

THE CRYSTAL STRUCTURE OF PARAGEORGBOKIITE, β -Cu₅O₂(SeO₃)₂Cl₂

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ABSTRACT

The crystal structure of parageorgbokiite, β -Cu₅O₂(SeO₃)₂Cl₂, a new mineral species from the fumaroles of the Great Fissure Tolbachik eruption, in the Kamchatka Peninsula, Russia, has been solved from single-crystal X-ray-diffraction data by direct methods and refined to $R_1 = 0.032$ for 1388 unique reflections with $|F_o| \geq 4\sigma_F$. The mineral is monoclinic, space group $P2_1/c$, a 5.3982(5), b 8.0543(8), c 11.1277(10) Å, β 99.258(2)°, V 477.52(8) Å³, $Z = 2$. The structure contains three symmetrically unique Cu positions, each octahedrally coordinated by O²⁻ and Cl⁻ anions. There is one symmetrically independent Se⁴⁺ cation coordinated by three O atoms, to form SeO₃ trigonal pyramids. The structure of parageorgbokiite is best described in terms of arrangements of the strong M -O bonds ($M = \text{Se}^{4+}$ and Cu^{2+}). The O1 atom is not bonded to Se⁴⁺ cations and is tetrahedrally coordinated by four Cu²⁺ cations, which results in the formation of an oxocentered O1Cu₄ tetrahedron. Two O1Cu₄ tetrahedra share a Cu3...Cu3 edge to form O₂Cu₆ dimers that are further linked by sharing the Cu2 corners to form O₂Cu₅ infinite chains parallel to the a axis. The SeO₃ pyramids are attached to the faces of the oxocentered tetrahedra in a "face-to-face" position to form complex $([\text{O}_2\text{Cu}_5][\text{SeO}_3]_2)^{2+}$ chains and a three-dimensional framework with channels occupied by the Cl⁻ anions. A comparison of parageorgbokiite and georbokiite shows that the two minerals have the same space group $P2_1/c$ (monoclinic), but differ in their unit-cell parameters. The structures of both minerals are based upon the same complex $([\text{O}_2\text{Cu}_5][\text{SeO}_3]_2)^{2+}$ chains. However, the arrangements of the chains in the structures are different. The channels in parageorgbokiite are larger than those in georbokiite. From the lower density of parageorgbokiite in comparison to georbokiite, we suggest that parageorgbokiite is a high-temperature modification of Cu₅O₂(SeO₃)₂Cl₂ that is either chemically or kinetically stabilized at ambient conditions.

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

SOMMAIRE

Nous avons résolu la structure cristalline de la parageorgbokiite, β -Cu₅O₂(SeO₃)₂Cl₂, espèce récemment découverte dans une fumerolle associée à la grande éruption fissurale de Tolbachik, péninsule de Kamchatka, en Russie, par diffraction X sur monocristal (méthodes directes), et nous l'avons affinée jusqu'à un résidu R_1 de 0.032 en utilisant 1388 réflexions uniques observées ayant $|F_o| \geq 4\sigma_F$. Il s'agit d'un minéral monoclinique, groupe spatial $P2_1/c$, a 5.3982(5), b 8.0543(8), c 11.1277(10) Å, β 99.258(2)°, V 477.52(8) Å³, $Z = 2$. La structure contient trois positions symétriquement uniques de Cu, dans chaque cas avec coordination octaédrique aux anions O²⁻ et Cl⁻. Il y a un cation Se⁴⁺ symétriquement indépendant et coordonné à trois atomes d'oxygène pour former une pyramide trigonale SeO₃. On a avantage à décrire la structure de la parageorgbokiite en termes de fortes liaisons M -O ($M = \text{Se}^{4+}$, Cu^{2+}). L'atome O1 n'est pas lié aux cations Se⁴⁺; il est en coordination tétraédrique avec quatre cations Cu²⁺ pour donner un tétraèdre oxocentré O1Cu₄. Deux tétraèdres O1Cu₄ partagent une arête Cu3...Cu3 pour former un dimère O₂Cu₆. Ces dimères sont aussi interliés par partage de coins Cu2 pour former des chaînes O₂Cu₅ infinies parallèles à l'axe a . Les pyramides SeO₃ sont rattachées aux faces des tétraèdres oxocentrés dans un agencement "face-à-face" pour donner des chaînes complexes $([\text{O}_2\text{Cu}_5][\text{SeO}_3]_2)^{2+}$ qui forment une trame tri-dimensionnelle ayant des canaux où logent les anions Cl⁻. Une comparaison de la parageorgbokiite avec la georbokiite montre que les deux minéraux partagent le même groupe spatial $P2_1/c$ dans le système monoclinique, mais leurs mailles élémentaires diffèrent. Les deux structures possèdent les mêmes chaînes $([\text{O}_2\text{Cu}_5][\text{SeO}_3]_2)^{2+}$ complexes. Toutefois, la disposition des chaînes dans les deux structures est différente. Les canaux sont plus

