

## THE CRYSTAL STRUCTURE OF ALLOCHALCOSELITE, $\text{Cu}^+\text{Cu}^{2+}_5\text{PbO}_2(\text{SeO}_3)_2\text{Cl}_5$ , A MINERAL WITH WELL-DEFINED $\text{Cu}^+$ AND $\text{Cu}^{2+}$ POSITIONS

SERGEY V. KRIVOVICHEV<sup>§</sup> AND STANISLAV K. FILATOV

Department of Crystallography, St. Petersburg State University, University Emb. 7/9, RU-199034 St. Petersburg, Russia

PETER C. BURNS

Department of Civil Engineering and Geological Sciences, University of Notre Dame,  
Notre Dame, Indiana 46556-0767, USA

LIDIYA P. VERGASOVA

Institute of Volcanology, Russian Academy of Sciences, Bulvar Piypa 9, RU-683006 Petropavlovsk-Kamchatskiy, Russia

### ABSTRACT

The crystal structure of allochalcoseelite,  $\text{Cu}^+\text{Cu}^{2+}_5\text{PbO}_2(\text{SeO}_3)_2\text{Cl}_5$ , a new mineral species from the fumaroles of the Great Tolbachik fissure eruption, in the Kamchatka Peninsula, Russia, has been solved from single-crystal X-ray-diffraction data by direct methods and refined to  $R_1 = 0.047$  for 1235 unique reflections with  $|F_o| \geq 4\sigma_F$ . The mineral is monoclinic, space group  $C2/m$ ,  $a$  18.468(2),  $b$  6.1475(8),  $c$  15.314(2) Å,  $\beta$  119.284(2)°,  $V$  1516.5(3) Å<sup>3</sup>,  $Z = 4$ . The structure contains one symmetrically unique Pb position coordinated by three O and four Cl atoms. There are two  $\text{Se}^{4+}$  cations, which form  $\text{SeO}_3$  trigonal pyramids. There are six symmetrically independent Cu sites in allochalcoseelite, four of which [Cu1–Cu4] are occupied by  $\text{Cu}^{2+}$  and two [Cu5 and Cu6] by  $\text{Cu}^+$  cations. The Cu1, Cu2, and Cu3 sites have distorted octahedral [4O + 2Cl], [(3O + Cl) + 2Cl], and [(3O + Cl) + 2Cl] coordinations, respectively. The Cu4 site forms a trigonal  $\text{CuO}_3\text{Cl}_2$  bipyramid with one equatorial and one apical vertex occupied by Cl. The  $\text{Cu}^+$  cations are both coordinated by two  $\text{Cl}^-$  anions to form linear anions  $[\text{Cu}^+\text{Cl}_2]^-$ , with Cl–Cu–Cl angles of 180°. The structure can be appropriately described in terms of arrangements of the strong  $M$ –O bonds ( $M = \text{Se}^{4+}$ ,  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$ ). These bonds are accumulated within layers parallel to (100), with some of the  $\text{Cl}^-$  anions sandwiched between them. The O4 and O5 atoms are not bonded to  $\text{Se}^{4+}$  cations, and are tetrahedrally coordinated by four metal atoms. The  $[\text{O4PbCu}_3]^{6+}$  and  $[\text{O5Cu}_4]^{6+}$  tetrahedra are linked *via* Cu1 atoms into  $[\text{O}_2\text{Cu}_5\text{Pb}]^{8+}$  chains extending parallel to the  $b$  axis. The  $[\text{SeO}_3]^{2-}$  pyramids are attached to oxocentered tetrahedra in “face-to-face” positions to form complex  $[(\text{O}_2\text{Cu}_5\text{Pb})[\text{SeO}_3]_2]^{4+}$  chains that are linked together to form a metal–oxygen layer parallel to (100). The layer has large pores that are occupied by the  $[\text{Cu}^+\text{Cl}_2]^-$  anions. These anions are held in the structure *via* weak  $\text{Cu}^{2+}$ – $\text{Cl}^-$  bonds ( $> 2.8$  Å) only. Thus allochalcoseelite can be considered as a kind of delicately balanced host–guest system with  $[\text{Cu}^+\text{Cl}_2]^-$  anions included into the  $\text{Cu}^{2+}$  oxoselenite chloride matrix. Relatively isolated and weakly bonded positions of the  $[\text{Cu}^+\text{Cl}_2]^-$  anions in the structure may indicate stability of these complexes as separate entities and their possible role in the  $\text{Cu}^+$  transport by volcanic gases.

**Keywords:** allochalcoseelite, crystal structure, copper, selenite, Tolbachik volcano, Russia.

### SOMMAIRE

Nous avons résolu la structure cristalline de l'allochalcoséélite,  $\text{Cu}^+\text{Cu}^{2+}_5\text{PbO}_2(\text{SeO}_3)_2\text{Cl}_5$ , nouvelle espèce minérale provenant des fumarolles du volcan Tolbachik, dans la péninsule de Kamchatka, en Russie, avec des données en diffraction X prélevées sur monocristal, traitées par méthodes directes, et affinées jusqu'à un résidu  $R_1$  de 0.047 pour 1235 réflexions uniques ayant  $|F_o| \geq 4\sigma_F$ . Il s'agit d'un minéral monoclinique, groupe spatial  $C2/m$ ,  $a$  18.468(2),  $b$  6.1475(8),  $c$  15.314(2) Å,  $\beta$  119.284(2)°,  $V$  1516.5(3) Å<sup>3</sup>,  $Z = 4$ . La structure contient une position symétriquement unique pour le Pb, coordonné par trois atome de O et quatre de Cl. Il y a deux cations  $\text{Se}^{4+}$ , formant des pyramides trigonales  $\text{SeO}_3$ . Il y a six sites de Cu symétriquement indépendants, parmi lesquels quatre [Cu1–Cu4] contiennent  $\text{Cu}^{2+}$  et deux [Cu5 et Cu6] contiennent  $\text{Cu}^+$ . Les sites Cu1, Cu2, et Cu3 possèdent des coordinences octaédriques difformes [4O + 2Cl], [(3O + Cl) + 2Cl], et [(3O + Cl) + 2Cl], respectivement. Le site Cu4 forme une pyramide  $\text{CuO}_3\text{Cl}_2$  trigonale ayant le Cl à un coin équatorial et à un vertex apical. Les deux cations  $\text{Cu}^+$  sont coordonnés à deux anions  $\text{Cl}^-$  pour former des anions linéaires  $[\text{Cu}^+\text{Cl}_2]^-$ , avec un angle Cl–Cu–Cl de 180°. On peut décrire la structure en termes d'agencements de liaisons  $M$ –O fortes ( $M = \text{Se}^{4+}$ ,  $\text{Cu}^{2+}$  et  $\text{Pb}^{2+}$ ). Ces liaisons sont accumulées à l'intérieur

