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Lead-tellurium oxysalts from Otto Mountain near Baker, California: III. Thorneite, $Pb_6(Te_2^{6+}O_{10})(CO_3)Cl_2(H_2O)$, the first mineral with edge-sharing octahedral tellurate dimers

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Abstract

Thorneite, $Pb_6(Te_2^{6+}O_{10})(CO_3)Cl_2(H_2O)$, is a new tellurate from Otto Mountain near Baker, California, named in honor of Brent Thorne. The new mineral occurs on fracture surfaces and in small vugs in brecciated quartz veins. Thorneite is directly associated with acanthite, cerussite, gold, hessite, iodargyrite, khinite, wulfenite, and three other new tellurates: housleyite, markcooperite, and ottoite. Various other secondary minerals occur in the veins, including three other new secondary tellurium minerals: paratimroseite, telluroperite, and timroseite. Thorneite is monoclinic, space group *C*2/*c*, *a* = 21.305(1), *b* = 11.059(1), *c* = 7.564(1) Å, β = 101.112(4)°, *V* = 1748.8(4) Å^3, and *Z* = 4. Crystals are prismatic to bladed with elongation and striations parallel to **c** and typically occur in parallel and random aggregates. It is yellow and transparent, with pale yellow streak and adamantine luster. Mohs hardness is estimated at 2. The mineral is brittle, with an irregular to splintery fracture and good {100} cleavage. The calculated density is 6.828 g/cm^3. Thorneite is biaxial (+), with large 2*V*, but indices of refraction are too high to be measured. The optic orientation is *Y* = **b**, *Z* ^ **a** = 29° in obtuse β. No pleochroism was observed. Electron microprobe analysis provided PbO 73.90, ZnO 0.03, TeO_3 20.35, Cl 2.29, H_2O 1.28 (structure), CO_2 2.29 (structure), O≡Cl –0.52, total 99.62 wt%; the empirical formula (based on O+Cl = 16) is $(Pb_{5.94}Zn_{0.01})(Te^{6+}_{2.08}O_{10})(C_{1.00}O_3)[Cl_{1.16}O_{0.34}(OH)_{0.50}](H_2O)$. The strongest powder X-ray diffraction lines are [d_{obs} in Å (*hkl*) *I*]: 10.43 (200) 35, 3.733 ($\bar{5}11$, $\bar{2}02$, 002) 27, 3.595 ($\bar{4}21$) 33, 3.351 (112) 66, 3.224 (511, 131) 100, 3.093 ($\bar{2}22$, $\bar{3}31$) 30, 2.900 ($\bar{6}21$) 44, 2.133 (821, 622, 223, 731, 242) 38. The crystal structure (R_1 = 0.028) contains edge-sharing octahedral tellurate dimers, $[Te_2^{6+}O_{10}]^{8-}$ that bond to Pb atoms, which in turn are linked via bonds to Cl atoms, CO_3 triangles, and H_2O molecules.

Keywords: Thorneite, new mineral, tellurate, crystal structure, Otto Mountain, California

Introduction

Thorneite, $Pb_6(Te_2^{6+}O_{10})(CO_3)Cl_2(H_2O)$, is one of seven new secondary lead-tellurium minerals discovered recently at Otto Mountain near Baker, California. Detailed information on the mining history, geology, mineralogy, and mineral paragenesis of the deposit, as well as the discovery of the new minerals, is provided in Kampf et al. (2010a).

Thorneite is named in honor of Brent Thorne (b. 1951) of Bountiful, Utah, the discoverer of the mineral. Brent Thorne is an avid field collector and regular contributor to Mindat.org with over 1100 photographs posted on the Mindat website. He has collected and provided specimens for the description of the new mineral plumbophyllite (Kampf et al. 2009) and for continuing studies of other new and existing minerals from Otto Mountain and the nearby Blue Bell claims. Thorne has agreed to the naming of the mineral in his honor. The new mineral and name have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2009-023). Four cotype specimens are deposited in the Natural History Museum of Los Angeles County, catalog numbers 62257, 62258, 62259, and 62260.

Occurrence

Thorneite was found in the Bird Nest drift on the southwest flank of Otto Mountain, approximately 2 km northwest of Baker, San Bernardino County, California. The Bird Nest drift (35° 16.606′N, 116° 05.956′W) is located 0.7 km northwest of the Aga mine (35° 16.399′N, 116° 05.665′W).

