

NEW MINERALS FROM THE REDMOND MINE, NORTH CAROLINA, USA: II. CUBOTHIOPLUMBITE AND HEXATHIOPLUMBITE, TWO NEW MINERALS CONTAINING THE CUBANE-LIKE $[\text{Pb}_4(\text{OH})_4]^{4+}$ STRUCTURAL UNIT

ANTHONY R. KAMPF[§]

Mineral Sciences Department, Natural History Museum of Los Angeles County, 900 Exposition Boulevard, Los Angeles, California 90007, USA

JASON B. SMITH

2148 McClintock Rd., Charlotte, North Carolina 28205, USA

JOHN M. HUGHES

Department of Geology, University of Vermont, Burlington, Vermont 05405, USA

CHI MA

Division of Geological and Planetary Sciences, California Institute of Technology, 1200 East California Boulevard, Pasadena, California 91125, USA

CHRISTOPHER EMPROTO

Department of Earth and Environmental Sciences, University of Michigan, 1100 North University Avenue, Ann Arbor, Michigan 48109, USA

ABSTRACT

The new minerals cubothioplumbite (IMA2021-091) and hexathioplumbite (IMA2021-092), both with the ideal formula $[\text{Pb}_4(\text{OH})_4]\text{Pb}(\text{S}_2\text{O}_3)_3$, were found in the Redmond mine, Haywood County, North Carolina, USA, where they occur together in a highly unusual secondary assemblage that comprises a variety of rare Pb-Zn-Cu sulfates, thiosulfates, and carbonates. Cubothioplumbite has the following properties: yellow equant crystals to about 0.5 mm; white streak; adamantine luster; brittle; Mohs hardness 3; conchoidal fracture; no cleavage; 5.748 g/cm^3 calculated density; isotropic with $n > 2.00$. Hexathioplumbite has the following properties: colorless hexagonal prisms to about 1 mm; white streak; adamantine luster; brittle; Mohs hardness $2\frac{1}{2}$; curved fracture; no cleavage; 5.531 g/cm^3 calculated density; uniaxial (–) with $\omega = 2.005(5)$ and $\varepsilon = 1.995(5)$. Electron probe microanalyses provided the empirical formulae $[\text{Pb}_4(\text{OH})_4]\text{Pb}(\text{S}_2\text{O}_3)_{2.72}(\text{SO}_4)_{0.28}$ and $[\text{Pb}_4(\text{OH})_4]\text{Pb}(\text{S}_2\text{O}_3)_{2.68}(\text{SO}_4)_{0.32}$ for cubothioplumbite and hexathioplumbite, respectively. Cubothioplumbite is cubic, $P\bar{a}3$, $a = 14.9179(13) \text{ \AA}$, $V = 3319.9(9) \text{ \AA}^3$, and $Z = 8$. Hexathioplumbite is hexagonal, $P6_3$, $a = 10.7213(10)$, $c = 8.6541(6) \text{ \AA}$, $V = 861.49(17) \text{ \AA}^3$, and $Z = 2$. The structures of cubothioplumbite ($R_1 = 0.0354$ for $1090 I > 2\sigma I$) and hexathioplumbite ($R_1 = 0.0791$ for $1062 I > 2\sigma I$) both contain cubane-like $[\text{Pb}_4(\text{OH})_4]^{4+}$ structural units.

Keywords: cubothioplumbite, hexathioplumbite, new mineral, crystal structure, thiosulfate, Pb^{2+} lone-pair electrons, cubane-like $[\text{Pb}_4(\text{OH})_4]^{4+}$ cluster, Redmond mine, North Carolina, USA.

[§] Corresponding author e-mail address: akampf@nhm.org

INTRODUCTION

The Redmond mine, a very small and long-inactive lead-zinc mine in western North Carolina, was recently found to host a highly unusual secondary assemblage of Pb-Zn-Cu sulfates, thiosulfates, and carbonates. To date, we have identified at least 20 new Pb and Zn sulfate and thiosulfate phases in this assemblage. Of particular note is the fact that the crystal structures of many of these new phases contain rare and, in some cases, novel clusters involving short $\text{Pb}^{2+}\text{-O}$ bonds. In the first paper on the new minerals from the Redmond mine, the new species redmondite, hydroredmondite, and sulfator-edmondite were described (Kampf *et al.* 2023). In the present paper, two new dimorphous minerals, cubothioplumbite (IMA2021-091) and hexathioplumbite (IMA2021-092), are described. Both are ideally $[\text{Pb}_4(\text{OH})_4]\text{Pb}(\text{S}_2\text{O}_3)_3$ and have crystal structures containing the same cubane-like $[\text{Pb}_4(\text{OH})_4]^{4+}$ cluster.

The names of the two minerals are based on their respective crystal systems, cubic (cubo) and hexagonal (hexa), and on their composition, both being thiosulfates (thio) of lead (plumb). The new minerals and their names have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association. Type specimens are deposited in the collections of the Natural History Museum of Los Angeles County, Los Angeles, California, USA. Three cotype specimens of cubothioplumbite have catalogue numbers 76184, 76185, and 76186. Three cotype specimens of hexathioplumbite have catalogue numbers 76187, 76188, and 76189.

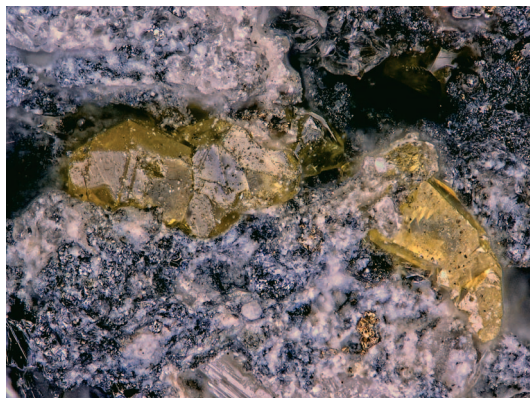


FIG. 1. Crystals of cubothioplumbite on cotype specimen #76184. The field of view is 0.68 mm across.



FIG. 2. A divergent group of prisms of hexathioplumbite on cotype specimen #76187. Note the tapered base of the prisms. The field of view is 0.36 mm across.



