

NEW MINERALS FROM THE REDMOND MINE, NORTH CAROLINA, USA: I. REDMONDITE, HYDROREDMONDITE, AND SULFATOREDMONDITE, THREE MINERALS CONTAINING THE NOVEL $[\text{Pb}_8\text{O}_2\text{Zn}(\text{OH})_6]^{8+}$ STRUCTURAL UNIT

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ABSTRACT

The new minerals redmondite (IMA2021–072), $[\text{Pb}_8\text{O}_2\text{Zn}(\text{OH})_6](\text{S}_2\text{O}_3)_4$, hydroredmondite (IMA2021–073), $[\text{Pb}_8\text{O}_2\text{Zn}(\text{OH})_6](\text{S}_2\text{O}_3)_4 \cdot 2\text{H}_2\text{O}$, and sulfatoredmondite (IMA2021–089), $[\text{Pb}_8\text{O}_2\text{Zn}(\text{OH})_6](\text{SO}_4)_4 \cdot 6\text{H}_2\text{O}$, 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. The properties of redmondite are as follows: colorless to shades of brown, transparent equant rhombs to about 1 mm; white streak; adamantine luster; brittle; Mohs hardness 2; conchoidal fracture; no cleavage; 5.757 g/cm³ calculated density; biaxial with $\alpha = 1.96\text{--}1.97$, $\beta = 1.97\text{--}1.98$, $\gamma = 1.97\text{--}1.98$; extreme dispersion. The properties of hydroredmondite are as follows: colorless, transparent prisms, blades, and tablets up to about 1 mm; white streak; adamantine luster; brittle; Mohs hardness 2; curved and stepped fracture; good cleavages on $\{101\}$ and $\{10\bar{1}\}$; 5.124 g/cm³ calculated density; biaxial (+) with $\alpha = 1.830(5)$, $\beta = 1.880(\text{calc})$, $\gamma = 1.950(\text{calc})$, $2V_{\text{meas}} = 83(1)^\circ$. The properties of sulfatoredmondite are as follows: colorless, transparent wedge-shaped crystals to about 2 mm; white streak; adamantine luster; brittle; Mohs hardness 2; curved, irregular fracture; no cleavage; 5.173 g/cm³ calculated density; biaxial (+), $\alpha = 1.780(5)$, $\beta = 1.850(\text{calc})$, $\gamma = 1.860(\text{calc})$, $2V_{\text{meas}} = 40(3)^\circ$; moderate $r > v$ dispersion. Electron probe microanalyses provided the empirical formulae: $\text{Pb}_{8.16}\text{Zn}_{1.00}\text{S}^{6+}_{3.97}\text{S}^{2-}_{3.97}\text{O}_{20}\text{H}_{5.79}$, $\text{Pb}_{8.00}\text{Zn}_{1.00}\text{S}^{6+}_{4.00}\text{S}^{2-}_{4.00}\text{O}_{22}\text{H}_{9.98}$, and $\text{Pb}_{8.00}\text{Zn}_{0.99}\text{S}^{6+}_{4.00}\text{S}^{2-}_{0.89}\text{O}_{29.11}\text{H}_{17.98}$ for redmondite, hydroredmondite, and sulfatoredmondite, respectively. Redmondite is monoclinic, $P2_1/c$, $a = 9.1672(4)$, $b = 10.6576(4)$, $c = 14.0620(10)$ Å, $\beta = 101.173(7)^\circ$, $V = 1347.83(12)$ Å³, and $Z = 2$. Hydroredmondite is monoclinic, $P2_1/n$, $a = 12.5991(9)$, $b = 9.2819(4)$, $c = 12.9774(9)$ Å, $\beta = 90.443(6)^\circ$, $V = 1517.57(16)$ Å³, and $Z = 2$. Sulfatoredmondite is monoclinic, $C2/m$, $a = 17.294(2)$, $b = 7.3668(9)$, $c = 12.7271(18)$ Å, $\beta = 110.622(9)^\circ$, $V = 1517.5(4)$ Å³, and $Z = 2$. The crystal structures of redmondite ($R_1 = 0.0346$ for 2061 $I > 2\sigma I$), hydroredmondite ($R_1 = 0.0346$ for 3022 $I > 2\sigma I$), and sulfatoredmondite ($R_1 = 0.0344$ for 1661 $I > 2\sigma I$) are all based on the same $[\text{Pb}_8\text{O}_2\text{Zn}(\text{OH})_6]^{8+}$ structural unit.