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volumineux dans la parageorgbokiite; ainsi, la densité plus faible de la parageorgbokiite fait penser que cette dernière serait la modification de $\text{Cu}_5\text{O}_2(\text{SeO}_3)_2\text{Cl}_2$ stable à une température plus élevée, et stabilisée aux conditions ambiantes pour des raisons soit chimiques, soit cinétiques.

(Traduit par la Rédaction)

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

INTRODUCTION

Parageorgbokiite, $\beta\text{-Cu}_5\text{O}_2(\text{SeO}_3)_2\text{Cl}_2$, has recently been described by Vergasova *et al.* (2006) from the fumaroles of the Great fissure Tolbachik eruption, in the Kamchatka Peninsula, Russia. The mineral was found as green, transparent plates up to 0.1 mm in maximum dimension and in close intergrowths with cotunnite and other copper selenite chlorides: ilinskite, $\text{NaCu}_5\text{O}_2(\text{SeO}_3)_2\text{Cl}_3$ (Vergasova *et al.* 1997), chloromenite, $\text{Cu}_9\text{O}_2(\text{SeO}_3)_4\text{Cl}_6$ (Vergasova *et al.* 1999b), burnsite, $\text{KCaCu}_7\text{O}_2(\text{SeO}_3)_2\text{Cl}_9$ (Krivovichev *et al.* 2002) and allochalcocelinite, $\text{Cu}^+\text{Cu}^{2+}_3\text{PbO}_2(\text{SeO}_3)_2\text{Cl}_5$ (Vergasova *et al.* 2005). The initial chemical analysis indicated that the mineral has the formula $\text{Cu}_5\text{O}_2(\text{SeO}_3)_2\text{Cl}_2$, identical to that of georgbokiite, a mineral that has also been described from the Tolbachik fumaroles (Vergasova *et al.* 1999a, Krivovichev *et al.* 1999a). However, parageorgbokiite crystals are green and show pleochroism in green hues, whereas georgbokiite grains are invariably dark brown to black. A determination of the crystal structure of the green mineral indicated that, indeed, its chemical formula is $\text{Cu}_5\text{O}_2(\text{SeO}_3)_2\text{Cl}_2$. However, the structure is different from that of georgbokiite; thus these two minerals are dimorphs. Consequently, the new mineral was named parageorgbokiite in order to emphasize its relation to georgbokiite (Vergasova *et al.* 2006). The purpose of the present paper is to report details of the crystal structure of parageorgbokiite as well as to compare it to that of georgbokiite.

EXPERIMENTAL

The crystal of parageorgbokiite used in this study was taken from the holotype specimen described by Vergasova *et al.* (2006). It was mounted on a Bruker three-circle X-ray diffractometer operated at 50 kV and 40 mA and equipped with a 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° in ω , and with 60 s spent counting 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 with a semiempirical 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 0.032, calculated for the 1388 unique observed ($|F_o| \geq 4\sigma_F$) reflections (see Table 1 for further details). Final atomic 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 Brese & O'Keeffe (1991). Calculated and observed structure-factors are available from the Depository of Unpublished Data on the MAC web site [document Parageorgbokiite CM45_929].