FIG. 3. Subparallel clusters of prisms of hexathioplumbite joined at their bases on cotype specimen #76189. This is presumed to be due to twinning on $\{001\}$. The field of view is 0.56 mm across.

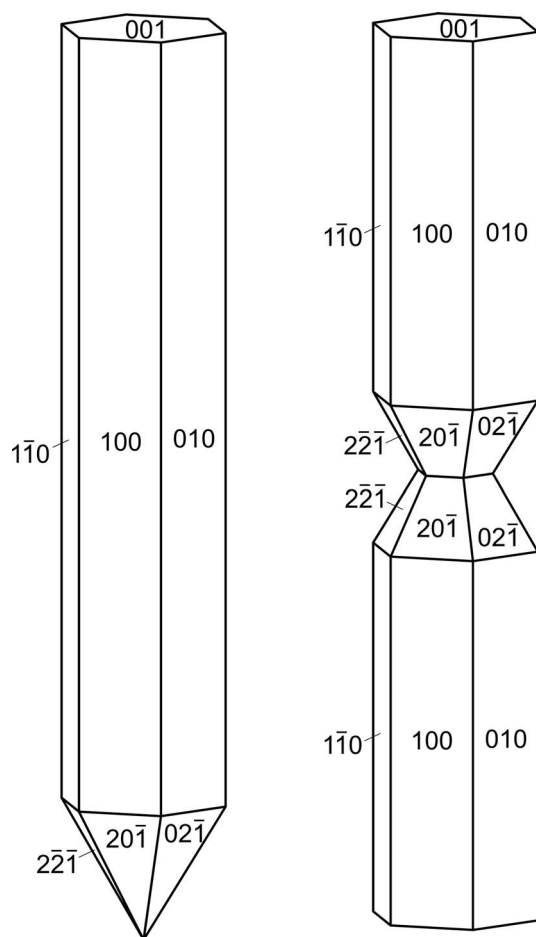


FIG. 4. Crystal drawings (clinographic projections) of hexathioplumbite: untwinned (left) and twinned by reflection on (001) (right).

OCCURRENCE

Cubothioplumbite and hexathioplumbite were found by one of the authors (JBS) underground at the Redmond mine, Haywood County, North Carolina, USA (35°40'55"N, 83°0'56"W). The ore, consisting mainly of galena and sphalerite with lesser chalcopyrite, occurs in an epithermal vein system consisting of disconnected sulfide-bearing quartz lenses near the contact between a granite gneiss and a mica schist (Espenshade *et al.* 1947). The new minerals occur in a localized, unusual secondary mineral assemblage that has been discussed in detail in our first paper in this series (Kampf *et al.* 2023). Cubothioplumbite and hexathioplumbite occur together in vugs in massive galena-sphalerite-chalcopyrite-quartz in close association with anglesite, cerussite, fassinaite, hydroredmondite, lanarkite, and steverustite.

PHYSICAL AND OPTICAL PROPERTIES

Cubothioplumbite

Cubothioplumbite crystals occur as yellow, transparent, cubic crystals up to about 0.5 mm in diameter (Fig. 1), consisting of various combinations of the forms {111} (octahedron), {110} (rhombic dodecahedron), {210} (pentagonal dodecahedron), and {211} (trapezohedron). No twinning was observed. The streak is white and the luster is adamantine. The mineral does not fluoresce under long- or short-wave ultraviolet light. The Mohs hardness is about 3 based on scratch tests. The tenacity is brittle, the fracture is conchoidal, and there is no cleavage. The density could not be measured because crystals exceed the density of available density fluids. The calculated density is 5.748 g/cm³ for the empirical formula and 5.763 g/cm³ for the ideal formula. In room-tempera-

TABLE 1. ANALYTICAL DATA (FOUR POINTS EACH) IN wt.% FOR CUBOTHIOPLUMBITE AND HEXATHIOPLUMBITE

Constituent	cubothioplumbite				hexathioplumbite				Ideal	Standard
	Mean	Range	S.D.	Norm.	Mean	Range	S.D.	Norm.		
PbO	73.81	73.41–74.16	0.33	77.74	71.30	71.16–71.15	0.16	77.75	77.48	PbS
SO ₃	(30.26)	30.10–30.47	0.17		(29.07)	28.80–29.36	0.23			anhydrite
SO ₃ *	15.87			16.71	15.35			16.74	16.68	
S*	5.76			6.07	5.49			5.99	6.68	
H ₂ O [§]	2.38			2.51	2.30			2.51	2.50	
O=S	–2.87			–3.02	–2.74			–2.99	–3.33	
Total	94.95			100.01	91.70			100.00	100.01	

* Allocated based on the structure (S₂O₃ + SO₄ = 3)

§ Based on the structure (O + S = 19 apfu)

Cubothioplumbite empirical formula: [Pb₄(OH)₄]Pb(S₂O₃)_{2.72}(SO₄)_{0.28}

Hexathioplumbite empirical formula: [Pb₄(OH)₄]Pb(S₂O₃)_{2.68}(SO₄)_{0.32}

Ideal formulae: [Pb₄(OH)₄]Pb(S₂O₃)₃

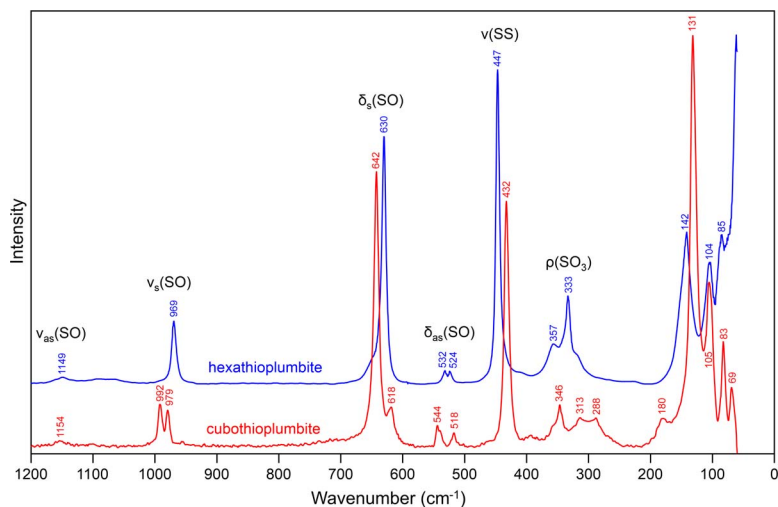


FIG. 5. The Raman spectra of cubothioplumbite and hexathioplumbite recorded with a 785 nm laser.

