

## NEW Cu<sup>2+</sup> COORDINATION POLYHEDRA IN THE CRYSTAL STRUCTURE OF BURNSITE, KCdCu<sub>7</sub>O<sub>2</sub>(SeO<sub>3</sub>)<sub>2</sub>Cl<sub>9</sub>

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### ABSTRACT

The crystal structure of burnsite, KCdCu<sub>7</sub>O<sub>2</sub>(SeO<sub>3</sub>)<sub>2</sub>Cl<sub>9</sub>, a new mineral species from fumaroles of the Tolbachik volcano, Kamchatka, Russia, has been solved by direct methods and refined on the basis of  $F^2$  for all unique data collected with monochromatic MoK $\alpha$  X-radiation and a CCD (charge-coupled device) detector to an agreement factor ( $R_1$ ) of 1.9%, calculated using the 460 unique observed reflections ( $|F_o| = 4\sigma_F$ ). The mineral is hexagonal, space group  $P6_3/mmc$ ,  $a$  8.7805(8),  $c$  15.521(2) Å,  $V$  1036.3(2) Å<sup>3</sup>,  $Z$  = 2. There are two non-equivalent Cu<sup>2+</sup> cations in the structure of burnsite. The Cu(1) cation is coordinated by three atoms of O and three of Cl; this is the first example of this type of mixed-ligand Cu<sup>2+</sup>φ<sub>6</sub> (φ: O<sup>2-</sup>, Cl<sup>-</sup>) octahedron in a mineral. The octahedron is (2 + 4)-distorted owing to the Jahn-Teller effect, in contrast to the vast majority of Cu<sup>2+</sup> oxyx salt minerals that contain (4 + 2)-distorted Cu<sup>2+</sup> octahedra. The Cu(2) cation is coordinated by two O and three Cl anions arranged at the vertices of a trigonal bipyramidal; this is the first occurrence of a mixed-ligand Cu<sup>2+</sup>O<sub>2</sub>Cl<sub>3</sub> trigonal bipyramidal in a mineral. The single symmetrically independent Cd<sup>2+</sup> cation is coordinated by six Cl anions located at the vertices of a regular octahedron. The structure contains one symmetrically independent K cation that is coordinated by six Cl anions in a trigonal prismatic arrangement. There is one unique Se<sup>4+</sup> cation that is strongly bonded to three O anions on one side of the cation, owing to the presence of a  $s^2$  lone-electron pair. The structure is described both in terms of cation-centered polyhedra and oxocentered OCu<sub>4</sub> tetrahedra. The structure of burnsite is closely related to the structures of other natural copper oxide chloride selenites discovered in the Tolbachik fumaroles (chloromenite, georgbokiite, ilinskite).

**Keywords:** burnsite, crystal structure, copper selenites, oxocentered tetrahedra.

### SOMMAIRE

Nous avons résolu la structure cristalline de la burnsite, KCdCu<sub>7</sub>O<sub>2</sub>(SeO<sub>3</sub>)<sub>2</sub>Cl<sub>9</sub>, nouvelle espèce minérale provenant des fumerolles du volcan Tolbachik, péninsule de Kamchatka, en Russie, par méthodes directes, et nous l'avons affiné en utilisant les facteurs  $F^2$  des réflexions uniques prélevées avec rayonnement monochromatique MoK $\alpha$  et un détecteur CCD à couplage de charges, jusqu'à un facteur de concordance ( $R_1$ ) de 1.9%, calculé pour les 460 réflexions uniques observées ( $|F_o| = 4\sigma_F$ ). Il s'agit d'un minéral hexagonal, groupe spatial  $P6_3/mmc$ ,  $a$  8.7805(8),  $c$  15.521(2) Å,  $V$  1036.3(2) Å<sup>3</sup>,  $Z$  = 2. La structure contient deux cations non équivalents de Cu<sup>2+</sup>. Le cation Cu(1) est coordonné à trois atomes de O et trois de Cl; c'est en fait le premier exemple de ce type de ligand mixte Cu<sup>2+</sup>φ<sub>6</sub> (φ: O<sup>2-</sup>, Cl<sup>-</sup>) octaédrique dans un minéral. L'octaèdre montre une distortion (2 + 4) due à l'effet Jahn-Teller, contrairement à la grande majorité d'oxyxalys de Cu<sup>2+</sup>, minéraux qui contiennent des octaèdres à Cu<sup>2+</sup> montrant la distortion (4 + 2). Le cation Cu(2) est coordonné à deux atomes de O et trois anions de Cl aux coins d'une bipyramide trigonale. C'est le premier exemple d'un ligand mixte Cu<sup>2+</sup>O<sub>2</sub>Cl<sub>3</sub> en bipyramide trigonale dans un minéral. Le cation unique Cd<sup>2+</sup> est symétriquement indépendant et coordonné à six anions de Cl situés aux coins d'un octaèdre régulier. La structure contient un cation K symétriquement indépendant, coordonné par six anions Cl dans un agencement prismatique trigonal. Il y a un cation Se<sup>4+</sup> unique avec fortes liaisons à trois atomes O d'un côté du cation, à cause de la présence d'une paire isolée d'électrons  $s^2$ . Nous décrivons la structure à la fois en termes de polyèdres entourant un cation et de tétraèdres OCu<sub>4</sub> ayant un atome d'oxygène au centre. La structure de la burnsite montre des ressemblances étroites avec la structure d'autres sélénites chlorurés naturels de cuivre découverts dans les fumerolles à Tolbachik (chloroménite, georgbokiite, ilinskite).