<sup>§</sup> E-mail address: skrivovi@mail.ru

de couches parallèles à (100), avec certains des anions  $\text{Cl}^-$  intercalés entre ces feuillets. Les atomes O4 et O5 ne sont pas liés aux cations  $\text{Se}^{4+}$ , et possèdent une coordinence tétraédrique avec quatre atomes métalliques. Les tétraèdres  $[\text{O}4\text{PbCu}_3]^{6+}$  et  $[\text{O}5\text{Cu}_4]^{6+}$  sont connectés grâce aux atomes Cu1 pour former des chaînes  $[\text{O}_2\text{Cu}_5\text{Pb}]^{8+}$  parallèles à l'axe  $b$ . Les pyramides  $[\text{SeO}_3]^{2-}$  sont rattachées aux tétraèdres oxocentrés dans un agencement "face-à-face" pour former des chaînes complexes de stoechiométrie  $([\text{O}_2\text{Cu}_5\text{Pb}][\text{SeO}_3]_2)^{4+}$ , qui sont liées ensemble pour former une couche métal-oxygène parallèle à (100). Cette couche possède de larges pores qu'occupent les anions  $[\text{Cu}^+\text{Cl}_2]^-$ . Ces anions sont retenus dans la structure seulement grâce à de faibles liaisons  $\text{Cu}^{2+}-\text{Cl}^-$  ( $>2.8 \text{ \AA}$ ). On pourrait considérer l'allochalcosélénite comme une sorte de système hôte-inclusion délicatement balancé, avec les anions  $[\text{Cu}^+\text{Cl}_2]^-$  inclus dans la matrice d'oxosélénite chlorurée de  $\text{Cu}^{2+}$ . La position relativement isolée et faiblement retenue des anions  $[\text{Cu}^+\text{Cl}_2]^-$  indique une certaine stabilité de ces complexes comme entités distinctes et leur rôle possible dans le transfert du  $\text{Cu}^+$  dans les gaz volcaniques.

(Traduit par la Rédaction)

*Mots-clés:* allochalcosélénite, structure cristalline, cuivre, sélénite, volcan Tolbachik, Russie.

## INTRODUCTION

Materials with transition-metal cations in two oxidation states have received considerable attention because of their interesting magnetic properties. Among them,  $\text{Cu}^+-\text{Cu}^{2+}$  systems are of special interest owing to the interplay between  $d^9-d^{10}$  electronic configurations (see, e.g., Etheredge & Hwu 1995). The only mineral known that contains both univalent and divalent copper cations is paramelaconite. Datta & Jefferey (1978) assigned to that mineral the chemical formula  $\text{Cu}^{2+}_{12}\text{Cu}^+_{4}\text{O}_{14}$  with  $\text{Cu}^{2+}-\text{Cu}^+$  disorder, whereas O'Keeffe & Bovin (1978) established the composition  $\text{Cu}^+_{2}\text{Cu}^{2+}_{2}\text{O}_4$  with fully ordered  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  sites (see also Morgan *et al.* 1996).

Recently, Vergasova *et al.* (2005) described the second mineral species containing both  $\text{Cu}^{2+}$  and  $\text{Cu}^+$  cations, allochalcosélénite,  $\text{Cu}^+\text{Cu}^{2+}_5\text{PbO}_2(\text{SeO}_3)_2\text{Cl}_5$ . It was found within the fumaroles of the Great fissure Tolbachik eruption (Kamchatka Peninsula, Russia). Allochalcosélénite occurs as dark brown prismatic crystals in association with sophiite,  $\text{Zn}_2(\text{SeO}_3)\text{Cl}_2$  (Vergasova *et al.* 1989), ilinskite,  $\text{NaCu}_5\text{O}_2(\text{SeO}_3)_2\text{Cl}_3$  (Vergasova *et al.* 1997), georgbokiite,  $\text{Cu}_5\text{O}_2(\text{SeO}_3)_2\text{Cl}_2$  (Vergasova *et al.* 1999a) and burnsite,  $\text{KCdCu}_7\text{O}_2(\text{SeO}_3)_2\text{Cl}_9$  (Krivovichev *et al.* 2002, Burns *et al.* 2002). After these minerals and chloromenite,  $\text{Cu}_9\text{O}_2(\text{SeO}_3)_4\text{Cl}_6$  (Vergasova *et al.* 1999b), and francisite,  $\text{Cu}_3\text{Bi}(\text{SeO}_3)_2\text{O}_2\text{Cl}$  (Pring *et al.* 1990), allochalcosélénite is the seventh known anhydrous selenite chloride of natural origin. In this paper, we report the details of its structure and compare it with that of related minerals and inorganic compounds.

## EXPERIMENTAL

The crystal of allochalcosélénite used in this study was taken from the holotype specimen described by Vergasova *et al.* (2005). It was mounted on a Bruker three-circle X-ray diffractometer operated at 50 kV and 40 mA and equipped with an SMART APEX CCD area detector. More than a hemisphere of data was collected using monochromatic  $\text{MoK}\alpha$  X-radiation, with frame

widths of  $0.3^\circ$  in  $\omega$ , and with a 60 s count for each frame. The unit-cell parameters (Table 1) were refined using least-squares techniques. The intensity data were integrated and corrected for Lorentz, polarization, and background effects using the Bruker program SAINT. The absorption correction was done by semi-empirical pseudo- $\Psi$ -scan method by modeling the crystal as an ellipsoid.

The Bruker SHELXTL Version 5 system of programs was used for determination and refinement of the crystal structure. The structure was solved by direct methods and refined to an  $R_1$  value of 0.047, calculated for the 1235 unique observed ( $|F_o| \geq 4\sigma_F$ ) reflections. Final coordinates and anisotropic displacement parameters of the atoms are given in Table 2, selected interatomic distances are in Table 3. Table 4 provides a bond-valence analysis calculated using bond-valence parameters taken from Krivovichev & Brown (2001) for the  $\text{Pb}^{2+}-\text{O}$  bonds and from Brese & O'Keeffe (1991) for other bonds. Calculated and observed structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2, Canada.