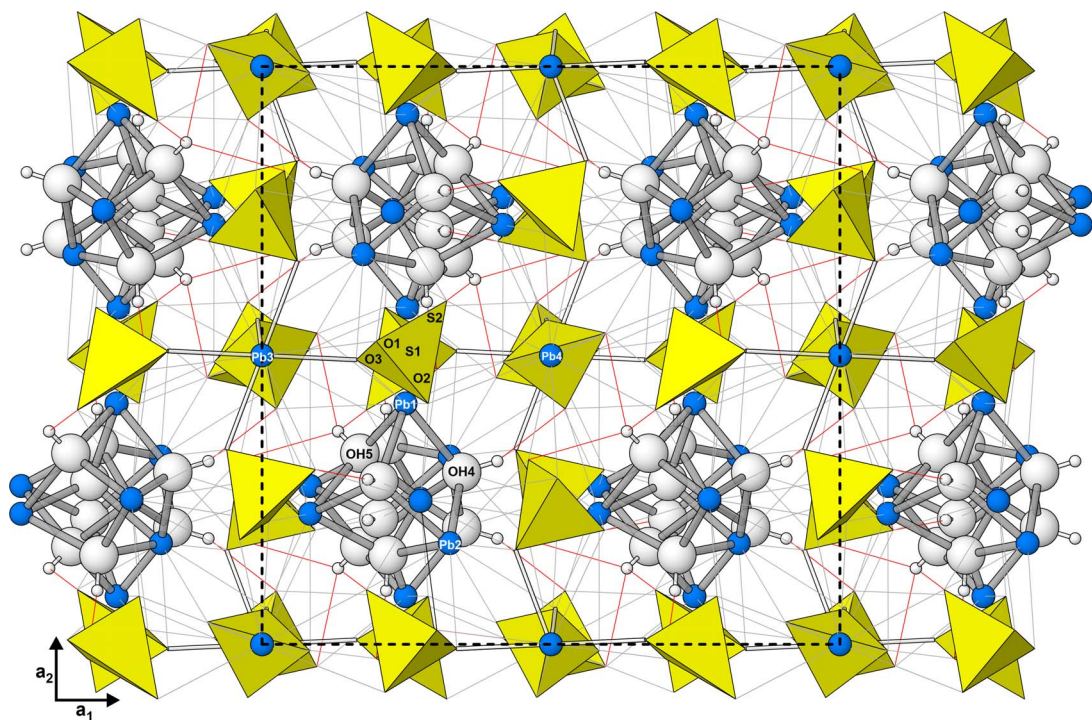


FIG. 6. The crystal structure of cubothioplumbite. Short (strong) Pb–O bonds are shown as thick gray sticks, medium length (moderately strong) Pb–O bonds are shown as white sticks, long (weak) Pb–O bonds are shown as thin gray lines, and hydrogen bonds are shown as thin red lines. The outline of the unit cell is shown by black dashed lines.

TABLE 2. DATA COLLECTION AND CRYSTAL-STRUCTURE REFINEMENT DETAILS FOR CUBOTHIOLPLUMBITE AND HEXATHIOLPLUMBITE

Mineral	cubothioplumbite	hexathioplumbite
Diffractometer	Rigaku R-Axis Rapid II	
X-ray rad. / power	MoK α ($\lambda = 0.71075$ Å) / 50 kV, 40 mA	
Temperature	293(2) K	
Structural formula (incl. unlocated H)	[Pb ₄ (OH) ₄]Pb(S ₂ O ₃) ₃	
Space group	<i>Pa</i> $\bar{3}$ (#205)	<i>P6</i> ₃ (#173)
Unit cell dimensions	<i>a</i> = 14.9179(13) Å	<i>a</i> = 10.7213(10) Å <i>c</i> = 8.6541(6) Å
<i>V</i>	3319.9(9) Å ³	861.49(17) Å ³
<i>Z</i>	8	2
Density (calc.)	5.753 g/cm ³	5.552 g/cm ³
Absorption coefficient	51.355 mm ⁻¹	49.476 mm ⁻¹
<i>F</i> (000)	4912	1228
Crystal size	170 × 170 × 130 μm	200 × 25 × 25 μm
θ range	3.35 to 27.43°	3.22 to 27.39°
Index ranges	−11 ≤ <i>h</i> ≤ 13 −15 ≤ <i>k</i> ≤ 19 −19 ≤ <i>l</i> ≤ 18	−13 ≤ <i>h</i> ≤ 13 −13 ≤ <i>k</i> ≤ 13 −7 ≤ <i>l</i> ≤ 11
Refl. collected	10556	4849
Independent reflections	1274; <i>R</i> _{int} = 0.116	1151; <i>R</i> _{int} = 0.060
Refl. with <i>I</i> > 2 σ	1090	1062
Completeness to $\theta_{\max}$	99.6 %	99.4 %
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Parameters/restraints	79/2	75/1
Goodness-of-fit	1.107	1.151
Final <i>R</i> indices [<i>I</i> > 2 σ]	<i>R</i> ₁ = 0.0353 <i>wR</i> ₂ = 0.0781 <i>R</i> ₁ = 0.0438 <i>wR</i> ₂ = 0.0813	<i>R</i> ₁ = 0.0791 <i>wR</i> ₂ = 0.1999 <i>R</i> ₁ = 0.0843 <i>wR</i> ₂ = 0.2120
<i>R</i> indices (all data)		0.07(6)
Absolute structure parameter		0.0011(9)
Extinction coefficient	0.00035(3)	
Largest diff. peak/hole	+2.03/−1.60 e Å ⁻³	+8.87/−2.61 e Å ⁻³

$R_{\text{int}} = \Sigma |F_o^2 - F_c^2(\text{mean})| / \Sigma [F_o^2]$. 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 $P = [2F_c^2 + \text{Max}(F_o^2, 0)] / 3$; for cubothioplumbite, *a* is 0.0308 and *b* is 15.5 and for hexathioplumbite, *a* is 0.1467 and *b* is 20.5677.

ture dilute HCl, cubothioplumbite becomes birefringent and then very slowly dissolves. Cubothioplumbite is optically isotropic. The index of refraction is higher than available liquids. The Gladstone-Dale relationship (Mandarino 1976) predicts 2.002 for the empirical formula and 2.021 for the ideal formula.