(Traduit par la Rédaction)

**Mots-clés:** burnsite, structure cristalline, sélénites de cuivre, tétraèdres oxo-centrés.

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## INTRODUCTION

Burnsite,  $KCdCu_7O_2(SeO_3)_2Cl_9$ , is a new potassium cadmium copper oxide chloride selenite mineral species that was recently described by Krivovichev *et al.* (2002) from the fumaroles of the Tolbachik volcano, Kamchatka, Russia. It forms aggregates of dark red transparent isometric grains up to 0.1 mm in maximum dimension. The crystal structure, which provides the first mineral examples of two new  $Cu^{2+}$  coordination polyhedra, is reported herein.

## EXPERIMENTAL

## X-ray diffraction

A single crystal of burnsite was selected by optical examination and mounted on a Bruker PLATFORM three-circle goniometer equipped with a 1K SMART CCD (charge-coupled device) detector and a crystal-to-detector distance of 5 cm. More than a hemisphere of three-dimensional intensity data was collected using monochromatic MoK $\alpha$  X-radiation and frame widths of  $0.3^\circ$  in  $\omega$ . The unit-cell dimensions (Table 1) were refined from 2697 reflections using least-squares techniques. The data were integrated and corrected for Lorentz, polarization and background effects using the

Bruker program SAINT. A semi-empirical correction for absorption was done using 2003 intense reflections with the crystal modeled as an ellipsoid; the  $R_{\text{int}}$  was lowered from 8.36 to 3.97%. Additional information pertinent to the data collection is given in Table 1.

## Structure solution and refinement

Scattering curves for neutral atoms, together with anomalous-dispersion corrections, were taken from International Tables for X-Ray Crystallography, Vol. IV (Ibers & Hamilton 1974). The Bruker SHELXTL Version 5 system of programs was used for the determination and refinement of the structure. It was solved by direct methods and refined on the basis of  $F^2$  for all unique data. The final refinement included all atomic positional parameters not restricted by symmetry, with an allowance for anisotropic displacement of all atoms, and a weighting scheme of the structure factors. The refinement converged to an agreement index ( $R1$ ) of 1.9%, calculated for the 460 unique observed reflections ( $F_o > 4\sigma_F$ ). Final atomic parameters and selected interatomic distances are presented in Tables 2 and 3, respectively. Observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

## DESCRIPTION OF THE CATION POLYHEDRA

The coordination environments of the various cations in the structure of burnsite are illustrated in Figure 1. The coordination polyhedra about the two symmetrically distinct  $Cu^{2+}$  cations are most unusual. The  $Cu(1)$  site is coordinated by three O and three Cl anions arranged at the vertices of a distorted octahedron. Burns & Hawthorne (1995b) examined the geometries of mixed-ligand  $Cu^{2+}\phi_6$  ( $\phi$ :  $O^{2-}$ ,  $OH^-$ ,  $H_2O$ ,  $Cl^-$ ) octahedra, with an emphasis on the stereochemical details of observed octahedra and prediction of the polyhedron geometries using Hartree-Fock calculations. The  $Cu(1)\phi_6$  octahedron in burnsite is the first example in a mineral of a mixed-ligand  $Cu^{2+}\phi_6$  octahedron that con-

TABLE I. CRYSTALLOGRAPHIC DATA FOR BURNSITE

$a$ (Å)	8.7805(8)	$c$ (Å)	15.521(2)
$V$ (Å $^3$ )	1036.3(2)	Space group	$P\bar{6}/mmc$
$F_{\text{obs}}$	1110	Radiation	MoK $\alpha$
Crystal size (mm)	0.09 × 0.08 × 0.04	Unique reflections	532
Total reflections	6211		
Unique $F_o \geq 4\sigma_F$	460		
$R1$	0.019	$wR2$	0.046
$S$	0.99		
Formula	$KCdCu_7O_2(SeO_3)_2Cl_9$	$\mu$ (cm $^{-1}$ )	129.4
$Z$	2		
$D_{\text{calc}}$ (g/cm $^3$ )	3.85		
$R1 = \sum (F_o - F_c) / \sum F_o \times 100$			
$wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_c^2)]^{1/2}$			
$w = 1/[a^2(F_o^2) + (0.0314 \times P)^2]$ , $P = [\max(F_o^2, 0) + 2 \times F_c^2]/3$			
$S = [\sum w(F_o - F_c)^2 / (m - n)]^{1/2}$ , for 532 observations and 36 parameters			