Thorneite is rare and occurs mostly on fracture surfaces and in small vugs in quartz veins. Species observed in direct association with the new mineral include acanthite, cerussite, gold, hessite, iodargyrite, khinite, wulfenite, and three other new tellurates: housleyite $[Pb_6Cu^{2+}Te_4^{6+}O_{18}(OH)_2]$ (IMA2009-024; Kampf et al. 2010b), markcooperite $[Pb_2(UO_2)Te^{6+}O_6]$ (IMA2009-045; Kampf et al. 2010c), and ottoite $[Pb_2Te^{6+}O_5]$ (IMA2009-063; Kampf et al. 2010a). Other species identified in the Otto Mountain assemblages include: anglesite, atacamite, boleite, brochantite, burckhardtite, calcite, caledonite, celestine, chalcopyrite, bromine-rich chlorargyrite, chrysocolla, devilline, diaboleite, fluorite, fornacite, galena, goethite, jarosite, kuranakhite, linarite, malachite, mimetite, mottramite, munakataite, murdochite,

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muscovite, perite, phosphohedyphane, plumbojarosite, pyrite, schieffelinite, vanadinite, vauquelinite, and three other new minerals: paratimroseite [$Pb_2Cu_4^{2+}(Te^{6+}O_6)_2(H_2O)_2$] (IMA2009-065; Kampf et al. 2010d), telluroperite [$Pb_3Te^{4+}O_4Cl_2$] (IMA2009-044; Kampf et al. 2010e), and timroseite [$Pb_2Cu_5^{2+}(Te^{6+}O_6)_2(OH)_2$] (IMA2009-064; Kampf et al. 2010d). Other potentially new species are still under investigation.

Thorneite and most of the other secondary minerals of the quartz veins are interpreted as having formed from the partial oxidation of primary sulfides (e.g., galena) and tellurides (e.g., hessite) during or following brecciation of the quartz veins.

Physical and optical properties

The mineral occurs as prismatic to bladed crystals (Fig. 1) with elongation and striations parallel to **c**. They typically occur in parallel and random intergrowths and are up to 0.5 mm in length. Crystals exhibit the forms {100}, {010}, {110}, and {21$\bar{1}$} (Fig. 2). Crystal intergrowths are common, but no systematic crystallographic orientation was observed.

Thorneite is yellow and transparent, with pale yellow streak and adamantine luster. The mineral is non-fluorescent. The Mohs hardness is estimated at 2 based upon behavior of crystals when broken. The tenacity is brittle and the fracture is irregular to splintery. Crystals are very fragile and easily crushed. Cleavage is good on {100}. The density could not be measured because it is greater than those of available high-density liquids and there is insufficient material for physical measurement. The calculated density is 6.790 g/cm^3 for the empirical formula and 6.829 g/cm^3 for formula based on refined occupancies in structure (see below). Thorneite turns opaque and dissolves slowly in HCl.

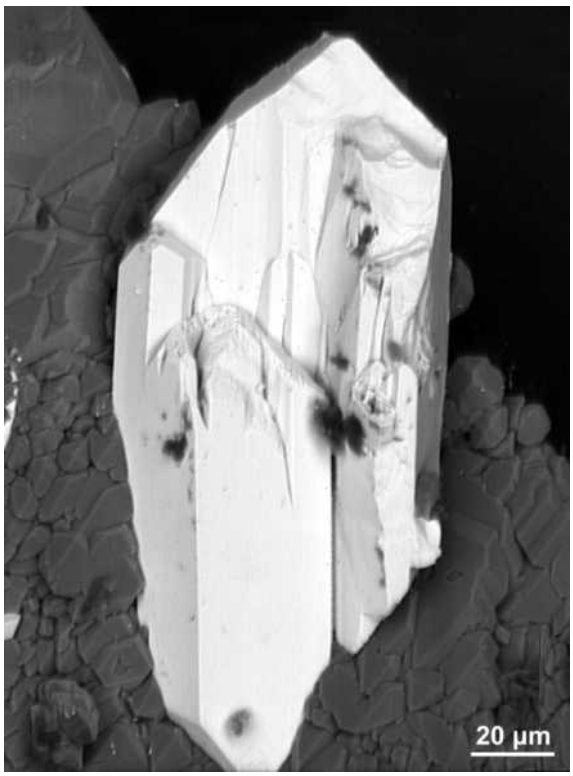

Figure 1. Backscatter SEM image of thorneite.