Hexathioplumbite

Crystals of hexathioplumbite occur as colorless, transparent, hexagonal prisms up to about 1 mm in length (Figs. 2 and 3). The crystals are hemimorphic with flat (basal) terminations and tapering bases, exhibiting the forms {100}, {001}, and {20 $\bar{1}$ }. Prisms often are joined at their tapering bases in an apparent twin relationship (Fig. 4). Twinning is observed, probably by reflection on {00 $\bar{1}$ } and rotation on

{001}. The streak is white and the luster is adamantine. The mineral does not fluoresce under long- or short-wave ultraviolet light. The Mohs hardness is about 2½ based on scratch tests. The tenacity is brittle, the fracture is curved, and there is no cleavage. The density could not be measured because crystals exceed the density of available density fluids. The calculated density is 5.531 g/cm³ for the empirical formula and 5.552 g/cm³ for the ideal formula. The mineral slowly dissolves in room-temperature dilute HCl.

Hexathioplumbite is optically uniaxial (−) with $\omega = 2.005(5)$ and $\varepsilon = 1.995(5)$, determined in white light. Note that ε was bracketed between 1.99 and 2.00 liquids, whereas ω was observed to be slightly greater than 2.00. The $\omega - \varepsilon$ birefringence measured with a Berek compensator is about 0.01, supporting $\omega =$

TABLE 3. ATOM COORDINATES AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS ($\text{\AA}^2$) FOR CUBOTHIOPLUMBITE

	x/a	y/b	z/c	U_{eq}		
Pb1	0.58314(3)	0.22600(3)	0.75169(3)	0.01548(17)		
Pb2	0.82483(3)	0.17517(3)	0.67517(3)	0.0151(2)		
Pb3	0.5	0.5	0.5	0.0204(3)		
Pb4	0.5	0.5	0	0.0344(3)		
S1	0.49888(16)	0.49387(17)	0.73490(17)	0.0118(6)		
S2	0.59473(18)	0.53880(18)	0.81950(19)	0.0170(6)		
O1	0.5247(6)	0.4077(5)	0.6975(5)	0.0226(17)		
O2	0.4166(5)	0.4887(6)	0.7875(6)	0.0269(19)		
O3	0.4923(5)	0.5612(5)	0.6630(5)	0.0237(19)		
OH4	0.7178(5)	0.1545(5)	0.7978(5)	0.0132(15)		
H4	0.715(7)	0.093(3)	0.817(7)	0.020		
OH5	0.6692(4)	0.3308(4)	0.8308(4)	0.009(3)		
H5	0.6315(13)	0.3685(13)	0.8685(13)	0.013		
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pb1	0.0094(2)	0.0190(3)	0.0181(3)	-0.00083(16)	-0.00061(15)	-0.00393(15)
Pb2	0.0151(2)	0.0151(2)	0.0151(2)	-0.00244(15)	0.00244(15)	0.00244(15)
Pb3	0.0204(3)	0.0204(3)	0.0204(3)	-0.0052(2)	-0.0052(2)	-0.0052(2)
Pb4	0.0344(3)	0.0344(3)	0.0344(3)	-0.0053(3)	0.0053(3)	0.0053(3)
S1	0.0139(14)	0.0117(13)	0.0100(13)	-0.0011(9)	0.0012(10)	0.0008(10)
S2	0.0144(13)	0.0169(13)	0.0197(14)	-0.0021(11)	-0.0050(11)	-0.0037(11)
O1	0.035(5)	0.012(4)	0.021(4)	-0.002(3)	0.005(4)	0.004(3)
O2	0.011(4)	0.042(5)	0.028(5)	-0.005(4)	0.006(4)	-0.003(4)
O3	0.032(5)	0.019(4)	0.020(4)	0.005(3)	-0.005(4)	0.011(3)
OH4	0.014(4)	0.008(3)	0.018(4)	0.004(3)	0.005(3)	0.002(3)
OH5	0.009(3)	0.009(3)	0.009(3)	-0.001(3)	0.001(3)	0.001(3)

2.005. The Gladstone-Dale compatibility 1 – (K_p/K_c) is -0.041 (good) for the empirical formula and -0.019 (superior) for the ideal formula (Mandarino 2007).

RAMAN SPECTROSCOPY

Raman spectra were collected with a Horiba XploRAPLUS system, a 785 nm diode laser, 200 μm slit, 1800 gr/mm diffraction grating, and a 100 $\times$ (0.9 NA) objective. Hexathioplumbite and its dimorph cubothioplumbite are very sensitive under the laser. They burn even under the lowest power of a 532 nm laser. The spectra of hexathioplumbite and cubothioplumbite were recorded from 2000 to 60 cm^{-1} . As they are featureless from 2000 to 1200 cm^{-1} , only spectra from 1200 to 60 cm^{-1} are shown in Figure 5. The spectra of hexathioplumbite and cubothioplumbite are quite similar and both exhibit numerous bands attributable to the various stretching, bending, and rotation modes of $(\text{S}_2\text{O}_3)^{2-}$ (see Gabelica 1980, Bindi *et al.* 2011). These are labeled in Figure 4 as follows: $\nu_{\text{as}}(\text{SO})$ = S–O asymmetric stretching, $\nu_{\text{s}}(\text{SO})$ = S–O symmetric stretching, $\delta_{\text{s}}(\text{SO})$ = S–O symmetric deformation, $\delta_{\text{as}}(\text{SO})$ = S–O asymmetric deformation,

$\nu(\text{SS})$ = S–S stretching, and $\rho(\text{SO}_3) = \text{SO}_3$ rotation. At least some of the bands between 400 and 100 cm^{-1} are probably related to Pb–O stretching and bending modes (see Jensen 2002, Welch *et al.* 2016).