RESULTS

Cation coordination

The structure of parageorgbokiite contains three symmetrically unique Cu positions, each of which is octahedrally coordinated by O^{2-} and Cl^- anions (Fig. 1). As is typical for Cu^{2+} cations (Burns & Hawthorne 1995a, b), the $\text{Cu}^{2+}\phi_6$ octahedra (ϕ : O, Cl) are distorted owing to the Jahn–Teller effect (Jahn & Teller 1937); there are four short equatorial Cu– ϕ bonds complemented by two long apical Cu– ϕ bonds. The Cu1 site is coordinated by three O and one Cl atoms forming a distorted square. The apical positions are occupied by O and Cl. The Cu2 atom has a planar coordination defined by four O atoms, complemented by two additional long Cu–Cl bonds (3.194 Å). The bond

TABLE 1. CRYSTALLOGRAPHIC DATA AND REFINEMENT PARAMETERS FOR PARAGEORGBOKIITE

a (Å)	5.3982(5)	Crystal size (mm)	$0.06 \times 0.04 \times 0.02$
b (Å)	8.0543(8)	Radiation	$\text{MoK}\alpha$
c (Å)	11.1277(10)	$2\theta_{\text{max}}$ ($^\circ$)	68.99
β ($^\circ$)	99.258(2)	Total reflections	5207
V (Å ³)	477.52(8)	Unique reflections	1957
Space group	$P2_1/c$	Unique $ F_o \geq 4\sigma_F$	1388
F_{000}	622	R_1	0.032
m (cm ⁻¹)	191.56	wR_2	0.062
Z	2	S	0.680
D_{calc} (g/cm ³)	4.69	$r_{\text{max}}, r_{\text{min}}$ ($e/\text{Å}^3$)	1.47, -2.74

Note: $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$; $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$; $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$, 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.

TABLE 2. COORDINATES AND DISPLACEMENT PARAMETERS OF ATOMS IN PARAGEORGBOKIITE

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃	
Cu1	0.52244(10)	0.20949(7)	0.38388(4)	0.0136(1)	0.0163(3)	0.0145(3)	0.0108(2)	-0.0029(2)	0.0044(2)	-0.0039(2)
Cu2	0	½	½	0.0126(2)	0.0096(3)	0.0174(4)	0.0107(3)	-0.0010(3)	0.0020(3)	-0.0025(3)
Cu3	0.47613(10)	0.57640(6)	0.38012(4)	0.0116(1)	0.0128(2)	0.0133(3)	0.0094(2)	0.0012(2)	0.0034(2)	0.00218(19)
Se	0.13167(8)	0.90880(5)	0.28438(4)	0.0108(1)	0.0117(2)	0.0123(2)	0.0090(2)	0.0003(1)	0.0033(2)	-0.00031(15)
Cl	0.7221(2)	0.8513(1)	0.47423(9)	0.0197(2)	0.0215(5)	0.0244(6)	0.0149(5)	-0.0016(4)	0.0076(4)	-0.0057(4)
O1	0.6724(5)	0.3980(3)	0.4729(2)	0.0108(6)	0.0102(13)	0.0138(14)	0.0088(12)	-0.0005(10)	0.0030(11)	-0.0010(11)
O2	0.3464(6)	0.0584(4)	0.2599(3)	0.0153(6)	0.0184(16)	0.0175(15)	0.0114(13)	-0.0045(11)	0.0063(12)	-0.0089(12)
O3	0.2846(6)	0.7324(4)	0.2511(2)	0.0135(6)	0.0171(15)	0.0125(14)	0.0114(13)	0.0047(11)	0.0035(12)	0.0051(11)
O4	-0.0834(6)	0.9311(4)	0.1590(3)	0.0151(6)	0.0119(14)	0.0221(17)	0.0118(13)	0.0051(12)	0.0036(12)	0.0006(12)

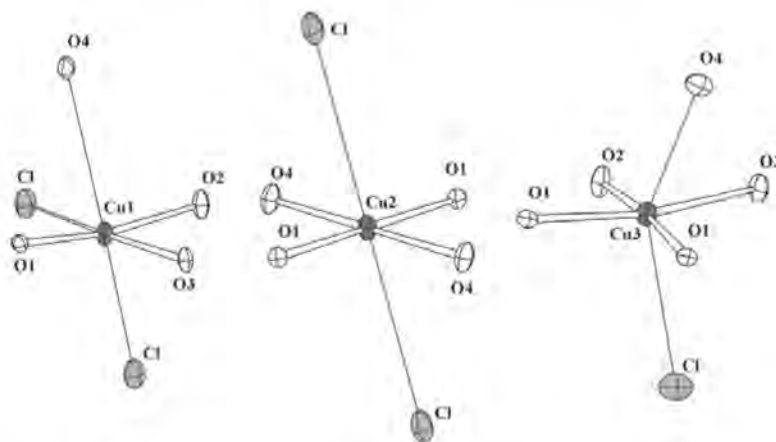
FIG. 1. The coordination of Cu²⁺ cations in the structure of parageorgbokiite. Ellipsoids are drawn at 50% probability level.

