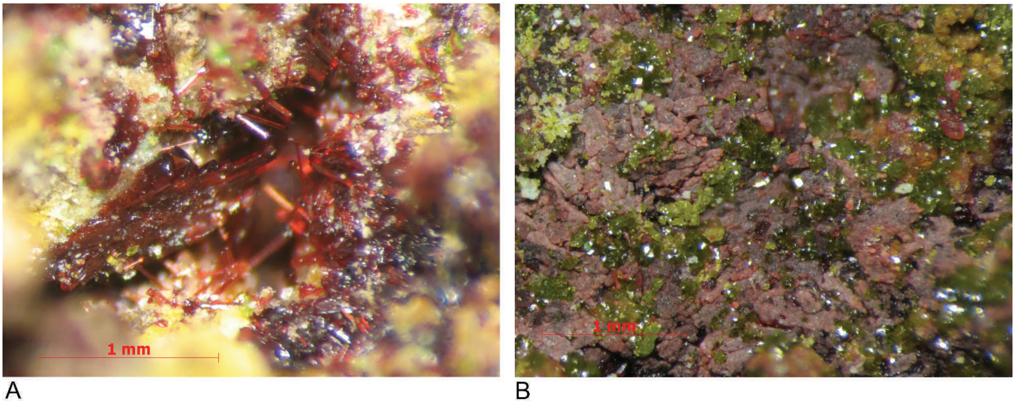

FIG. 2. Sanguite: (a) unaltered, long prismatic bright red crystals in a cavity of basalt scoria; (b) slightly altered, dull reddish coarse prismatic crystals forming a massive, parquet-like crust, with olive green belloite. FOV width: (a) 2.75 mm, (b) 3.4 mm. Photo: I.V. Pekov and A.V. Kasatkin.

mineralization occurs in the outer, moderately hot (110 °C) zone on the northern flank of the fumarole. Chlorides are major constituents of this zone, occurring as a lenticular body about 1.5 m long and up to 0.2 m thick (Fig. 1a). They are represented by belloite, avdoninite, eriochalcite, sylvite, halite, carnallite, mitscherlichite, sanguite, chrysothallite, romanorlovite, mellizinkalite $K_3Zn_2Cl_7$ (Pekov *et al.* 2015b), and an incompletely studied K-Pb-Cu hydroxychloride mineral. Other minerals in this zone are gypsum, chlorothionite, kainite, sellaite, and earlier hematite, tenorite, and chalcocyanite. In this sulfate-chloride zone, OH- and H_2O-bearing minerals play a signiicant role, unlike the above-mentioned hottest oxide-sulfate zone (350–360 °C), in which only anhydrous minerals are present.

Sanguite is common in the sulfate-chloride zone of the Glavnaya Tenoritovaya fumarole. Some areas contain up to 10–15 vol.% of this mineral (Fig. 1b). Sanguite forms prismatic (short to long, elongated along [100]) crystals in cavities. The crystals are up to 1 mm long and up to 0.2 mm thick, typically combined in groups (Figs. 2a and 3), dense clusters, or crusts (Fig. 2b). Some sanguite crusts are up to several dozens of cm^2 in area (Fig. 1b). Granular aggregates up to 1 mm across in polycomponent chloride incrustations are also observed. Some cavities ("bubbles" up to 0.5 mm in diameter) in basalt scoria are completely filled by sanguite.

The major forms of sanguite crystals are {011}, {100}, and {010} (Fig. 4); subordinate faces belonging to the zones {0*kl*} and {*h*0*l*} are present on some crystals. Areas

