THE CRYSTAL STRUCTURE OF ALLOCHALCOSELITE, $Cu^+Cu^{2+}_5PbO_2(SeO_3)_2Cl_5$, A MINERAL WITH WELL-DEFINED Cu^+ AND Cu^{2+} POSITIONS

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ABSTRACT

The crystal structure of allochalcoselite, $Cu^+Cu^{2+}_5PbO_2(SeO_3)_2Cl_5$, 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, β 119.284(2)°, V 1516.5(3) Å^3, $Z = 4$. The structure contains one symmetrically unique Pb position coordinated by three O and four Cl atoms. There are two Se^{4+} cations, which form SeO_3 trigonal pyramids. There are six symmetrically independent Cu sites in allochalcoselite, four of which [Cu1–Cu4] are occupied by Cu^{2+} and two [Cu5 and Cu6] by 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 CuO_3Cl_2 bipyramid with one equatorial and one apical vertex occupied by Cl. The Cu^+ cations are both coordinated by two Cl^- anions to form linear anions $[Cu^+Cl_2]^-$, with Cl–Cu–Cl angles of 180°. The structure can be appropriately described in terms of arrangements of the strong M–O bonds ($M = Se^{4+}$, Cu^{2+} and Pb^{2+}). These bonds are accumulated within layers parallel to (100), with some of the Cl^- anions sandwiched between them. The O4 and O5 atoms are not bonded to Se^{4+} cations, and are tetrahedrally coordinated by four metal atoms. The $[O4PbCu_3]^{6+}$ and $[O5Cu_4]^{6+}$ tetrahedra are linked *via* Cu1 atoms into $[O_2Cu_5Pb]^{8+}$ chains extending parallel to the b axis. The $[SeO_3]^{2-}$ pyramids are attached to oxocentered tetrahedra in "face-to-face" positions to form complex $([O_2Cu_5Pb][SeO_3]_2)^{4+}$ chains that are linked together to form a metal–oxygen layer parallel to (100). The layer has large pores that are occupied by the $[Cu^+Cl_2]^-$ anions. These anions are held in the structure *via* weak Cu^{2+}–Cl^- bonds (> 2.8 Å) only. Thus allochalcoselite can be considered as a kind of delicately balanced host–guest system with $[Cu^+Cl_2]^-$ anions included into the Cu^{2+} oxoselenite chloride matrix. Relatively isolated and weakly bonded positions of the $[Cu^+Cl_2]^-$ anions in the structure may indicate stability of these complexes as separate entities and their possible role in the Cu^+ transport by volcanic gases.

Keywords: allochalcoselite, crystal structure, copper, selenite, Tolbachik volcano, Russia.

SOMMAIRE

Nous avons résolu la structure cristalline de l'allochalcosélite, $Cu^+Cu^{2+}_5PbO_2(SeO_3)_2Cl_5$, nouvelle espèce minérale provenant des fumerolles 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, β 119.284(2)°, V 1516.5(3) Å^3, $Z = 4$. 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 Se^{4+}, formant des pyramides trigonales SeO_3. Il y a six sites de Cu symétriquement indépendants, parmi lesquels quatre [Cu1–Cu4] contiennent Cu^{2+} et deux [Cu5 et Cu6] contiennent 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 CuO_3Cl_2 trigonale ayant le Cl à un coin équatorial et à un vertex apical. Les deux cations Cu^+ sont coordonnés à deux anions Cl^- pour former des anions linéaires $[Cu^+Cl_2]^-$, avec un angle Cl–Cu–Cl de 180°. On peut décrire la structure en termes d'agencements de liaisons M–O fortes ($M = Se^{4+}$, Cu^{2+} et Pb^{2+}). Ces liaisons sont accumulées à l'intérieur

