Lead-tellurium oxysalts from Otto Mountain near Baker, California: II. Housleyite, Pb₆CuTe₄O₁₈(OH)₂, a new mineral with Cu-Te octahedral sheets

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ABSTRACT

Housleyite, Pb₆CuTe₄O₁₈(OH)₂, is a new tellurate from Otto Mountain near Baker, California, named in honor of Robert M. Housley. The new mineral occurs on fracture surfaces and in small vugs in brecciated quartz veins. Housleyite is directly associated with acanthite, cerussite, gold, iodargyrite, khinite-40, wulfenite, and three other new tellurates: markcooperite, ottoite, and thorneite. A variety of other secondary minerals occur in the veins, including three other new secondary tellurium minerals, paratimroseite, telluroperite, and timroseite. Housleyite is monoclinic, space group $P2_1/n$, a = 7.8552(5), b = 10.4836(7), c = 11.0426(8) Å, $\beta = 95.547(2)^{\circ}$, and Z = 2. Crystals are prismatic to bladed with elongation parallel to **b** and typically occur in bow tie-like aggregates, drusy balls, and irregular sprays. It is pale to medium greenish blue and transparent, with pale blue streak and adamantine luster. Mohs hardness is estimated at 3. The mineral is brittle, with an irregular fracture. Cleavage was not observed, but is likely on $\{10\overline{1}\}$. The calculated density is 7.845(1) g/cm³. Housleyite is biaxial (+), with $2V = 50^{\circ}$ to 60° and strong inclined dispersion, r > v, but indices of refraction are too high to be measured. The optic orientation is $Y = \mathbf{b}$, $Z^{\wedge} \mathbf{c} \approx 40^{\circ}$ in obtuse β and pleochroism is Y (medium green-blue) > Z (light green-blue) > X. Energy dispersive spectroscopy provided PbO 62.53, CuO 3.77, TeO₃ 32.85, H_2O 0.84 (structure), total 99.99 wt%; the empirical formula (based on O =20) is $Pb_{5.99}Cu_{1.01}Te_{4.00}O_{18}(OH)_2$. The strongest powder X-ray diffraction lines are $[d_{obs} \text{ in } \text{\AA} (hkl) I]$: 3.336 (202, 031, 122) 69, 3.292 (113) 50, 3.195 (130, 103) 100, 3.068 (221, 202) 47, 3.007 (023) 49, 2.942 (032, 212) 80, 2.723 (123, $\overline{2}13$, 132) 29, 2.580 (230, $\overline{3}01$, $\overline{2}31$) 38. The crystal structure (R_1 = (0.028) consists of corner-sharing chains of TeO₆ octahedra along [101] linked into slabs parallel to {101} by sharing edges and corners with strongly Jahn-Teller (4+2) distorted and severely skewed CuO₆ octahedra. Lead (Pb) atoms in lopsided nine- and elevenfold coordinations form additional links within and between the octahedral sheets.

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

INTRODUCTION

Housleyite, Pb₆CuTe₄O₁₈(OH)₂, is one of seven new secondary 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. (2010b).

Housleyite is named in honor of Robert M. Housley (b. 1934), Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California, U.S.A. Robert Housley's scientific career in experimental solid-state physics and materials characterization has spanned nearly five decades. While much of his professional work has focused on planetary/meteoritic materials, he has always had a strong interest in terrestrial mineralogy. In recent years, his personal mineral collecting efforts have brought to light many unusual occur-

OCCURRENCE

Housleyite was found at the Aga mine, (35° 16.399'N 116° 05.665'W) on Otto Mountain, ~2 km northwest of Baker, San Bernardino County, California, U.S.A., and in the Bird Nest drift on the southwest flank of Otto Mountain 0.7 km northwest of the Aga mine (35° 16.606'N 116° 05.956'W).

rences of rare minerals in southern California and surrounding areas. His chemical analytical work has served to identify and characterize several new minerals. He has been very involved in work on the unusual secondary tellurium mineral assemblages in the mine workings on Otto Mountain near Baker, California. Robert Housley 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 2009-024). Three cotype specimens are deposited in the Natural History Museum of Los Angeles County, catalog numbers 62261, 62262, and 62263.

