
Revision 1

Prewittite, $\text{KPb}_{1.5}\text{Cu}_6\text{Zn}(\text{SeO}_3)_2\text{O}_2\text{Cl}_{10}$, a new mineral from Tolbachik fumaroles, Kamchatka peninsula, Russia: description and crystal structure

Running title: Prewittite, $\text{KPb}_{1.5}\text{Cu}_6\text{Zn}(\text{SeO}_3)_2\text{O}_2\text{Cl}_{10}$, a new mineral

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Abstract

Prewittite, ideally $\text{K}_{0.53}\text{Pb}_{1.33}\text{Cu}_{5.87}\text{Zn}_{1.38}\text{Se}_{1.99}\text{O}_{7.67}\text{Cl}_{10.33}$, was found in the fumarole field of the Second cinder cone of the North Breach of the Great fissure Tolbachik eruption (1975-1976, Kamchatka peninsula, Russia). It occurs as separate olive-green tabular crystals up to 0.2 mm in maximum dimension. It has vitreous luster and brownish-green streak. Prewittite is orthorhombic, space group $Pn\bar{m}$, $a = 9.132(2)$, $b = 19.415(4)$, $c = 13.213(3)$ Å, $V = 2342.6(9)$ Å³, $Z = 4$, $D_{\text{calc}} = 3.89$ g/cm³, $D_{\text{meas}} = 3.90(2)$ g/cm³. The eight strongest lines of the powder X-ray diffraction pattern are [I (d (Å)) hkl]: 70 (8.26) 110; 60 (7.53) 101; 90 (4.111) 220, 132, 141; 100 (3.660) 212, 123; 40 (2.996) 223; 50 (2.887) 062; 40 (2.642) 322, 214; 40 (2.336) 073, 180, 244. Prewittite is biaxial (-). The optical orientation is $X = a$, $Y = c$, $Z = b$. The mineral has clear pleochroism: X , Y – olive green, Z – red-brown. The mineral is very brittle with the perfect cleavage on (010) and (101). The most developed crystal forms are {010}, {001} and {101}. The chemical composition determined by the electron-microprobe is (wt. %): K₂O 1.76, PbO 21.18, CuO 33.24, ZnO 8.00, SeO₂ 15.74, Cl 26.06, O = Cl – 5.88, total 100.10. The empirical formula derived on the basis of O + Cl = 18 and sum of positive charges of cations equal to 26 is $\text{K}_{0.53}\text{Pb}_{1.33}\text{Cu}_{5.87}\text{Zn}_{1.38}\text{Se}_{1.99}\text{O}_{7.67}\text{Cl}_{10.33}$. The crystal structure was solved by direct methods and refined to an agreement index $R1 = 0.034$ on the basis of 1522 independent reflections with $I \geq 2\sigma_I$. It is based upon metal oxide selenite chloride layers parallel to (010) and linked through K-Cl and Pb-Cl bonds to the K and Pb atoms located in the interlayer. The mineral name honors Professor Charles T. Prewitt (b. 1933) in recognition of his important contributions to crystal chemistry of minerals and planetary materials.

Keywords: prewittite, new mineral, crystal structure, copper selenite chloride, fumaroles, Tolbachik volcano, Kamchatka peninsula, Russia.

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Abstract

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48 Introduction

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50 The Great fissure Tolbachik eruption (GFTE) that occurred in 1975-76 in Kamchatka
51 peninsula, Russia (Fedotov 1984), was followed by exceptional fumarolic activity and formation of
52 unique assemblages of anhydrous mineral species. More than 30 new minerals have been discovered
53 at this locality so far. One of the most interesting and structurally complex group of Tolbachik
54 minerals are copper and zinc selenite chlorides. Seven minerals of this group have been first
55 described and known from Tolbachik only: sophiite, $\text{Zn}_2(\text{SeO}_3)\text{Cl}_2$ (Vergasova et al. 1989), ilinskite,
56 $\text{NaCu}_5(\text{SeO}_3)_2\text{O}_2\text{Cl}_3$ (Vergasova et al. 1997), chloromenite, $\text{Cu}_9(\text{SeO}_3)_4\text{O}_2\text{Cl}_6$ (Vergasova et al.
57 1999a), georgbokiite, $\alpha\text{-Cu}_5(\text{SeO}_3)_2\text{O}_2\text{Cl}_2$ (Vergasova et al. 1999b), burnsite, $\text{KCdCu}_7(\text{SeO}_3)_2\text{O}_2\text{Cl}_9$
58 (Krivovichev et al. 2002), parageorgbokiite, $\beta\text{-Cu}_5(\text{SeO}_3)_2\text{O}_2\text{Cl}_2$ (Vergasova et al. 2006), and
59 allochalcoseelite, $\text{Cu}^+\text{Cu}^{2+}_5\text{PbO}_2(\text{SeO}_3)_2\text{Cl}_5$ (Vergasova et al. 2005). In 1983, another complex copper
60 selenite chloride, ideally $\text{KPb}_{1.5}\text{Cu}_6\text{Zn}(\text{SeO}_3)_2\text{O}_2\text{Cl}_{10}$ was discovered in the Tolbachik fumaroles and
61 named prewittite, in honor of Professor Charles T. Prewitt (b. 1933), in recognition of his important
62 contributions to to crystal chemistry of minerals and planetary materials. The mineral was approved
63 by the Commission on New Minerals and Mineral Names of the International Mineralogical
64 Association (2002-041). Type material is deposited at the Mining Museum, St. Petersburg Mining
65 Institute, St. Petersburg, Russia (specimen No. 29/2002). According to its chemical composition,
66 single crystal and powder X-ray diffraction data prewittite has no close analogues among known
67 minerals and inorganic compounds. In this paper, we report on its occurrence, physical properties,
68 and crystal structure.