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Keywords: redmondite, hydroredmondite, sulfatoredmondite, new mineral, crystal structure, sulfate, thiosulfate, Pb^{2+} lone-pair electrons, Redmond mine, North Carolina, USA.

INTRODUCTION

The Redmond mine, a lead-zinc vein discovered in about 1905 and operated sporadically on a small scale until the mid-1940s, was recently found to host a highly unusual secondary mineral assemblage that includes a variety of rare Pb-Zn-Cu sulfates, thiosulfates, and carbonates (see below), including at least 20 new Pb and/or Zn sulfate and thiosulfate minerals. Of particular note is the fact that the crystal structures of many of these potentially new minerals contain rare, and in some cases novel, clusters characterized by short Pb^{2+} -O bonds. This paper, the first in a series, describes the new minerals redmondite (IMA2021-072), $[\text{Pb}_8\text{O}_2\text{Zn}(\text{OH})_6](\text{S}_2\text{O}_3)_4$, hydroredmondite (IMA2021-073), $[\text{Pb}_8\text{O}_2\text{Zn}(\text{OH})_6](\text{S}_2\text{O}_3)_4 \cdot 2\text{H}_2\text{O}$, and sulfatoredmondite (IMA2021-089), $[\text{Pb}_8\text{O}_2\text{Zn}(\text{OH})_6](\text{SO}_4)_4 \cdot 6\text{H}_2\text{O}$, all of which have crystal structures based on the same novel $[\text{Pb}_8\text{O}_2\text{Zn}(\text{OH})_6]^{8+}$ structural unit. Redmondite is named for the mine and hydroredmondite for its compositional and structural similarity to redmondite, but with the addition of an interstitial H_2O group (hydro-). Sulfatoredmondite is named for its compositional and structural similarity to both redmondite and hydroredmondite, in addition to having interstitial sulfate (sulfato-) instead of thiosulfate.

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 redmondite have catalog numbers 76160, 76161, and 76162. Four cotype specimens of hydroredmondite have catalog numbers 76163, 76164, 76165, and 76166. Three cotype specimens of sulfatoredmondite have catalog numbers 76181, 76182, and 76183.

OCCURRENCE

Redmondite, hydroredmondite, and sulfatoredmondite were found by one of the authors (JBS) underground at the Redmond mine, Haywood County, North Carolina, USA ($35^\circ 40' 55''\text{N}$, $83^\circ 0' 56''\text{W}$). The ore, consisting mainly of galena and sphalerite with lesser amounts of 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 secondary assemblage that comprises a variety of rare Pb-Zn-Cu sulfates, thiosulfates, and carbonates, including bechererite, chenite, elyite, fassinaite, lahnsteinite, lanarkite, lauenthalite, namuwite, redgillite, osakaite, sidpietersite, steverustite, and susannite, as well as some more common secondary minerals such as anglesite, brochantite, caledonite, cerussite, langite, leadhillite, linarite, malachite, posnjakite, schulenbergite, and wroewolfeite. Redmondite, hydroredmondite, and sulfatoredmondite occur together in vugs in massive galena-sphalerite-chalcopyrite-quartz, in close association with anglesite, cerussite, chenite, elyite, gypsum, hydroredmondite, lanarkite, redmondite, steverustite, susannite, and several other potentially new minerals.