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Housleyite is rare and occurs on fracture surfaces and in small vugs in quartz veins. Species observed in direct association with the new mineral include acanthite, cerussite, gold, iodargyrite, khinite-40, wulfenite, and three other new tellurates: markcooperite [Pb₂(UO₂)TeO₆] (IMA2009-045; Kampf et al. 2010a), ottoite [Pb₂TeO₅] (IMA2009-063; Kampf et al. 2010b), and thorneite $[Pb_{6}(Te_{2}O_{10})(CO_{3})Cl_{2}(H_{2}O)]$ (IMA2009-023; Kampf et al. 2010c). Other species identified in the assemblages include: anglesite, atacamite, boleite, brochantite, burckhardtite, calcite, caledonite, celestine, chalcopyrite, bromine-rich chlorargyrite, chrysocolla, devilline, diaboleite, fluorite, fornacite, galena, goethite, hessite, jarosite, kuranakhite, linarite, malachite, mimetite, mottramite, munakataite, murdochite, muscovite, perite, phosphohedyphane, plumbojarosite, pyrite, schieffelinite, vanadinite, vauquelinite, and three other new minerals: paratimroseite [Pb₂Cu²⁺₄(Te⁶⁺O₆)₂(H₂O)₂] (IMA2009-065; Kampf et al. 2010d), telluroperite [Pb₃Te⁴⁺O₄Cl₂] (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.

Housleyite and most other secondary minerals of the quartz veins are interpreted as having formed from the partial oxidation of primary sulfides (e.g., galena and chalcopyrite) 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 with elongation parallel to **b**. They are up to 0.15 mm in length and typically occur in bow tie-like aggregates, drusy balls, and irregular sprays (Fig. 1). Crystals exhibit the forms $\{001\}$, $\{10\overline{1}\}$, $\{011\}$, and $\{010\}$ (Fig. 2). Penetration twinning appears to occur occasionally with individual prisms intersecting at about 60°, the plane containing the intersecting crystals being parallel to one of the prominent prism faces. Unfortunately, efforts to remove an intact twin from matrix for study were unsuccessful, so the twin law could not be determined.

Housleyite is pale to medium greenish blue and transparent, with pale blue streak. The luster is adamantine, although crystal faces are sometimes frosted giving them a dull luster. The mineral is nonfluorescent. The Mohs hardness is estimated at 3. The tenacity is brittle and the fracture is irregular. Cleavage was not observed, but is likely on $\{10\overline{1}\}$ based upon the crystal structure. The density could not be measured because it is greater than



FIGURE 1. Backscatter SEM image of housleyite crystals on quartz (FOV $120 \ \mu m$).

those of available high-density liquids and there is insufficient material for physical measurement. The density calculated for the ideal formula is 7.845(1) g/cm³.

The indices of refraction exceed those of available index fluids. The Gladstone-Dale relationship (Mandarino 1981) predicts $n_{av} = 2.169$ based on the ideal formula. Orthoscopic and conoscopic optical examination using a Leitz Ortholux I polarizing microscope equipped with a Supper spindle stage showed housleyite to be biaxial (+), with $2V = 50^{\circ}$ to 60° and strong inclined dispersion, r > v. Because the interference figure is relatively diffuse, the 2V could not be determined more precisely. The optic orientation is $Y = \mathbf{b}$, $Z \wedge \mathbf{c} \approx 40^{\circ}$ in obtuse β . The mineral is pleochroic with Y (medium green-blue) > Z (light green-blue) > X.

CHEMISTRY

Three chemical analyses carried out using a JEOL8200 electron microprobe (WDS mode, 15 kV, 15 nA, 5 μ m beam diameter) at the Division of Geological and Planetary Sciences, California Institute of Technology, provided the averages (and ranges): PbO 58.93 (57.67–59.95), TeO₃ 33.22 (32.43–33.98), CuO 3.48 (3.37–3.56), H₂O 0.84 (structure), total 96.47 (95.32–97.36) wt%. Note that the crystals are prone to electron beam damage. This and sample porosity contributes to the low analytical total, even though we used the mildest analytical conditions feasible. This problem of sample instability in the electron beam appears to be common in tellurates (cf. Grundler et al. 2008; Mills et al. 2008, 2009b, 2010). We found that beam damage tends to yield significantly lower Pb and Cu contents relative to Te. Standards used were PbS, Cu metal, and Te metal.