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de couches parallèles à (100), avec certains des anions Cl⁻ intercalés entre ces feuillets. Les atomes O4 et O5 ne sont pas liés aux cations Se^{4+}, et possèdent une coordinence tétraédrique avec quatre atomes métalliques. Les tétraèdres [O4PbCu$_3$]$^{6+}$ et [O5Cu$_4$]$^{6+}$ sont connectés grâce aux atomes Cu1 pour former des chaînes [O$_2$Cu$_5$Pb]$^{8+}$ parallèles à l'axe *b*. Les pyramides [SeO$_3$]$^{2-}$ sont rattachées aux tétraèdres oxocentrés dans un agencement "face-à-face" pour former des chaînes complexes de stoechiométrie ([O$_2$Cu$_5$Pb][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 [Cu$^+$Cl$_2$]⁻. Ces anions sont retenus dans la structure seulement grâce à de faibles liaisons Cu^{2+}–Cl⁻ (>2.8 Å). On pourrait considérer l'allochalcosélite comme une sorte de système hôte–inclusion délicatement balancé, avec les anions [Cu$^+$Cl$_2$]⁻ inclus dans la matrice d'oxosélénite chlorurée de Cu^{2+}. La position relativement isolée et faiblement retenue des anions [Cu$^+$Cl$_2$]⁻ indique une certaine stabilité de ces complexes comme entités distinctes et leur rôle possible dans le tranfert du Cu$^+$ dans les gaz volcaniques.

(Traduit par la Rédaction)

Mots-clés: allochalcosélite, 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, Cu$^+$–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 Cu$^{2+}_{12}$Cu$^+_4$O$_{14}$ with Cu^{2+}–Cu$^+$ disorder, whereas O'Keeffe & Bovin (1978) established the composition Cu$^+_2$Cu$^{2+}_2$O$_4$ with fully ordered Cu$^+$ and Cu^{2+} sites (see also Morgan *et al.* 1996).

Recently, Vergasova *et al.* (2005) described the second mineral species containing both Cu^{2+} and Cu$^+$ cations, allochalcoselite, Cu$^+$Cu$^{2+}_5$PbO$_2$(SeO$_3$)$_2$Cl$_5$. It was found within the fumaroles of the Great fissure Tolbachik eruption (Kamchatka Peninsula, Russia). Allochalcoselite occurs as dark brown prismatic crystals in association with sophiite, Zn$_2$(SeO$_3$)Cl$_2$ (Vergasova *et al.* 1989), ilinskite, NaCu$_5$O$_2$(SeO$_3$)$_2$Cl$_3$ (Vergasova *et al.* 1997), georgbokiite, Cu$_5$O$_2$(SeO$_3$)$_2$Cl$_2$ (Vergasova *et al.* 1999a) and burnsite, KCdCu$_7$O$_2$(SeO$_3$)$_2$Cl$_9$ (Krivovichev *et al.* 2002, Burns *et al.* 2002). After these minerals and chloromenite, Cu$_9$O$_2$(SeO$_3$)$_4$Cl$_6$ (Vergasova *et al.* 1999b), and francisite, Cu$_3$Bi(SeO$_3$)$_2$O$_2$Cl (Pring *et al.* 1990), allochalcoselite 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 allochalcoselite 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 Mo*K*α X-radiation, with frame widths of 0.3° in ω, 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-Ψ-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 Pb^{2+}–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 allochalcoselite 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 Cl⁻ anions. The coordination of the Pb^{2+} cation is highly asymmetrical owing to the localized 6s^2 lone pair of electrons. The character of the Pb^{2+} coordination (short Pb^{2+}–O^{2-} bonds in one half of the coordination sphere and long Pb^{2+}–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 Se^{4+} cations in the structure, coordinated by three O atoms each, to form SeO$_3$ trigonal
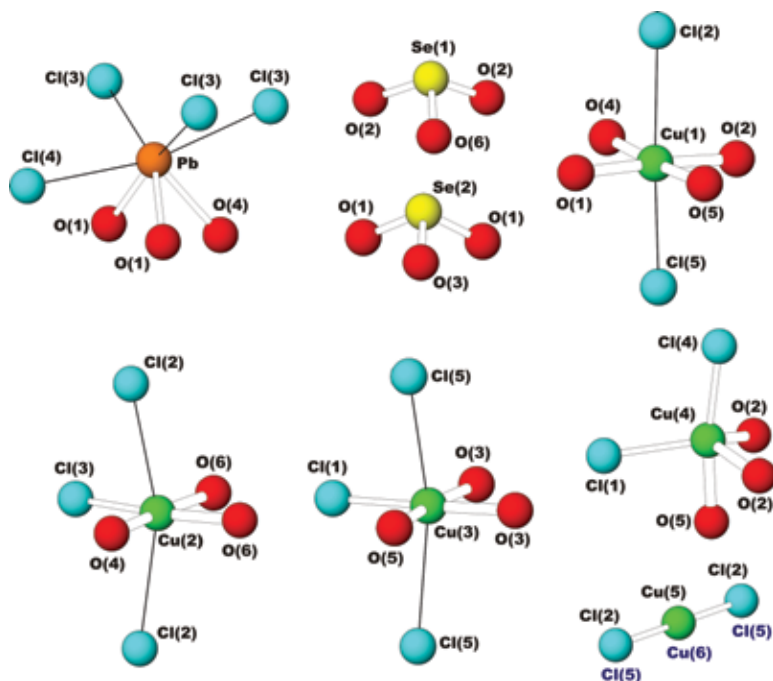
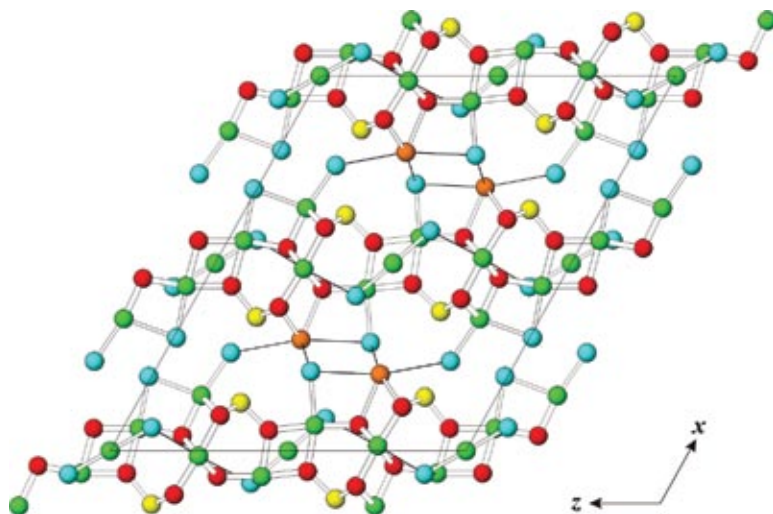FIG. 1.   Coordination of cations in the structure of allochalcoselite.