The indices of refraction exceed those of available index fluids. The Gladstone-Dale relationship (Mandarino 1981) predicts n_{av} = 2.021 based on the empirical formula. Birefringence is very low (~0.01), suggesting that all indices of refraction are in the 2.01 to 2.03 range. Orthoscopic and conoscopic optical examination using a Leitz Ortholux I polarizing microscope equipped with a Supper spindle stage showed thorneite to be biaxial (+), with large 2V. No dispersion was observed. The optical orientation is Y = **b**, Z ^ **a** = 29° in obtuse β. The mineral is non-pleochroic.

Raman spectroscopy

Raman spectroscopic micro-analysis was carried out using a Renishaw M1000 micro-Raman spectrometer system. Spectra were obtained using a 514.5 nm laser with a 100× objective producing a spot about 2 µm in diameter with about 5 mW power. Peak positions were calibrated against a silicon standard. Spectra were obtained with a dual-wedge polarization scrambler inserted directly above the objective lens to minimize the effects of polarization. Raman measurements were made on an isolated 150 µm × 50 µm thorneite crystal on quartz matrix. Spectra obtained with the light propagating parallel and perpendicular to the **c** axis of the crystal were found to be very similar. The spectra with the light propagating parallel to the **c** axis are shown in Figure 3a (100 to 1600 cm^{-1} range) and Figure 3b (0 to 4000 cm^{-1} range with the vertical scale expanded).

The sharp peak at 1056 cm^{-1} is in the shift range where the strongest carbonate peak typically occurs. The broad peak at about 3300 cm^{-1} is attributable to OH stretching modes and the peak at about 1630 cm^{-1} is attributable to the HOH bending mode of water. The Raman spectroscopy, therefore, corroborates the presence of carbonate and water indicated by the structure determination (see below).

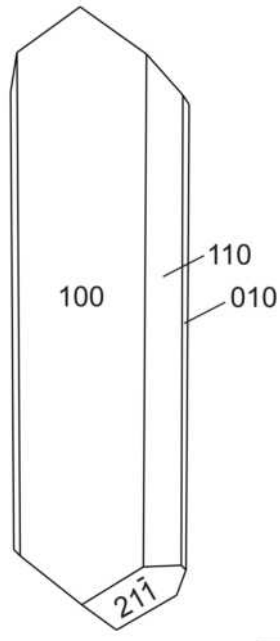

Figure 2. Crystal drawing of thorneite (clinographic projection).

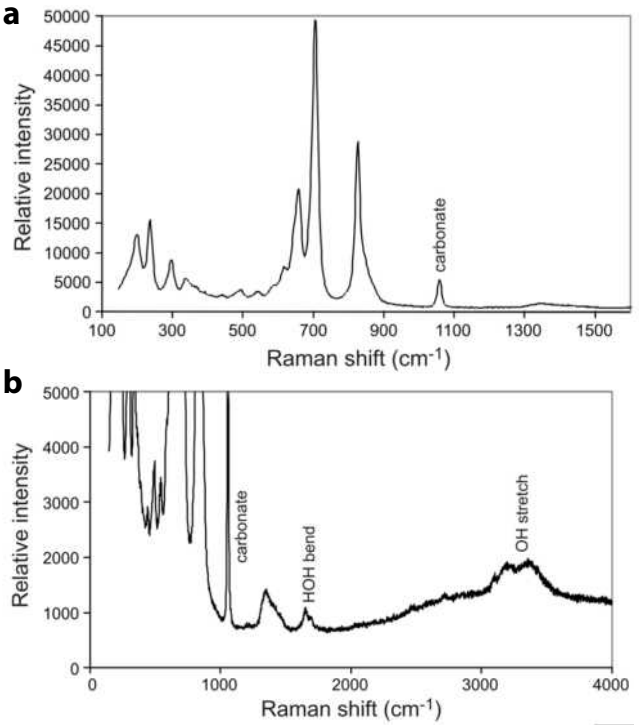

FIGURE 3. Raman spectra for thorneite (**a**) covering the range 100 to 1600 cm^{-1} and (**b**) covering the range 0 to 4000 cm^{-1} with expanded vertical scale.