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

Cu1-O1	1.919(3)	Cu3-O1	1.945(3)
Cu1-O2	1.966(3)	Cu3-O2	1.961(3)
Cu1-O3	1.970(3)	Cu3-O3	1.975(3)
Cu1-Cl	2.268(1)	Cu3-O4	2.056(3)
Cu1-O4	2.944(3)	Cu3-Cl	2.399(3)
Cu1-Cl	3.185(1)	Cu3-Cl	2.704(1)
<Cu1-φ>	2.375	<Cu3-φ>	2.173
Cu2-O1	1.929(3) 2×	Se-O4	1.675(3)
Cu2-O4	1.974(3) 2×	Se-O3	1.714(3)
Cu2-Cl	3.194(1) 2×	Se-O2	1.724(3)
<Cu2-φ>	2.366	<Se-O>	1.704

φ: O, Cl

valence of the Cu2–Cl bond is rather low (0.04 valence units, *vu*), but the positions of the Cl atoms above and below the Cu₂O₄ square are likely to be essential for the stabilization of the Cu₂O₄Cl₂ polyhedron. The Cu3 site is coordinated by four O atoms that form a Cu₃O₄ square. The square is further coordinated by one O and one Cl atom (Fig. 1).

There is one symmetrically independent Se⁴⁺ cation in the structure; it is coordinated by three O atoms, forming SeO₃ trigonal pyramids, an arrangement that is typical of the structures of selenites (Hawthorne *et al.* 1987).

Description of the structure

Projections of the structure of parageorgbokiite in Cu-centered coordination polyhedra are shown

in Figure 2. The $\text{Cu1}\phi_6$ and $\text{Cu1}\phi_6$ octahedra share edges to form sheets parallel to (100). The $\text{Cu2}\phi_6$ octahedra share faces with two $\text{Cu1}\phi_6$ octahedra of the adjacent sheets, which results in the formation of a three-dimensional framework of octahedra. The SeO_3 trigonal bipyramids share corners with the Cu-centered octahedra.

However, as in the case of georgbokiite (Krivovichev *et al.* 1999a), the structure of parageorgbokiite is best described in terms of arrangements of the strong $M\text{--O}$ bonds ($M = \text{Se}^{4+}$ and Cu^{2+}). We note that the O1 atom is not bonded to Se^{4+} cations and thus is not a part of the SeO_3 group. This atom is tetrahedrally coordinated by four Cu^{2+} cations, resulting in the formation of oxocentered O1Cu_4 tetrahedra. Two O1Cu_4 tetrahedra share the $\text{Cu3}\dots\text{Cu3}$ edge to form a O_2Cu_6 dimer. It is interesting that such dimers are present in the structures of two other fumarolic minerals, euchlorine, $\text{NaKCu}_3\text{O}(\text{SO}_4)_3$ (Scordari & Stasi 1990), and fedotovite, $\text{K}_2\text{Cu}_3\text{O}(\text{SO}_4)_3$ (Vergasova *et al.* 1988, Starova *et al.* 1991). The dimers are further linked by sharing the Cu2 corners to form O_2Cu_5 infinite chains parallel to the a axis (Fig. 3a). The SeO_3 pyramids are attached to the faces of the oxocentered tetrahedra in a "face-to-face" arrangement (Krivovichev *et al.* 1999b, Krivovichev & Filatov 2001) to form the complex $([\text{O}_2\text{Cu}_5][\text{SeO}_3]_2)^{2+}$ chain shown in Figure 3b. These complex metal oxoselenite chains are linked together to form a three-dimensional framework with channels occupied by Cl^- anions (Fig. 4b).