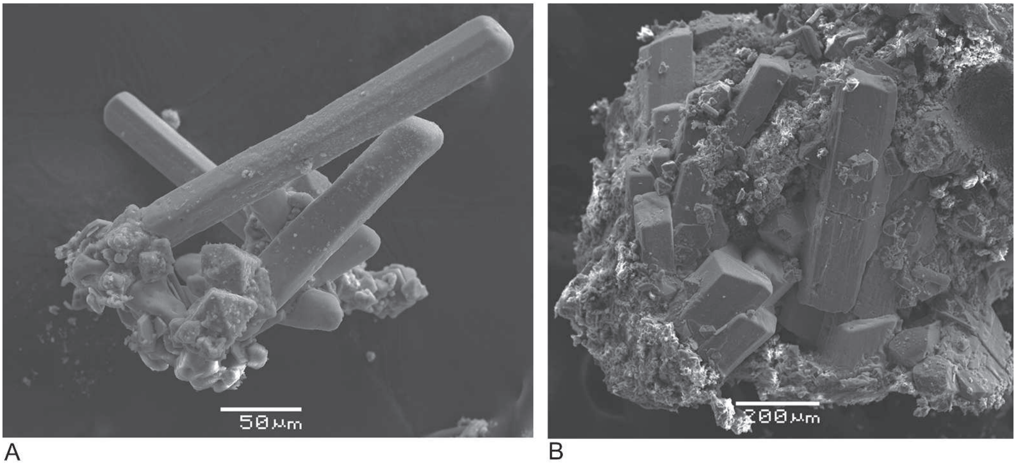

FIG. 3. Groups of sanguite crystals: (a) long-prismatic crystals with halite octahedra; (b) short-prismatic crystals overgrowing basalt scoria altered by fumarolic gas. SEM (SE) images.

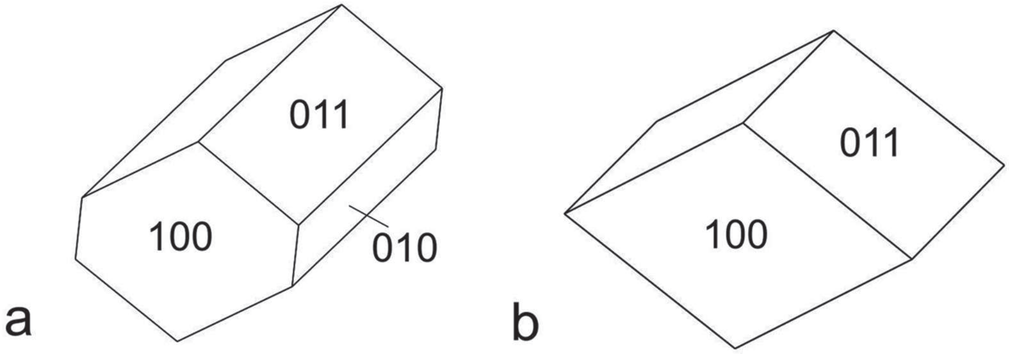

FIG. 4. Idealized crystals of sanguite.

with polysynthetic twinning were observed in several crystals under the microscope, on the section coplanar to (010); the twin lamellae are wedge-shaped and elongated along [100].

PHYSICAL PROPERTIES AND OPTICAL CHARACTERISTICS

Sanguite is bright red; slightly altered samples are dark red to brownish red (Figs. 1b and 2). Its streak is reddish orange. The mineral is transparent and has vitreous luster. Sanguite is very brittle. The Mohs' hardness is about 3. Cleavage is perfect on (010); another distinct cleavage observed under the microscope is probably on $(10\overline{2})$, based on angles measured on cleaved pieces and by analogy with the synthetic crystals reported by Goto *et al.* (2006). The fracture is stepped. The density measured by flotation in heavy liquids (bromoform + hexane) is 2.86(1) g cm^{-3}. The density calculated using the empirical formula is 2.88 g cm^{-3}.

Sanguite is optically biaxial (–), with α 1.653(3), β 1.780(6), γ 1.900(8) (589 nm), $2V_{meas} = 85(5)°$, and $2V_{calc} = 82°$. Dispersion of the optical axes is very strong, $r > v$. Pleochroism is strong: Z (brownish red) $>$ Y (grey to pinkish grey) $>$ X (yellowish grey to colorless). The optical orientation is: $Y = b$, $Z \wedge a = 48°$.

RAMAN SPECTROSCOPY

The Raman spectrum of sanguite (Fig. 5) was recorded using a HORIBA Scientific XploRA System (Jobin Yvon) with a green laser (532 nm) at room temperature. The power of the laser beam at the sample was about 3 mW. The spectrum was processed using the LabSpec 5 program from 100 to 3800 cm^{-1} with a diffraction grating of 1800 mm^{-1}. The diameter of the focal spot on the sample was about 15 μm. The backscattered Raman signal was collected with a 50 × objective. Signal acquisition time for a single scan of the spectral range was 100 s and the signal was averaged over five scans. The spectrum was acquired from a randomly oriented crystal.