Three other analyses were carried out using a Philips XL30 FESEM equipped with an Oxford Inca thin-window EDS detector and IMIX data analysis software (EDS mode, 15 kV, low beam current) providing the averages (and ranges): PbO 62.53 (60.74–64.09), CuO 3.77 (3.17–3.72), TeO₃ 32.85 (32.66–32.96), H₂O 0.84 (structure), total 99.99 wt%. Oxygen was determined by stoichiometry and individual analysis totals (excluding H₂O) were between 98 and 100 wt%. Standards used were PbF₂, Cu metal, and HgTe.

The EMP (after normalization) and EDS empirical formulae (based on O = 20) are $Pb_{5.74}Cu_{0.95}Te_{4.11}O_{18}(OH_{0.98})_2$ and $Pb_{5.99}Cu_{1.01}Te_{4.00}O_{18}(OH)_2$, respectively. The simplified formula is $Pb_6CuTe_4O_{18}(OH)_2$ that requires PbO 62.60, CuO 3.72, TeO₃ 32.84, H₂O 0.84, 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.



FIGURE 2. Housleyite crystal drawing (clinographic projection).

The powder data presented in Table 1 show good agreement with the pattern calculated from the structure determination.

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 OH) is bonded to an H atom. A difference Fourier revealed a likely location for this H atom, the position of which was constrained to an H-OH distance of 0.90(3) Å in the final refinement.

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. Note that structure factors and CIF data are on deposit¹.

¹ Deposit item AM-10-043, structure factors and CIF. 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.

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TABLE 2. Data collection and structure refinement details for housleyite

Diffractometer	Rigaku R-Axis Spider with curved imaging plate
X-ray radiation/power	MoKα (λ = 0.71075 Å)/50 kV, 40 mA
Temperature	298(2) K
Formula	Pb ₆ CuTe₄O ₁₈ (OH) ₂
Space group	P2 ₁ /n
Unit-cell dimensions	<i>a</i> = 7.8552(5) Å
	<i>b</i> = 10.4836(7) Å
	<i>c</i> = 11.0426(8) Å
	$\beta = 95.547(2)^{\circ}$
Ζ	2
Volume	905.1(1) Å ³
Density (for ideal formula)	7.845(1) g/cm ³
Absorption coefficient	63.168 mm ⁻¹
F(000)	1780
Crystal size	$0.045 \times 0.035 \times 0.015 \text{ mm}^3$
θrange	3.05° to 27.48°
Index ranges	$-10 \le h \le 10, -13 \le k \le 12, -14 \le l \le 14$
Reflections collected/unique	19181/2071 [R _{int} = 0.0718]
Reflections with $F_{o} > 4\sigma F$	1832
Completeness to $\theta = 27.50^{\circ}$	99.6%
Max. and min. transmission	0.4509 and 0.1633
Refinement method	Full-matrix least-squares on F ²
Parameters refined	146
GoF	1.090
Final <i>R</i> indices $[F_o > 4\sigma F]$	$R_1 = 0.028$, w $R_2 = 0.048$
R indices (all data)	$R_1 = 0.036$, w $R_2 = 0.050$
Largest diff. peak/hole	1.755/–1.849 e/ų
Notes: $R_{\rm int} = \Sigma F_{\rm o}^2 - F_{\rm o}^2({\rm mean}) /2$	$\Sigma[F_o^2]$. GoF = S = { $\Sigma[w(F_o^2 - F_o^2)^2]/(n-p)$ } ^{1/2} . $R_1 = \Sigma F_o ^2$

 $-|F_c||/\Sigma|F_o|.wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}.w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP] \text{ where } a$ is 0.0020, b is 19.9615, and P is [2F_c²+Max(F_o²,0)]/3.