TABLE 2. ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS FOR BURNSITE

	$x$	$y$	$z$	* $U_{\text{eq}}$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{11}$	$U_{12}$
Cd	0	0	0	0.0205(2)	0.0212(2)	0.0212(2)	0.0192(3)	0	0	0	0.0106(1)
Se	- $\frac{2}{3}$	$\frac{1}{3}$	0.09730(4)	0.0131(2)	0.0147(2)	0.0147(2)	0.0099(3)	0	0	0	0.0073(1)
Cu(1)	-0.45264(3)	-0.54736(3)	0.09057(3)	0.0157(2)	0.0200(2)	0.0200(2)	0.0137(2)	0.0013(1)	-0.0013(1)	0.0150(2)	
Cu(2)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	0.0134(2)	0.0169(3)	0.0169(3)	0.0063(5)	0	0	0	0.0085(2)
K	0	0	$\frac{1}{4}$	0.0609(9)	0.080(1)	0.080(1)	0.023(1)	0	0	0	0.0398(7)
Cl(1)	-0.13697(8)	-0.2739(1)	0.10178(7)	0.0402(3)	0.0571(6)	0.0221(5)	0.0299(6)	0.0041(5)	0.0020(2)	0.0110(3)	
Cl(2)	-0.4945(1)	-0.5055(1)	$\frac{1}{4}$	0.0352(4)	0.0433(7)	0.0433(7)	0.0370(8)	0	0	0	0.0350(8)
O(1)	$\frac{1}{3}$	$\frac{2}{3}$	0.1267(2)	0.0112(8)	0.012(1)	0.012(1)	0.010(2)	0	0	0	0.0058(6)
O(2)	-0.5696(2)	-0.1392(3)	0.0447(2)	0.0210(6)	0.026(1)	0.011(1)	0.021(1)	-0.001(1)	-0.0005(5)	0.0053(6)	

\*  $U_{\text{eq}} = (1/3) \sum U_{ij} a_i^* a_j^*$

tains three Cl anions; such an octahedron occurs in the synthetic compound Cu(OH)Cl (Effenberger 1981). Examples of Cu<sub>6</sub> octahedra with one, two and four Cl are listed in Burns & Hawthorne (1995b).

The distribution of bond lengths in the Cu(1) $\phi_6$  octahedron is worthy of comment. The expected Cu<sup>2+</sup>-O

and Cu<sup>2+</sup>-Cl bond lengths from sums of effective ionic radii are 2.09 and 2.40 Å, respectively [Cu<sup>2+</sup> = 0.73 Å, O<sup>2-</sup> = 1.36 Å (Shannon 1976); Cl<sup>-</sup> = 1.67 Å (Whittaker & Muntus 1970)]. However, as noted by Burns & Hawthorne (1995b), mixed-ligand Cu<sup>2+</sup> $\phi_6$  octahedra invariably involve bond-length distortion owing to the Jahn-Teller effect (Jahn & Teller 1937). Although a holosymmetric coordination about the Cu<sup>2+</sup> cation is impossible because the ligands are mixed, a pseudo-holosymmetric octahedral geometry would involve a near-degenerate electronic state, and either an elongation [(4+2) distortion] or a compression [(2+4) distortion] of the ligand geometry will likely occur, removing the near-degenerate electronic state and resulting in a net stabilization of the octahedron. The Cu(1) $\phi_6$  octahedron involves two compressed Cu<sup>2+</sup>-O bond lengths of 1.899(1) and 1.916(3) Å, with the corresponding ligands in a *trans* arrangement. There is also one Cu<sup>2+</sup>-O bond-length of 2.126(3) Å, which is longer than the expected distance for an undistorted octahedron. The three Cu(1)-Cl bond lengths range from 2.5554(6) to 2.612(1) Å, and are thus longer than the expected distance for an undistorted octahedron. The four elongate Cu<sup>2+</sup>- $\phi$  bonds extend to ligands in the equatorial posi-

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) IN THE STRUCTURE OF BURNSITE

Cd-C(1),a,b,c,d,e	2.614(1) 6x	K-Cl(1),i,j,k,l,c	3.104(1) 6x
Se-O(2),f,g	1.687(3) 3x	O(1)-Cu(1),h,j	1.899(1) 3x
Cu(1)-O(1)	1.899(1)	O(1)-Cu(2)	1.914(4)
Cu(1)-O(2)g	1.916(3)	<O(1)-Cu>	1.90
Cu(1)-O(2)e	2.126(3)	Cu(1)-Cu(1),h,j	3.1426(8) 2x
Cu(1)-Cl(2)	2.5554(6)	Cu(1)-h-Cu(1)j	3.1426(8)
Cu(1)-Cl(1),h	2.612(1) 2x	Cu(2)-Cu(1),h,j	3.0685(5) 3x
Cu(2)-O(1),i	1.914(4) 2x	<Cu-Cu>	3.106
Cu(2)-Cl(2),h,j	2.452(2) 3x		

a = -y-1, x-y, z; b = x-y, -x-1, z; c = y-y-1, x, -z; d = x, y, -z+1/2; e = -y-1, x-y-1, z+1/2; f = -y-1, x-y+1, z; g = -y, x-y, z; h = -x-1, -y-1, -z; i = -x+y-1, x-1, z; j = y, -x+y, -z; k = -x+y, -x-1, -z+1/2; l = -x, -y, -z