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70 Locality and occurrence

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72 Prewittite was found in the fumarole 'Melanotallitovaya' (the name reflects abundance of

73 melanothallite, Cu_2OCl_2) on the Second cinder cone of the Northern Breach of the GFTE. The
74 fumarole situated at the bottom of an open fracture approximately 1 meter in width, with vertical
75 walls from 1 to 2 meters high. The fumarole walls consisted of magnesian basalt pyroclastic
76 material. The maximum temperature in the fumarole could have been more than 400 °C based on the
77 occurrence of spherical aggregates of flattened tenorite crystals (Filatov and Vergasova 1983).
78 Prewittite was found in close association with melanothallite, Cu_2OCl_2 (Vergasova and Filatov
79 1982), chloromenite, sophiite, and an unidentified Zn,Cl-bearing mineral. The mineral occurs as
80 olive-green tabular crystals up to 0.2 mm in maximum dimension (Fig. 1). The crystals are elongated
81 along [100] and flattened on (010). Three crystals of prewittite were measured using 2-circle
82 Goldschmidt goniometer. They have approximately the same habit with the well-developed forms
83 {010}, {001}, {101} and less-developed {011} - (Fig. 2). The axial ratio $a : b : c = 0.483 : 1 : 0.711$
84 derived from crystal morphology is close to the ratio 0.470 : 1 : 0.681 calculated on the basis of X-
85 ray diffraction data.

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87 Chemical composition

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89 The chemical composition of prewittite was studied on three grains by means of the
90 CamScan 4DV electron microprobe instrument operated at 30 kV and 10 nA with a Link AN-10000
91 energy-dispersive detector. The following average chemical composition was obtained from 10
92 analyses (wt% (min-max; standard deviation)): K_2O 1.76 (1.53-1.99; 0.15), PbO 21.18 (20.41-21.94;
93 0.51), CuO 33.24 (32.60-33.87; 0.42), ZnO 8.00 (7.93-8.08; 0.05), SeO_2 15.74 (15.58-15.91; 0.11),
94 Cl 26.06 (24.96-27.16; 0.74), $\text{O} = \text{Cl} - 5.88$, total 100.10 wt%. The following standards were used:
95 sanidine (K); galena (Pb); pure elements (Cu, Zn and Se); synthetic chlorapatite (Cl). The empirical
96 formula calculated on the basis of $\text{O} + \text{Cl} = 18$ and the sum of positive charges of cations equal to
97 26, is $\text{K}_{0.53}\text{Pb}_{1.33}\text{Cu}_{5.87}\text{Zn}_{1.38}\text{Se}_{1.99}\text{O}_{7.67}\text{Cl}_{10.33}$, which is in general agreement with the results of

98 crystal-structure analysis (see below). The idealized chemical formula can be written as
99 $\text{KPb}_{1.5}\text{Cu}_6\text{Zn}(\text{SeO}_3)_2\text{O}_2\text{Cl}_{10}$, which requires the following ideal composition: K_2O 3.28, PbO 23.30,
100 CuO 33.21, ZnO 5.66, SeO_2 15.44, Cl 24.67, $\text{O} = \text{Cl} - 5.56$, total 100 wt%.

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102 Physical and optical properties

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104 Prewittite is olive-green and transparent. It has vitreous luster and brownish-green streak.
105 The mineral grains are very brittle and have perfect cleavage along $\{010\}$ and $\{101\}$. Hardness of
106 prewittite was not measured, because under even small VHN loads, the crystals tested were
107 completely destroyed. Density, measured using Clerici solution, is $3.90(1) \text{ g/cm}^3$. It is slightly higher
108 than the density of 3.844 g/cm^3 calculated on the basis of empirical chemical formula.

109 Prewittite is biaxial negative, $X = a$, $Y = c$, $Z = b$. The pleochroism is clear: X , Y – olive-
110 green, Z – red-brown. Refraction indices were not measured because of the rapid decomposition of
111 the mineral upon contact with the immersion liquids. An average refractive index of 1.81 was
112 calculated using Gladstone-Dale relationship (Mandarino 1981) according to the empirical formula
113 $\text{K}_{0.53}\text{Pb}_{1.33}\text{Cu}_{5.87}\text{Zn}_{1.38}\text{Se}_{1.99}\text{O}_{7.67}\text{Cl}_{10.33}$ and calculated density.