CHEMICAL COMPOSITION

Chemical analyses for cubothioplumbite and hexathioplumbite (four points for each) were performed at Caltech with a JEOL 8200 electron microprobe operating in WDS mode. Analytical conditions were 15 kV accelerating voltage, 10 nA beam current, and 10 μm beam diameter. For these and several other new phases in this assemblage, it has been generally observed that analyses for S are somewhat lower than expected for thiosulfate phases and somewhat higher than expected for sulfate phases. This appears to be due to the substitution of a small amount of sulfate for thiosulfate or thiosulfate for sulfate in their crystal structures. This was clearly observed in the structure refinement for sulfatoredmondite (Kampf *et al.* 2023); however, it was not observed in the refinements of the structures of cubothioplumbite and hexathioplumbite, presumably because of the much smaller amount of

TABLE 4. ATOM COORDINATES AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS ($\text{\AA}^2$) FOR HEXATHIOPLUMBITE

	x/a	y/b	z/c	U_{eq}		
Pb1	0.58314(3)	0.22600(3)	0.75169(3)	0.01548(17)		
Pb1	0.14950(15)	0.44866(15)	0.5000(3)	0.0348(7)		
Pb2	2/3	1/3	0.3634(3)	0.0268(7)		
Pb3	0	0	0.3000(5)	0.0564(11)		
S1	0.8159(9)	0.1274(9)	0.5595(12)	0.0209(17)		
S2	0.6917(12)	0.0245(11)	0.3754(14)	0.036(2)		
O1	0.832(3)	0.268(3)	0.570(5)	0.033(7)		
O2	0.753(3)	0.041(3)	0.700(4)	0.036(7)		
O3	0.957(3)	0.136(3)	0.534(4)	0.033(8)		
OH4	0.822(3)	0.350(3)	0.154(4)	0.023(6)		
OH5	1/3	2/3	0.374(9)	0.030(11)		
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pb1	0.0265(9)	0.0283(8)	0.0366(12)	−0.0097(8)	−0.0045(7)	0.0038(6)
Pb2	0.0320(9)	0.0320(9)	0.0166(12)	0.000	0.000	0.0160(4)
Pb3	0.0741(17)	0.0741(17)	0.0208(17)	0.000	0.000	0.0371(8)
S1	0.020(4)	0.019(4)	0.020(5)	0.003(3)	0.000(3)	0.008(3)
S2	0.047(5)	0.029(4)	0.017(5)	0.005(4)	−0.003(5)	0.007(4)
O1	0.032(14)	0.023(13)	0.05(2)	−0.011(13)	−0.010(13)	0.019(11)
O2	0.020(12)	0.042(16)	0.017(15)	−0.008(14)	−0.004(11)	−0.007(11)
O3	0.035(14)	0.020(12)	0.04(2)	−0.001(12)	0.004(13)	0.014(11)
OH4	0.013(11)	0.021(12)	0.033(17)	0.009(11)	0.009(10)	0.008(9)
OH5	0.025(12)	0.025(12)	0.04(3)	0.000	0.000	0.012(6)

substitution involved. The low analytical totals are attributed to the irregular surfaces of the crystals. Insufficient material is available for the determination of H_2O , so it is calculated based on the structures ($\text{O} + \text{S} = 19 \text{ apfu}$). Analytical data are given in Table 1.

X-RAY CRYSTALLOGRAPHY

Powder X-ray studies were done using a Rigaku R-Axis Rapid II curved imaging plate microdiffractom-

eter, with monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71075 \text{ \AA}$). A Gandolfi-like motion on the ϕ and ω axes was used to randomize the orientations of the samples. Observed d values and intensities were derived by profile fitting using JADE Pro software (Materials Data, Inc.). Data are deposited as Supplementary Tables S1 and S2.

Single-crystal data were collected using the same diffractometer and radiation noted above. The Rigaku

TABLE 5. SELECTED BOND LENGTHS (IN $\text{\AA}$) AND ANGLES (IN $^\circ$) FOR CUBOTHIOPLUMBITE

Pb1–OH5	2.342(4)	Pb2–OH4 ($\times 3$)	2.448(7)	S1–O1	1.454(8)
Pb1–OH4	2.375(7)	Pb2–S2 ($\times 3$)	3.196(3)	S1–O2	1.458(8)
Pb1–OH4	2.441(7)	Pb2–O3	3.219(9)	S1–O3	1.473(8)
Pb1–O2	2.737(8)	$\langle \text{Pb2–O}_{sh} \rangle$	2.448	S1–S2	2.021(4)
Pb1–O1	2.959(7)	$\langle \text{Pb2–}\phi_{lg} \rangle$	3.208	$\langle \text{S2–O} \rangle$	1.462
Pb1–O3	2.988(8)				
Pb1–S2	3.241(3)	Pb3–O3 ($\times 6$)	2.600(8)		
Pb1–O1	3.366(8)	Pb3–O1 ($\times 6$)	3.273(8)		
Pb1–O2	3.589(9)				
$\langle \text{Pb1–O}_{sh} \rangle$	2.386	Pb4–S2 ($\times 6$)	3.096(3)		
$\langle \text{Pb1–}\phi_{lg} \rangle$	3.147	Pb4–O2 ($\times 6$)	3.410(9)		
Hydrogen bonds	D–H	H...A	D...A	$\angle \text{DHA}$	
OH4–H4...O1	0.96(3)	2.23(5)	3.150(11)	159(9)	
OH5–H5...S2	0.97(3)	2.700(17)	3.300(8)	120.3(6)	

TABLE 6. SELECTED BOND LENGTHS (IN Å) FOR HEXATHIOPLOMBITE

Pb1–OH4	2.30(3)	Pb2–OH4 (×3)	2.41(3)	S1–O1	1.44(2)
Pb1–OH4	2.43(3)	Pb2–O1 (×3)	2.84(3)	S1–O2	1.47(4)
Pb1–OH5	2.44(3)	Pb2–S2 (×3)	3.454(12)	S1–O3	1.49(3)
Pb1–O3	2.94(3)	<Pb2–O _{sh} >	2.41	S1–S2	2.015(15)
Pb1–O2	3.01(3)	<Pb2–φ _{lg} >	3.15	<S1–O>	1.47
Pb1–O1	3.02(3)				
Pb1–S2	3.201(10)	Pb3–O3 (×3)	2.66(3)	Hydrogen bond	
Pb1–S2	3.497(12)	Pb3–O3 (×3)	2.88(3)	OH4...O2	2.76(3)
Pb1–O2	3.62(3)	Pb3–O2 (×3)	3.02(3)		
<Pb1–O _{sh} >	2.39	Pb3–S2 (×3)	3.505(13)		
<Pb1–φ _{lg} >	3.22	<Pb3–φ _{lg} >	3.02		