DISCUSSION

Parageorgbokiite is a dimorph of georgbokiite, $\text{Cu}_5\text{O}_2(\text{SeO}_3)_2\text{Cl}_2$. A comparison of the crystallographic parameters of the two minerals is given in Table 5. Both parageorgbokiite and georgbokiite have the same space-group, $P2_1/c$ (monoclinic), but differ in their unit-cell parameters. Moreover, structural studies of the two minerals have demonstrated that both are based upon the same complex $([\text{O}_2\text{Cu}_5][\text{SeO}_3]_2)^{2+}$ chains (= 1D modules), represented in Figure 3. However, the arrangements of the chains in the structures are different, as shown in Figure 4. In georgbokiite, $\alpha\text{-Cu}_5\text{O}_2(\text{SeO}_3)_2\text{Cl}_2$ (Fig. 4a), the chains are linked into layers that are parallel to (100), such that the structure has channels parallel to the c axis ($c = 5.579 \text{ \AA}$) that are occupied by the Cl^- anions. It is very likely that these

TABLE 4. BOND-VALENCE ANALYSIS (vii) FOR PARAGEORGBOKIITE

	Cl	O1	O2	O3	O4	Σ
Cu1	0.48, 0.04	0.52	0.46	0.46	0.03	1.99
Cu2	0.04 ^{2x}	0.51 ^{2x}			0.45 ^{2x}	2.00
Cu3	0.15	0.49, 0.45	0.47	0.36	0.14	2.06
Se			1.27	1.30	1.44	4.01
Σ	0.71	1.97	2.10	2.12	2.08	

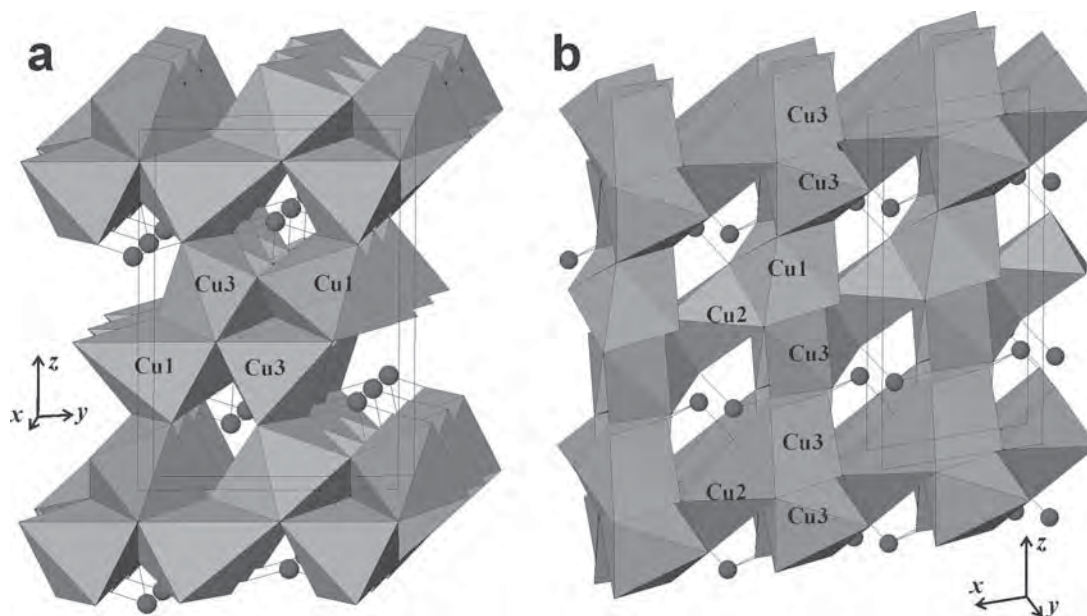


FIG. 2. The structure of parageorgbokiite shown in terms of Cu-centered octahedra approximately along the a (a) and b (b) axes. The Se^{4+} cations are shown as circles.

channels also accommodate lone-electron pairs on the Se^{4+} cations, as the apical vertices of the SeO_3 pyramids are oriented toward the Cl^- anions. The same situation is observed for parageorgbokiite (Fig. 4b). However, in this case, the arrangement of the 1D metal–oxygen modules is different. Thus, the two structures represent an interesting case of modular arrangements, similar to those that have received considerable attention in the mineralogical and crystallographic literature recently (Ferraris *et al.* 2004).