114 In order to exclude the possibility of the NH_4^+ ion to accommodate into the structure of
115 prewittite (ammonium is a typical constituent of some fumarolic minerals (Demartin et al. 2009,
116 2010a, b)), infrared spectra for the two crystals of prewittite were measured on the Bruker Vertex 70
117 FTIR spectrometer using the MIRacle ATR attachment with a Ge crystal and a pressure clamp in the
118 region $650\text{-}1500 \text{ cm}^{-1}$. An extended ATR correction was applied using the OPUS v. 6.5 software.
119 The obtained spectrum was of rather poor quality, but bands typical for selenite groups were
120 observed in the region $700\text{-}800 \text{ cm}^{-1}$. At the same time, the strong band at $\sim 1400 \text{ cm}^{-1}$ typical for the
121 NH_4^+ ions was not registered, which points out to the absence of any detectable amounts of
122 ammonium in prewittite.

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Powder X-ray diffraction data

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Weissenberg techniques and $\text{CuK}\alpha$ radiation were used to establish that prewittite has

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orthorhombic symmetry and two possible space groups, $Pnn2$ and $Pnmm$, according to the reflection

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conditions $h0l: h + l = 2n$ and $0kl: k + l = 2n$. The unit cell parameters derived from the single crystal

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structure refinement are: $a = 9.132(2)$, $b = 19.415(4)$, $c = 13.213(3)$ Å, $V = 2342.6(9)$ Å³.

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Powder X-ray diffraction data were collected using a Debye-Scherrer powder camera ($D =$

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114.6 mm) and $\text{CuK}\alpha$ radiation (Table 1). Because of the small amount of the material, the sample

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was prepared as a sphere (~ 0.1 mm in diameter) from a mixture of natural resin and mineral powder

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with Ge as an internal standard. The unit cell parameters refined from the powder data are: $a =$

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$9.142(6)$, $b = 19.40(2)$, $c = 13.200(9)$ Å, $V = 2341(6)$ Å³, and are in good agreement with those

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determined from the structure refinement.

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Crystal structure

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Experimental

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Single-crystal X-ray diffraction data for prewittite were collected using a four-circle single

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crystal diffractometer Syntex P2₁. Crystallographic positions of Pb atoms were determined by direct

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methods using SIR-97 (Altomare et al. 1997). Positions of other atoms were located by inspection of

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difference Fourier electron density maps. The final refinement of the crystal structure was performed

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using SHELXL-97 (Sheldrick 2008) in the space group $Pnmm$ to an agreement index $R1 = 0.034$

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using 1522 independent reflections with $I \geq 2\sigma_I$. The occupancy factor of the Pb1 site was refined

148 using the Pb scattering curve and then re-calculate for the mixed Pb-K occupancy. Details on the X-
149 ray data collection are given in Table 2, fractional atomic coordinates and displacement parameters
150 are given in Table 3, selected interatomic distances and bond angles are given in Table 5.

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152 Cation coordination

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154 The structure of prewittite contains five symmetrically independent Cu sites (Fig. 3). The
155 Cu1 and Cu2 atoms have square pyramidal coordination consisting of four equatorial ligands (2O +
156 2Cl in *cis*-configuration). It is noteworthy that the Cu1 site has a low occupancy (s.o.f. = 0.15) and is
157 located 1.038 Å apart from the Pb2 site (s.o.f. = 0.85). Other Cu sites have Jahn-Teller-distorted
158 octahedral coordination with different ligands: the Cu3 site has coordination [4O+2Cl], whereas the
159 Cu4 and Cu5 sites have coordination [(3O+Cl)+2Cl]. All types of Cu coordination have been
160 previously observed in minerals and inorganic compounds. The square-pyramidal [(2O+2Cl)-*cis*+Cl]
161 coordination has been observed for the Cu2 site in K₂Cu₅Cl₈(OH)₄(H₂O)₂ (Kahlenberg 2004).
162 Octahedral [(3O+Cl)+2Cl] coordination can be found in the same structure for the Cu3 site and in
163 the structure of belloite, Cu(OH)Cl (Effenberger 1984). The [4O+2Cl] octahedra are the most
164 common mixed-ligand Cu-O-Cl coordination polyhedron in copper oxysalt chlorides and was
165 observed, e.g. in atacamite and clinoatacamite, Cu₂(OH)₃Cl (Parise and Hyde 1986; Malcherek and
166 Schlueter 2009), chloroxiphite, Pb₃CuO₂(OH)₂Cl₂ (Siidra et al. 2008), leningradite, PbCu₃(VO₄)₂Cl₂
167 (Siidra et al. 2007), etc.

168 There are two Pb sites in the structure of prewittite. The Pb1 site is occupied by Pb and K and
169 has the site occupancy Pb_{0.60}K_{0.40}. It has symmetrical octahedral coordination to six Cl⁻ anions (Fig.
170 3). The coordination of the Pb2 site is strongly asymmetrical with two strong Pb2-O1 and four Pb2-
171 Cl bonds located in one hemisphere. This type of coordination is typical for Pb²⁺ cations in Pb

172 oxychlorides and is usually explained in terms of stereoactive behaviour of the $6s^2$ lone electron pair
173 (Krivovichev and Burns 2001, 2002).

174 The structure contains one low-occupied K1 site with trigonal prismatic coordination to six
175 Cl^- anions. This site cannot have more than 50%-occupancy, since the adjacent equivalent K1 site is
176 2.814 Å apart. There is one Zn site tetrahedrally coordinated by four Cl^- anions. Taking into account
177 the results of the chemical analyses given above (the amount of Zn is 1.38 per formula unit), it is
178 very likely that Zn also enters other cation sites, presumably the Pb1 site with octahedral
179 coordination (see below). The Se^{4+} cation has a trigonal pyramidal coordination, typical for selenites.