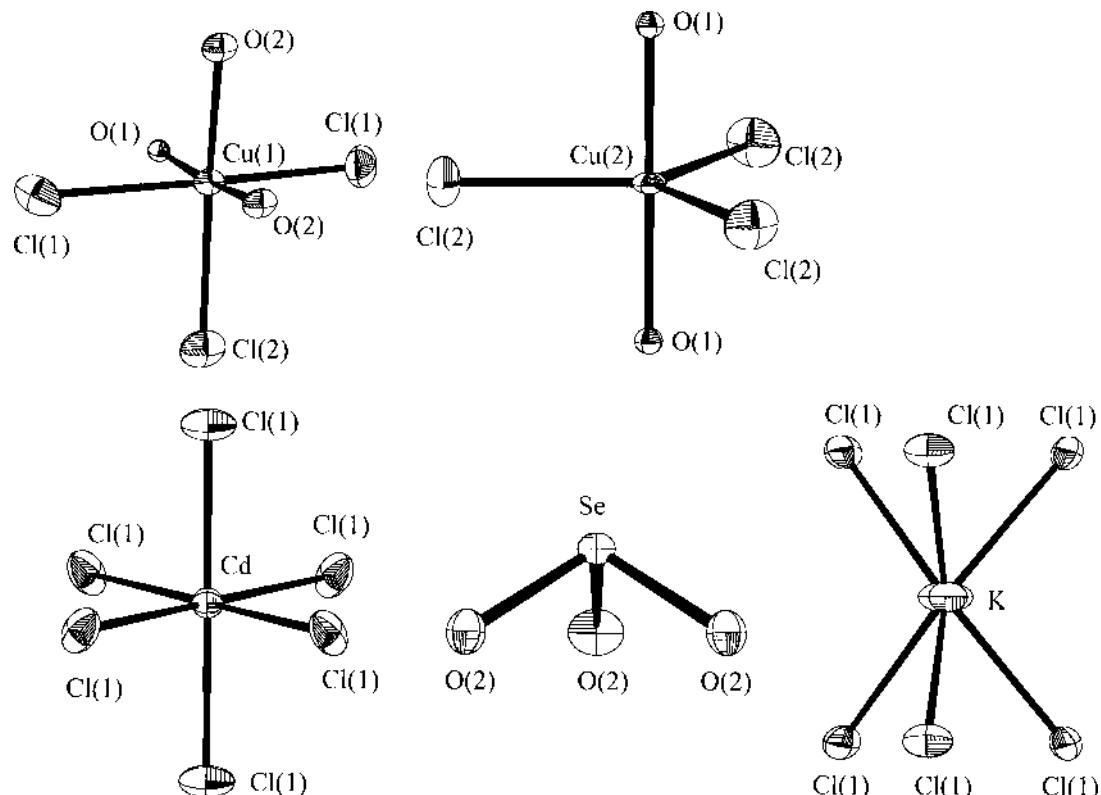


FIG. 1. Cation coordination polyhedra in the structure of burnsite.

tions of the octahedron, with the compressed bonds extending to the two apical ligands of the octahedron. The Cu(1) $\phi_6$  octahedron may therefore be described as (2 + 4)-distorted, which is extremely unusual in Cu<sup>2+</sup> oxysalt minerals (Burns & Hawthorne 1996).

Burns & Hawthorne (1996) proposed that some Cu<sup>2+</sup> octahedra in minerals may involve a dynamic Jahn-Teller distortion, in which case the structure determined by X-ray diffraction reveals coordination polyhedra with time-averaged geometries. Given the rarity of (2 + 4)-distorted Cu<sup>2+</sup> octahedra in minerals, is it possible that the Cu(1) $\phi_6$  octahedron in burnsite involves a dynamic distortion? If this is the case, the dynamic interchange of elongation directions of (4 + 2)-distorted octahedra may result in an apparent (2 + 4)-distorted octahedron. Dynamic Jahn-Teller distortion of an octahedron involves movement of the ligands approximately parallel to the bond lengths, and thus should be reflected by anisotropic displacement ellipsoids that are elongate (sub)parallel to the bond direction. Inspection of the displacement ellipsoids for the ligands of the Cu(1) octahedron (Fig. 1) shows that they are somewhat elongate (sub)perpendicular to the bond direction, which is inconsistent with a dynamic distortion of the octahedron. The Cu(1) $\phi_6$  octahedron thus appears to be a persuasive example of a (2 + 4)-distorted octahedron.

The Cu(2) cation is coordinated by five ligands in a symmetric trigonal bipyramidal arrangement. The coordination polyhedron contains two O anions located in the apical positions, and three of Cl in the equatorial positions. Although Cu<sup>2+</sup> occurs in trigonal prismatic coordination in several minerals (Burns & Hawthorne 1995a), burnsite is the first mineral to contain a mixed-ligand Cu<sup>2+</sup>O<sub>2</sub>Cl<sub>3</sub> trigonal bipyramidal.

There is a single symmetrically distinct Cd<sup>2+</sup> cation that is coordinated by six Cl(1) anions arranged at the

vertices of an octahedron. The K cation is coordinated by six Cl(1) anions in a trigonal prismatic arrangement. The structure contains one symmetrically distinct Se<sup>4+</sup> cation, which is coordinated by three atoms of O that are arranged at the vertices of a trigonal pyramid. Note that all of the O atoms are located on the same side of the Se<sup>4+</sup> cation, owing to the presence of a  $s^2$  lone-electron pair on the other side of the cation.