TABLE 7. BOND-VALENCE SUMS (IN VALENCE UNITS) FOR CUBOTHIOPLOMBITE

	Pb1	Pb2	Pb3	Pb4	S1	Hydrogen bonds		sum
						Donated	Accepted	
O1	0.12, 0.05		0.06 ^{×6↓}		1.61		0.05	1.89
O2	0.20, 0.03			0.04 ^{×6↓}	1.59			1.87
O3	0.11	0.07 ^{×3↓}	0.28 ^{×6↓}		1.53			1.99
OH4	0.46, 0.40	0.39 ^{×3↓}				–0.05		1.20
OH5	0.50 ^{×3→}					–0.08		1.42
S2	0.15	0.17 ^{×3↓}		0.22 ^{×6↓}	1.14		0.03	1.71
sum	1.97	1.89	2.04	1.56	5.87			

Non-hydrogen bond-valence parameters are from Gagné & Hawthorne (2015). Hydrogen bond-valence parameters are from Adams *et al.* (2004).

CrystalClear software package was used for processing the data, including the application of empirical absorption corrections using the multi-scan method with ABCOR (Higashi 2001). The crystal structures of both minerals were solved using SHELXT (Sheldrick 2015a) and SHELXL-2016 (Sheldrick 2015b) was used for the refinements. For the crystal structure of cubothioplumbite, difference-Fourier mapping was used to locate probable H atom sites, and these were subsequently refined with soft restraints of 0.97(3) Å on the O–H distances and with the U_{eq} of each H set to 1.5 times that of its donor O atom. For the crystal structure of hexathioplumbite, difference-Fourier mapping failed to locate the H atom sites. Data collection and refinement details are given in Table 2, atom coordinates and displacement parameters in Tables 3 and 4, selected bond distances in Tables 5 and 6, and bond-valence analyses in Tables 7 and 8. CIF files have been deposited and are available from the Depository of Unpublished Data on the MAC website.¹

ATOMIC ARRANGEMENT

The structures of the dimorphs cubothioplumbite (Fig. 6) and hexathioplumbite (Fig. 7) share several features. They contain Pb²⁺ cations both with and without stereoactive 6s² lone-pair electrons. The Pb²⁺ cations with stereoactive 6s² lone-pair electrons (Pb1 and Pb2 in both structures) each form three short bonds with OH groups forming strongly bonded cubane-like [Pb₄(OH)₄]⁴⁺ cluster structural units (Fig. 8). In the cubothioplumbite structure, Pb1 forms long bonds to one S2 and five O vertices of thiosulfate groups and to an OH group in another [Pb₄(OH)₄]⁴⁺ cluster. The Pb2 forms long bonds to three S2 and three O3 vertices of thiosulfate groups. In the hexathioplumbite structure, the Pb1 forms long bonds to two S2 and four O vertices of thiosulfate groups. The Pb2 forms long bonds to three S2 and three O1 vertices of thiosulfate groups.

The Pb²⁺ cations without stereoactive 6s² lone-pair electrons (Pb3 and Pb4 in the cubothioplumbite structure; Pb3 in the hexathioplumbite structure) are all 12-coordinated. The cubothioplumbite Pb3 and Pb4 are both located on centers of symmetry and bond only to vertices of thiosulfate groups. The hexathioplumbite Pb3 is located on the 6₃ axis and its coordination may

¹ Supplementary Data are available from the Depository of Unpublished Data on the MAC website (<http://mineralogicalassociation.ca/>), document “Cubothioplumbite and Hexathioplumbite, CM61, 22-00070”.

TABLE 8. BOND-VALENCE SUMS (IN VALENCE UNITS) FOR HEXATHIOPLUMBITE

	Pb1	Pb2	Pb3	S1	H-bonds	sum
O1	0.11	$0.16 \times 3_{\downarrow}$		1.66		1.93
O2	0.11, 0.03		$0.11 \times 3_{\downarrow}$	1.54	0.20	1.99
O3	0.13		$0.24 \times 3_{\downarrow}$, $0.15 \times 3_{\downarrow}$	1.47		1.99
OH4	0.55, 0.41	$0.43 \times 3_{\downarrow}$			-0.20	1.19
OH5	$0.40 \times 3_{\rightarrow}$					1.20
S2	0.17, 0.08	$0.08 \times 3_{\downarrow}$	$0.07 \times 3_{\downarrow}$	1.16		1.56
sum	1.97	2.01	1.71	5.83		

Bond-valence parameters are from Gagné & Hawthorne (2015). Hydrogen bond contributions estimated from $O_D \cdots O_A$ distances using Ferraris & Ivaldi (1988). Negative values indicate the amount of hydrogen bond valence donated. Note that there is no likely hydrogen bond receptor for OH5.