180 Bond-valence sums for atom sites in the structure of prewittite are given in Table 3. In
181 general, they are in agreement with the expected oxidation states, except that for Cu1 (1.44 v.u.),
182 which is much lower than the expected value of 2.0. However, this site is only 15%-occupied and its
183 coordination and bond-valence characteristics cannot be evaluated properly.

184

185 Structure description

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187 The structure of prewittite is shown in Figure 4. It is based upon well-defined metal-oxide
188 layers parallel to (010), in good agreement with the perfect cleavage observed for the same direction.
189 The layers are comprised of Cu^{2+} cations, SeO_3^{2-} pyramids, and O1 and Pb2 atoms and are
190 surrounded by Cl^- anions. The K and Pb1 atoms are located in between the layers, providing three-
191 dimensional integrity of the structure.

192 The topological structure of the metal-oxide-chloride layers is rather complex and can be
193 described using a simplified model based upon separation of O1-centered polyhedral building blocks
194 (Fig. 5a). The $\text{Pb}_2\text{O}_2\text{Cl}_4$ polyhedra, and $\text{Cu}_3\text{O}_4\text{Cl}_2$, $\text{Cu}_4\text{O}_3\text{Cl}_3$, and $\text{Cu}_5\text{O}_3\text{Cl}_3$ octahedra share a
195 common Cl-O1 edges to form octahedral tetramers. In the tetramers, O1 atom is common to all four
196 coordination polyhedra, and the Cu/Pb-O1 bonds are the shortest and the strongest metal-oxygen

197 bonds in the structure. The O1 atom is central for OCu_3Pb tetrahedron or OCu_4 tetrahedron, taking
198 into account the observed Pb2-Cu1 disorder. Two adjacent OCu_3Pb tetrahedra share common Cu-Pb
199 edge to form a tetrahedral $[\text{O}_2\text{Cu}_5\text{Pb}]$ dimer shown in Figure 5b. The SeO_3 groups are attached to the
200 Cu-Cu-Cu triangular faces of the OCu_3Pb tetrahedra in a ‘face-to-face’ fashion (Krivovichev et al.
201 1999; Krivovichev and Filatov 1999) to form $[\text{OCu}_3\text{Pb}](\text{SeO}_3)_2$ clusters shown in Figure 5c.

202 The structure the complex metal oxide chloride layers can be described as built in the
203 sequence of steps presented in Figure 6. First, the $[\text{O}_2\text{Cu}_5\text{Pb}]$ dimers are arranged parallel to each
204 other within the (010) plane (Fig. 6a). Attachment of the SeO_3 pyramids and additional Cu2 sites
205 results in the porous metal-oxide sheet shown in Figure 6b. Surrounding the sheet by the Cl^- anions
206 complements the construction (Fig. 6c). The Zn^{2+} atoms are located in the pores of the metal-oxide-
207 chloride structure, and the resulting layers are linked together by the K^+ and Pb^{2+} cations.

208

209 Crystal-chemical formula

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211 According to the crystal-structure refinement, the crystal-chemical formula of prewittite can
212 be written as $(\square_{0.77}\text{K}_{0.22})(\text{Pb}_{0.60}\text{K}_{0.40})[(\text{Pb}_{0.85}\text{Cu}_{0.15})]\text{Cu}_6\text{Zn}(\text{SeO}_3)_2\text{O}_2\text{Cl}_{10}$ ($Z = 4$) or
213 $\text{K}_{0.62}\text{Pb}_{1.45}\text{Cu}_{6.15}\text{ZnSe}_2\text{O}_8\text{Cl}_{10}$ with the positive charge deficiency of 0.18. This formula is in general
214 agreement with the results of microprobe analysis, which also shows the slight excess of Zn (1.38
215 against the ideal value of 1.00). We suggest that some amount of Zn is present in the K1 and Pb1
216 sites, thus compensating for the observed charge deficiency. The idealized chemical formula for
217 prewittite is $\text{KPb}_{1.5}\text{Cu}_6\text{Zn}(\text{SeO}_3)_2\text{O}_2\text{Cl}_{10}$ ($Z = 2$) or $\text{K}_2\text{Pb}_3\text{Cu}_{12}\text{Zn}_2(\text{SeO}_3)_4\text{O}_4\text{Cl}_{20}$ ($Z = 4$). It is
218 achieved when the K1, Pb1, and Pb2 sites have the occupancies equal to $\text{K}_{0.50}$, $\text{Pb}_{0.50}\text{K}_{0.50}$, and
219 $\text{Pb}_{1.00}$, respectively.