## RESULTS

### Cation coordination

The structure of allochalcosélénite contains one symmetrically unique Pb position. It is coordinated by three O atoms located on one side of its coordination sphere (Fig. 1). On the other side, the coordination is complemented by four  $\text{Cl}^-$  anions. The coordination of the  $\text{Pb}^{2+}$  cation is highly asymmetrical owing to the localized  $6s^2$  lone pair of electrons. The character of the  $\text{Pb}^{2+}$  coordination (short  $\text{Pb}^{2+}-\text{O}^{2-}$  bonds in one half of the coordination sphere and long  $\text{Pb}^{2+}-\text{Cl}^-$  bonds in the other) is typical of Pb oxide chlorides (Krivovichev & Burns 2001, 2002, Pasero & Vacchiano 2000, Keller *et al.* 2001).

There are two  $\text{Se}^{4+}$  cations in the structure, coordinated by three O atoms each, to form  $\text{SeO}_3$  trigonal

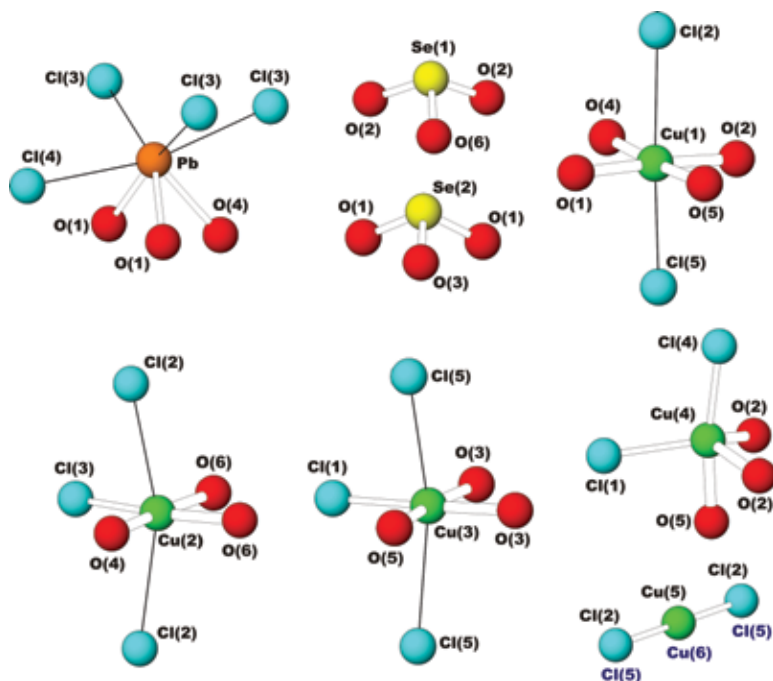


FIG. 1. Coordination of cations in the structure of allochalcocelite.

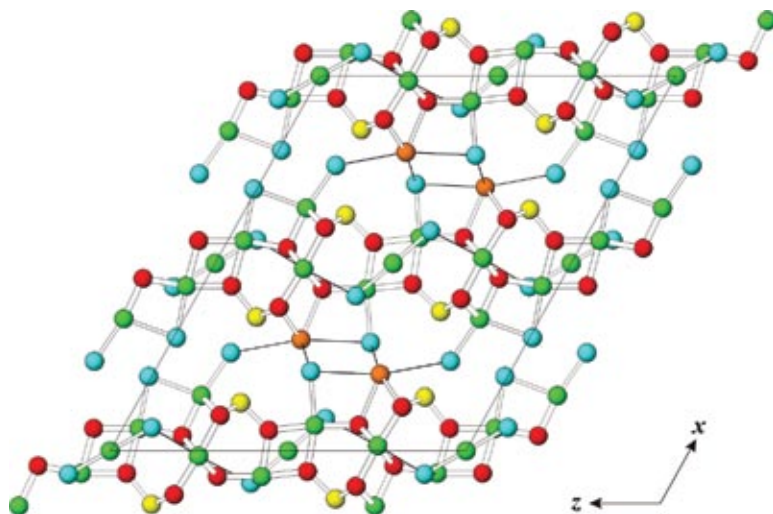


FIG. 2. The crystal structure of allochalcocelite projected along the  $b$  axis. Legend: O: red, Se: yellow, Cu: green, Cl: light blue, Pb: orange.

pyramids, an arrangement that is typical of the structures of selenites (Hawthorne *et al.* 1987).

There are six symmetrically independent Cu positions, four of which [Cu1–Cu4] are occupied by  $\text{Cu}^{2+}$  and two [Cu5 and Cu6] by  $\text{Cu}^+$  cations (Fig. 1, Table 4). The Cu1 site is coordinated by four  $\text{O}^{2-}$  anions at the vertices of a square and two apical  $\text{Cl}^-$  anions, such that an elongate  $[\text{CuO}_4\text{Cl}_2]$  octahedron is formed. A similar coordination has been observed for the Cu2 site in georgbokitite (Krivovichev *et al.* 1999a) and for the Cu5 site in chloromenite (Krivovichev *et al.* 1998). The Cu2 and Cu3 positions are coordinated by three O and one Cl atoms, forming a distorted square, and two additional apical  $\text{Cl}^-$  anions. It should be noted that the  $\text{Cu}^{2+}$ – $\text{Cl}^-$  distances corresponding to the apical

vertices of the  $\text{CuO}_3\text{Cl}_3$  octahedra are rather long ( $\sim 3.12 \text{ \AA}$ ); however, their bond valences are  $\geq 0.05$  valence units (*vu*), and their inclusion into the  $\text{Cu}^{2+}$  coordination sphere seems reasonable from the viewpoint of stereochemistry. A similar coordination polyhedron with composition  $\text{CuO}_3\text{Cl}_3$  has been observed in the structure of belloite,  $\text{Cu}(\text{OH})\text{Cl}$  (Itaka *et al.* 1961, Effenberger 1984, Schlüter *et al.* 2000). The octahedral coordinations of  $\text{Cu}^{2+}$  are distorted owing to the Jahn–Teller effect (Jahn & Teller 1937, Burns & Hawthorne 1995a, b). The Cu4 site has trigonal bipyramidal coordination, with one equatorial and one apical vertex occupied by Cl. This unusual  $\text{CuO}_3\text{Cl}_2$  coordination polyhedron has not been previously found in a mineral. The Cu5 and Cu6 positions are occupied by  $\text{Cu}^+$  cations; both are coordinated by two  $\text{Cl}^-$  anions to form linear anions  $[\text{Cu}^+\text{Cl}_2]^-$  with  $\text{Cl}$ – $\text{Cu}$ – $\text{Cl}$  angles of  $180^\circ$ .

