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BURNSITE, $KCdCu_7O_2(SeO_3)_2Cl_9$, A NEW MINERAL SPECIES FROM THE TOLBACHIK VOLCANO, KAMCHATKA PENINSULA, RUSSIA

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ABSTRACT

Burnsite, ideally $KCdCu_7O_2(SeO_3)_2Cl_9$, occurs in a fumarole in the North Breach of the great fissure Tolbachik volcano eruption (1975–1976), Kamchatka Peninsula, Russia. It occurs as dark red, anhedral, equidimensional grains. Associated minerals are cotunnite, sophiite, chloromenite, georgbokiite, ilinskite and an undefined Cu–Pb selenite. Burnsite is very rare and has only been found as several dozen grains that do not exceed 0.1 mm in maximum dimension. It is very similar megascopically to georgbokiite and the undefined Cu–Pb selenite, but differs from them by its red color. Burnsite has a strongly vitreous (metalloid) luster and a red streak. The mineral is brittle, opaque to translucent, with an uneven fracture. Cleavage is good on the (001) plane. Hardness VHN = 12 kg/mm^2. The calculated density is 3.85 g/cm^3. It is nonfluorescent. It is uniaxial negative, E 1.912(5), O 1.920(5), with weak bireflectance and no pleochroism. Burnsite is hexagonal, space group $P6_3/mmc$, *a* 8.7805(8), *b* 15.521(2) Å, *V* 1036.3(2) Å^3, $Z = 2$. The strongest eight lines of the X-ray powder-diffraction pattern [*d* in Å (*I*)(*hkl*)] are: 7.779(100)(002), 6.823(50)(101), 4.391(60)(100), 3.814(80)(200), 3.066(70)(203), 2.582(50)(006), 2.501(60)(213) and 2.190(50)(220). Electron-microprobe analyses yield K_2O 4.30, CuO 46.74,CdO 10.45, SeO_2 19.91, Cl 25.46, less $O{=}Cl_2$ –5.75, total 101.11 wt. %. The empirical formula, derived from the crystal-structure analysis and electron-microprobe analyses, is $K_{1.08}Cd_{0.97}Cu_{6.98}O_{2.05}(Se_{1.07}O_{3.21})_2Cl_{8.53}$, on the basis of O + Cl = 17. The mineral name honors Professor Peter C. Burns, University of Notre Dame, Indiana, in recognition of his important contributions to structural mineralogy.

Keywords: burnsite, new mineral species, potassium cadmium copper oxy-selenite chloride, Tolbachik volcano, Kamchatka Peninsula, Russia.

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SOMMAIRE

La burnsite, dont la formule idéale est $KCdCu_7O_2(SeO_3)_2Cl_9$, a été découverte dans une fumerolle dans la brèche du Nord de la grande éruption fissurale du volcan Tolbachik (1975–1976), dans la péninsule de Kamchatka, en Russie. Elle se présente en grains rouge foncé, xénomorphes, équidimensionnels. Lui sont associés cotunnite, sophiite, chloroménite, georgbokiite, ilinskite et un sélénite Cu–Pb non défini. La burnsite est considérée rarissime, n'ayant été trouvée que dans quelques douzaines de grains qui ne dépassent pas 0.1 mm. Elle ressemble beaucoup à la georgbokiite et au sélénite de Cu–Pb non défini, mais s'en distingue par sa couleur rouge. La burnsite a un éclat fortement vitreux (métalloïde) et une rayure rougeâtre. C'est un minéral cassant, opaque à translucide, avec une cassure inérale. Le clivage est bon le long du plan (001). La dureté VHN est égale à 12 kg/mm^2. La densité calculée est égale à 3.85 g/cm^3. Elle est non fluorescente. La burnsite est uniaxe négative, E 1.912(5), O 1.920(5), avec une faible biréflectance et sans pléochroïsme. Elle est hexagonale, groupe spatial $P6_3/mmc$, a 8.7805(8), b 15.521(2) Å, V 1036.3(2) Å^3, Z = 2. Les huit raies les plus intenses du spectre de diffraction. méthode des poudres [d en Å (I)(hkl)] sont: 7.779(100)(002), 6.823(50)(101), 4.391(60)(100), 3.814(80)(200), 3.066(70)(203), 2.582(50)(006), 2.501(60)(213) et 2.190(50)(220). Les analyses à la microsonde électronique ont donné K_2O 4.30, CuO 46.74,CdO 10.45, SeO_2 19.91, Cl 25.46, moins $O{=}Cl_2$ –5.75, pour un total de 101.11% (poids). La formule empirique, dérivée à partir de la détermination de la structure et des données chimiques, est $K_{1.08}Cd_{0.97}Cu_{6.98}O_{2.05}(Se_{1.07}O_{3.21})_2Cl_{8.53}$, sur une base de O + Cl = 17. Le nom choisi honore Peter C. Burns, professeur ;a l'Université de Notre Dame, Indiana, pour souligner ses contributions importantes à la minéralogie structurale.