l _{obs}	$d_{\rm obs}$		$d_{ m calc}$	I _{calc}	hkl	lobs	$d_{ m obs}$		d_{calc}	I _{calc}	hkl
16	6.681		6.689	27	101 *			ſ	2.030	6	143
11	6.119		6.112	15	101 *	16	2.026	Į	2.028	5	115
17	4.743		4.736	21	021 *			1	2.028	6	150
10	3.968		3.988	12	112 *				2.007	6	125
8	3.805		3.796	12	022 *			ſ	2.007	8	332
13	3.579		3.579	15	211 *	27	2.002	Į	2.003	19	151 *
18	3.460		3.460	18	013 *			1	1.994	17	224 *
			3.392	15	211	6	1.921	, c	1.926	10	410
		ſ	3.344	48	202 *	6	1 000	ſ	1.908	6	332
69	3.336	Į	3.334	11	031	0	1.900	1	1.899	6	323
			3.331	25	122			-	1.873	8	412
50	3.292	•	3.276	58	113			ſ	1.869	15	225 *
		ſ	3.205	12	103	29	1.867	Į	1.867	19	411 *
100	3.195	Į	3.194	100	130 *			1	1.861	14	324
			3.139	40	220	27	1 001	ŕ	1.806	16	341*
17	3 068	7	3.081	43	221 *	27	1.801	1	1.796	16	116 *
7/	5.000	1	3.056	34	202 *	15	1 78/	Ì	1.789	8	4 22
49	3.007	-	3.005	58	023 *	15	1.704	1	1.774	7	4 13
		ſ	2.952	56	032 *	12	1 740	ć	1.756	7	153
80	2.942	Į	2.934	69	212 *	15	1.749	1	1.743	10	315
			2.882	17	123	18	1.728	-	1.730	15	026*
13	2.811		2.810	14	132 *			ſ	1.711	11	324
			2.749	20	004	26	1.697	Į	1.699	20	343 *
		ſ	2.735	11	123			1	1.696	10	422
29	2.723	Į	2.717	23	213 *	15	1 682	ŕ	1.685	4	045
			2.717	16	132	15	1.002	1	1.682	7	161
13	2.653	•	2.659	19	014	8	1 668	Ì	1.668	7	431
		ſ	2.609	18	230	0	1.000	1	1.666	4	244
38	2.580	Į	2.597	17	301	8	1 636	Ì	1.640	6	162
			2.576	37	231 *	0	1.050	1	1.636	4	350
12	2.538	•	2.534	9	310	14	1 6 1 9	Ì	1.623	6	253
16	2.522		2.521	13	311	14	1.015	1	1.621	14	162 *
15	2.481		2.485	14	213 *	6	1.582	-	1.584	12	216
15	2.447		2.443	14	141 *			ſ	1.560	7	163 *
8	2.296		2.301	12	214 *	6	1.557	Į	1.552	4	117
7	2.248		2.248	8	321			1	1.518	6	055
		ſ	2.133	10	043 *	17	1 507	ζ	1.512	10	414 *
13	2.125	۲.	2.125	8	134 *	17	1.507	1	1.509	7	155
		1	2.117	10	241 *	Notes: I	based upon	peak height	s. Intercalculated	d from the cr	vstal structu
13	2 059	ז	2.067	8	105 *	using P	owder Cell (Kra	us and Nolze	e 1996), <i>d</i> _{est} has	sed on the ce	ell refined fro
	2.039	1	2.062	11	051*	tho nov	udor data (*) uci	ng UnitColl (Holland and Por	dforp 1007) E	ofined cells

ire m a =ing Ur 7.871(1), b = 10.495(1), c = 11.046(1) Å, $\beta = 95.46(1)^{\circ}$, V = 908.5(1) Å³.