The highest frequency absorption band has a maximum at 547 cm^{-1} and corresponds to Cu^{2+}–Cl stretching vibrations. Several bands with frequencies below 300 cm^{-1} correspond to lattice modes involving K–Cl stretching and Cu^{2+}–Cl bending vibrations. The absence of absorption bands in the region higher than 600 cm^{-1} indicates the absence of O–H, Be–O, Li–O, and C-, N-, and B-bearing groups in sanguite.

CHEMICAL DATA

Chemical data for sanguite were obtained with 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. The following standards were used: microcline (K), $CuFeS_2$ (Cu), and NaCl (Cl).

The average (six spot analyses) chemical composition of sanguite (wt.%, ranges are in parentheses) is:

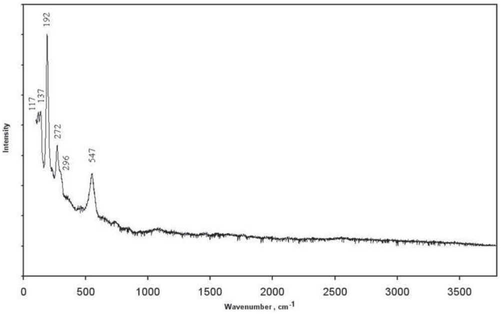

FIG. 5. The Raman spectrum of sanguite.

TABLE 1. POWDER X-RAY DIFFRACTION DATA FOR SANGUITE

I_{obs}	d_{obs}, Å	I_{calc}*	d_{calc}, Å**	$h\ k\ l$
78	7.36	73	7.337	011
100	6.92	100	6.895	020
45	5.415	45	5.396	021
15	4.344	6	4.333	002
35	4.137	20	4.134	012
41	4.080	29	4.061	031
69	3.684	74	3.676	$11\bar{1}$
4	3.449	3	3.448	040
15	3.359	13, 8	3.364, 3.338	111, $12\bar{1}$
64	3.146	20, 60	3.153, 3.139	032, $10\bar{2}$
63	3.068	81	3.060	$11\bar{2}$
73	2.857	94	2.857	$12\bar{2}$
29	2.771	6, 20	2.771, 2.769	102, 131
82	2.709	51, 44	2.717, 2.698	112, 042
43	2.635	27, 38	2.664, 2.628	023, 051
56	2.574	56	2.571	122
4	2.456	4	2.453	$11\bar{3}$
8	2.371	7	2.373	132
16	2.327	11	2.327	052
34	2.271	48	2.270	150
31	2.220	26, 16	2.222, 2.214	061, 043
9	2.166	10, 7, 1	2.186, 2.160, 2.159	113, 142, 151
6	2.108	9	2.108	123
10	2.068	14	2.067	024
44	2.002	26, 9, 46	2.020, 2.012, 1.998	$14\bar{3}$, $10\bar{4}$, 200
14	1.965	6, 17	1.969, 1.960	$16\bar{1}$, 034
13	1.921	2, 8, 4, 8	1.923, 1.921, 1.919, 1.916	$22\bar{1}$, 071, 220, 161
18	1.861	23	1.863	143
9	1.796	17	1.793	072
19	1.754	9, 6, 13	1.753, 1.753, 1.750	231, 124, $17\bar{1}$
15	1.705	13	1.704	054
18	1.689	3, 11	1.690, 1.686	$16\bar{3}$, 134
12	1.624	3, 2, 7	1.628, 1.626, 1.623	073, $15\bar{4}$, 232
6	1.607	2, 2	1.606, 1.604	172, 144
9	1.567	5, 4, 8, 2	1.571, 1.569, 1.568, 1.563	$18\bar{1}$, $25\bar{2}$, $13\bar{5}$, 251
12	1.549	7, 6	1.550, 1.549	242, 045
9	1.538	8, 11	1.544, 1.530	181, $22\bar{4}$
9	1.513	3, 5, 11	1.515, 1.514, 1.510	154, $16\bar{4}$, $26\bar{1}$
3	1.483	6	1.485	$23\bar{4}$
4	1.471	2, 2, 2, 1	1.473, 1.472, 1.468, 1.468	233, 173, 252, $26\bar{2}$
4	1.446	7, 1, 1	1.445, 1.445, 1.444	135, 092, 006
10	1.416	6, 11	1.418, 1.414	243, 026
8	1.407	4, 7	1.404, 1.402	$27\bar{1}$, 191
6	1.359	5	1.364	$25\bar{4}$
7	1.356	11, 4	1.354, 1.353	093, $13\bar{6}$
2	1.337	6	1.336	$31\bar{1}$
2	1.321	4	1.320	$30\bar{2}$
4	1.305	1, 3	1.306, 1.305	$28\bar{1}$, 280
4	1.302	2	1.302	272