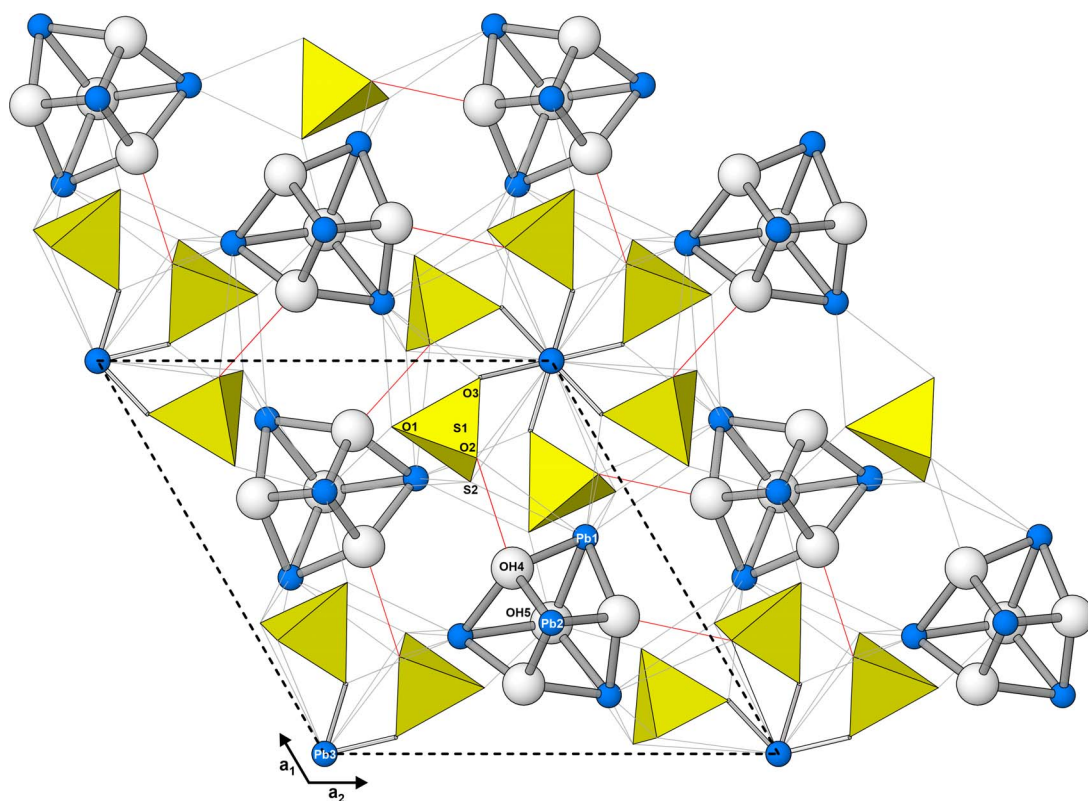


FIG. 7. The crystal structure of hexathioplumbite. Short (strong) Pb–O bonds are shown as thick gray sticks, medium length (moderately strong) Pb–O bonds are shown as white sticks, long (weak) Pb–O bonds are shown as thin gray lines, and hydrogen bonds are shown as thin red lines. The outline of the unit cell is shown by black dashed lines.

exhibit a weak lone-pair effect with bonds of $2.66 \text{ \AA}$ to three O3 all on one side and bonds of $2.88 \text{ \AA}$ to three O3 on the opposite side. Longer bonds of $3.02 \text{ \AA}$ to three O2 and $3.505 \text{ \AA}$ to three S2 sites are distributed around the girdle of the coordination sphere (Fig. 9).

The remaining bonds in the structures are hydrogen bonds from the OH groups of the $[\text{Pb}_4(\text{OH})_4]^{4+}$

clusters to the vertices of the thiosulfate groups. In the crystal structure of cubothioplumbite, the hydrogen bonds are $\text{OH4} \cdots \text{H4} \cdots \text{O1}$ and $\text{OH5} \cdots \text{H5} \cdots \text{S2}$ (trifurcated). In the crystal structure of hexathioplumbite, only the $\text{OH4} \cdots \text{O2}$ hydrogen bond could be discerned; no likely receptor for a hydrogen bond from OH5 could be identified.

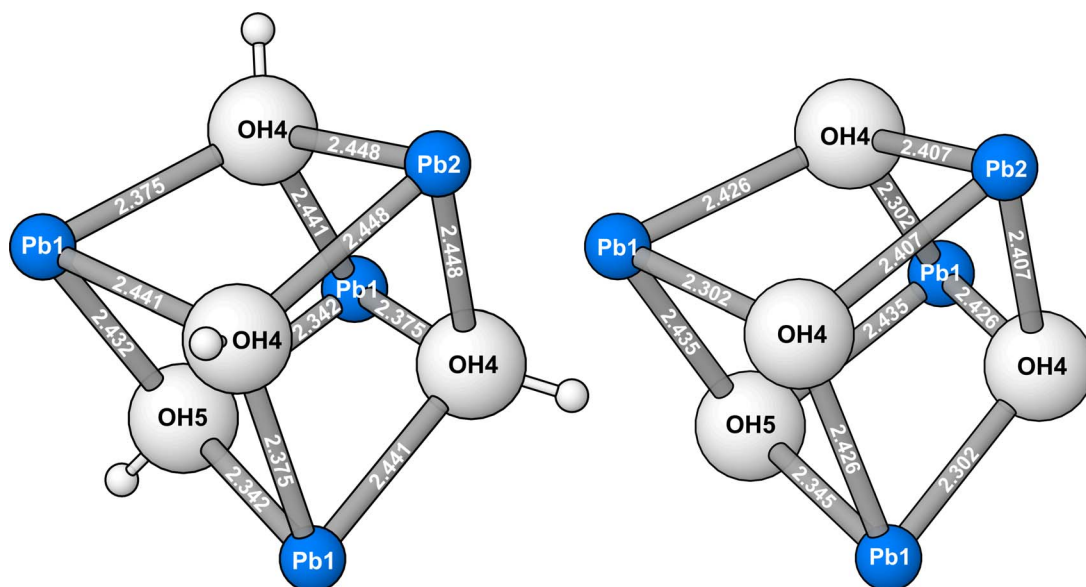


FIG. 8. The $[\text{Pb}_4(\text{OH})_4]^{4+}$ cluster in the structures of cubothioplumbite (left) and hexathioplumbite (right). Note that hydrogen atom positions were not determined for hexathioplumbite and, therefore, are not shown.

Kolitsch & Tillmanns (2003) reviewed $\text{Pb}-(\text{O},\text{OH})$ clusters. They noted that the cubane-like $[\text{Pb}_4(\text{OH})_4]^{4+}$ cluster occurs in several synthetic phases and that it is a component of the structure of maricopaite, $(\text{Pb}_7\text{Ca}_2)[\text{Al}_{12}\text{Si}_{36}(\text{O},\text{OH})_{100}] \cdot n(\text{H}_2\text{O},\text{OH})$, $n \approx 32$ (Rouse & Peacor 1994). They also noted that the similar $[\text{Pb}_4(\text{OH})_2\text{F}_2]^{4+}$ unit occurs in the structure of bidauxite, $\text{Pb}^{2+}_2\text{Ag}^+\text{Cl}_3\text{F}(\text{OH})$ (Cooper *et al.* 1999). Rumsey *et al.* (2017) reported the $[\text{Pb}_4(\text{OH})_4]^{4+}$ cluster in the structure of siidraite, $\text{Pb}_2\text{Cu}(\text{OH})_2\text{I}_3$, and it occurs in the recently approved mineral nitroplumbite, $[\text{Pb}_4(\text{OH})_4](\text{NO}_3)_4$ (Kampf *et al.* 2022), which is

equivalent to one of the synthetic phases noted by Kolitsch & Tillmanns (2003).