CHEMISTRY

Three chemical analyses were carried out using a JEOL8200 electron microprobe (WDS mode, 15 kV, 10 nA, focused beam) at the Division of Geological and Planetary Sciences, California Institute of Technology. The H_2O and CO_2 were calculated by stoichiometry from the results of the crystal-structure analysis. The averages (and ranges) of the analyses are: PbO 73.90 (73.74–73.98), ZnO 0.03 (0.02–0.05), TeO_3 20.35 (20.05–20.76), Cl 2.29 (1.75–2.98), H_2O 1.26 (structure), CO_2 2.45 (structure), O≡Cl –0.52, total 99.76 wt%. Standards used were PbS, ZnO, Te metal, and sodalite (for Cl). There was some evidence of beam damage during the EMP analyses; however, the final totals are close to 100% and the empirical formula derived from the analyses fits the structural formula well.

The empirical formula (based on O + Cl = 16) is $(Pb_{5.94}Zn_{0.01})(Te^{6+}_{2.08}O_{10})(C_{1.00}O_3)(Cl_{1.16}O_{0.34}(OH)_{0.50})(H_2O)$. The simplified formula is $Pb_6(Te^{6+}_2O_{10})(CO_3)(Cl_{1.50}(OH)_{0.50})(H_2O)$, based on the structure with refined Cl and OH occupancies for the Cl/OH site. The end-member formula is $Pb_6(Te^{6+}_2O_{10})(CO_3)Cl_2(H_2O)$, which requires PbO 74.10, TeO_3 19.43, CO_2 2.44, H_2O 1.00, Cl 3.92, O≡Cl –0.89, total 100.00 wt%.

X-RAY CRYSTALLOGRAPHY AND STRUCTURE DETERMINATION

Both powder and single-crystal X-ray diffraction data were obtained on a Rigaku R-Axis Spider curved imaging plate microdiffractometer utilizing monochromatized Mo$K\alpha$ radiation. The powder data presented in Table 1 show good agreement with the pattern calculated from the structure determination.

TABLE 1. X-ray powder-diffraction data for thorneite

I_{obs}	d_{obs}	d_{calc}	I_{calc}	$h\,k\,l$
35	10.430	10.452	60	2 0 0*
14	9.740	9.775	25	1 1 0
6	5.550	5.529	14	0 2 0*
10	5.040	5.033	12	$\bar{3}$ 1 1*
13	4.940	4.888	12	2 2 0
6	4.440	4.434	9	0 2 1*
18	4.270	4.288	14	3 1 1*
10	3.900	3.911	16	5 1 0*
		3.797	11	$\bar{4}$ 2 0
27	3.733	3.750	11	$\bar{5}$ 1 1
		3.731	18	$\bar{2}$ 0 2*
		3.711	13	0 0 2
33	3.595	3.591	47	$\bar{4}$ 2 1*
		3.400	15	$\bar{3}$ 1 2
66	3.351	3.370	38	1 1 2*
		3.305	21	$\bar{1}$ 3 1
		3.302	14	2 0 2
100	3.224	3.228	73	5 1 1*
		3.219	100	$\bar{1}$ 3 1*
30	3.093	3.093	26	$\bar{2}$ 2 2*
		3.088	21	$\bar{3}$ 3 1*
21	2.969	2.973	31	$\bar{5}$ 1 2
		2.932	10	$\bar{3}$ 1 2
44	2.900	2.907	55	$\bar{6}$ 2 1*
		2.883	18	$\bar{7}$ 1 0
		2.874	23	$\bar{7}$ 1 1
		2.835	11	$\bar{2}$ 2 2
6	2.691	2.706	7	$\bar{5}$ 3 1
		2.673	10	2 4 0
8	2.606	2.613	5	8 0 0
		2.598	4	6 2 1
6	2.581	2.591	7	0 4 1
		2.444	8	$\bar{4}$ 4 0
12	2.428	2.427	18	$\bar{3}$ 1 3*
8	2.361	2.363	4	$\bar{8}$ 2 0
		2.362	12	$\bar{8}$ 0 2*
3	2.285	2.292	4	$\bar{2}$ 2 3
6	2.226	2.221	6	$\bar{2}$ 4 2
		2.220	7	$\bar{4}$ 2 3
26	2.153	2.159	13	3 1 3
		2.146	11	8 2 1
		2.144	16	6 2 2
38	2.133	2.131	11	2 2 3
		2.126	20	7 3 1
		2.120	14	$\bar{2}$ 4 2
4	2.075	2.078	5	$\bar{7}$ 1 3
		2.060	5	$\bar{3}$ 5 1
15	1.969	1.973	16	$\bar{5}$ 3 3*
		1.966	8	8 0 2
		1.955	12	5 5 0
		1.875	5	$\bar{10}$ 2 2
		1.873	9	11 1 0*
		1.866	9	$\bar{4}$ 0 4*
15	1.863	1.858	7	$\bar{9}$ 1 3
		1.843	12	0 6 0
		1.798	10	$\bar{5}$ 5 2
		1.789	11	$\bar{2}$ 2 4
		1.780	9	6 4 2
22	1.782	1.777	17	7 5 0*
		1.773	9	2 4 3
3	1.737	1.742	8	12 0 0
		1.737	4	5 3 3
4	1.684	1.693	7	3 1 4
6	1.665	1.665	6	4 4 3
6	1.617	1.617	7	$\bar{10}$ 4 2*
		1.614	4	10 2 2
5	1.574	1.579	4	7 3 3
		1.561	3	$\bar{12}$ 2 1
10	1.555	1.561	9	$\bar{2}$ 4 4
		1.547	3	$\bar{9}$ 5 2
12	1.493	1.497	7	$\bar{13}$ 3 1*
		1.496	5	3 7 1