220

221

Discussion

222

223 Prewittite is yet another complex copper oxide selenite chloride from the Tolbachik
224 fumaroles. This group of minerals have no analogues among known mineral species, except
225 francisite, $\text{Cu}_3\text{Bi}(\text{SeO}_3)_2\text{O}_2\text{Cl}$ (Pring et al. 1990). However, there are many synthetic copper oxide
226 selenite chlorides prepared using chemical transport reactions that involve transport of gases under
227 continuous temperature gradient in a reaction vessel (evacuated glass or quartz ampules) (Berrigan
228 and Gatehouse, 1996; Millet et al. 2000, 2001; Krivovichev et al. 2004; Becker et al. 2007;
229 Berdonosov et al. 2009; Zhang et al. 2010). Filatov et al. (1992) proposed that polynuclear
230 complexes similar to those shown in Figure 5 may play the role of clusters stable in the gaseous
231 phase and able to be transported by the gas flow. Indeed, tetrahedral dimers similar to the one
232 depicted in Figure 5b and surrounded by sulfate groups have been observed in the structures of
233 fumarolic minerals fedotovite, $\text{K}_2\text{Cu}_3\text{O}(\text{SO}_4)_3$ (Starova et al. 1991), and euchlorine, $\text{KNaCu}_3\text{O}(\text{SO}_4)_3$
234 (Scordari and Stasi 1990). The $[\text{O}_2\text{Cu}_6]$ dimers of edge-sharing OCu_4 tetrahedra are also present in
235 the structures of two $\text{Cu}_4\text{O}(\text{SeO}_3)_3$ polymorphs prepared by Effenberger and Pertlik (1986) using
236 chemical transport reactions. These observations provide additional evidences that oxocentered
237 tetrahedral groups may indeed be formed and transported by volcanic gases in fumaroles.

238

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- 351

352 **Table 1.** Powder X-ray diffraction pattern for prewittite*

I_{meas}	d_{meas} (Å)	hkl	I_{calc}	d_{calc} (Å)
70	8.26	110	42	8.26
60	7.53	101	100	7.50
30	7.02	111	67	7.00
<10	5.749	031	36	5.811
10	5.483	022	7	5.458
<10	4.924	131	5	4.902
90	4.111	220	8	4.132
		132	19	4.123
		141	8	4.076
10	3.905	103	11	3.964
100	3.660	212	17	3.687
		123	15	3.670
10	3.189	241	2	3.225
20	3.113	213	17	3.127
		024	9	3.124
40	2.996	223	57	3.012
50	2.887	062	32	2.905
<10	2.692	071	14	2.714
		252	6	2.699
40	2.642	322	21	2.658
		214	9	2.650
<10	2.572	340	5	2.579
		224	2	2.578
30	2.466	313	36	2.483
		234	8	2.472
<10	2.390	342	7	2.402
		350	2	2.396
40	2.336	073	14	2.346
		180	2	2.346
		244	5	2.342
10	2.271	410	4	2.267
<10	2.197	006	16	2.200
<10	2.149	412	3	2.144
		280	2	2.143
		116	11	2.126
30	2.079	245	6	2.068
		440	7	2.066
		264	4	2.062
<10	2.021	371	3	2.026
10	1.932	093	2	1.937
		433	8	1.934
20	1.861	292	13	1.870
		443	2	1.870
		414	2	1.869
<10	1.796	037	3	1.810
		501	7	1.809
10	1.5176	620	4	1.5036
		505	5	1.5020
<10	1.4955	563	5	1.4958
20	1.3429	653	4	1.3488
		662	4	1.3482
10	1.3160	319	7	1.3182

353 * the experimental errors for the d-spacings are 0.02 Å for the
354 low-angle and 0.03 Å for the high-angle values.

Table 2. Crystal data, data collection and structure refinement

Crystal data	
Temperature	293 K
Radiation, wavelength	MoK α , 0.71073 Å
Crystal system	orthorhombic
Space group	<i>Pnmm</i>
Unit-cell dimensions <i>a</i> , <i>b</i> , <i>c</i> (Å)	9.132(2), 19.415(4), 13.213(3)
Unit-cell volume (Å ³)	2342.6(9)
<i>Z</i>	4
Calculated density (g/cm ³)	3.889
Absorption coefficient (mm ⁻¹)	20.53
Crystal size (mm ³)	0.22×0.14×0.05
Data collection	
θ range	1.86 – 34.94°
<i>h</i> , <i>k</i> , <i>l</i> ranges	0 → 14, 0 → 30, 0 → 21
Total reflections collected	4352
Unique reflections (R_{int})	1695 (0.043)
Unique reflections $F > 4\sigma(F)$	1522
Structure refinement	
Refinement method	Full-matrix least-squares on F^2
Weighting coefficients <i>a</i> , <i>b</i>	0.0317, 5.4632
Extinction coefficient	0.00004(5)
Data/restraints/parameters	1522/0/161
R_1 [$F > 4\sigma(F)$], wR_2 [$F > 4\sigma(F)$],	0.034, 0.073
R_1 all, wR_2 all	0.039, 0.078
Goodness-of-fit on F^2	1.108
Largest diff. peak and hole, e Å ⁻³	0.850, -1.080

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Table 3. Fractional atomic coordinates, bond-valence sums* (BVS, v.u. = valence units), site occupation factors (s.o.f.), and anisotropic displacement parameters (10^{-4} \AA^2) for prewittite