The primary and secondary assemblages of the Redmond mine bear a strong resemblance to those of similar Pb-Zn veins in central Wales (*e.g.*, Frongoch mine) and southern Scotland (*e.g.*, Susanna mine) where the secondary assemblages also include basic Pb, Zn, and Cu sulfate and carbonate minerals, as well as the thiosulfate mineral steverustite (Cooper *et al.* 2009). Although the ore mineralization at the Redmond mine is very similar to that of the Welsh and Scottish occurrences, the secondary mineral assemblage here is distinguished from any analogous Pb-Zn vein known, based on the astonishing diversity of new and/or rare sulfate and thiosulfate minerals found within it. The formation (or preservation) of the new sulfate and thiosulfate minerals appears to have been limited to small vugs within the galena-rich ore where exotic metal coordination complexes were stabilized in stagnant solutions under supergene conditions. The formation of rarer, more basic sulfate and carbonate minerals is thought to arise from the dearth of pyrite in these types of epithermal Pb-Zn veins, limiting the formation of sulfuric acid and allowing natural buffers to maintain a near-neutral pH within groundwater and mine runoff (Bearcock *et al.* 2010). At the Redmond mine, the occurrence of minerals with the $\text{Pb}_4(\text{OH})_4^{4+}$ cluster in the thiosulfate assemblage suggests that at least some thiosulfate precipitation occurred at near-neutral pH conditions in the weathered ore lenses (Rumsey *et al.* 2017). However, the extant groundwater within the flooded adit sampled by one of the authors (JBS) was observed to be slightly alkaline (*ca.* 8.5 pH). In fact, the mineralization at the Redmond mine was originally discovered after an assay of the water flowing from a nearby spring showed it to be



FIG. 1. Redmondite crystals on cotype specimen #76161. The field of view is 0.4 mm across.

alkaline with a high Pb content, leading prospectors to the vein (Redmond family, *pers. commun.*). Basic and reducing spring waters are also reported from the nearby Hot Springs, North Carolina, area (Hobba *et al.* 1979). The weathering of the pyrite-poor Pb-Zn vein by alkaline and reducing spring waters rather than by more neutral or slightly acidic waters would serve to further inhibit the onset of acidic conditions, thus

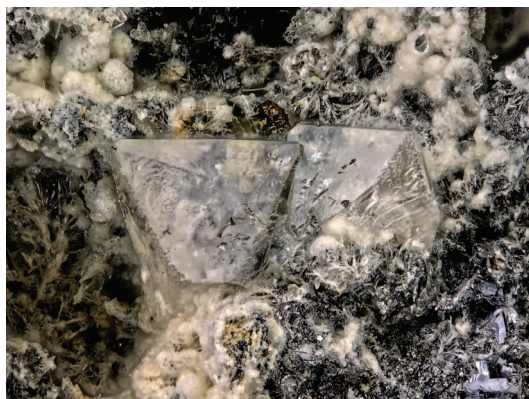


FIG. 2. Redmondite crystals with white balls of susannite on the cotype specimen #76160. The field of view is 1.14 mm across.

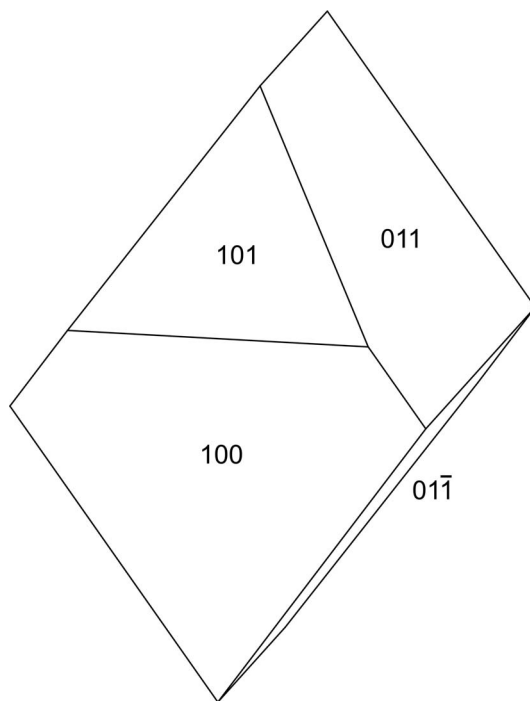


FIG. 3. Crystal drawing of redmondite; clinographic projection in standard orientation.

allowing thiosulfate to remain stable long enough to form metal thiosulfate complexes, which have larger Eh-pH stability fields than thiosulfate under supergene conditions (Aylmore & Muir 2001). An alkaline/reducing spring water contribution would set Redmond apart from other similar Pb-Zn veins and may explain the uniqueness of the Redmond mine assemblage.