Notes: I_{obs} based upon peak heights. I_{calc} calculated from the crystal structure using Powder Cell (Kraus and Nolze 1996). d_{calc} based on the cell refined from the powder data (*) using UnitCell (Holland and Redfern 1997). Refined cell: a = 21.226(3), b = 11.106(2), c = 7.548(1) Å, β = 101.33(2)°, V = 1744.6(4) Å^3.

The Rigaku CrystalClear software package was used for processing the structure data, including the application of an empirical absorption correction. The structure was solved by direct methods using SIR92 (Altomare et al. 1994) and the location of all non-hydrogen atoms was straightforward. The SHELXL-97 software (Sheldrick 2008) was used, with neutral atom scattering factors, for the refinement of the structure. Bond-valence calculations indicate that one O atom (designated OW) is a water molecule. A difference Fourier map revealed the H atom site corresponding to both H atoms of the water molecule. The position of the H site was constrained to an OW-H distance of 0.90(3) Å and an H-H distance of 1.45(3) Å in the final refinement. The structure refinement indicated the Cl site to be jointly occupied by Cl and OH [$Cl_{0.75}(OH)_{0.25}$]. It was not possible to locate the 0.25 H atom associated with this site.

The details of the data collection and the final structure refinement are provided in Table 2. The final atomic coordinates and displacement parameters are in Table 3. Selected interatomic distances are listed in Table 4 and bond valences in Table 5. CIF and structure factors are on deposit[1].

TABLE 2. Data collection and structure refinement details for thorneite

Diffractometer	Rigaku R-Axis Spider
X-ray radiation/power	Mo$K\alpha$ (λ = 0.71075 Å)/50 kV, 40 mA
Temperature	298(2) K
Structural formula	$Pb_6(Te_2^{6+}O_{10})(CO_3)(Cl_{1.50}(OH)_{0.50})(H_2O)$
Space group	*C*2/*c*
Unit-cell dimensions	*a* = 21.305(1) Å
	b = 11.059(1) Å
	c = 7.564(1) Å
	β = 101.112(4)°
Z	4
Volume	1748.8(4) Å^3
Density (for above formula)	6.829 g/cm^3
Absorption coefficient	61.129 mm^{-1}
F(000)	3016
Crystal size	85 × 70 × 15 µm
θ range	3.46 to 23.24°
Index ranges	$-23 \le h \le 23$, $-12 \le k \le 12$, $-7 \le l \le 8$
Reflections collected/unique	8170/1255 [R_{int} = 0.0610]
Reflections with $F_o > 4\sigma F$	1135
Completeness to θ = 27.50°	99.7%
Max. and min. transmission	0.4608 and 0.0782
Refinement method	Full-matrix least-squares on F^2
Parameters refined	120
GoF	1.069
Final *R* indices [$F_o > 4\sigma F$]	R_1 = 0.028, wR_2 = 0.054
R indices (all data)	R_1 = 0.033, wR_2 = 0.055
Largest diff. peak/hole	1.395/–1.327 *e*/Å^3

Notes: $R_{int} = \Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma[F_o^2]$. GoF = $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$. $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where *a* is 0, *b* is 107.075, and *P* is $[2F_c^2 + \text{Max}(F_o^2, 0)]/3$.