FIG. 2.   The crystal structure of allochalcoselite 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 Cu^{2+} and two [Cu5 and Cu6] by Cu^+ cations (Fig. 1, Table 4). The Cu1 site is coordinated by four O^{2-} anions at the vertices of a square and two apical Cl^- anions, such that an elongate $[CuO_4Cl_2]$ octahedron is formed. A similar coordination has been observed for the Cu2 site in georgbokiite (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 Cl^- anions. It should be noted that the Cu^{2+}–Cl^- distances corresponding to the apical vertices of the CuO_3Cl_3 octahedra are rather long (~3.12 Å); however, their bond valences are ≥0.05 valence units (*vu*), and their inclusion into the Cu^{2+} coordination sphere seems reasonable from the viewpoint of stereochemistry. A similar coordination polyhedron with composition CuO_3Cl_3 has been observed in the structure of belloite, Cu(OH)Cl (Iitaka *et al.* 1961, Effenberger 1984, Schlüter *et al.* 2000). The octahedral coordinations of 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 CuO_3Cl_2 coordination polyhedron has not been previously found in a mineral. The Cu5 and Cu6 positions are occupied by Cu^+ cations; both are coordinated by two Cl^- anions to form linear anions $[Cu^+Cl_2]^-$ with Cl–Cu–Cl angles of 180°.

Description of the structure

The structure of allochalcoselite 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 = Se^{4+}, Cu^{2+} and Pb^{2+}). These bonds are accumulated within the layers parallel to (100), with some of the 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 1. CRYSTALLOGRAPHIC DATA AND
REFINEMENT PARAMETERS FOR ALLOCHALCOSELITE

a (Å)	18.468(2)	D_{calc} (g/cm^3)	4.606
b (Å)	6.1475(8)	Crystal size (mm)	0.08 × 0.04 × 0.008
c (Å)	15.314(2)	Radiation	Mo$K\alpha$
b (°)	119.284(2)	Total reflections	5536
V (Å^3)	1516.5(3)	Unique reflections	1878
Space group	$C2/m$	Unique $|F_o| \geq 4\sigma_F$	1235
F_{000}	1892	R_1	0.047
μ (cm^{-1})	25.019	wR_2	0.098
Z	8	S	0.995