#### DESCRIPTION OF THE STRUCTURE

The structure of burnsite is complex in that it involves five different types of cation coordination polyhedra. Here we provide two alternative descriptions of the structure, one based upon cation-centered polyhedra, and the other involving anion-centered tetrahedra. We consider each of these approaches to be of merit; both emphasize important structural features and facilitate comparison with related structures.

##### *Description of the structure using cation-centered polyhedra*

The structure of burnsite is shown projected along [001] in Figure 2a, and onto (100) in Figure 2b, with cation polyhedra shown in each case. From these projections, it is apparent that burnsite possesses a complex framework structure. Description of the structure is facilitated by considering first the Cu(1) $\phi_6$  octahedra. As illustrated in Figure 3a, Cu(1) $\phi_6$  octahedra occur as trimers of octahedra formed by the sharing of edges, with all three octahedra sharing the O(1) vertex. Each trimer is linked to three identical trimers by the sharing of O(2)–O(2) octahedron edges, resulting in layers of octahedra that are parallel to (001) that involve linkages only by the sharing of octahedron edges. The

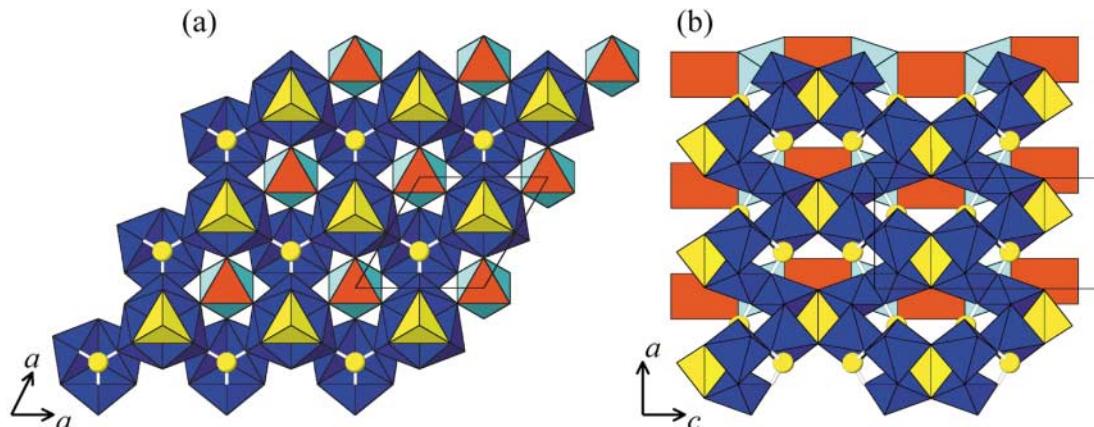


FIG. 2. Polyhedral representations of cation-centered polyhedra in the structure of burnsite. Legend: Cu(1) $\phi_6$  octahedra: dark blue, Cu(2)O<sub>2</sub>Cl<sub>3</sub> triangular bipyramids: yellow, CdCl<sub>6</sub> octahedra: light blue, KCl<sub>6</sub> trigonal prisms: red, and Se atoms: yellow balls.

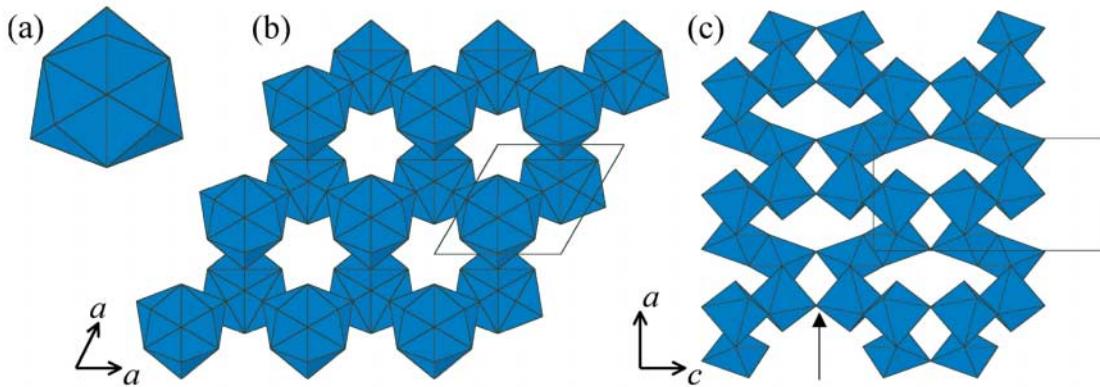


FIG. 3. The framework of  $\text{Cu}(1)\phi_6$  octahedra in the structure of burnsite. (a) The trimer of edge-sharing  $\text{Cu}(1)\phi_6$  octahedra, (b) the layer of edge-sharing octahedra parallel to (001), (c) linkage of layers of edge-sharing octahedra to form a framework. The  $\text{Cl}(2)$  vertex, which is shared between adjacent layers, is indicated by the arrow. The unit cell is outlined in each case.

layers of  $\text{Cu}(1)\phi_6$  octahedra are stacked along [001], and are connected by sharing the  $\text{Cl}(2)$  vertex (shown by an arrow in Fig. 3c), resulting in a framework of  $\text{Cu}(1)\phi_6$  octahedra that share vertices and edges.