DESCRIPTION OF THE STRUCTURE

The most distinctive unit in the structure (Fig. 4) is an edge-sharing octahedral tellurate dimer, $[Te_2^{6+}O_{10}]^{8-}$. The octahedral dimers bond to Pb atoms, which in turn are linked via bonds to Cl atoms, CO_3 triangles, and H_2O molecules. The thorneite structure is unique and is not closely related to that of any other mineral.

The average Te-O bond length in thorneite, 1.934 Å, is typical of octahedrally coordinated Te^{6+} [e.g., frankhawthorneite, 1.939 Å (Grice and Roberts 1995); jensenite, 1.936 Å (Grice et al. 1996); leisingite, 1.922 Å (Margison et al. 1997); khinite, 1.962 Å (Cooper et al. 2008); ottoite, 1.942 Å (Kampf et al. 2010a,); housleyite, 1.931 and 1.942 Å (Kampf et al. 2010b); markcooperite, 1.95 Å (Kampf et al. 2010c); timroseite, 1.933 Å

[1] Deposit item AM-10-045, CIF and structure factors. Deposit items are available two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. For an electronic copy visit the MSA web site at http://www.minsocam.org, go to the *American Mineralogist* Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.

TABLE 4. Selected bond distances (Å) for thorneite

Te-O3	1.889(10)	Pb1-O6	2.297(9)
Te-O4	1.901(9)	Pb1-O3	2.360(10)
Te-O6	1.930(9)	Pb1-O5	2.423(9)
Te-O5	1.931(9)	Pb1-O2	2.777(12)
Te-O7	1.974(9)	Pb1-O6	3.016(9)
Te-O7	1.979(8)	Pb1-O1	3.155(1)
<Te-O>	1.934	Pb1-Cl	3.456(7)
		Pb1-O2	3.472(13)
C-O2(×2)	1.269(15)	Pb1-O4	3.728(10)
C-O1	1.291(26)	Pb1-O3	3.806(10)
<C-O>	1.276	<Pb1-O,Cl>	3.086
Pb2-O4	2.439(9)	Pb3-O4	2.317(10)
Pb2-O5	2.490(9)	Pb3-O6	2.404(9)
Pb2-O3	2.554(10)	Pb3-O2	2.406(12)
Pb2-O5	2.661(9)	Pb3-O1	2.679(10)
Pb2-O7	2.718(9)	Pb3-OW	2.758(16)
Pb2-Cl	2.968(6)	Pb3-Cl	3.360(6)
Pb2-O3	3.096(11)	Pb3-Cl	3.489(7)
Pb2-Cl	3.599(7)	Pb3-O2	3.699(12)
Pb2-O7	3.808(8)	Pb3-O7	3.788(9)
<Pb2-O,Cl>	2.991	<Pb3-O,Cl>	3.068

Hydrogen bonds (D = donor, A = acceptor)

D-H	d(D-H)	d(H-A)	D-H-A	d(D-A)	A	H-D-H
OW-H	0.92(3)	2.69(21)	114°	3.175(6)	Cl	104°
OW-H	0.92(3)	2.71(21)	128°	3.355(6)	Cl	