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

TABLE 2. COORDINATES AND DISPLACEMENT PARAMETERS OF ATOMS IN ALLOCHALCOSELITE

Atom	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
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(2)	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 Se^{4+} cations, and they are tetrahedrally coordinated by four metal atoms. The O4 atom is coordinated by three Cu^{2+} and one Pb^{2+} cations, and the O5 atom, by four Cu^{2+} cations. The $[O4PbCu_3]^{6+}$ and $[O5Cu_4]^{6+}$ tetrahedra are linked *via* Cu1 atoms into $[O_2Cu_5Pb]^{8+}$ chains that extend parallel to the *b* axis (Fig. 3c). The $[SeO_3]^{2-}$ 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 $([O_2Cu_5Pb][SeO_3]_2)^{4+}$ 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 $[Cu^+Cl_2]^-$ anions. These anions are held in the structure *via* weak Cu^{2+}–Cl^- bonds (>2.8 Å) only. Thus, allochalcoselite can be considered as a kind of delicately balanced host–guest system with $[Cu^+Cl_2]^-$ anions included into the Cu^{2+} oxoselenite chloride matrix. We note that the linear $[Cu^+Cl_2]^-$ anion

has been previously observed in the structure of freedite, $Pb_8Cu^+(As^{3+}O_3)_2O_3Cl_5$ (Pertlik 1987).

DISCUSSION

Allochalcoselite is the second copper oxoselenite chloride containing both Cu^+ and Cu^{2+} anions. Recently, Krivovichev *et al.* (2004) reported the synthesis, by a vapor-transport technique, and the structure of $Cu^+Cu^{2+}{}_4O(SeO_3)Cl_5$. As in allochalcoselite, the structure of this compound contains additional O atoms that are coordinated by four Cu^{2+} cations to form $[OCu_4]^{6+}$ tetrahedra that are linked into infinite $[O_2Cu_6]^{8+}$ chains. However, the Cu^+ cations are tetrahedrally coordinated by four Cl^- anions, which is common for Cu^+ chlorides (see, *e.g.,* Geller & Sishen 1986, Becker *et al.* 2003).

Chains of composition $[O_2M_6]^{8+}$ that are similar to those shown in Figure 3c, with M = Cu or Zn, have also been observed in the structures of chloromenite (Krivovichev *et al.* 1998), vergasovaite, $[Cu_3O]((Mo,S)O_4)(SO_4)$ (Berlepsch *et al.* 1999), kamchatkite, $[Cu_3O]Cl(SO_4)_2$ (Varaksina *et al.* 1990), $[Cu_3O](MoO_4)_2$ (Steiner & Reichelt 1997), $[Cu_3O](V_2O_7)(H_2O)$ (Leblanc & Feréy 1990), $Na_2Cu^+[Cu^{2+}{}_3O](PO_4)_2Cl$ (Etheredge & Hwu 1995), $[Zn_3O](SO_4)_2$ (Bald & Gruehn 1981), and $[Zn_3O](MoO_4)_2$ (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 allochalcoselite is two-dimensional and is shown in Figure 4. It can be considered as a distorted *kagomé* net expanded by inclusion of the Cu^+ cations. It is impossible to measure magnetic properties of allochalcoselite 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