 TABLE 3.
 Atomic coordinates and displacement parameters (Å²) for housleyite

	х	У	Z	$U_{\rm eq}$	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Cu	0.5000	0.5000	1.0000	0.0099(4)	0.0108(8)	0.0094(8)	0.0092(9)	-0.0006(7)	-0.0009(7)	-0.0012(7)
Te1	0.15518(8)	0.36603(6)	0.80124(6)	0.0064(1)	0.0069(3)	0.0071(3)	0.0050(3)	-0.0001(2)	-0.0003(2)	-0.0001(2)
Te2	0.79491(8)	0.24012(6)	0.60876(6)	0.0067(1)	0.0071(3)	0.0075(3)	0.0055(3)	0.0002(2)	-0.0001(2)	-0.0002(2)
Pb1	0.34533(5)	0.18063(4)	0.57768(4)	0.0127(1)	0.0139(2)	0.0141(2)	0.0098(2)	0.0007(2)	-0.0005(2)	0.0011(2)
Pb2	0.45212(6)	0.53120(4)	0.66438(4)	0.0195(1)	0.0243(2)	0.0236(2)	0.0117(2)	-0.0038(2)	0.0075(2)	-0.0124(2)
Pb3	0.97051(5)	0.62715(4)	0.60367(4)	0.0184(1)	0.0143(2)	0.0239(2)	0.0166(2)	0.0046(2)	-0.0009(2)	-0.0046(2)
01	0.9867(9)	0.1837(7)	0.5294(6)	0.011(2)	0.011(3)	0.014(4)	0.011(4)	0.003(3)	0.006(3)	0.000(3)
02	0.3556(8)	0.4708(6)	0.8464(6)	0.009(1)	0.006(3)	0.012(4)	0.009(4)	0.002(3)	-0.002(3)	-0.006(3)
O3	0.6314(8)	0.1811(7)	0.4692(6)	0.008(1)	0.008(3)	0.014(3)	0.002(3)	0.001(3)	0.001(3)	-0.004(3)
04	0.9378(8)	0.2708(6)	0.7623(6)	0.009(1)	0.006(3)	0.011(3)	0.008(4)	0.001(3)	-0.003(3)	-0.003(3)
O5	0.2719(8)	0.2069(6)	0.7829(6)	0.009(1)	0.012(3)	0.008(3)	0.006(3)	0.002(3)	-0.002(3)	0.005(3)
06	0.1875(9)	0.4107(7)	0.6398(6)	0.015(2)	0.020(4)	0.019(4)	0.005(3)	0.000(3)	0.000(3)	-0.009(3)
07	0.4811(9)	0.0130(7)	0.6798(7)	0.012(2)	0.012(3)	0.010(3)	0.016(4)	-0.001(3)	0.004(3)	-0.001(3)
08	0.8162(9)	0.4033(7)	0.5396(7)	0.016(2)	0.020(4)	0.011(4)	0.016(4)	0.002(3)	-0.002(3)	-0.001(3)
09	0.5924(9)	0.2811(7)	0.6814(6)	0.014(2)	0.013(4)	0.021(4)	0.009(4)	-0.002(3)	0.002(3)	-0.003(3)
OH	0.7945(9)	0.0613(7)	0.6673(7)	0.015(2)	0.009(4)	0.020(4)	0.015(4)	0.004(3)	0.000(3)	0.000(3)
н	0.695(10)	0.081(14)	0.697(13)	0.050						