TABLE 1. (CONTINUED)

I_{obs}	d_{obs}, Å	I_{calc}*	d_{calc}, Å**	*h k l*
1	1.284	1	1.284	126
2	1.261	2	1.260	$15\bar{6}$
2	1.257	1	1.257	136
3	1.241	2, 1	1.243, 1.241	340, 0.11.1
4	1.236	3, 1	1.238, 1.235	254, 1.10.2
4	1.229	5	1.227	$22\bar{6}$
3	1.219	1, 1	1.219, 1.219	$19\bar{4}$, 027

* Only reflections with $I_{calc} \geqslant 1$ are taken into account; **calculated for the unit cell parameters obtained from single-crystal data.

K 18.57 (17.91–19.02), Cu 29.79 (29.18–30.30), Cl 50.66 (49.87–51.17), total 99.02. Contents of other elements with atomic numbers higher than carbon are below detection limits.

The empirical formula calculated based on the sum of atoms = 5 *pfu* is: $K_{1.00}Cu_{0.99}Cl_{3.01}$. The idealized formula $KCuCl_3$ requires K 18.71, Cu 30.41, Cl 50.88, total 100.00 wt.%.

Sanguite dissolves very easily in H_2O at room temperature. In humid air the mineral is unstable and alters to an aggregate of eriochalcite $CuCl_2{\bullet}2H_2O$ and sylvite KCl after several weeks.

X-RAY CRYSTALLOGRAPHY AND CRYSTAL STRUCTURE

Powder X-ray diffraction data (Table 1) for sanguite were collected with a STOE IPDS II diffractometer equipped with an image plate area detector, using the Gandolfi method (Mo$K\alpha$-radiation; detector-to-sample distance: 200 mm). The parameters of the monoclinic unit cell refined from the powder data are: *a* 4.027(4), *b* 13.79(1), *c* 8.734(8) Å, β 97.17(7)°, and *V* 481(1) Å^3.

Single-crystal X-ray studies were carried out using an Xcalibur S CCD diffractometer. Crystal data, data collection information, and structure refinement details are given in Table 2. The data were corrected for Lorentz and polarization effects. An absorption correction was applied according to the shape of the crystal. The structure was solved by direct methods and refined with the use of the SHELX software package (Sheldrick 2008) on the basis of 874 independent reflections with $I > 2\sigma(I)$ to $R = 0.0545$. Atom coordinates and displacement parameters are given in Table 3 and selected interatomic distances in Table 4.

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

Formula	$KCuCl_3$
Formula weight	208.99
Crystal system, space group	monoclinic, $P2_1/c$
Unit cell parameters (Å,°)	a = 4.0281(2) b = 13.7906(5) c = 8.7335(4) β = 97.137(4)°
V (Å^3)	481.38(3)
Z	4
F(000)	396
Absorption coefficient μ (mm^{-1})	6.867
Diffractometer	Xcalibur S CCD
λ (Mo$K\alpha$) (Å), T (K)	0.71073, 293(2)
Crystal-detector distance (mm)	45 (full) sphere
Collection mode, 2θ$_{max}$ (°)	
θ range for data collection(°)	2.78–26.37
Crystal size (mm)	0.06 × 0.09 × 0.11
h, k, l ranges	–5/5, –17/17, –10/10
Reflections collected	6927
Unique reflections	976 (R_{int} = 0.0733)
Reflections with $I > 2\sigma(I)$	874
Structure solution	direct methods
Refinement method	full-matrix least-squares on F^2
No. of refined parameters	52
Extinction coefficient	0.0024(10)
Weighting scheme	$1/[\sigma^2(F_o{}^2) + (0.0178P)^2 + 0.6474P]$, $P = [\max(F_o)^2 + 2(F_c)^2]/3$
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0545, w$R2$ = 0.0767
R indices (all data)	$R1$ = 0.0660, w$R2$ = 0.0797
GoF	1.349
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e/Å^3)	–0.664, 0.590