Atom	BVS	x	y	z	s.o.f.	U_{eq}	U_{11}	U_{22}	U_{33}	U_{13}	U_{23}	U_{12}
Se	4.20	0.4124(1)	0.34134(5)	0.22085(7)	Se	275(2)	306(5)	266(4)	253(4)	26(5)	-7(4)	13(5)
K1	0.90	0.3982(23)	0.4456(9)	½	$K_{0.22(1)}$	497(63)	514(126)	516(106)	462(107)	0	0	-69(105)
Pb1	2.34	½	0	0.3409(1)	$Pb_{0.60(4)}K_{0.40(4)}$	673(9)	979(14)	431(9)	609(11)	0	0	-106(7)
Pb2	2.24	0.4046(1)	0.09061(5)	0	$Pb_{0.85(4)}$	435(3)	497(6)	413(5)	395(5)	0	0	-2(5)
Cu1	1.44	0.3302(18)	0.1310(7)	0	$Cu_{0.15(4)}$	449(54)	529(105)	333(80)	484(85)	0	0	17(72)
Cu2	2.04	0.4242(3)	0.4248(1)	0	Cu	413(6)	626(16)	316(9)	297(10)	0	0	117(10)
Cu3	2.02	0.4174(2)	0.26232(9)	0	Cu	308(4)	345(11)	320(9)	257(8)	0	0	-16(10)
Cu4	2.04	0.0824(2)	0.30985(6)	0.3150(1)	Cu	332(3)	351(8)	283(6)	360(7)	-73(7)	-37(6)	22(7)
Cu5	1.99	0.2302(2)	0.19533(7)	0.1792(1)	Cu	312(3)	308(7)	314(6)	314(7)	-76(6)	17(6)	20(6)
Zn	1.95	0.3971(2)	0.1928(1)	½	Zn	377(4)	334(11)	388(10)	408(10)	0	0	-8(10)
Cl1	0.90	0	0	0.3768(3)	Cl	508(12)	692(35)	396(21)	435(25)	0	0	104(23)
Cl2	0.74	0.2211(5)	0.2788(2)	½	Cl	429(10)	412(26)	458(24)	418(24)	0	0	77(21)
Cl3	0.83	0.1114(5)	0.2487(2)	0	Cl	408(10)	401(27)	450(22)	374(20)	0	0	-43(21)
Cl4	1.42	0.1611(6)	0.4495(3)	0	Cl	584(13)	489(30)	620(31)	643(32)	0	0	-69(26)
Cl5	0.77	0.1694(4)	0.0842(2)	0.1376(2)	Cl	455(8)	514(20)	400(16)	451(17)	-16(16)	-9(14)	20(14)
Cl6	1.01	0.3606(4)	0.1341(2)	0.3546(2)	Cl	495(8)	591(22)	478(17)	416(16)	-72(16)	-29(14)	24(15)
Cl7	1.14	0.1374(4)	0.4223(1)	0.3357(2)	Cl	433(7)	465(18)	369(14)	463(17)	-13(15)	-26(14)	28(12)
O1	1.97	0.4120(8)	0.1911(3)	0.1050(5)	O	309(15)	361(39)	268(31)	299(34)	-4(40)	-59(29)	9(38)
O2	2.33	0.0444(8)	0.2145(4)	0.2555(5)	O	320(18)	355(42)	325(38)	281(38)	-36(34)	-29(33)	43(31)
O3	2.18	0.2608(8)	0.2910(3)	0.2330(6)	O	314(17)	264(40)	254(36)	422(45)	-44(36)	-21(33)	22(30)
O4	2.18	0.4242(9)	0.3431(4)	0.0919(6)	O	354(17)	411(48)	309(34)	342(37)	4(40)	15(32)	-1(37)

362

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* calculated using bond-valence parameters from Krivovichev and Brown (2001) for the Pb^{2+} -O bonds and Brese and O'Keeffe (1991) for other bonds

364
365

Table 4. Selected interatomic distances (Å) in the crystal structure of prewittite

Se-O2	1.651(7)	Cu3-O1	1.960(7) 2x
Se-O3	1.702(7)	Cu3-O4	1.985(7) 2x
Se-O4	1.708(7)	Cu3-Cl3	2.807(5)
<Se-O>	1.687	Cu3-Cl2	2.885(5)
K1-Cl5	3.13(2) 2x	Cu4-O1	1.881(8)
K1-Cl7	3.25(2) 2x	Cu4-O3	1.990(7)
K1-Cl5	3.31(2) 2x	Cu4-O2	2.041(7)
<K1-Cl>	3.23	Cu4-Cl7	2.257(3)
		Cu4-Cl2	2.818(3)
Pb1-Cl4	2.747(4) 2x	Cu4-Cl6	3.211(4)
Pb1-Cl6	2.904(3) 2x		
Pb1-Cl7	3.049(4) 2x	Cu5-O1	1.930(8)
<Pb1-Cl>	2.900	Cu5-O2	2.008(7)
		Cu5-O3	2.008(8)
Pb2-O1	2.395(6) 2x	Cu5-Cl5	2.295(3)
Pb2-Cl5	2.817(4) 2x	Cu5-Cl3	2.803(3)
Pb2-Cl7	3.048(3) 2x	Cu5-Cl6	2.863(4)
Cu1-O1	1.96(1) 2x	Zn-Cl6	2.259(3) 2x
Cu1-Cl5	2.51(1) 2x	Zn-Cl3	2.263(5)
Cu1-Cl3	3.04(1)	Zn-Cl2	2.318(5)
		<Zn-Cl>	2.275
Cu2-O4	1.998(7) 2x		
Cu2-Cl1	2.294(4) 2x	O1-Cu4	1.881(8)
Cu2-Cl4	2.450(6)	O1-Cu5	1.930(8)
		O1-Cu3	1.959(7)
		O1-Pb2	2.395(6)
		O1-Cu1	1.96(1)

366

367

368 Figure captions

369

370 **Figure 1.** SEM photos of crystals of prewittite.