TABLE 4. Selected bond distances (Å) for housleyite

Pb1-07	2.294(7)	Pb2-O2	2.305(7)	Pb3-05	2.423(6)
Pb1-09	2.399(7)	Pb2-06	2.426(7)	Pb3-08	2.434(8)
Pb1-05	2.408(7)	Pb2-OH	2.608(7)	Pb3-01	2.510(7)
Pb1-O3	2.647(7)	Pb2-05	2.651(7)	Pb3-07	2.668(7)
Pb1-01	2.816(7)	Pb2-O4	2.753(7)	Pb3-08	2.704(7)
Pb1-06	2.826(8)	Pb2-09	2.843(7)	Pb3-06	2.843(8)
Pb1-O2	2.879(7)	Pb2-08	3.012(7)	Pb3-06	2.877(7)
Pb1-O4	3.661(7)	Pb2-O3	3.394(7)	Pb3-09	2.951(7)
Pb1-OH	3.792(7)	Pb2-08	3.555(8)	Pb3-OH	3.496(8)
Pb1-O3	3.834(7)	<pb2-0></pb2-0>	2.839	<pb3-o></pb3-o>	2.767
Pb1-07	3.849(7)				
<pb1-0></pb1-0>	3.037				
Cu-01	1.957(7)	Te1-06	1.884(7)	Te2-08	1.887(7)
Cu-01	1.957(7)	Te1-07	1.899(7)	Te2-09	1.899(7)
Cu-02	1.971(7)	Te1-05	1.923(7)	Te2-01	1.909(7)
Cu-02	1.971(7)	Te1-O2	1.944(6)	Te2-04	1.967(7)
Cu-OH	2.648(8)	Te1-O3	1.946(7)	Te2-OH	1.984(8)
Cu-OH	2.648(8)	Te1-04	1.989(6)	Te2-O3	2.006(6)
<cu-0></cu-0>	2.192	<te1-0></te1-0>	1.931	<te2-0></te2-0>	1.942
Hydrogen	bonds (D = d	lonor, A = acc	eptor)		
D-H	d(D-H)	d(H-A)	D-H-A	d(D-A)	Α
OH-H	0.90(3)	1.81(11)	135°	2.530(10)	07
OH-H	0.90(3)	2.25(13)	120°	2.811(11)	09

DESCRIPTION OF THE STRUCTURE

The structure of housleyite (Fig. 3) consists of corner-sharing chains of TeO₆ octahedra along [101] linked into undulating sheets parallel to $\{10\overline{1}\}$ by sharing edges and corners with CuO₆ octahedra. Bonds to Pb atoms form additional links within and between the octahedral sheets.

The TeO₆ octahedra exhibit moderate distortion. For the Te1 and Te2 octahedra, Te-O distances range from 1.884 to 1.989 Å and from 1.887 to 2.006 Å, respectively, and O-Te-O angles range from 85.4 to 97.7° and from 83.3 to 97.8°. The CuO₆ octahedra

 TABLE 5.
 Bond-valence analysis for housleyite

are strongly Jahn-Teller (4+2) distorted and severely skewed. The Cu forms short bonds to O1 of 1.957 (×2) and to O2 of 1.971 Å (×2) yielding a fairly regular square-planar array with O-Cu-O angles of 87.4 and 92.6°. The apical OH atoms of the Cu octahedron are at distances of 2.648 Å and have O1-Cu-OH angles of 66.4 and 113.6° and O2-Cu-OH angles of 77.1 and 102.9°. The Pb atoms have lopsided nine- and elevenfold coordinations (Fig. 4) attributable to the 6s² lone-electron-pair effect typically exhibited by Pb2+ (e.g., Moore 1988; Cooper and Hawthorne 1994; Kharisun et al. 1997; Mills et al. 2009a). In fact, the Pb atoms in the structures of all seven recently discovered new minerals from Otto Mountain exhibit this effect. The hydrogen atom of the hydroxyl group appears to form a bifurcated hydrogen bond to O7 and O9. The hydrogen bond to O9 is unusual in that OH and O9 form one of the edges of the Te2 octahedron; however, the bonding geometry (Fig. 5) and bond-valence analysis (Table 5) support this H bond assignment.

A corner-sharing chain of $Te^{6+}O_6$ octahedra is found in one other mineral, ottoite (Kampf et al. 2010b); however, the configurations of the chains in the two structures are different. The octahedral chains in housleyite consist of two different $Te^{6+}O_6$ octahedra that alternate along the chains. The Te1 octahedra share *cis* corners and the Te2 octahedra share *trans* corners. In ottoite there is only one type of $Te^{6+}O_6$ octahedron and it links to equivalent octahedra by sharing *trans* corners. Another difference is that the chains in ottoite are linked to one another only via Pb-O bonds.