The  $\text{Cu}(2)\text{O}_2\text{Cl}_3$  trigonal bipyramidal is located between two translationally equivalent trimers of  $\text{Cu}(1)\phi_6$  octahedra, which belong to adjacent layers of edge-sharing  $\text{Cu}(1)\phi_6$  octahedra (Figs. 2a, b). The  $\text{Cl}(2)$  vertices shared between adjacent layers of  $\text{Cu}(1)\phi_6$  octahedra constitute the equatorial ligands of the trigonal bipyramidal, with the apical ligands corresponding to  $\text{O}(1)$ , which are shared between the three  $\text{Cu}(1)\phi_6$  octahedra of each trimer. The  $\text{SeO}_3$  trigonal pyramids are linked to the trimers of  $\text{Cu}(1)\phi_6$  octahedra by sharing the  $\text{O}(2)$  vertices, but on the side opposite the  $\text{Cu}(2)\text{O}_2\text{Cl}_3$  trigonal bipyramidal. The  $\text{SeO}_3$  trigonal pyramid is located toward the center of individual layers of  $\text{Cu}(1)\phi_6$  octahedra (Fig. 2b).

The  $\text{KCl}_6$  trigonal prisms and  $\text{CdCl}_6$  octahedra are linked to form columns that are parallel to [001] by the sharing of triangular faces (Fig. 2b). The columns extend through the framework of  $\text{Cu}(1)\phi_6$  octahedra, and are linked to the framework by the sharing of each of their ligands with the  $\text{Cu}(1)\phi_6$  octahedra (Figs. 2a, b).

#### Description of the structure using anion-centered tetrahedra

The two symmetrically distinct atoms of O in the structure of burnsite assume very different chemical roles. The  $\text{O}(2)$  atom is strongly bonded to a  $\text{Se}^{4+}$  cation, as well as to two  $\text{Cu}(1)$  cations. The  $\text{O}(1)$  atom is tetrahedrally coordinated by three  $\text{Cu}(1)$  and one  $\text{Cu}(2)$  atoms, thus forming an  $\text{OCu}_4$  oxocentered tetrahedron. The  $\text{OCu}_4$  tetrahedron is common in structures of  $\text{Cu}^{2+}$  oxyxalts that also contain O atoms that are not part of

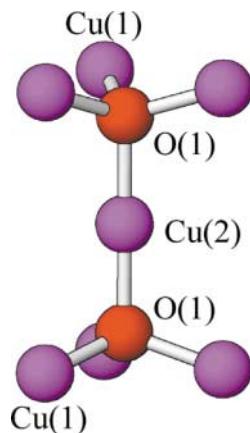


FIG. 4. The  $\text{O}_2\text{Cu}_7$  finite clusters in the structure of burnsite.

the oxocentered tetrahedra (Effenberger 1985, Filatov *et al.* 1992, Starova *et al.* 1991, 1997, 1998, Gorskaya *et al.* 1992, Krivovichev *et al.* 1998a, 1999b). The mean  $\langle \text{O}(1)-\text{Cu} \rangle$  bond length in burnsite is 1.90 Å, which is in accord with the typical  $\langle \text{O}-\text{Cu} \rangle$  bond length in  $\text{OCu}_4$  tetrahedra (Effenberger 1985, Filatov *et al.* 1992). The mean  $\langle \text{Cu}-\text{Cu} \rangle$  distance in the  $\text{OCu}_4$  tetrahedron in burnsite is 3.106 Å, in good agreement with the average value of 3.14 Å for such tetrahedra given by Krivovichev & Filatov (1999a).

In the structure of burnsite, two  $\text{OCu}_4$  tetrahedra are linked by a common vertex, resulting in the  $\text{O}_2\text{Cu}_7$  unit shown in Figure 4. The connectivity of this unit is analogous to the  $\text{Si}_2\text{O}_7$  group in silicates, except that the cations and anions are inverted.

The bond valences associated with cation–anion bonds in the structure of burnsite may be grouped according to their approximate strengths (Table 4):  $\text{Se}^{4+}$ –O bonds [1.40 valence units (*vu*)],  $\text{Cu}^{2+}$ –O bonds [except the Cu(1)–O(2) bond; 0.53–0.55 *vu*] and other bonds (0.19–0.35 *vu*). The structure may be described on the basis of the polymerization of those polyhedra of higher bond-valence (Hawthorne 1983). The  $\text{SeO}_3$  trigonal pyramid involves the strongest bonds, followed by the  $\text{Cu}^{2+}$ –O bonds. The  $\text{Cu}^{2+}$ –O bonds are of two types, those that are incident upon the O(1) atom (bonds within the  $\text{OCu}_4$  tetrahedron), and those that link  $\text{OCu}_4$  tetrahedra and  $\text{SeO}_3$  trigonal pyramids. The  $\text{OCu}_4$  tetrahedra and  $\text{SeO}_3$  pyramids are linked to each other according to the “face-to-face” principle (Krivovichev *et al.* 1999b); their Cu–Cu–Cu and O–O–O triangular

faces are parallel to each other and have the same orientation. The  $\text{Cu}^{2+}$ –O and  $\text{Se}^{4+}$ –O bonds thus form an extended three-dimensional  $[\text{O}_2\text{Cu}_7](\text{SeO}_3)_2$  framework, which is illustrated in Figure 5a. The columns formed by the sharing of triangular faces of  $\text{CdCl}_6$  octahedra and  $\text{KCl}_6$  trigonal prisms (Fig. 5b) are located within large channels in the  $[\text{O}_2\text{Cu}_7](\text{SeO}_3)_2$  framework (Fig. 6).