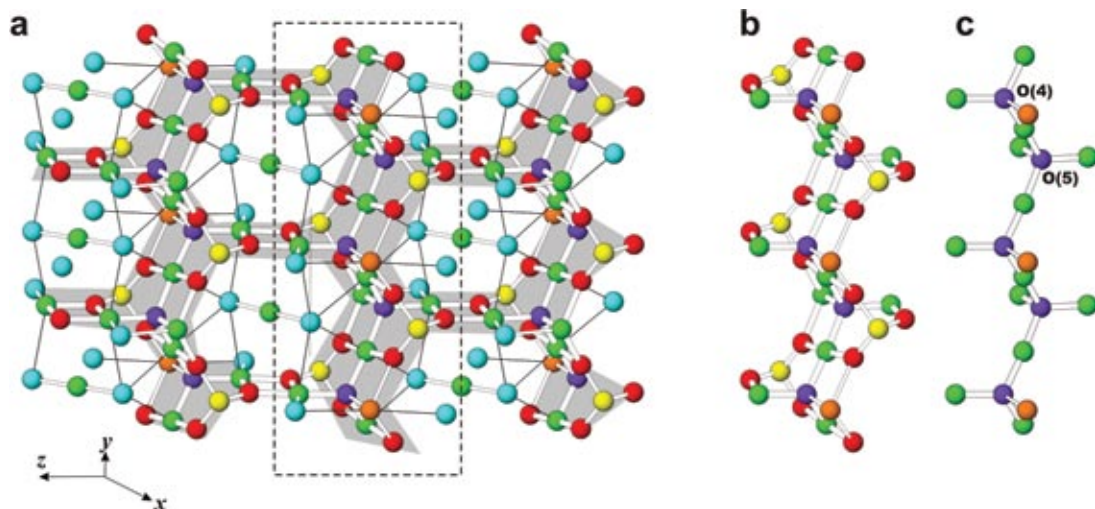|	Cl1	Cl2	Cl3	Cl4	Cl5	O1	O2	O3	O4	O5	O6	Σ
Pb			0.29, 0.38[×2-]	0.23		0.38[×2-]			0.44			1.92
Se1							1.41[×2-]				1.38	4.21
Se2						1.39[×2-]		1.29				4.07
Cu1		0.07[×2↓]			0.11[×2↓]	0.44	0.43		0.51[×2↓]	0.52[×2↓]		2.09
Cu2		0.05[×2-↓]	0.43						0.55		0.44,0.41	1.93
Cu3	0.49				0.05[×2-↓]			0.48,0.42		0.57		2.05
Cu4	0.34			0.54			0.32[×2-]			0.53		2.03
Cu5		0.47[×2-]										0.94
Cu6					0.58[×2-]							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 allochalcoselite (a), complex ([O$_2$Cu$_5$Pb][SeO$_3$]$_2$)$^{4+}$ oxoselenite chain (b) and [O$_2$Cu$_5$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.
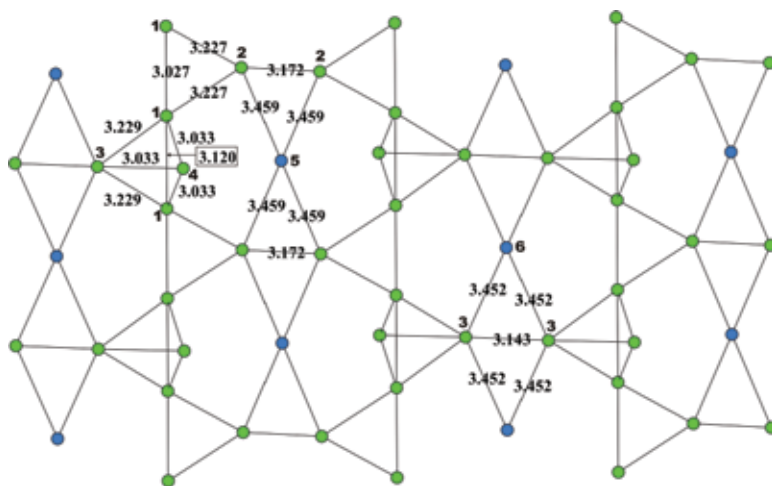

FIG. 4.   Two-dimensional copper substructure in allochalcoselite. Legend: Cu^{2+} cations are shown in green, and Cu$^+$ cations, in blue. The Cu–Cu distances are given in Å.

The presence of the [Cu$^+$Cl$_2$]$^-$ anions in allochalcoselite 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 allochalcoselite crystallized. Thus, the [Cu$^+$Cl$_2$]$^-$ complexes may reflect a form of 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 Cu$^+$ and Cu^{2+} simultaneously in gaseous phase has been demonstrated under laboratory conditions by the synthesis of Cu$^+$Cu^{2+}$_4$O(SeO$_3$)Cl$_5$ (Krivovichev *et al.* 2004) which, along with allochalcoselite, contains independent crystallographic positions for the Cu$^+$ and 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.

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