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Quetzalcoatlite: A new octahedral-tetrahedral structure from a $2 \times 2 \times 40 \mu\text{m}^3$ crystal at the Advanced Photon Source-GSE-CARS Facility

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ABSTRACT

The structure of quetzalcoatlite, $\text{Zn}_6\text{Cu}_3(\text{TeO}_3)_2\text{O}_6(\text{OH})_6(\text{Ag}_x\text{Pb}_y)\text{Cl}_{x+y}$, $x + y \leq 2$, $Z = 1$, was solved and refined using data collected at the Advanced Photon Source-GSE-CARS facility, using a $2 \times 2 \times 40 \mu\text{m}^3$ single crystal. The structure is trigonal, space group $P\bar{3}1m$, $a = 10.145(1)$, $c = 4.9925(9)$ Å, $V = 445.0(1)$ Å³, and was refined to $R = 5.1$ for 395 unique observed reflections. Te^{6+}O_6 octahedra and Jahn-Teller distorted $\text{Cu}^{2+}\text{O}_4(\text{OH})_2$ octahedra share edges to form layers parallel to (001), and $\text{ZnO}_2(\text{OH})_2$ tetrahedra share vertices to form six-member rings parallel to (001). Layers of octahedra and tetrahedra alternate along c , and form a new framework structure by vertex sharing. Channels through the framework parallel to c are occupied by Ag, Pb, and Cl ions. Electron microprobe analysis revealed Ag and Cl overlooked in the original microchemical analysis. Up to one-third of the Ag was substituted by Pb, and a Pb-rich analog may exist.

INTRODUCTION

Complex assemblages of fine-grained low-temperature minerals challenge our understanding of mineralogy, both chemically and geologically. Crystal structures of minerals in complex geochemical environments should be related to the paragenetic sequences of the minerals (Hawthorne 1979; Moore 1973). Establishing such relationships would promote understanding of complex mineral occurrences. Solving the structures of crystals with effective volume $< 20 \mu\text{m}^3$ has been recently made possible by that the introduction of synchrotron radiation (Smith 1995) and CCD-based detectors (Burns 1998) to mineralogy.

In principle, synchrotron X-ray sources should permit the structure determination for crystals as small as $1 \mu\text{m}^3$ (Smith 1995; Smith and Rivers 1995; Coppens 1997). It is possible to obtain direct chemical information using a combination of diffraction, fluorescence and absorption experiments on the same crystal. The first example of a mineral structure determination using synchrotron radiation was first done at the European Synchrotron Radiation Facility in Grenoble, France, using half of a needle $3 \times 3 \times 65 \mu\text{m}^3$ of raite (Pluth et al. 1998). The present study refines an even smaller ($2 \times 2 \times 40 \mu\text{m}^3$) crystal of structurally complex quetzalcoatlite at the Geo/Soil/Enviro-CARS Sector 13 at the Advanced Photon Source in Argonne. The elec-

tron density map required revision of the chemical formula, as subsequently quantified by electron microprobe analysis.

EXPERIMENTAL METHODS

The crystals used in this study were collected by RMH during a San Bernardino County Museum study trip to the Blue Bell claims, San Bernardino County, California. An unusual assemblage of Te oxyalts was found by breaking a 0.5 m diameter rock consisting mostly of iron oxides and skarn minerals that was lying at the bottom of a short 2.5 m deep exploration shaft. This shaft is part of the 2D site that also includes another short shaft and a short adit nearby (Maynard et al. 1984). Probably, metal was not produced, but the mineralogy is extraordinarily complex, with 22 species identified including murdochite, perite, kettnerite, fluorite, embolite, hemimorphite, diopside, and acicular chrysocholla pseudomorphs, probably after aurichalcite. From a qualitative chemical analysis and crystal morphology, the radiating blue microcrystals were identified as talocite, the only mineral then known to contain both Te and Cl. However, the identification remained tentative owing to the presence of substantial Ag in the crystal, in contradiction to the description of talocite (Williams 1975). The crystallographic data collected at the synchrotron matched quetzalcoatlite, originally described by Williams (1973), but with a modified chemical formula.

Scanning electron micrographs (Fig. 1) illustrate the typical occurrence of quetzalcoatlite needles ($\sim 2 \mu\text{m}$ across; up to $100 \mu\text{m}$ long) and tabular crystals of kettnerite.