The crystal structure of sanguite (Figs. 6 and 7), as well as its synthetic analogue (Willett *et al.* 1963), contains almost planar, discrete dimers $[Cu^{2+}{}_2Cl_6]$ with Cu–Cl distances in the range 2.25 to 2.33 Å. We note that the Cu–centered polyhedra could be considered as significantly distorted octahedra with two additional elongated bonds, Cu–Cl(2) with distance 2.9323(17) Å and Cu–Cl(3) with distance 3.1104(17) Å. The contribution of

TABLE 3. ATOM COORDINATES, DISPLACEMENT PARAMETERS (Å^2), AND BOND VALENCE SUMS (ΣS) FOR SANGUITE

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}	Σs
Cu	0.24055(19)	0.04990(6)	0.15765(8)	0.0200(3)	1.82*
K	0.2178(3)	–0.17062(10)	0.44269(17)	0.0268(4)	1.26
Cl(1)	0.2738(4)	0.19899(11)	0.26298(18)	0.0245(4)	1.11
Cl(2)	0.6794(4)	–0.00779(11)	0.32167(17)	0.0211(4)	0.96*
Cl(3)	–0.1806(4)	0.09868(11)	–0.03440(17)	0.0214(4)	1.01*

* The values could be increased by taking into account the elongated Cu–Cl distances (see italicized distances in Table 4): to 1.95 for Cu, 1.04 for Cl(2), and 1.06 *v.u.* for Cl(3). Parameters for bond valence calculations were taken from Brese & O'Keeffe (1991).

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

Cu–Cl(1)	2.2497(17)	K–Cl(1)	3.082(2)
–Cl(2)	2.2762(16)	–Cl(1)	3.106(2)
–Cl(3)	2.3133(16)	–Cl(2)	3.179(2)
–Cl(3)	2.3316(16)	–Cl(2)	3.201(2)
<Cu–Cl>	2.293	–Cl(2)	3.208(2)
–Cl(2)	2.9323(17)	–Cl(3)	3.289(2)
–Cl(3)	3.1104(17)	–Cl(1)	3.401(2)
		–Cl(1)	3.456(2)
		–Cl(3)	3.686(2)
		<K–Cl>	3.290

these bonds to the bond valences is 0.08 and 0.05, respectively. For better clarity the Cu-centered polyhedra are shown in Figures 6 and 7 as planar squares. The KCl_9 polyhedra are connected *via* common faces (Fig. 7) to form interrupted layers in the *ac* plane. Neighboring layers are linked to each other by the common edges of the K-centered polyhedra. Such an arrangement of K atoms makes the structure quasi-layered and probably results in the perfect cleavage on (010).

DISCUSSION

Sanguite is a representative of the well-known family of compounds with the structural archetype