(Traduit par la Rédaction)

Mots-clés: burnsite, nouvelle espèce minérale, oxy-sélénite chloruré de potassium, cadmium et cuivre, volcan Tolbachik, péninsule de Kamchatka, Russie.

INTRODUCTION

A new potassium cadmium copper oxy-selenite chloride, ideally $KCdCu_7O_2(SeO_3)_2Cl_9$, was discovered within a fumarole in the North Breach of the great fissure Tolbachik eruption (GFTE) (1975–1976), in Kamchatka Peninsula, Russia. The mineral is named *burnsite* in honor of Professor Peter C. Burns (b. 1966), Canadian-born mineralogist and structural crystallographer presently at the University of Notre Dame, Notre Dame, Indiana, U.S.A., in recognition of his important contributions to structural mineralogy and, in particular, to knowledge about the structures of Cu^{2+} oxysalt minerals (Burns 1998; Burns & Hawthorne 1993, 1995a, b, c, 1996; Burns *et al.* 1991, 1995a, b, 2000a, b, c, 2002). Type material is deposited in the Mining Museum, Mining Institute, St. Petersburg, Russia. The mineral and mineral name have been approved by the Commission on New Minerals and Mineral Names, IMA (2000–50). According to the chemical composition and crystal-structure data, burnsite has no known analogues among minerals and inorganic compounds. In this paper, we describe the physical and chemical attributes of this new mineral species.

LOCALITY AND OCCURRENCE

The GFTE is the largest basaltic eruption in modern history (Fedotov 1984). It was active in 1975–1976 and consisted of two Breaches (North and South) and seven cones (see Vergasova *et al.* 1999c for more details). Beginning in the late 1970s, fumarolic activity of the GFTE resulted in the crystallization of a unique mineral assemblage, with twenty-four new mineral species discovered to date. Beginning from the eruption in 1976 and up to the present, an interesting association of selenite-bearing minerals has been detected, from which sophiite, $Zn_2(SeO_3)_2Cl_2$ (Vergasova *et al.* 1989), ilinskite, $NaCu_5O_2(SeO_3)_2Cl_3$ (Vergasova *et al.* 1997), georgbokiite, $Cu_5O_2(SeO_3)_2Cl_3$ (Vergasova *et al.* 1999a), and chloromenite, $Cu_9O_2(SeO_3)_4Cl_6$ (Vergasova *et al.* 1999b), have been approved as new mineral species. Burnsite is the fifth selenite chloride discovered within the Tolbachik fumaroles. Grains of this mineral were found in products of fumarolic activity on the second cinder cone of the North breach of GFTE.

Burnsite is associated with cotunnite ($PbCl_2$), sophiite, ilinskite, georgbokiite, chloromenite and an undefined Cu–Pb selenite. The latter mineral and burnsite are quite rare and have only been found as several dozen grains that do not exceed 0.1 mm in maximum dimension. Burnsite is megascopically very similar to georgbokiite and the undefined Cu–Pb selenite, but differs from them by its red color. The crystals of burnsite are very rarely well formed and usually occur as round anhedral equidimensional grains with no obvious crystal forms (Fig. 1).

CHEMICAL COMPOSITION

Two small grains of burnsite (< 0.1 mm in size) were mounted in epoxy and chemically analyzed at 15 kV and 10 nA with a Cameca SX–50 electron microprobe. The following standards were used: microcline (K), Cu metal (Cu), synthetic CdS (Cd), Se metal (Se) and synthetic chlorapatite (Cl). No elements other than those mentioned above were detected. The results of the analyses are summarized in Table 1. The empirical for-