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X-ray diffraction

Many crystals of quetzalcoatlite were studied optically, a crystal $2 \times 2 \times 40 \mu\text{m}^3$ with sharp extinction between crossed polarizers was selected and mounted on the tip of a glass rod tapered to $1 \mu\text{m}$. Data were collected at the Geo/Soil/Enviro-CARS (Consortium for Advanced Radiation Sources) beamline at the Advanced Photon Source, Argonne, Illinois. A horizontal KB mirror rejected high-energy harmonics. X-radiation from the undulator was focused to $\sim 100 \mu\text{m}$ by a cylindrical mirror, and monochromatized to a wavelength of 0.61993 \AA (20 keV). Data were collected using a Bruker 2K SMART CCD (charge-coupled device) detector by scanning in ϕ , with 1000 frame widths of 0.3° and 10 s spent counting per frame. Unit-cell dimensions (Table 1) were refined by least squares using 2250 reflections. Data were integrated and corrected for Lorentz, polarization, and background effects using the Bruker program SAINT. A correction for systematic errors such as beam decay and absorption was done using the program SADABS (G. Sheldrick, unpublished) on the basis of the intensities of equivalent reflections. A total of 2713 reflections was collected from $2\theta = 3$ to 56.7° , of the 410 unique reflections ($R_{\text{int}} = 12.9\%$), 395 were classed as observed ($|F_o| \geq 4\sigma_F$).

Chemical analysis

Clusters of fibers from three specimens including that used for structure determination were mounted in epoxy. Polishing exposed some fibers of each at low angle to the surface giving sufficient area for microprobe analysis. Each, however, was $\sim 3 \mu\text{m}$ wide and $\sim 1.5 \mu\text{m}$ thick. Analyses were done in wavelength-dispersion-spectroscopy mode with a Cameca SX-50 electron microprobe. Following carbon coating, analyses were obtained at 15 kV and 25 nA incident current in a focused beam. Each point was located by imaging the fiber and locating the

beam in the center and verifying the material with qualitative EDS observation. Analyses were made for Te, Ag, Pb, and Cu (metal standards) and Cl (synthetic Cl-apatite) and Zn (synthetic ZnO). Three analyses were obtained for each of the three samples (Table 2); because Ag anticorrelates with Pb a substitution series is possible. H_2O was calculated from the stoichiometry obtained from the crystal-structure analysis.

Structure solution and refinement

Structure solution and refinement methods follow Burns (1998). The space group $P\bar{3}1m$ was verified by successful solution and refinement of the structure by direct methods. The structure model was checked for higher symmetry using the program MISSYM (Le Page 1987). The final refinement in-

TABLE 1. Unit-cell parameters, crystallographic parameters, and atomic parameters for quetzalcoatlite

a (Å)	10.145(1)	Crystal size (μm^3)	$2 \times 2 \times 40$
c (Å)	4.9925(9)	Radiation	0.61993 \AA
V (Å ³)	445.0(1)	Total refl.	2713
		Unique refl.	410
Space group	$P\bar{3}1m$	R_{int} (%)	12.9
$F(000)$	588	Unique $ F_o \geq 4\sigma_F$	395
D_{calc} (g/cm ³)	4.82	Final R^* (%)	5.1
		S^\dagger	1.16
Unit-cell contents: $\text{Zn}_6\text{Cu}_3(\text{TeO}_3)_2\text{O}_6(\text{OH})_6(\text{Ag,Pb}_y)\text{Cl}_{x+2y}$, $x+y \leq 2$			
	x	y	z
Te	$1/3$	$2/3$	$1/2$
Zn	0.20371(6)	0.4074(1)	0
Cu	$1/2$	0	$1/2$
O	0.3508(6)	0.5190(6)	0.2850(8)
OH	0	0.2772(9)	0.158(1)
Ag	0	0	0
Cl	0	0	$1/2$
			U_{eq}^\ddagger
			95(5)
			140(5)
			180(6)
			143(10)
			290(18)
			594(16)
			211(17)

* $R = S(|F_o| - |F_c|) / S|F_o|$.

$^\dagger S = [S \sum (|F_o| - |F_c|)^2 / (m-n)]^{1/2}$, for m observations and n parameters.