PHYSICAL AND OPTICAL PROPERTIES

Redmondite

Redmondite crystals occur as colorless, transparent, equant rhombs up to about 1 mm in diameter (Figs. 1 and 2), exhibiting the forms $\{100\}$, $\{011\}$, and $\{101\}$ (Fig. 3). Crystals sometimes show varying shades of brown, possibly due to inclusions or underlying minerals. 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 2 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 5.757 g/cm^3 for the empirical formula and 5.680 g/cm^3 for the ideal formula. In room-temperature dilute HCl,



FIG. 4. Twinned blades of hydroredmondite on the cotype specimen #76163. The field of view is 0.3 mm across.

redmondite immediately becomes opaque and then slowly dissolves.

High indices of refraction and extreme dispersion (as suggested by the development of anomalous interference colors when crystals are viewed in some directions) made complete optical determinations impractical. Redmondite is biaxial, with $\alpha = 1.96$ – 1.97 , $\beta = 1.97$ – 1.98 , and $\gamma = 1.97$ – 1.98 . The optic sign, $2V$, and optical orientation could not be determined. No pleochroism was noted. The Gladstone-Dale compatibility is $1 - (K_p/K_c) = 0.011$ (superior) for the empirical formula and 0.003 (superior) for the ideal formula, assuming an average index of refraction of 1.97 .

Hydroredmondite

Hydroredmondite crystals occur as colorless, transparent prisms, blades, and tablets up to about 1 mm in maximum dimension (Fig. 4). Crystals are elongated on $[010]$, more or less flattened on $\{101\}$, and exhibit the forms $\{101\}$, $\{10\bar{1}\}$, and $\{011\}$ (Fig. 5). Twinning is common by 180° rotation on $[001]$ with the composition plane $\{10\bar{1}\}$. The streak is white and the luster is adamantine. The mineral does not fluoresce under long- or short-wave ultraviolet light.

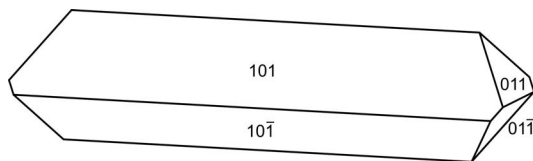


FIG. 5. Crystal drawing of hydroredmondite; clinographic projection in standard orientation.

The Mohs hardness is about 2 based on scratch tests. The tenacity is brittle, the fracture is curved and stepped, and there is good cleavage on $\{101\}$ and $\{10\bar{1}\}$. The density could not be measured because it exceeded that of the available density fluids. The calculated density is 5.124 g/cm^3 for the empirical formula and 5.123 g/cm^3 for the ideal formula. In room-temperature dilute HCl, redmondite immediately becomes opaque and then slowly dissolves.

Direct measurement of all indices of refraction proved very difficult because of their high values. Liquids with indices >1.8 are too dark to use in the cell of the spindle stage. The value of α was measured in grain mounts; γ was then calculated from the $\gamma - \alpha$ retardation (0.12), after which β was calculated from α , γ , and $2V$. Hydroredmondite is biaxial (+), with $\alpha = 1.830(5)$, $\beta = 1.880(\text{calc})$, and $\gamma = 1.950(\text{calc})$; $2V_{\text{meas}} = 83(1)^\circ$ from extinction data using EXCALIBURW (Gunter *et al.* 2004). The dispersion could not be observed. The partial optical orientation is $X = \mathbf{b}$ (length slow) and there is no pleochroism. The Gladstone-Dale compatibility is $1 - (K_p/K_c) = 0.004$ (superior) for both the empirical and ideal formulae.