## DISCUSSION

Burnsite,  $\text{KCdCu}_7\text{O}_2(\text{SeO}_3)_2\text{Cl}_9$ , was found in close association with other rare copper oxide selenite chlorides that have been described from the Tolbachik fumaroles: georgbokiite,  $\text{Cu}_5\text{O}_2(\text{SeO}_3)_2\text{Cl}_2$ , chloromenite,  $\text{Cu}_9\text{O}_2(\text{SeO}_3)_4\text{Cl}_6$ , ilinskite,  $\text{NaCu}_5\text{O}_2(\text{SeO}_3)_2\text{Cl}_3$ , and an unnamed selenite with the ideal formula  $[\text{Cu}^+\text{Cl}_2]\text{Pb Cu}_5\text{O}_2(\text{SeO}_3)_2\text{Cl}_3$ . Each of these minerals involve structures based upon structural units composed of oxo-centered tetrahedra. However, the coordination polyhedra about  $\text{Cu}^{2+}$  are variable in these structures, and include square planar arrangements, triangular bipyramids and octahedra.

The  $\text{OCu}_4$  oxocentered tetrahedra combine in a variety of ways in the structures of Tolbachik minerals. In burnsite, two  $\text{OCu}_4$  tetrahedra form  $\text{O}_2\text{Cu}_7$  finite clusters, whereas in chloromenite,  $\text{OCu}_4$  tetrahedra are

TABLE 4. BOND-VALENCE\* (*vu*) ANALYSIS FOR BURNSITE

Atom	Cd	K	$\text{Cu}(1)$	$\text{Cu}(2)$	$\text{Se}(1)$	$\Sigma$
Cl(1)	0.35 <sup>a1</sup>	0.21 <sup>a1</sup>	0.19 <sup>a1</sup>			0.75
Cl(2)			0.22 <sup>a2</sup>	0.30 <sup>a1</sup>		0.74
O(1)			0.55 <sup>a3</sup>	0.53 <sup>a1</sup>		2.18
O(2)			0.53, 0.30		1.40 <sup>a1</sup>	2.23
$\Sigma$	2.10	1.26	1.98	1.96	4.20	

\*calculated using parameters from Busey & O’Keeffe (1991)

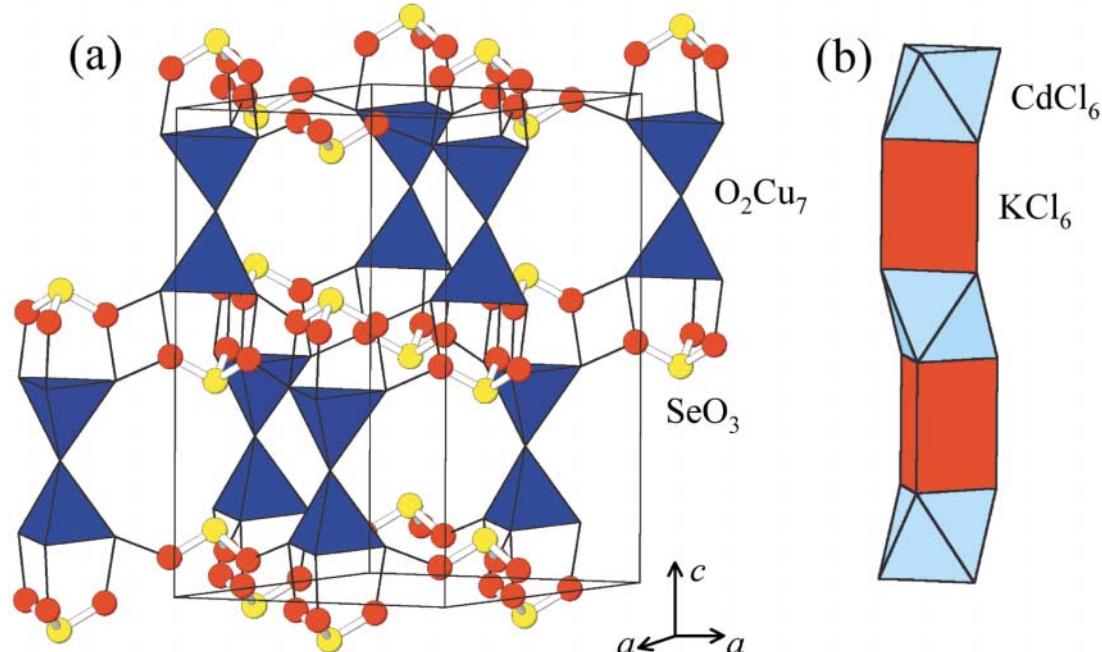


FIG. 5. Framework of  $\text{O}_2\text{Cu}_7$  units and  $\text{SeO}_3$  groups (a) and column of face-sharing  $\text{CdCl}_6$  octahedra and  $\text{KCl}_6$  trigonal prisms (b) in the structure of burnsite.