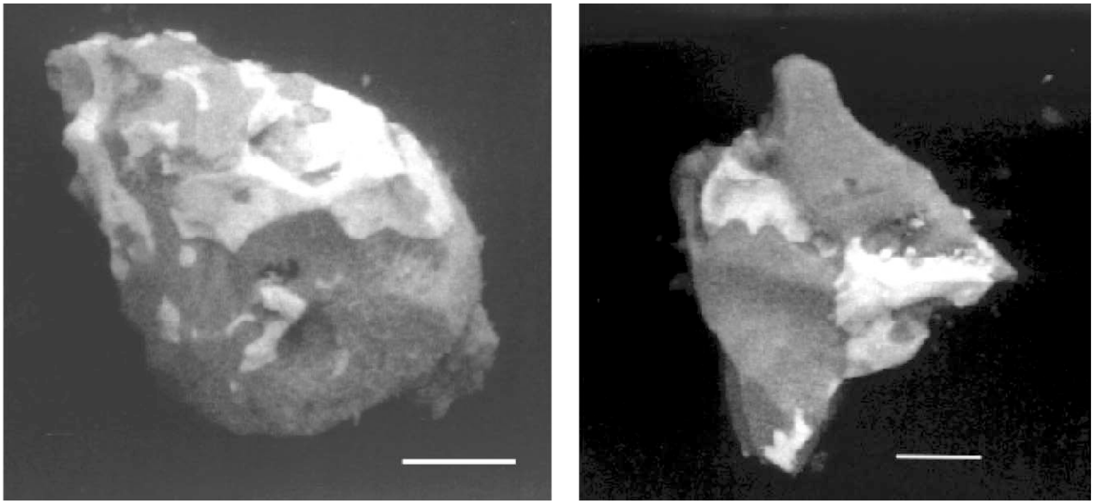

FIG. 1. Images of burnsite grains (dark) in intimate intergrowth with cotunnite (light). Images obtained by scanning electron microscopy. Scale bar: 20 μm.

TABLE 1. CHEMICAL COMPOSITION OF BURNSITE

		Range	Theoretical
K_2O wt%	4.3	4.25–4.40	3.92
CuO	46.74	46.07–47.60	46.35
CdO	10.45	10.25–10.80	10.69
SeO_2	19.91	19.42–20.30	18.47
Cl	25.46	24.48–26.39	26.56
$O{=}Cl_2$	–5.75	–(5.57–6.82)	–5.99
Total	101.11		100

Empirical formula: $K_{1.08}Cd_{0.97}Cu_{6.98}O_{2.05}(Se_{1.07}O_{3.21})_2Cl_{8.53}$
Theoretical formula: $KCdCu_7O_2(SeO_3)_2Cl_9$

mula of burnsite, $K_{1.08}Cd_{0.97}Cu_{6.98}O_{2.05}(Se_{1.07}O_{3.21})_2Cl_{8.53}$, calculated on the basis of O + Cl = 17 atoms per formula unit (*apfu*), is close to the ideal, $KCdCu_7O_2(SeO_3)_2Cl_9$, which requires: K_2O 3.92, CuO 46.35,CdO 10.69, SeO_2 18.47, Cl 26.56, sum 105.99, less $O = Cl_2$ – 5.99, total 100.00 wt. %. The chemical formula of burnsite is confirmed by the crystal-structure analysis (Burns *et al.* 2002).

PHYSICAL AND OPTICAL PROPERTIES

Burnsite is dark red in color, with a strongly vitreous (metalloid) luster and a red streak. The mineral is brittle, opaque to translucent, with an uneven fracture. According to optical examination, burnsite has a good cleavage on the (001) plane. Hardness VHN measured by micro-identation is 12 kg/mm^2, which corresponds to 1–1½ on the Mohs scale. The calculated density for Z = 2 is 3.85 g/cm^3. The density of the mineral was not measured owing to a dearth of material and size limitations. The mineral does not fluoresce in either short- or long-wave ultraviolet radiation.

Study of the optical properties of burnsite was very difficult, because the crystals react with high-index immersion liquids in 20–30 seconds. Most grains have an undulatory extinction, probably due to compositionally distinct micro-domains, which results in a pseudo-biaxial interference figure. The mineral is optically negative, $n_e = 1.912(5)$, $n_o = 1.920(5)$. Bireflectance is weak and can be estimated as 0.01. No pleochroism has been observed. The average index of refraction, calculated from the ideal formula using the Gladstone–Dale equation, is 1.804. This means that the compatibility is very poor. However, the same situation holds for other natural copper oxide selenite chlorides, such as chloromenite, georgbokiite and ilinskite.

X-RAY CRYSTALLOGRAPHY

Unit-cell parameters of burnsite were determined using a three-circle Bruker AXS diffractometer equipped with a 1K SMART CCD (charge-coupled device) detector and were further refined by crystal-structure analysis. The mineral is hexagonal, space group *P*6_3*/mmc*, *a* 8.7805(8), *c* 15.521(2) Å, *V* 1036.3(2) Å^3, *c/a* = 1.768. As a very small amount of material was available for study, X-ray powder-diffraction data (Table 2) were obtained using a Debye–Scherrer powder camera, 114.6 mm in diameter. The refined unit-cell parameters, *a* 8.761(3), *c* 15.507(6) Å, *V* 1030.7(7)

Å^3, *c/a* 1.770, are based on 21 X-ray powder diffraction lines between 3.456 and 1.461 Å for which unambiguous indexing was possible. All indexed reflections were confirmed using the calculated intensities derived from the crystal structure. Diffraction lines solely ascribable to admixed cotunnite have been deleted from the table.

The details of a crystal-structure determination will be reported by Burns, Krivovichev & Filatov (in prep.).