371

372 **Figure 2.** Ideal prewittite crystal drawn on the basis of goniometric measurements: $b = \{010\}$, $c = \{001\}$,
373 $d = \{101\}$, $n = \{011\}$.

374

375 **Figure 3.** Coordination geometries of cation sites in the structure of prewittite. Legend: Pb = light-brown;
376 Cu = green; K = dark grey; Zn = light grey; O = red; Cl = blue. Displacement ellipsoids are drawn at 50%
377 probability level.

378

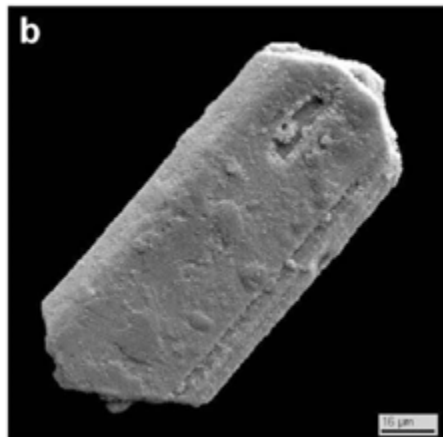
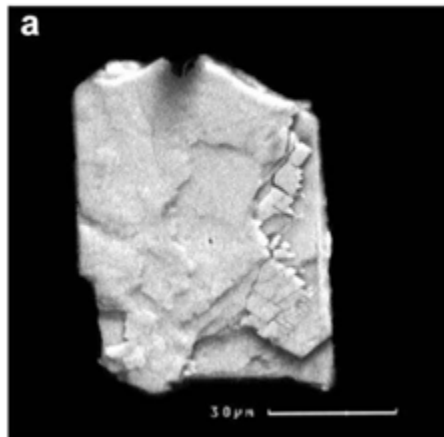
379 **Figure 4.** Crystal structure of prewittite with K-Cl, Zn-Cl and Pb-Cl bond omitted for clarity. Legend as in
380 Figure 3. Displacement ellipsoids are drawn at 50% probability level.

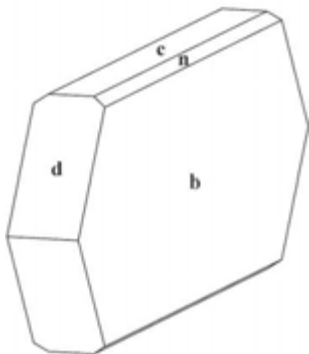
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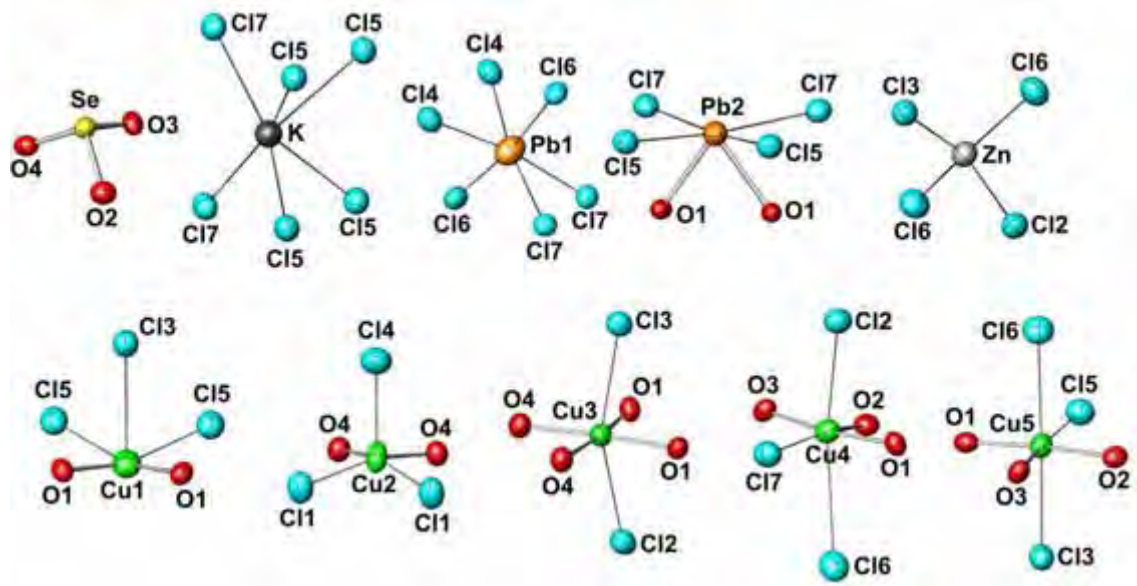
382 **Figure 5.** Fundamental building blocks in the structure of prewittite: (a) coordination environment of the
383 O1 atom consisting of four cation coordination polyhedra; (b) the $O_2Cu_5(Pb,Cu)$ dimer of two oxocentered
384 OM_4 tetrahedra ($M = Cu, Pb$) linked by sharing a common edge (note the Pb2-Cu1 disordered
385 configuration); (c) the O_2Cu_5Pb dimer surrounded by two SeO_3 groups. Legend as in Figure 3.
386 Displacement ellipsoids are drawn at 50% probability level.