TABLE 1. CRYSTALLOGRAPHIC DATA AND REFINEMENT PARAMETERS FOR ALLOCHALCOSELITE

<i>a</i> (Å)	18.468(2)	<i>D</i> <sub>calc</sub> (g/cm <sup>3</sup> )	4.606
<i>b</i> (Å)	6.1475(8)	Crystal size (mm)	0.08 × 0.04 × 0.008
<i>c</i> (Å)	15.314(2)	Radiation	MoKα
<i>b</i> (°)	119.284(2)	Total reflections	5536
<i>V</i> (Å <sup>3</sup> )	1516.5(3)	Unique reflections	1878
Space group	<i>C2/m</i>	Unique $ F_o  \geq 4\sigma_r$	1235
<i>F</i> <sub>calc</sub>	1892	<i>R</i> <sub>1</sub>	0.047
<i>μ</i> (cm <sup>-1</sup> )	25.019	<i>wR</i> <sub>2</sub>	0.098
<i>Z</i>	4	<i>S</i>	0.995

Note:  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ;  $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)] \}^{1/2}$ ;  $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ , where  $P = (F_o^2 + 2F_c^2) / 3$ ;  $S = \{ \sum [w(F_o^2 - F_c^2)] / (n - p) \}^{1/2}$ , where *n* is the number of reflections and *p* is the number of refined parameters.

### Description of the structure

The structure of allochalcoseelite is shown in Figure 2. Because of irregular and variable coordinations of the cations, its description in terms of coordination polyhedra of cations is not appropriate. Thus the structure is better described in terms of arrangements of the strong *M*–O bonds (*M* =  $\text{Se}^{4+}$ ,  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$ ). These bonds are accumulated within the layers parallel to (100), with some of the  $\text{Cl}^-$  anions sandwiched between them. The structure of the metal–oxygen layer is shown in Figure 3. Its description can be given as follows. The O4 and O5 atoms are “additional”, *i.e.*,

TABLE 2. COORDINATES AND DISPLACEMENT PARAMETERS OF ATOMS IN ALLOCHALCOSELITE

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>23</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>12</sub>
Pb	0.79657(6)	0	0.63877(7)	0.0152(3)	0.0089(5)	0.0217(5)	0.0134(5)	0	0.0042(4)	0
Se1	0.12845(13)	0	0.70903(16)	0.0113(5)	0.0053(11)	0.0192(11)	0.0093(11)	0	0.0034(10)	0
Se2	0.85671(13)	½	0.79940(16)	0.0118(5)	0.0071(11)	0.0189(11)	0.0100(12)	0	0.0047(10)	0
Cu1	0.98610(11)	0.2462(3)	0.74348(13)	0.0136(4)	0.0094(10)	0.0166(9)	0.0155(10)	-0.0042(7)	0.0067(9)	-0.0019(7)
Cu2	0.93169(17)	0	0.5343(2)	0.0196(7)	0.0094(15)	0.0437(18)	0.0070(15)	0	0.0050(13)	0
Cu3	0.93998(17)	½	0.0455(2)	0.0153(6)	0.0084(15)	0.0296(15)	0.0075(14)	0	0.0035(12)	0
Cu4	0.64740(18)	0	0.8306(2)	0.0197(7)	0.0145(16)	0.0284(15)	0.0222(17)	0	0.0137(14)	0
Cu5	½	0	½	0.0291(10)	0.024(3)	0.032(2)	0.032(3)	0	0.015(2)	0
Cu6	0	0	0	0.0427(14)	0.064(4)	0.038(3)	0.042(3)	0	0.038(3)	0
Cl1	0.6982(3)	0	0.0082(4)	0.0222(12)	0.008(3)	0.041(3)	0.012(3)	0	0.001(3)	0
Cl2	0.5865(4)	0	0.4462(5)	0.0312(15)	0.028(4)	0.039(4)	0.024(4)	0	0.011(3)	0
Cl3	0.7886(4)	0	0.4388(4)	0.0221(13)	0.013(3)	0.036(3)	0.019(3)	0	0.008(3)	0
Cl4	0.7613(4)	0	0.8150(5)	0.0275(14)	0.017(3)	0.044(4)	0.026(4)	0	0.013(3)	0
Cl5	0.0623(4)	0	0.9198(5)	0.0314(15)	0.040(4)	0.032(3)	0.016(3)	0	0.009(3)	0
O1	0.8829(6)	0.7134(16)	0.7511(7)	0.016(2)	0.014(6)	0.023(6)	0.013(6)	0.001(4)	0.008(5)	0.000(5)
O2	0.0946(7)	0.2154(17)	0.7468(8)	0.022(3)	0.016(6)	0.027(6)	0.028(7)	-0.009(5)	0.015(6)	-0.004(5)
O3	0.9401(9)	½	0.9184(10)	0.016(3)	0.012(7)	0.031(7)	0.003(6)	0	0.003(6)	0
O4	0.9317(9)	0	0.6582(10)	0.011(3)	0.009(8)	0.015(7)	0.013(8)	0	0.008(7)	0
O5	0.0401(9)	½	0.8211(10)	0.012(3)	0.002(7)	0.024(8)	0.005(8)	0	-0.001(6)	0
O6	0.0551(10)	0	0.5867(11)	0.026(4)	0.014(9)	0.056(11)	0.001(8)	0	-0.002(8)	0