TABLE 3. Atomic coordinates and displacement parameters (Å^2) for thorneite

	x	*y*	*z*	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pb1	0.63753(3)	0.09635(5)	0.15303(7)	0.0186(2)	0.0139(3)	0.0241(3)	0.0165(3)	–0.0012(2)	–0.0005(2)	0.0015(3)
Pb2	0.69515(3)	0.41296(5)	0.96922(8)	0.0220(2)	0.0218(4)	0.0233(3)	0.0195(3)	–0.0021(3)	0.0007(3)	–0.0020(3)
Pb3	0.55264(3)	0.24366(6)	0.52254(8)	0.0283(2)	0.0177(4)	0.0376(4)	0.0279(4)	–0.0047(3)	0.0006(3)	0.0056(3)
Te	0.78842(5)	0.30010(8)	0.36271(12)	0.0134(2)	0.0114(5)	0.0160(5)	0.0128(5)	–0.0008(4)	0.0024(4)	–0.0030(4)
C	0.5	0.9822(20)	0.25	0.025(6)	0.028(16)	0.017(13)	0.025(13)	0.0	–0.010(11)	0.0
Cl*	0.5884(3)	0.3933(6)	0.1682(8)	0.057(3)	0.032(4)	0.080(6)	0.059(5)	–0.002(3)	0.009(3)	0.006(3)
O1	0.5	0.0990(15)	0.25	0.052(5)	0.034(12)	0.033(11)	0.079(14)	0.0	–0.015(10)	0.0
O2	0.5487(6)	0.9265(11)	0.2183(17)	0.044(3)	0.022(7)	0.049(8)	0.063(9)	–0.009(7)	0.013(6)	0.001(6)
O3	0.7815(5)	0.4526(9)	0.2479(13)	0.026(3)	0.024(7)	0.028(6)	0.021(6)	0.008(5)	–0.006(5)	–0.011(5)
O4	0.6451(5)	0.2717(9)	0.7367(12)	0.020(2)	0.016(6)	0.028(6)	0.016(5)	–0.012(5)	0.003(5)	–0.008(5)
O5	0.7269(5)	0.2338(8)	0.1654(12)	0.016(2)	0.013(6)	0.019(6)	0.014(5)	0.004(4)	–0.004(4)	–0.004(4)
O6	0.6435(4)	0.1381(8)	0.4534(12)	0.014(2)	0.008(5)	0.025(6)	0.010(5)	–0.002(4)	0.003(4)	–0.001(4)
O7	0.7201(4)	0.3460(8)	0.4937(12)	0.012(2)	0.011(6)	0.013(5)	0.014(5)	–0.003(4)	0.008(4)	0.002(4)
OW	0.5	0.391(2)	0.75	0.089(8)	0.095(24)	0.094(20)	0.081(20)	0.0	0.022(17)	0.0
H	0.525(8)	0.442(5)	0.829 (19)	0.08(8)						

* Refined Cl:OH occupancy: 0.75(4):0.25(4).

TABLE 5. Bond-valence analysis for thorneite

	O1	O2	O3	O4	O5	O6	O7	OW	Cl	Sum
Te			1.079	1.044	0.963	0.965	0.857, 0.846			5.754
C	1.307	1.387 ×2→								4.080
Pb1	0.088 ×2↓	0.190, 0.046	0.445, 0.023	0.027	0.391	0.506, 0.117			0.125	1.958
Pb2			0.299, 0.099	0.379	0.341, 0.241		0.214, 0.023		0.339, 0.094	2.029
Pb3	0.232 ×2↓	0.405, 0.029		0.486		0.407	0.024	0.197 ×2↓	0.152, 0.117	2.049
H								0.926	0.074	1.000
H′								0.931	0.069	1.000
Sum	1.946	2.057	1.945	1.936	1.936	1.994	1.964	2.252	0.970	

Notes: Values are expressed in valence units. Multiplicity is indicated by ×→↓; Pb^{2+}-O bond strengths from Krivovichev and Brown (2001); Pb^{2+}-Cl bond strengths from Brese and O'Keeffe (1991); Te^{6+}-O bond strengths and hydrogen-bond strengths based on H···Cl/H···O bond lengths from Brown and Altermatt (1985); bond strength for Cl site assigned in accord with refined site occupancy $[Cl_{0.75}(OH)_{0.25}]$.