$^\ddagger U_{\text{eq}} = U_{\text{eq}} \text{ \AA}^2 \times 10^4$.

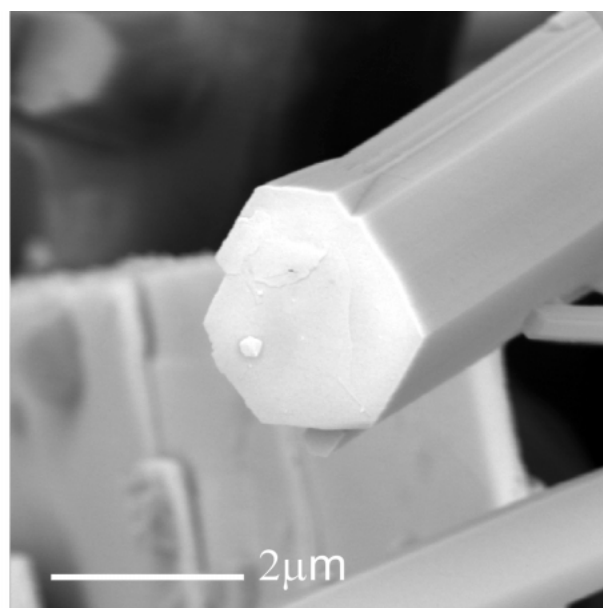
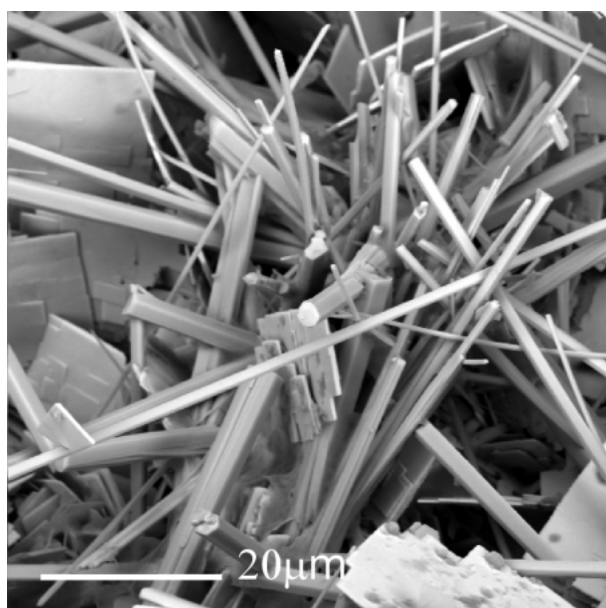


FIGURE 1. Backscattered electron images of a typical assemblage of quetzalcoatlite and kettnerite.

TABLE 2. Chemical analysis for quetzalcoatlite

	wt%									
	1	2	3	4	5	6	7	8	9	
TeO ₃	29.6	29.0	29.3	27.0	29.1	27.3	30.2	28.6	25.6	
Ag ₂ O	4.44	4.44	4.23	5.04	5.24	5.46	3.03	3.58	3.53	
Cl	2.27	2.66	2.78	2.29	2.65	2.34	2.11	2.38	2.06	
PbO	0.00	0.05	0.00	0.13	0.14	0.16	3.22	2.09	1.71	
ZnO	38.2	38.3	39.0	38.2	38.8	38.2	39.0	39.1	38.7	
CuO	18.6	18.3	18.8	18.0	17.7	18.3	18.2	17.1	18.7	
H ₂ O*	4.43	4.40	4.45	4.25	4.39	4.29	4.50	4.36	4.22	
O=Cl	-0.51	-0.60	-0.63	-0.52	-0.60	-0.53	-0.48	-0.54	-0.46	
Total	97.1	96.5	97.9	94.4	97.4	95.5	99.7	96.7	94.0	
Formula based on 15 O										
Te	2.06	2.03	2.03	1.95	2.04	1.96	2.06	2.02	1.87	
Ag	0.47	0.47	0.44	0.55	0.56	0.59	0.31	0.38	0.39	
Cl	0.78	0.92	0.95	0.82	0.92	0.83	0.71	0.83	0.74	
Pb	0.00	0.00	0.00	0.01	0.01	0.01	0.17	0.12	0.10	
Zn	5.73	5.86	5.82	5.97	5.87	5.92	5.75	5.95	6.09	
Cu	2.86	2.82	2.87	2.88	2.73	2.90	2.74	2.67	3.00	