not bonded to  $\text{Se}^{4+}$  cations, and they are tetrahedrally coordinated by four metal atoms. The O4 atom is coordinated by three  $\text{Cu}^{2+}$  and one  $\text{Pb}^{2+}$  cations, and the O5 atom, by four  $\text{Cu}^{2+}$  cations. The  $[\text{O4PbCu}_3]^{6+}$  and  $[\text{O5Cu}_4]^{6+}$  tetrahedra are linked *via* Cu1 atoms into  $[\text{O}_2\text{Cu}_5\text{Pb}]^{8+}$  chains that extend parallel to the *b* axis (Fig. 3c). The  $[\text{SeO}_3]^{2-}$  pyramids are attached to the faces of the oxocentered tetrahedra in a “face-to-face” position (Krivovichev *et al.* 1999b, Krivovichev & Filatov 2001) to form a complex  $[(\text{O}_2\text{Cu}_5\text{Pb})[\text{SeO}_3]_2]^{4+}$  chain (Fig. 3b). These complex metal oxoselenite chains are linked together to form the metal–oxygen layer mentioned above. The layer has large pores that are occupied by the dimeric  $[\text{Cu}^+\text{Cl}_2]^-$  anions. These anions are held in the structure *via* weak  $\text{Cu}^{2+}-\text{Cl}^-$  bonds ( $>2.8$  Å) only. Thus, allochalcocelinite can be considered as a kind of delicately balanced host–guest system with  $[\text{Cu}^+\text{Cl}_2]^-$  anions included into the  $\text{Cu}^{2+}$  oxoselenite chloride matrix. We note that the linear  $[\text{Cu}^+\text{Cl}_2]^-$  anion

has been previously observed in the structure of freedite,  $\text{Pb}_8\text{Cu}^+(\text{As}^{3+}\text{O}_3)_2\text{O}_3\text{Cl}_5$  (Pertlik 1987).

## DISCUSSION

Allochalcocelinite is the second copper oxoselenite chloride containing both  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  anions. Recently, Krivovichev *et al.* (2004) reported the synthesis, by a vapor-transport technique, and the structure of  $\text{Cu}^+\text{Cu}^{2+}_4\text{O}(\text{SeO}_3)\text{Cl}_5$ . As in allochalcocelinite, the structure of this compound contains additional O atoms that are coordinated by four  $\text{Cu}^{2+}$  cations to form  $[\text{OCu}_4]^{6+}$  tetrahedra that are linked into infinite  $[\text{O}_2\text{Cu}_6]^{8+}$  chains. However, the  $\text{Cu}^+$  cations are tetrahedrally coordinated by four  $\text{Cl}^-$  anions, which is common for  $\text{Cu}^+$  chlorides (see, *e.g.*, Geller & Sishen 1986, Becker *et al.* 2003).

Chains of composition  $[\text{O}_2\text{M}_6]^{8+}$  that are similar to those shown in Figure 3c, with  $\text{M} = \text{Cu}$  or  $\text{Zn}$ , have also been observed in the structures of chloromenite (Krivovichev *et al.* 1998), vergasovaite,  $[\text{Cu}_3\text{O}][(\text{Mo,S})\text{O}_4](\text{SO}_4)$  (Berlepsch *et al.* 1999), kamchatkite,  $[\text{Cu}_3\text{O}]\text{Cl}(\text{SO}_4)_2$  (Varaksina *et al.* 1990),  $[\text{Cu}_3\text{O}](\text{MoO}_4)_2$  (Steiner & Reichelt 1997),  $[\text{Cu}_3\text{O}](\text{V}_2\text{O}_7)(\text{H}_2\text{O})$  (Leblanc & Féry 1990),  $\text{Na}_2\text{Cu}^+[\text{Cu}^{2+}_3\text{O}](\text{PO}_4)_2\text{Cl}$  (Etheredge & Hwu 1995),  $[\text{Zn}_3\text{O}](\text{SO}_4)_2$  (Bald & Gruehn 1981), and  $[\text{Zn}_3\text{O}](\text{MoO}_4)_2$  (Söhnel *et al.* 1996).

The structures of anhydrous copper selenite chlorides possess interesting magnetic properties because of the finite Cu substructure immersed into an oxide matrix and insulated by dielectric layers of Cl atoms (Millet *et al.* 2001). The copper substructure in allochalcocelinite is two-dimensional and is shown in Figure 4. It can be considered as a distorted *kagomé* net expanded by inclusion of the  $\text{Cu}^+$  cations. It is impossible to measure magnetic properties of allochalcocelinite at the moment, owing to the paucity of natural material. The synthesis of its chemical analogue is presently being attempted by chemical transport reactions.

TABLE 3. SELECTED BOND-LENGTHS (Å) IN THE STRUCTURE OF ALLOCHALCOSELITE

Pb- O4	2.364(13)	Cu2- O4	1.898(13)
Pb- O1	2.434(10) 2×	Cu2- O6	1.984(15)
Pb- Cl3	2.993(6)	Cu2- O6	2.012(16)
Pb- Cl4	3.070(6)	Cu2- Cl3	2.312(7)
Pb- Cl3	3.392(3) 2×	Cu2- Cl2	3.122(1) 2×
Se1- O2	1.683(10) 2×	Cu3- O5	1.890(13)
Se1- O6	1.692(15)	Cu3- O3	1.948(14)
<Se1-O>	1.68	Cu3- O3	2.003(15)
		Cu3- Cl1	2.265(6)
Se2- O1	1.689(10) 2×	Cu3- Cl5	3.123(1) 2×
Se2- O3	1.717(14)		
<Se2-O>	1.70	Cu4- O5	1.914(14)
		Cu4- O2	2.106(10) 2×
Cu1- O5	1.919(8)	Cu4- Cl4	2.230(6)
Cu1- O4	1.930(9)	Cu4- Cl1	2.404(6)
Cu1- O1	1.981(10)		
Cu1- O2	1.988(10)	Cu5- Cl2	2.127(6) 2×
Cu1- Cl5	2.801(5)		
Cu1- Cl2	2.976(6)	Cu6- Cl5	2.052(6) 2×