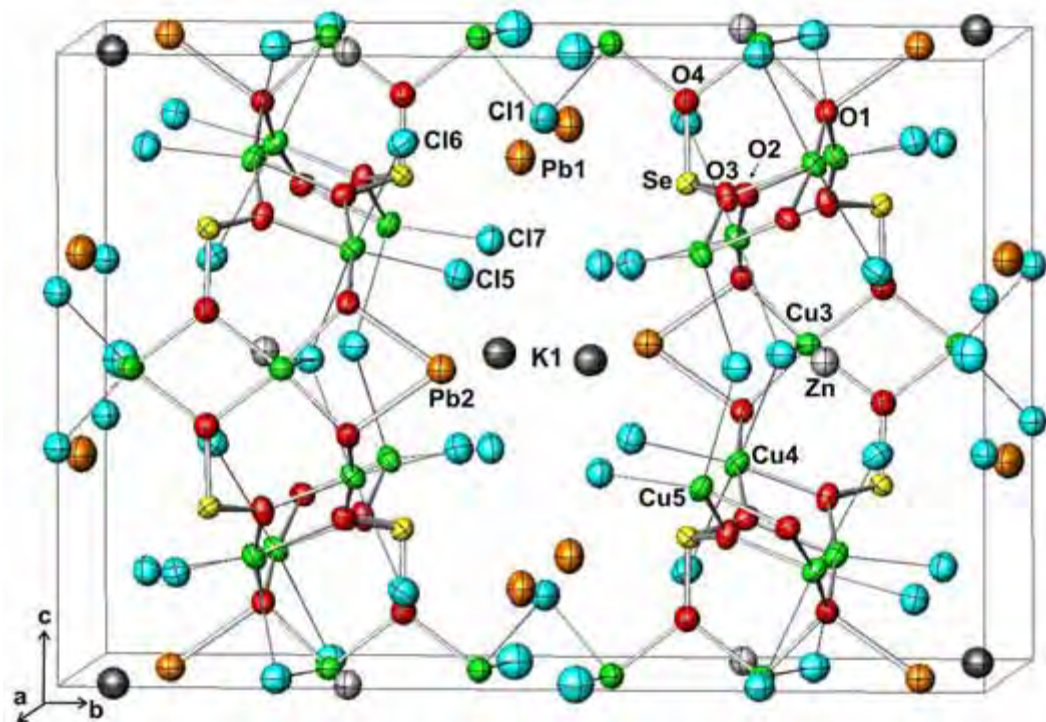
387

388 **Figure 6.** Step-by-step construction of the metal oxide selenite chloride layer in prewittite: (a) the
389 O_2Cu_5Pb dimers arranged within the (010) plane; (b) the O_2Cu_5Pb dimers surrounded and linked by SeO_3
390 groups and Cu2 atoms; (c) metal oxide selenite layer surrounded by Cl- anions. Legend as in Figure 3.
391 Displacement ellipsoids are drawn at 50% probability level.

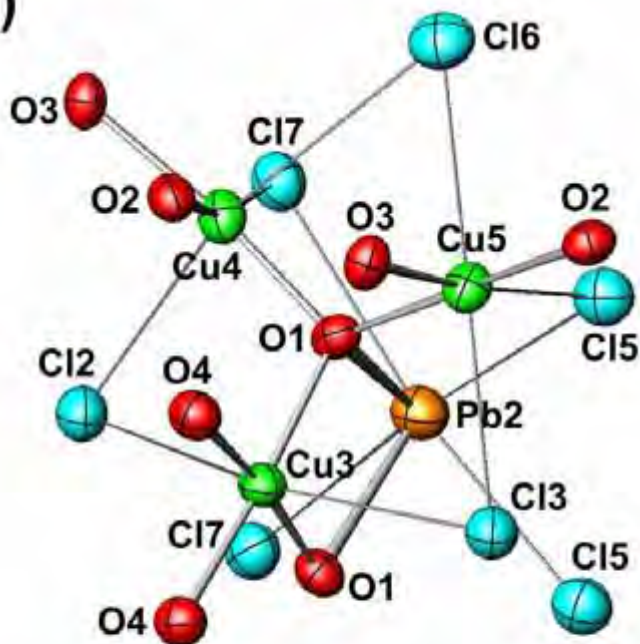




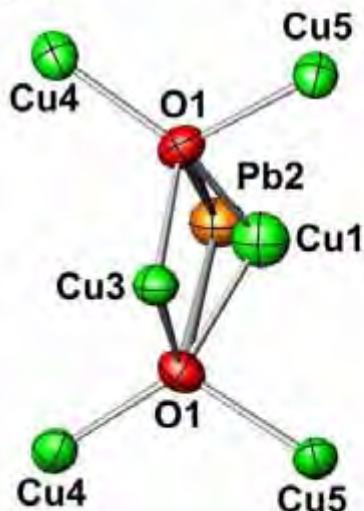




(a)



(b)



(c)