RELATIONSHIPS TO OTHER SPECIES AND FIELD OF STABILITY

The Tolbachik fumaroles represent an unique association of rare selenite chlorides. In addition to burnsite, four other selenite chlorides were discovered there (sophiite, georgbokiite, chloromenite and ilinskite) and several undefined minerals with similar composition await detailed characterization. From the above-mentioned minerals, three (georgbokiite, chloromenite and ilinskite) are copper oxide chloride selenites, similar in composition to burnsite. They contain "additional" O atoms that do not belong to SeO_3 groups, but are bonded only to Cu atoms. With the exception of the Tolbachik minerals, the only other known mineral that has these chemical and structural features is francisite, $Cu_3BiO_2(SeO_3)_2Cl$, which was described by Pring *et al.* (1990) from the Iron Monarch iron deposit in Australia. In contrast to the Tolbachik minerals, francisite forms from low-temperature hydrothermal fluids and can be synthesized using hydrothermal methods (Pring *et al.* 1990). Recently, Nazarchuk *et al.* (2000) and Millet *et al.* (2001) synthesized francisite using chemical transport reactions and solid-state reactions, respectively. These authors have shown therefore that francisite can crystallize from a gaseous phase, in the same manner as the selenites from the Tolbachik fumaroles do.

TABLE 2. X-RAY POWDER-DIFFRACTION DATA FOR BURNSITE

I_{est}		d_{meas}	d_{calc}	*hkl*	I_{est}		d_{meas}	d_{calc}	*hkl*
100		7.779	7.754	002	30	*	2.032	2.031	312
40		7.645	7.587	100	10	*	1.949	1.949	313
50		6.823	6.815	101	40	*	1.919	1.920	216
5		5.446	5.423	102	5		1.880	1.883	401
80		4.391	4.381	110				1.878	108
20		3.888	3.877	004	3		1.841	1.843	402
80		3.814	3.794	200	3	*	1.810	1.808	306
10		3.696	3.685	201	15		1.782	1.781	403
20	*	3.456	3.452	104	3	*	1.772	1.773	118
70	*	3.066	3.058	203	5		1.755	1.753	217
10	*	2.876	2.868	210	3	*	1.728	1.730	321
3		2.818	2.820	211	10		1.704	1.704	404
20	*	2.708	2.711	204	30	*	1.670	1.671	226
50	*	2.582	2.585	006				1.666	307
60	*	2.501	2.508	213	5		1.656	1.656	410
30	*	2.445	2.447	106	3		1.621	1.619	412
30	*	2.305	2.306	214	5b	*	1.578	1.577	413
40	*	2.272	2.272	303	3	*	1.555	1.551	00$\underline{10}$
50	*	2.190	2.190	220	5	*	1.538	1.539	308
3		2.122	2.127	107	5	*	1.516	1.517	500
			2.118	304	10		1.478	1.477	219
10b		2.099	2.104	310	20		1.461	1.460	330

Debye–Scherrer powder camera, 114.6 mm in diameter, Cu radiation and Ni filter (λ Cu*K*α 1.54178 Å); intensities estimated visually, b = broad line; not corrected for shrinkage and no internal standard. * Lines used for unit-cell refinement; indexed on *a* 8.761(3), *c* 15.507(6) Å. Values of *d* are expressed in Å.

Campostrini *et al.* (1999) described a lead selenite chloride hydrate, orlandiite, $Pb_3Cl_4(SeO_3)\bullet H_2O$, and an unnamed copper lead selenite chloride hydroxide, $Pb_4CuCl_3(SeO_3)_3(OH)$, from the oxidation zone at the old lead–arsenic mine of Baccu Locci, Sardinia, Italy. These phases are evidently of hydrothermal origin; we were able to synthesize crystals of orlandiite using low-temperature hydrothermal methods. However, as was noted by Campostrini *et al.* (1999), the conditions of formation of fumarolic and hydrothermal minerals are drastically different, since the absence of H_2O is crucial to the formation of copper oxide oxysalts in fumaroles. In the presence of H_2O, associations of copper hydroxysalts (*e.g.,* atacamite, brochantite, linarite) usually are observed.

Finally, it should be noted that copper oxysalts with "additional" O atoms are common in fumarolic deposits and, in addition to Tolbachik, were observed in fumaroles of the Vesuvius volcano, Italy [*e.g.*, euchlorine, $NaKCu_3O(SO_4)_3$ (Scordari *et al.* 1989)] and the Isalco volcano, El Salvador [*e.g.*, stoiberite, $Cu_5O_2(VO_4)_2$ (Birnie & Hughes 1979) and fingerite, $Cu_{11}O_2(VO_4)_6$ (Hughes & Hadidiacos 1985)].

On the basis of field measurements and high-temperature X-ray powder-diffraction studies of other copper oxide chloride selenites (georgbokiite, ilinskite, chloromenite, francisite), we estimate the temperature of formation of burnsite to be ~ 450–500°C.

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