Housleyite is chemically most closely allied with khinite (khinite-4*O* and khinite-3*T*), PbCu₃TeO₆(OH)₂ (Burns et al. 1995; Cooper et al. 2008; Hawthorne et al. 2009). Although all three structures are based upon layers of Te⁶⁺O₆ and Jahn-Teller

	01	02	O3	04	05	06	07	08	09	OH	Σv _c
Pb1	0.175	0.154	0.248 0.022	0.031	0.403	0.172	0.509 0.021		0.411	0.024	2.170
Pb2		0.498	0.054	0.199	0.246	0.389		0.118 0.039	0.166	0.268	1.977
Pb3	0.327				0.391	0.166 0.155	0.237	0.382 0.220	0.133	0.044	2.055
Cu	$0.472 \times 2 \rightarrow$	$0.454 \times 2 \rightarrow$								$0.073 \times 2 \rightarrow$	1.998
Te1		0.930	0.925	0.823	0.984	1.093	1.050				5.805
Te2	1.022		0.786	0.874				1.084	1.050	0.834	5.650
н							0.182		0.080	0.738	1.000
Σva	1.996	2.036	2.035	1.927	2.024	1.975	1.999	1.843	1.840	1.981	
Notes: streng	Values are exp ths and hydrog	ressed in valer en-bond strer	nce units. Multip ngths based on I	licity is indic ⊣…O bond le	ated by $\times \rightarrow$; ngths from B	Pb ²⁺ -O bond str rown and Alterr	rengths from F natt (1985).	(rivovichev and	Brown (200	01); Cu ²⁺ -O and Te	⁶⁺ -0 bond



FIGURE 3. Structure of housleyite viewed down [101] (top) and [101] (bottom). The Pb1, Pb2, and Pb3 atoms are shown as spheres.



FIGURE 4. Coordinations of the Pb1, Pb2, and Pb3 atoms in housleyite. The lopsided distributions of bond lengths are attributable to the localization of the lone-pair electrons. Bond lengths are given in angstroms.



FIGURE 5. Hydrogen bonding in housleyite.

distorted $Cu^{2+}O_6$ octahedra, the layers in the housleyite structure are quite different from those in the khinite polymorphs.

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REFERENCES CITED

- Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M.C., Polidori, G., and Camalli, M. (1994) SIR92—A program for automatic solution of crystal structures by direct methods. Journal of Applied Crystallography, 27, 435.
- Brown, I.D. and Altermatt, D. (1985) Bond-valence parameters from a systematic analysis of the inorganic crystal structure database. Acta Crystallographica, B41, 244–247.
- Burns, P.C., Cooper, M.A., and Hawthorne, F.C. (1995) Parakhinite, Pb²⁺Cu³⁺Te⁶⁺O₆(OH)₂: Crystal structure and revision of the chemical formula. Canadian Mineralogist, 33, 33–40.
- Cooper, M. and Hawthorne, F.C. (1994) The crystal structure of wherryite, Pb₇Cu₂(SO₄)₄(SiO₄)₂(OH)₂, a mixed sulfate-silicate with [^[6]M(TO₄)₂Φ] chains. Canadian Mineralogist, 32, 373–380.
- Cooper, M.A., Hawthorne, F.C., and Back, M.E. (2008) The crystal structure of khinite and polytypism in khinite and parakhinite. Mineralogical Magazine, 72, 763–770.
- Grundler, P., Brugger, J., Meisser, N., Ansermet, S., Borg, S., Etschmann, B., Testemale, D., and Bolin, T. (2008) Xocolatlite, Ca₂Mn₂⁴⁺Te₂O₁₂·H₂O, a new tellurate related to kuranakhite: Description and measurement of Te oxidation

state by XANES spectroscopy. American Mineralogist, 93, 1911-1920.