TABLE 4. BOND-VALENCE ANALYSIS (vu) FOR ALLOCHALCOSELITE

	Cl1	Cl2	Cl3	Cl4	Cl5	O1	O2	O3	O4	O5	O6	Σ
Pb			0.29, 0.38 <sup>*2-</sup>	0.23		0.38 <sup>*2-</sup>			0.44			1.92
Se1							1.41 <sup>*2-</sup>				1.38	4.21
Se2						1.39 <sup>*2-</sup>		1.29				4.07
Cu1		0.07 <sup>*21</sup>			0.11 <sup>*21</sup>	0.44	0.43		0.51 <sup>*21</sup>	0.52 <sup>*21</sup>		2.09
Cu2		0.05 <sup>*2-1</sup>	0.43						0.55		0.44, 0.41	1.93
Cu3	0.49				0.05 <sup>*2-1</sup>			0.48, 0.42		0.57		2.05
Cu4	0.34			0.54			0.32 <sup>*2-</sup>			0.53		2.03
Cu5		0.47 <sup>*2-</sup>										0.94
Cu6					0.58 <sup>*2-</sup>							1.16
Σ	0.83	0.71	1.00	0.77	0.90	2.21	2.16	2.19	2.01	2.14	2.23	

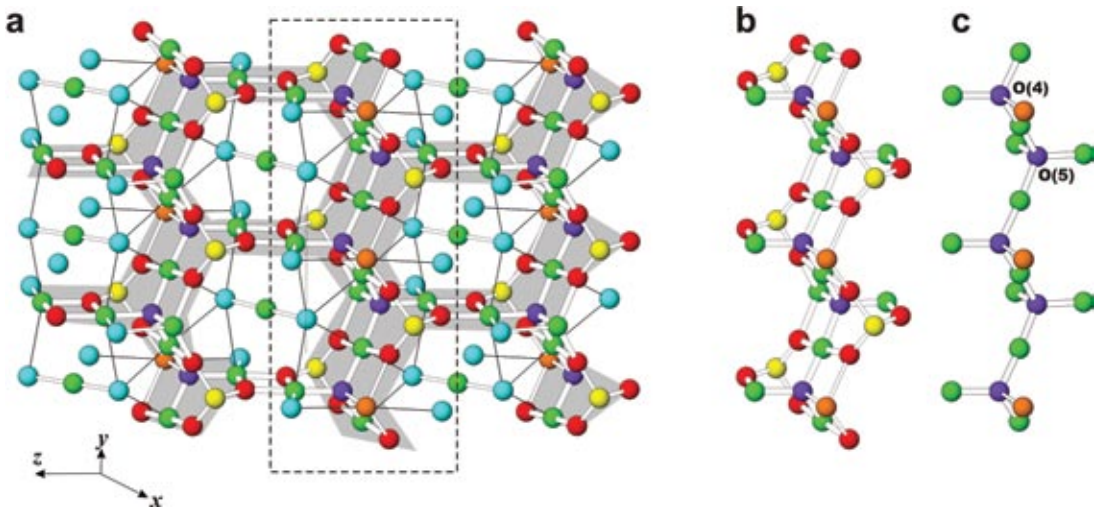


FIG. 3. The structure of metal-oxygen layer in allochalcocelite (a), complex  $[\text{O}_2\text{Cu}_5\text{Pb}][\text{SeO}_3]_2^{4+}$  oxoselenite chain (b) and  $[\text{O}_2\text{Cu}_5\text{Pb}]^{8+}$  chain of oxocentered tetrahedra. Legend: O atoms bonded to Se: red, “additional” O atoms: blue, Se: yellow, Cu: green, Cl: light blue, Pb: orange.

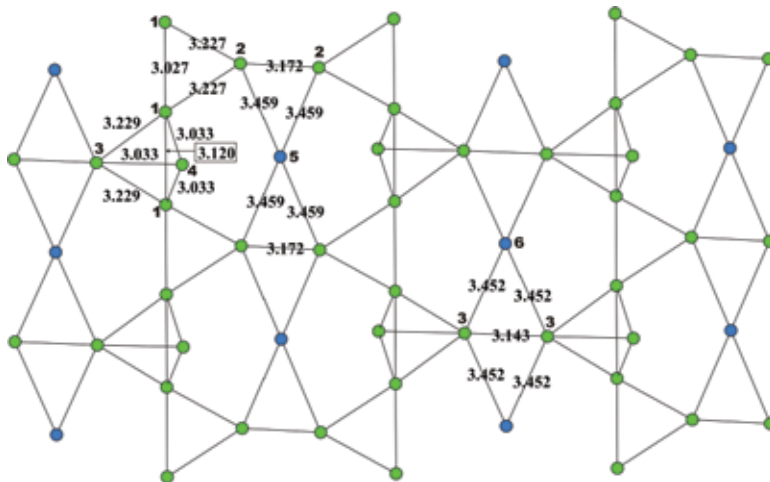


FIG. 4. Two-dimensional copper substructure in allochalcocelite. Legend:  $\text{Cu}^{2+}$  cations are shown in green, and  $\text{Cu}^+$  cations, in blue. The Cu-Cu distances are given in Å.

The presence of the  $[\text{Cu}^+\text{Cl}_2]^-$  anions in allochalcocelite also has some interesting geochemical implications. Their relatively isolated positions in the structure may indicate that these anions were stable and present as separate entities in a gaseous media from which allochalcocelite crystallized. Thus, the  $[\text{Cu}^+\text{Cl}_2]^-$  complexes may reflect a form of  $\text{Cu}^+$  transport by volcanic gases. If this is the case, the question arises concerning the

mobility of Cu in volcanic gases in both its monovalent and divalent forms. It should be noted that the possibility of transport of  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  simultaneously in gaseous phase has been demonstrated under laboratory conditions by the synthesis of  $\text{Cu}^+\text{Cu}^{2+}_4\text{O}(\text{SeO}_3)\text{Cl}_5$  (Krivovichev *et al.* 2004) which, along with allochalcocelite, contains independent crystallographic positions for the  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  cations. We speculate that

the same situation may also happen in nature, *e.g.*, in dry (~500–600°C) volcanic fumaroles such as those present in the Tolbachik fumarolic fields.

## ACKNOWLEDGEMENTS

We are grateful to Gerald Giester, Dieter Pohl, Associate Editor Uwe Kolitsch and Editor Robert F. Martin for their comments and corrections on the manuscript. This work was supported by the Russian Foundation for Basic Research (grant #03–05–64853) and the Russian Ministry of Science and Education program (grant RNP 2.1.1.3077).