* Calculated on the basis of stoichiometry; specimen 1 = points 1, 2, 3; specimen 2 = points 4, 5, 6; specimen 3 = points 7, 8, 9. All specimens were collected from the same 0.5 m diameter rock.

cluded positional parameters and anisotropic-displacement parameters for all atoms, and a weighting scheme of structure factors (details in Table 1). Final atomic parameters are given in Tables 1 and 3¹, and calculated and observed structure factors in Table 4.¹

RESULTS

The structure (Figs. 2 and 3) contains one symmetrically unique Te⁶⁺ cation, at the 2c position, that is octahedrally coordinated by O atoms, with a single unique Te-O bond length of 1.922(4) Å. The single unique Zn cation is located at the 6i position and is tetrahedrally coordinated by two atoms of O and two (OH) groups, with bond lengths 1.960(5) and 1.978(3) Å, respectively, and a $\langle\phi\text{-Zn-}\phi\rangle$ (ϕ : O, OH) bond angle of 109.4°. The unique Cu²⁺ cation is located on the 3g position, and occupies a strongly distorted octahedron owing to the Jahn-Teller effect associated with a d⁹ metal in an octahedral ligand field. The octahedron involves four short [1.942(4) Å] equatorial bonds to symmetrically equivalent O atoms and two long [2.834(4) Å] apical bonds to (OH)⁻ groups, a (4+2) distortion, as is common in Cu²⁺ octahedra (Burns and Hawthorne 1996).

Each TeO₆ octahedron shares three edges with three different Cu₆ octahedra, each of which share two trans edges with TeO₆ octahedra, resulting in layers of edge-sharing octahedra parallel to (001) (Fig. 3a). The Zn₄ tetrahedra share vertices, forming rings of six tetrahedra parallel to (001) (Fig. 3b), which define the edges of channels parallel to *c* (Fig. 2a). The structure is composed of alternating layers of octahedra and tetrahedra linked along [001] by vertex sharing (Fig. 2b).

The description of quetzalcoatlite by Williams (1973) involved neither Ag nor Cl. However, the X-ray data clearly in-

dicate that substantial electron density occurs in the channels through the structure along *c*, and prompted chemical analysis. Ag, Pb, and Cl occur within the channel at *z* = 0 (Ag, Pb) and 1/2 (Cl). Each Ag or Pb cation is bonded to two Cl anions at 2.4962(5) Å, and is further coordinated by six atoms of O at 2.920(9) Å. The Cl anions may accept H bonds from six symmetrically unique OH positions 3.293(8) Å from the Cl position. Because the framework of the structure is neutral, the total

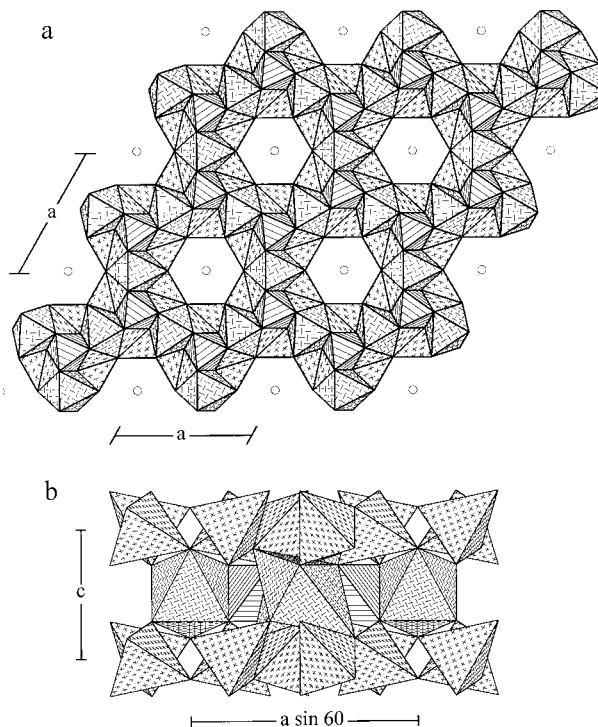


FIGURE 2. Polyhedral representations of the structure of quetzalcoatlite. Shading patterns: TeO₆ = parallel lines, ZnO₄ = crosses, CuO₆ = herringbone.