- Hawthorne, F.C., Cooper, M.A., and Back, M.E. (2009) Khinite-40 [= khinite] and khinite-3T [= parakhinite]. Canadian Mineralogist, 47, 473–476.
- Holland, T.J.B. and Redfern, S.A.T. (1997) Unit cell refinement from powder diffraction data: the use of regression diagnostics. Mineralogical Magazine, 61, 65–77.
- Kampf, A.R., Mills, S.J., Housley, R.M., Marty, J., and Thorne, B. (2010a) Lead-tellurium oxysalts from Otto Mountain near Baker, California: IV. The description and crystal structure of the new mineral markcooperite, Pb₂(UO₂) TeO₆. American Mineralogist, 95, in press.
- Kampf, A.R., Housley, R.M., Mills, S.J., Marty, J., and Thorne, B. (2010b) Lead-tellurium oxysalts from Otto Mountain near Baker, California: I. Ottoite, Pb₂TeO₅, a new mineral with chains of tellurate octahedra. American Mineralogist, 95, 1329–1336.
- Kampf, A.R., Housley, R.M., and Marty, J. (2010c) Lead-tellurium oxysalts from Otto Mountain near Baker, California: III. The description and crystal structure of the new mineral thorneite, Pb₆(Te₂O₁₀)(CO₃)Cl₂(H₂O). American Mineralogist, 95, in press.
- Kampf, A.R., Mills, S.J., Housley, R.M., Marty, J., and Thorne, B. (2010d) Lead-tellurium oxysalts from Otto Mountain near Baker, California: V. The description and crystal structure of the new minerals timroseite, Pb₂Cu³⁺₂(Te⁶⁺O₆)₂(OH)₂, and paratimroseite, Pb₂Cu³⁺₄(Te⁶⁺O₆)₂(H₂O)₂. American Mineralogist, 95, in press.
- (2010e) Lead-tellurium oxysalts from Otto Mountain near Baker, California: VI. The description and crystal structure of the new mineral telluroperite, Pb₃Te⁴⁺O₄Cl₂. American Mineralogist, 95, in press.
- Kharisun, Taylor, M.R., Bevan, D.J.M., Rae, A.D., and Pring, A. (1997) The crystal structure of mawbyite, PbFe₂(AsO₄)₂(OH)₂. Mineralogical Magazine, 61, 685–691.
- Kraus, W. and Nolze, G. (1996) POWDER CELL—a program for the representation and manipulation of crystal structures and calculation of the resulting X-ray powder patterns. Journal of Applied Crystallography, 29, 301–303.
- Krivovichev, S.V. and Brown, I.D. (2001) Are the compressive effects of encapsulation an artifact of the bond valence parameters? Zeitschrift f
 ür Kristallographie, 216, 245–247.
- Mandarino, J.A. (1981) The Gladstone-Dale relationship. IV. The compatibility concept and its application. Canadian Mineralogist, 19, 441–450.
- Mills, S.J., Groat, L.A., and Kolitsch, U. (2008) Te, Sb and W mineralization at the Black Pine mine, Montana. Poster, 18th Annual V.M. Goldschmidt Conference, Vancouver, Canada, July 13–18, 2008. Abstract in Geochimica et Cosmochimica Acta, 72, Special Supplement 12S, A632.
- Mills, S.J., Kampf, A.R., Raudsepp, M., and Christy, A.G. (2009a) The crystal structure of Ga-rich plumbogummite from Tsumeb, Namibia. Mineralogical Magazine, 73, 837–845.
- Mills, S.J., Kolitsch, U., Miyawaki, R., Groat, L.A., and Poirier, G. (2009b) Joëlbruggerite, Pb₃Zn₃(Sb⁵⁺,Te⁶⁺)As₂O₁₃(OH,O), the Sb⁵⁺ analog of dugganite, from the Black Pine mine, Montana. American Mineralogist, 94, 1012–1017.
- Mills, S.J., Kampf, A.R., Kolitsch, U., Housley, R.M., and Raudsepp, M. (2010) The crystal chemistry and crystal structure of kuksite, Pb₃Zn₃Te⁶⁺P₂O₁₄, and a note on the crystal structure of yafsoanite, (Ca,Pb)₃Zn(TeO₆)₂. American Mineralogist, 95, 933–938.
- Moore, P.B. (1988) The joesmithite enigma: Note on the 6s² Pb²⁺ lone pair. American Mineralogist, 73, 843–844.
- Sheldrick, G.M. (2008) A short history of SHELX. Acta Crystallographica, A64, 112–122.

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