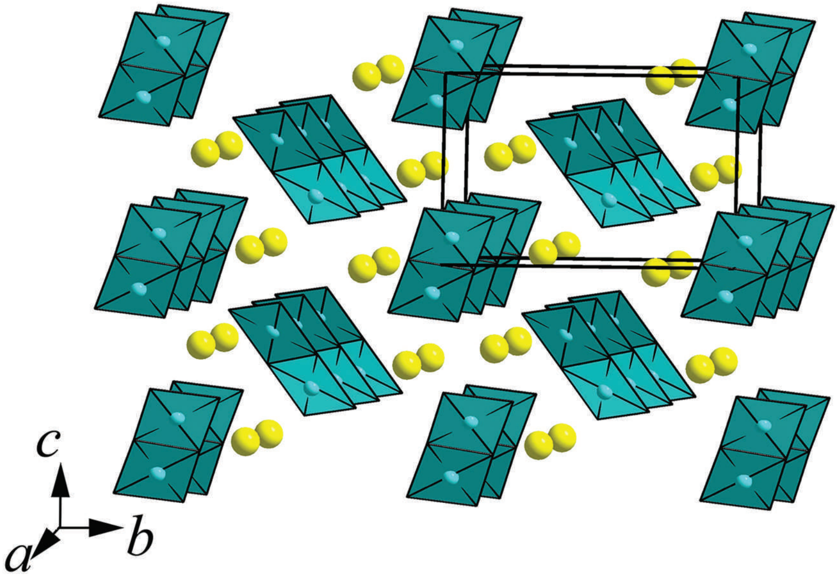

FIG. 6. Crystal structure of sanguite, general view. The $[Cu^{2+}{}_2Cl_6]$ dimers are blue and the K^+ ions are shown as yellow circles. The unit cell is outlined.

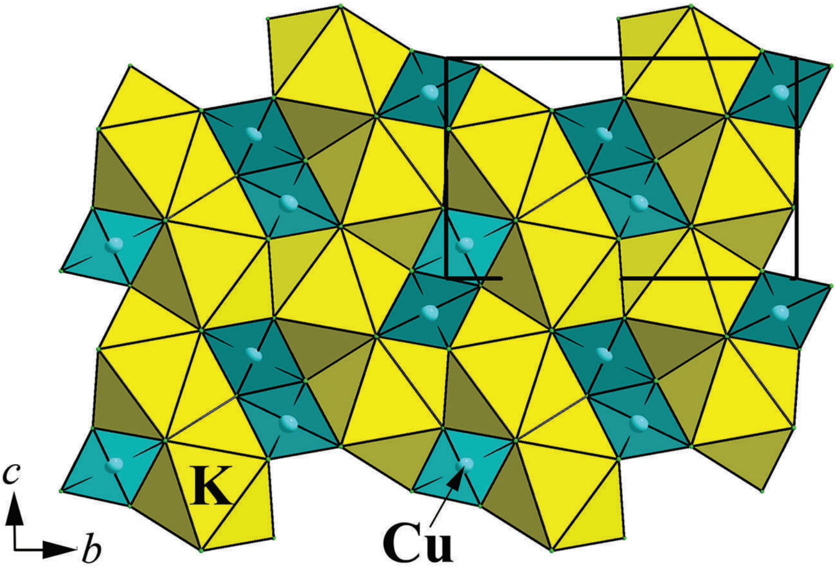

FIG. 7. Crystal structure of sanguite, the *bc* projection, with both Cu- and K-centered polyhedra shown. The unit cell is outlined.

$(NH_4)CdCl_3$ (Rolies & de Ranter 1978). No other natural halides structurally close to sanguite are known, but the sulfide minerals ottemannite Sn_2S_3 (Kniep *et al.* 1982) and suredaite $PbSnS_3$ (Paar *et al.* 2000) belong to this structural family.

The synthetic analogue of sanguite has been known since 1889 when "red $KCuCl_3$" was first synthesized and reported by Meyerhoffer; its crystal structure was studied by Willett *et al.* (1963). During the last few decades, this compound and related synthetic chlorides have been the focus of numerous studies because of their magnetic properties (*e.g.*, Kato *et al.* 1999, Goto *et al.* 2006).

Published data for synthetic $KCuCl_3$ show that its crystals can be grown using different methods over a wide temperature range, *e.g.*, at room temperature from aqueous solutions of KCl + $CuCl_2$ + HCl (Willett *et al.* 1963), or at 500 °C from a melt using the Bridgman method (Goto *et al.* 2006).

Sanguite occurs in the same assemblage as the OH- and H_2O-bearing minerals avdoninite, belloite, eriochalcite, mitscherlichite, carnallite, gypsum, kainite, chrysothallite, and romanorlovite, and commonly overgrows belloite and avdoninite. Based on this fact and on the temperature measurement of 110 °C at the site of formation, we conclude that the chloride mineralization in the Glavnaya Tenoritovaya fumarole did not form as the result of direct deposition from the gas phase (note that fumarolic gases of the second scoria cone are "dry" and contain no more than 1% H_2O: Zelenski *et al.* 2012). Rather, they formed from the interactions of earlier formed, high-temperature sublimate minerals, HCl-bearing fumarolic gas, and atmospheric water vapor at relatively low temperatures, presumably not higher than 110–150 °C.

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