¹For a copy of Tables 3 and 4, Document AM-00-041 contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue for price information). Deposit items may also be available on the American Mineralogist web site (www.minsocam.org).

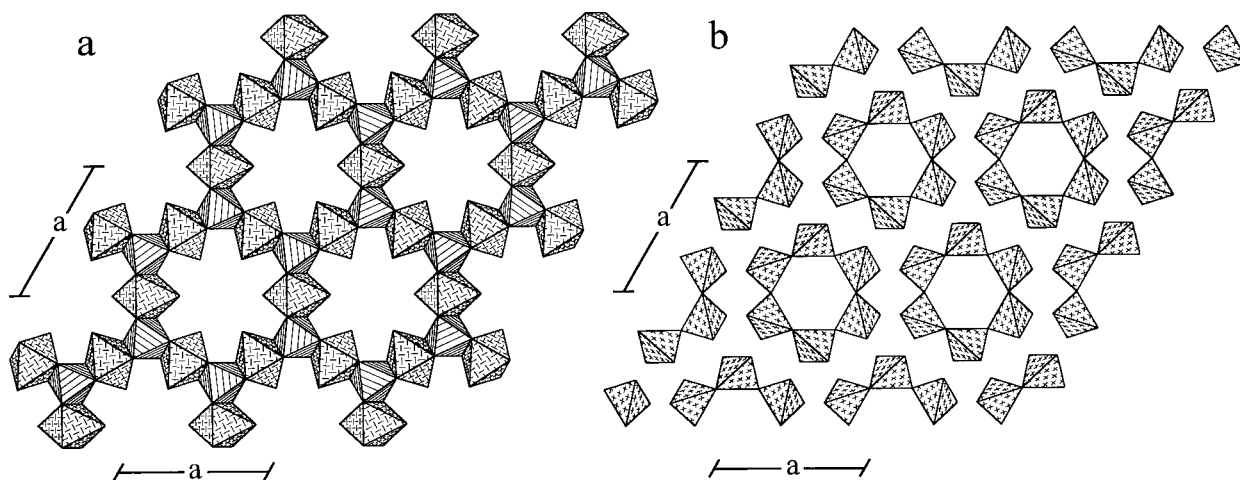


FIGURE 3. Polyhedral representations of the layers that occur in the structure of quetzalcoatlite. (a) Layer at $z = 1/2$. (b) Layer at $z = 0$.

charge associated with the channel constituents must be zero. The site scattering for the crystal studied is consistent with approximately 0.84 Cl, 0.30 Pb, and 0.24 Ag per formula unit. The chemical analysis of various crystals (Table 2) show that the concentrations of Ag and Pb are anti-correlated, indicating a solid-solution series exists involving $\text{Ag} \leftrightarrow \text{Pb}$ in the channel.

On the basis of the structure determination, the formula of quetzalcoatlite is $\text{Zn}_x\text{Cu}_3(\text{TeO}_3)_2\text{O}_6(\text{OH})_6(\text{Ag}_x\text{Pb}_y)\text{Cl}_{x+2y}$, $x + y \leq 2$, $Z = 1$, which may be compared to the formula $\text{Cu}_4\text{Zn}_3(\text{TeO}_3)_3(\text{OH})_{18}$ proposed by Williams (1973). The range of chemical analyses obtained for the microcrystals using the electron microprobe are in reasonable accord with the structural formula for just one crystal.

Eby and Hawthorne (1993) provide a comprehensive review and comparison of the structures of Cu^{2+} oxysalt minerals. Comparison to their figures indicates that the structure of quetzalcoatlite is unique among Cu oxysalts.

SIGNIFICANCE

Just as for raité (Pluth et al. 1998), the present work on quetzalcoatlite demonstrates the growing power of synchrotron diffraction techniques. Some hundreds of known minerals have proven too fine-grained for structure determination using laboratory X-ray sources, and a bonanza of new results can be expected. However, many problems can be expected for fine-grained materials growing at low temperatures, including metastable phase relations, chemical zoning, structural disorder, thermal, and electronic instability. It will be necessary to bring to bear all the "chemical microscopes" and to link micrometer synchrotron techniques to nanometer electron microscopy.

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