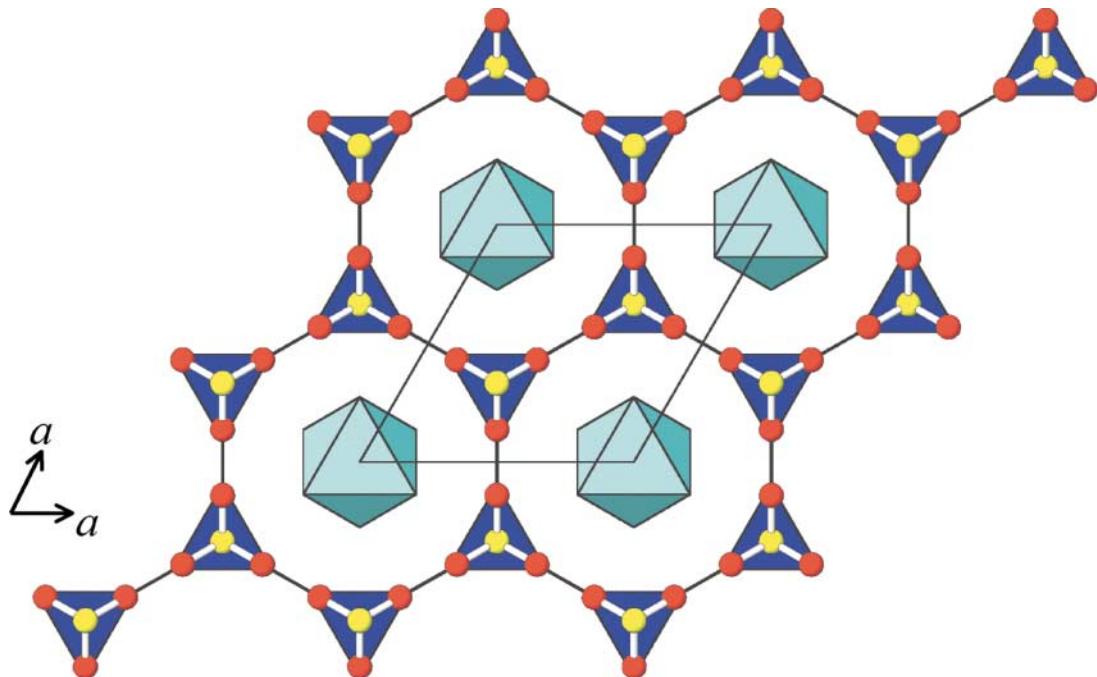


FIG. 6. Projection of the crystal structure of burnsite along the  $c$  axis showing the framework of  $\text{O}_2\text{Cu}_7$  units and  $\text{SeO}_3$  groups and the column of face-sharing  $\text{CdCl}_6$  octahedra and  $\text{KCl}_6$  trigonal prisms. The legend is the same as in Figure 5.

linked by corner-sharing into  $\text{O}_2\text{Cu}_6$  chains (Krivovichev *et al.* 1998a). Identical chains with a formula  $\text{O}_2\text{Cu}_5\text{Pb}$  occur in the structure of  $[\text{Cu}^+\text{Cl}_2]\text{PbCu}_5\text{O}_2(\text{SeO}_3)_2\text{Cl}_3$  (unpublished results). In georgbokiite,  $\text{OCu}_4$  tetrahedra are linked by sharing vertices and edges, resulting in  $\text{O}_2\text{Cu}_5$  chains (Krivovichev *et al.* 1999a). The structure of ilinksite is based upon  $\text{O}_2\text{Cu}_5$  sheets of corner-sharing  $\text{OCu}_4$  tetrahedra. Note that with the sole exception of  $[\text{Cu}^+\text{Cl}_2]\text{PbCu}_5\text{O}_2(\text{SeO}_3)_2\text{Cl}_3$ , this assemblage of minerals can be synthesized using chemical transport reactions (Galy *et al.* 1979, Shuvalov *et al.* 2000a, b, c, Bastide *et al.* 2000). In these experiments, crystals of the mineral analogues are formed directly from the gas phase. As noted by Filatov *et al.* (1992), the ability to synthesize these compounds by vapor transport provides evidence that oxocentered complexes may exist in gas phases, and they may play an important role in the transport of Cu and other metals involved in mineral-forming processes within fumaroles.

The description of structures of minerals and inorganic compounds in terms of anion-centered tetrahedra provides a useful tool for understanding occurrences of complex minerals such as those in the fumaroles of the Tolbachik volcano. For further references on anion-centered tetrahedra, see Krivovichev *et al.* (1998b, 2001),

Krivovichev & Burns (2000a, b, 2001a, b, 2002), Li *et al.* (2000, 2001), Hawthorne *et al.* (2000) and Krivovichev & Filatov (2001).

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