## REFERENCES

- BALD, L. & GRUEHN, R. (1981): Die Kristallstruktur von einem Sulfat-reichen Oxidsulfat des Zinks. *Naturwiss.* **68**, 39.
- BECKER, R., JOHNSON, M., KREMER, R. & LEMMENS, P. (2003): Crystal structure, magnetic properties and conductivity of  $\text{CuSbTeO}_3\text{Cl}_2$ . *Solid State Sci.* **5**, 1411–1416.
- BERLEPSCH, P., ARMBRUSTER, T., BRUGGER, J., BYKOVA, E.Y. & KARTASHOV, P.M. (1999): The crystal structure of vergasovaite  $\text{Cu}_3\text{O}[(\text{Mo,S})\text{O}_4\text{SO}_4]$ , and its relation to synthetic  $\text{Cu}_3\text{O}[\text{MoO}_4]_2$ . *Eur. J. Mineral.* **11**, 101–110.
- BRESE, N.E. & O'KEEFE, M. (1991): Bond-valence parameters for solids. *Acta Crystallogr.* **B47**, 192–197.
- BURNS, P.C. & HAWTHORNE, F.C. (1995a): Coordination-geometry structural pathways in  $\text{Cu}^{2+}$  oxy salt minerals. *Can. Mineral.* **33**, 889–905.
- BURNS, P.C. & HAWTHORNE, F.C. (1995b): Mixed-ligand  $\text{Cu}^{2+}\phi_6$  octahedra in minerals: observed stereochemistry and Hartree–Fock calculations. *Can. Mineral.* **33**, 1177–1188.
- BURNS, P.C., KRIVOVICHEV, S.V. & FILATOV S.K. (2002): New  $\text{Cu}^{2+}$  coordination polyhedra in the crystal structure of burnsite,  $\text{KCCu}_7\text{O}_2(\text{SeO}_3)_2\text{Cl}_9$ . *Can. Mineral.* **40**, 1587–1595.
- DATTA, N. & JEFFREY, J.W. (1978): The crystal structure of paramelaconite,  $\text{Cu}^{2+}_{12}\text{Cu}^4\text{O}_{14}$ . *Acta Crystallogr.* **B34**, 22–26.
- EFFENBERGER, H. (1984): Verfeinerung der Kristallstruktur von Kupfer(II)hydroxichlorid,  $\text{Cu}(\text{OH})\text{Cl}$ . *Monatsh. Chem.* **115**, 725–730.
- ETHEREDGE, K.M.S. & HWU, SHIOU-JYH (1995): A novel copper (I/II) oxophosphate chloride with a quasi-one-dimensional  $\mu_4$ -oxo-bridged copper(II) chain. Crystal structure and magnetic properties of  $[\text{Na}_2\text{Cu}^{\text{II}}_3(\text{PO}_4)_2][\text{Cu}^{\text{I}}\text{OCl}]$ . *Inorg. Chem.* **35**, 5278–5282.
- GELLER, S. & SISHEN, XIE (1986): Crystal structure and electrical conductivity of  $\text{Rb}_{18}\text{Cu}_{31}\text{Cl}_{49}$ . *J. Solid State Chem.* **63**, 316–325.
- HAWTHORNE, F.C., GROAT, L.A. & ERCIT, T.S. (1987): Structure of cobalt diselenite. *Acta Crystallogr.* **C43**, 2042–2044.
- ITAKA, Y., LOCCHI, S., & OSWALD, H.R. (1961) Die Kristallstruktur von  $\text{CuOHCl}$ . *Helv. Chim. Acta* **44**, 2095–2103.
- JAHN, H.A. & TELLER, E. (1937): Stability of polyatomic molecules in degenerate electronic states. I. Orbital degeneracy. *Proc. R. Soc., Ser. A* **161**, 220–235.
- KELLER, P., LISSNER, F. & SCHLEID, T. (2001): Damaraita,  $\text{Pb}_3\text{O}_2(\text{OH})\text{Cl}$ : crystal structure and new chemical formula. *Neues Jahrb. Mineral., Monatsh.*, 326–336.
- KRIVOVICHEV, S.V. & BROWN, I.D. (2001): Are the compressive effects of encapsulation an artifact of the bond valence parameters? *Z. Kristallogr.* **216**, 245–247.
- KRIVOVICHEV, S.V. & BURNS, P.C. (2001): Crystal chemistry of lead oxide chlorides. I. Crystal structures of synthetic mendipite,  $\text{Pb}_3\text{O}_2\text{Cl}_2$ , and synthetic damaraita,  $\text{Pb}_3\text{O}_2(\text{OH})\text{Cl}$ . *Eur. J. Mineral.* **13**, 801–809.
- KRIVOVICHEV, S.V. & BURNS, P.C. (2002): Crystal chemistry of lead oxide chlorides. II. Crystal structure of  $\text{Pb}_7\text{O}_4(\text{OH})_4\text{Cl}_2$ . *Eur. J. Mineral.* **14**, 135–139.
- KRIVOVICHEV, S.V. & FILATOV, S.K. (2001): *Crystal Chemistry of Minerals and Inorganic Compounds with Complexes of Anion-Centered Tetrahedra*. St. Petersburg University Press, St. Petersburg, Russia (in Russ.).
- KRIVOVICHEV, S.V., FILATOV, S.K., ARMBRUSTER, T. & PANKRATOVA, O.YU. (2004): Crystal structure of  $\text{Cu}(\text{I})\text{Cu}(\text{II})_4\text{O}(\text{SeO}_3)\text{Cl}_5$ , a new heterovalent copper compound. *Dokl. Chem.* **399**, 226–228.
- KRIVOVICHEV, S.V., FILATOV, S.K., SEMENOVA, T.F. & ROZHDESTVENSKAYA, I.V. (1998): Crystal chemistry of inorganic compounds based on chains of oxocentered tetrahedra. I. The crystal structure of chloromenite,  $\text{Cu}_9\text{O}_2(\text{SeO}_3)_4\text{Cl}_6$ . *Z. Kristallogr.* **213**, 645–649.
- KRIVOVICHEV, S.V., SHUVALOV, R.R., SEMENOVA, T.F. & FILATOV, S.K. (1999a): Crystal chemistry of inorganic compounds based on chains of oxocentered tetrahedra. III. Crystal structure of georgbokiite. *Z. Kristallogr.* **214**, 135–138.
- KRIVOVICHEV, S.V., STAROVA, G.L. & FILATOV, S.K. (1999b): “Face-to-face” relationships between oxocentered tetrahedra and cation-centered tetrahedral oxyanions in crystal structures of minerals and inorganic compounds. *Mineral. Mag.* **63**, 263–266.
- KRIVOVICHEV, S.V., VERGASOVA, L.P., STAROVA, G.L., FILATOV, S.K., BRITVIN, S.N., ROBERTS, A.C. & STEELE, I.M. (2002): Burnsite,  $\text{KCCu}_7\text{O}_2(\text{SeO}_3)_2\text{Cl}_9$ , a new mineral species from the Tolbachik volcano, Kamchatka Peninsula, Russia. *Can. Mineral.* **40**, 1171–1175.
- LEBLANC, M. & FERÉY, G. (1990): Room-temperature structures of oxocopper(II) vanadate(V) hydrates,