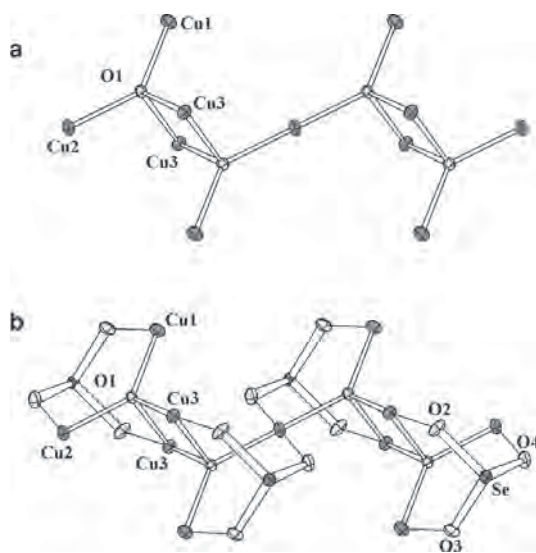


FIG. 3. The O_2Cu_5 chain of O1Cu_4 tetrahedra (a) and its coordination by SeO_3 groups (b) in the structure of parageorgbokiite.

It is noteworthy that the channels in parageorgbokiite are significantly larger than those in georgbokiite. This is apparent from the unit-cell volumes of the two minerals, 462.3(6) and 477.53(8) \AA^3 for the α and β modifications, respectively. Thus, the structure of parageorgbokiite is more open and of lower density than that of georgbokiite.

As the thermodynamic relationships between the two natural modifications of $\text{Cu}_5\text{O}_2(\text{SeO}_3)_2\text{Cl}_2$ are unknown, it is difficult to speculate on the stability of these compounds in Nature. However, from the lower density of parageorgbokiite in comparison to georgbokiite, one may conclude that parageorgbokiite is probably a high-temperature modification of $\text{Cu}_5\text{O}_2(\text{SeO}_3)_2\text{Cl}_2$ that is either chemically or kinetically stabilized at ambient conditions. This hypothesis is also supported by the much greater abundance of georgbokiite in comparison to parageorgbokiite.

TABLE 5. COMPARATIVE CHARACTERISTICS OF PARAGEORGBOKIITE AND GEORGBOKIITE

	Parageorgbokiite	Georgbokiite*
Chemical formula	$\beta\text{-Cu}_5\text{O}_2(\text{SeO}_3)_2\text{Cl}_2$	$\alpha\text{-Cu}_5\text{O}_2(\text{SeO}_3)_2\text{Cl}_2$
Space group	$P2_1/c$	$P2_1/c$
a , \AA	5.3982(5)	6.045(2)
b , \AA	8.0543(8)	13.778(2)
c , \AA	11.128(1)	5.579(5)
β , $^\circ$	99.258(2)	95.76(4)
V , \AA^3	477.53(8)	462.3(6)
Z	2	2
D_x , g/cm^3	4.84	4.70
Color	Brown	Green

* Vergasova *et al.* (1999a).

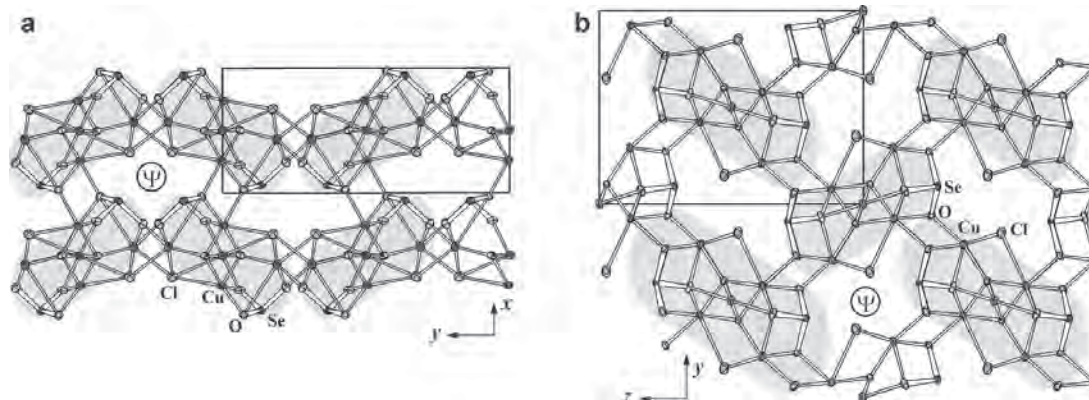


FIG. 4. The structures of georgbokiite (a) and parageorgbokiite (b) projected along the extension of the O_2Cu_5 chains (high-lighted). The location of channels occupied by the Cl^- anions and the lone pairs of electrons of the Se^{4+} cations is indicated by the symbol Ψ .

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