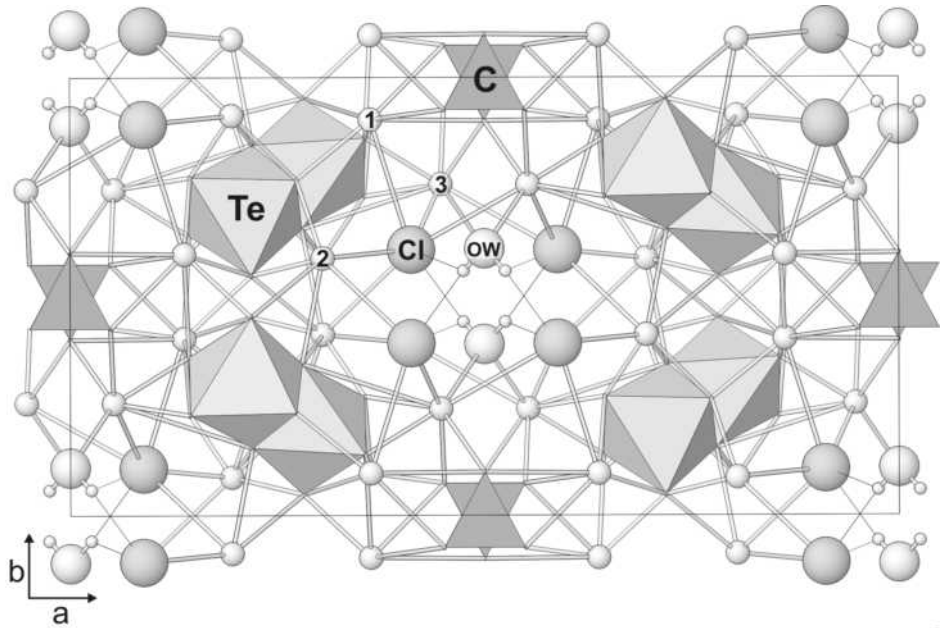

FIGURE 4. Structure of thorneite viewed down **c**. Numbered spheres are Pb atoms (Pb1, Pb2 and Pb3). Smallest spheres associated with OW are H atoms.

(Kampf et al. 2010d); and paratimroseite, 1.926 Å (Kampf et al. 2010d); however, the TeO_6 octahedron exhibits significant distortion, attributable to the repulsion between the Te^{6+} cations across the O7-O7 shared edge of the dimer. Te-O distances vary from 1.889 to 1.979 Å, O-Te-O angles vary from 77.3 to 100.9° and O-O distances vary from 2.469 to 2.923 Å. The Te-O7 distances are the longest, the O7-Te-O7 angle is the smallest and the O7-O7 edge is the shortest. The edge-sharing octahedral tellurate dimer, $[Te_2^{6+}O_{10}]^{8-}$, has not yet been found in any other mineral structure; however, it has been reported in synthetic compounds, cf. $K_4[Te_2^{6+}O_6(OH)_4](H_2O)_{7.3}$ (Lindqvist and Lundgren 1966), $Na_2K_4[Te_2^{6+}O_8(OH)_2](H_2O)_{14}$ (Lindqvist 1969), and Na_4TeO_5 (Untenecker and Hoppe 1987). Similar octahedral distortions related to Te^{6+} repulsions occur in all of these structures.

The Pb atoms have lopsided nine- and tenfold coordinations (Fig. 5) attributable to the $6s^2$ lone-electron-pair effect typically exhibited by Pb^{2+} (e.g., Moore 1988; Cooper and Hawthorne 1994; Kharisun et al. 1997; Mills et al. 2009). In fact, the Pb atoms in the structures of all seven recently discovered new minerals from Otto Mountain exhibit this effect.

The two equivalent H atoms of the OW group form bifurcated H bonds to two equivalent Cl sites (shown in Fig. 4). The H bonds are relatively long (2.68 and 2.71 Å), leaving OW relatively oversaturated. The 0.25 H atom associated with the 0.25 O at the Cl site may participate in an H bond to OW, but based upon the shortest Cl-OW bond length (3.175 Å) this would contribute a bond strength of about 0.005 valence units.

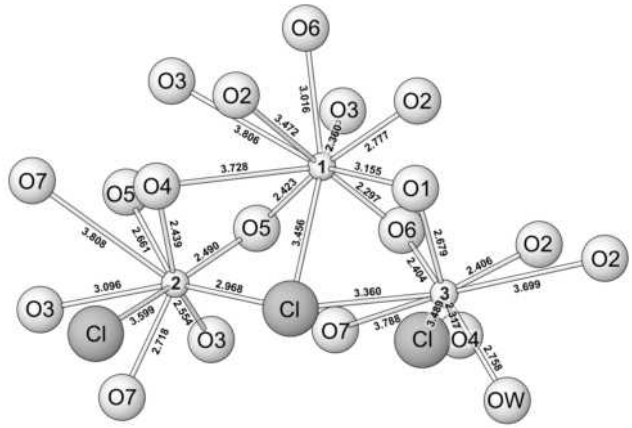

FIGURE 5. Coordinations of the Pb1, Pb2, and Pb3 atoms in thorneite. The lopsided distributions of bond lengths are attributable to the localization of the lone-pair electrons. Bond lengths are given in angstroms.

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