ACKNOWLEDGMENTS

One anonymous reviewer is thanked for constructive comments on the manuscript. A portion of this study was funded by the John Jago Trelawney Endowment to the Mineral Sciences Department of the Natural History Museum of Los Angeles County.

REFERENCES

- ADAMS, S., MORETZKI, O., & CANADELL, E. (2004) Global instability index optimizations for the localization of mobile protons. *Solid State Ionics* **168**, 281–290.
- BINDI, L., NESTOLA, F., KOLITSCH, U., GUASTONI, A., & ZORZI, F. (2011) Fassinaite, $\text{Pb}_2^{2+}(\text{S}_2\text{O}_3)(\text{CO}_3)$, the first mineral with coexisting thiosulphate and carbonate groups: Description and crystal structure. *Mineralogical Magazine* **75**, 2721–2732.
- COOPER, M.A., HAWTHORNE, F.C., MERLINO, S., PASERO, M., & PERCHIAZZI, N. (1999) Stereoactive lone-pair behavior of Pb in the crystal structure of bidauxite; $\text{Pb}^{2+}_2\text{Ag}^+\text{Cl}_3\text{F}(\text{OH})$. *The Canadian Mineralogist* **37**, 915–921.
- ESPENSHADE, G.H., STAATZ, M.H., & BROWN, E.A. (1947) *Preliminary Report, Redmond Lead-Zinc Mine, Haywood County, N.C.* United States Geological Survey, Open File Report 47-3. United States Geological Survey, Reston, Virginia, United States of America.

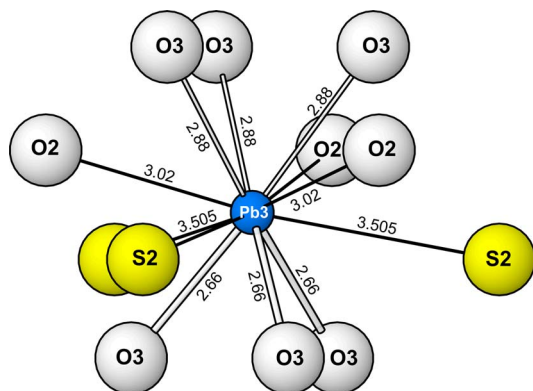


FIG. 9. Pb_3 coordination in the crystal structure of hexathioplumbite.

- FERRARIS, G. & IVALDI, G. (1988) Bond valence vs. bond length in O...O hydrogen bonds. *Acta Crystallographica* **B44**, 341–344.
- GABELICA, Z. (1980) Structural study of solid inorganic thiosulfates by infrared and Raman spectroscopy. *Journal of Molecular Structure* **60**, 131–138.
- GAGNÉ, O.C. & HAWTHORNE, F.C. (2015) Comprehensive derivation of bond-valence parameters for ion pairs involving oxygen. *Acta Crystallographica* **B71**, 562–578.
- HIGASHI, T. (2001) *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
- JENSEN, J.O. (2002) Vibrational frequencies and structural determinations of $\text{Pb}_4(\text{OH})_4^{4+}$. *Journal of Molecular Structure: THEOCHEM* **587**, 111–121.
- KAMPF, A.R., HUGHES, J.M., NASH, B.P., & MARTY, J. (2022) Nitroplumbite, $[\text{Pb}_4(\text{OH})_4](\text{NO}_3)_4$, a new mineral cubane-like $[\text{Pb}_4(\text{OH})_4]^{4+}$ clusters from the Burro mine, San Miguel County, Colorado, USA. *The Canadian Mineralogist* **60**, 787–795.
- KAMPF, A.R., SMITH, J.B., HUGHES, J.M., MA, C., & EMPROTO, C. (2023) New minerals from the Redmond Mine, North Carolina, U.S.A.: I. Redmondite, hydroredmondite, and sulfatoredmondite, three minerals containing the novel $[\text{Pb}_8\text{O}_2\text{Zn}(\text{OH})_6]^{8+}$ structural unit. *The Canadian Journal of Mineralogy and Petrology* **61**, 189–202.
- KOLITSCH, U. & TILLMANN, E. (2003) The crystal structure of anthropogenic $\text{Pb}_2(\text{OH})_3(\text{NO}_3)$, and a review of $\text{Pb}-(\text{O},\text{OH})$ clusters and lead nitrates. *Mineralogical Magazine* **67**, 79–93.
- MANDARINO, J.A. (1976) The Gladstone-Dale relationship; Part I, Derivation of new constants. *The Canadian Mineralogist* **14**, 498–502.
- MANDARINO, J.A. (2007) The Gladstone-Dale compatibility of minerals and its use in selecting mineral species for further study. *The Canadian Mineralogist* **45**, 1307–1324.
- ROUSE, R.C. & PEACOR, D.R. (1994) Maricopaite, an unusual lead calcium zeolite with an interrupted mordenite-like framework and intrachannel Pb_4 tetrahedral clusters. *American Mineralogist* **79**, 175–184.
- RUMSEY, M.S., WELCH, M.D., KLEPPE, A.K., & SPRATT, J. (2017) Siidraite, $\text{Pb}_2\text{Cu}(\text{OH})_2\text{I}_3$, from Broken Hill, New South Wales, Australia: The third halocuprate(I) mineral. *European Journal of Mineralogy* **29**, 1027–1030.
- SHELDRIK, G.M. (2015a) *SHELXT* – Integrated space-group and crystal-structure determination. *Acta Crystallographica* **A71**, 3–8.
- SHELDRIK, G.M. (2015b) Crystal Structure refinement with *SHELX*. *Acta Crystallographica* **C71**, 3–8.
- WELCH, M.D., RUMSEY, M.S., & KLEPPE, A.K. (2016) A naturally occurring new lead-based halocuprate(I). *Journal of Solid State Chemistry* **238**, 9–14.

Received December 6, 2022. Revised manuscript accepted February 2, 2023.

This manuscript was handled by Associate Editor James Evans and Editor Andrew McDonald.