- $\text{Cu}_3\text{V}_2\text{O}_8(\text{H}_2\text{O})$  and  $\text{CuV}_2\text{O}_6(\text{H}_2\text{O})_2$ . *Acta Crystallogr.* **C46**, 15-18.
- MILLET, P., BASTIDE, B., PASHCHENKO, V., GNATCHENKO, S., GAPON, V., KSARI, Y. & STEPANOV, A. (2001): Syntheses, crystal structures and magnetic properties of francisite compounds  $\text{Cu}_3\text{Bi}(\text{SeO}_3)_2\text{O}_2\text{X}$  (X = Cl, Br and I). *J. Mater. Chem.* **11**, 1152-1157.
- MORGAN, P.E.D., PARTIN, D.E., CHAMBERLAND, B.L. & O'KEEFFE, M. (1996): Synthesis of paramelaconite:  $\text{Cu}_4\text{O}_3$ . *J. Solid State Chem.* **121**, 33-37.
- O'KEEFFE, M. & BOVIN, J.-O. (1978): The crystal structure of paramelaconite,  $\text{Cu}_4\text{O}_3$ . *Am. Mineral.* **63**, 180-185.
- PASERO, M. & VACCHIANO, D. (2000): Crystal structure of mendipite,  $\text{Pb}_3\text{O}_2\text{Cl}_2$ . *Neues Jahrb. Mineral., Monatsh.*, 563-569.
- PERTLIK, F. (1987): The structure of freedite,  $\text{Pb}_8\text{Cu}(\text{AsO}_3)_2\text{O}_3\text{Cl}_5$ . *Mineral. Petrol.* **36**, 85-92.
- PRING, A., GATEHOUSE, B.M. & BIRCH, W.D. (1990): Francisite,  $\text{Cu}_3\text{Bi}(\text{SeO}_3)_2\text{O}_2\text{Cl}$ , a new mineral from Iron Monarch, South Australia: description and crystal structure. *Am. Mineral.* **75**, 1421-1425.
- SCHLÜTER, J., KLASKA, K.-H. & GEBHARD, G. (2000): Belloite,  $\text{Cu}(\text{OH})\text{Cl}$ , a new mineral from Sierra Gorda, Antofagasta, Chile. *Neues Jahrb. Mineral., Monatsh.*, 67-73.
- SÖHNEL, T., REICHEL, W., OPPERMAN, H., MATTAUSCH, HJ. & SIMON, A. (1996): Zum system Zn/Mo/O. I. Phasenbestand und Eigenschaften der ternären Zinkmolybdate; Struktur von  $\text{Zn}_3\text{Mo}_2\text{O}_9$ . *Z. Anorg. Allg. Chem.* **622**, 1274-1280.
- STEINER, U. & REICHEL, W. (1997): A reinvestigation of  $\text{Cu}_3\text{Mo}_2\text{O}_9$ , a compound containing copper (II) in compressed octahedral coordination. *Acta Crystallogr.* **C53**, 1371-1373.
- VARAKSINA, T.V., FUNDAMENSKY, V.S., FILATOV, S.K. & VERGASOVA, L.P. (1990): The crystal structure of kamchatkite, a new naturally occurring oxychloride sulphate of potassium and copper. *Mineral. Mag.* **54**, 613-616.
- VERGASOVA, L.P., FILATOV, S.K., SEMENOVA, T.F. & FILOSOFOVA, T.M. (1989): Sophiite,  $\text{Zn}_2(\text{SeO}_3)\text{Cl}_2$ , a new mineral from volcanic exhalations. *Zap. Vses. Mineral. Obshchest.* **118**(1), 65-69 (in Russ.).
- VERGASOVA, L.P., KRIVOVICHEV, S.V., BRITVIN, S.N., FILATOV, S.K., BURNS, P.C. & ANANIEV, V.V. (2005): Allochalcocelite,  $\text{Cu}^+\text{Cu}^{2+}_3\text{PbO}_2(\text{SeO}_3)_2\text{Cl}_5$  – a new mineral from volcanic exhalations. *Zap. Vser. Mineral. Obshchest.* **134**(3), 70-73 (in Russ.).
- VERGASOVA, L.P., KRIVOVICHEV, S.V., SEMENOVA, T.F., FILATOV, S.K. & ANANIEV, V.V. (1999b): Chloromenite,  $\text{Cu}_9\text{O}_2(\text{SeO}_3)_4\text{Cl}_6$ , a new mineral from the Tolbachik Volcano, Kamchatka, Russia. *Eur. J. Mineral.* **11**, 119-123.
- VERGASOVA, L.P., SEMENOVA, T.F., FILATOV, S.K., KRIVOVICHEV, S.V., SHUVALOV, R.R. & ANANIEV, V.V. (1999a): Georgbokiite,  $\text{Cu}_5\text{O}_2(\text{SeO}_3)_2\text{Cl}_2$ , a new mineral from volcanic exhalations. *Dokl. Akad. Nauk* **364**, 527-531 (in Russ.).
- VERGASOVA, L.P., SEMENOVA, T.F., SHUVALOV, R.R., FILATOV, S.K. & ANANIEV, V.V. (1997): Ilinskite,  $\text{NaCu}_5\text{O}_2(\text{SeO}_3)_2\text{Cl}_3$ , a new mineral from volcanic exhalations. *Dokl. Akad. Nauk* **353**, 641-644 (in Russ.).

Received April 17, 2005, revised manuscript accepted October 8, 2005.