Sulfatoredmondite

Sulfatoredmondite crystals occur as colorless, transparent stout prisms with wedge-shaped terminations up to about 2 mm in maximum dimension (Fig. 6). Crystals are sometimes flattened on $\{100\}$ and exhibit the forms $\{100\}$, $\{001\}$, $\{110\}$, and $\{011\}$ (Fig. 7). 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 2 based on scratch tests. The tenacity is brittle, the fracture is curved and irregular, and there is no cleavage. The density could not be measured because it exceeded that of the available density fluids. The calculated density is 5.173 g/cm^3 for the empirical formula and 5.177 g/cm^3 for the ideal formula. In room-temperature dilute HCl, redmondite immediately becomes opaque and then slowly dissolves.

Direct measurement of all indices of refraction proved very difficult because of their high values. Liquids with indices >1.8 are too dark to use in the



FIG. 6. Sulfatoredmondite crystal on the cotype specimen #76163. The field of view is 0.63 mm across.

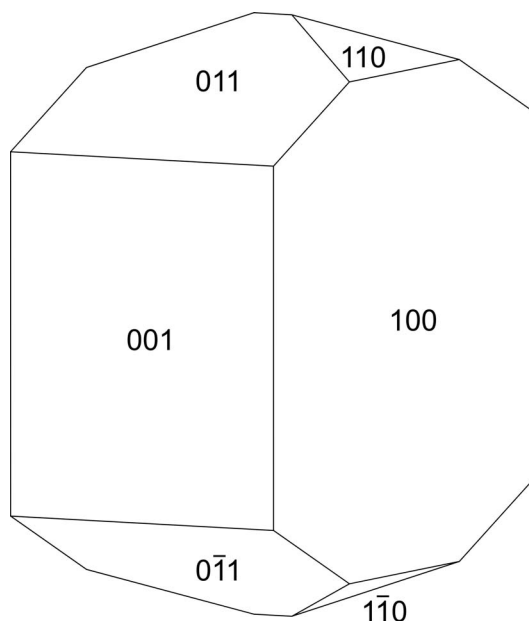


FIG. 7. Crystal drawing of sulfatoredmondite; clinographic projection in nonstandard orientation, **b** vertical.

cell of the spindle stage. The value of α was measured on the spindle stage; β and γ were then calculated from the $\gamma - \beta$ retardation (0.10) and $2V$. Sulfatoredmondite is biaxial (+), with $\alpha = 1.780(5)$, $\beta = 1.850(\text{calc})$, and $\gamma = 1.860(\text{calc})$; $2V_{\text{meas}} = 40(3)^\circ$ measured directly on a spindle stage. Moderate $r > v$ dispersion was observed. The optical orientation is $Z = \mathbf{b}$, $X \wedge a = 28^\circ$ in the obtuse angle β . The mineral is nonpleochroic. The Gladstone-Dale compatibility is $1 - (K_p/K_c) = -0.004$ (superior) for the empirical formula.

RAMAN SPECTROSCOPY

Raman spectroscopy was done on a Horiba XploRA PLUS micro-Raman spectrometer using an incident wavelength of 532 nm, 200 μm slit, 1800 gr/mm diffraction grating, and a 100 $\times$ (0.9 NA) objective. The spectra of redmondite, hydroredmondite, and sulfatoredmondite from 3800 to 100 cm^{-1} are shown in Figure 8. In the spectra of hydroredmondite and sulfatoredmondite, prominent, broad bands centered at about 3409 and 3405 cm^{-1} , respectively, are assigned to O–H stretching. These bands are probably due principally to O–H associated with the H_2O groups, because no such band was detected in the spectrum of redmondite, which has the same structural components as hydroredmondite and sulfatoredmondite, but lacks interstitial H_2O groups. The spectra are essentially featureless between 3200 and 1200 cm^{-1} . Although the complexity of the Raman spectra between 1200 and 100 cm^{-1} makes a comprehensive

assignment of bands impossible, the bands observed between 1200 and 400 cm^{-1} in the redmondite and hydroredmondite spectra are all likely due to various stretching, bending, and rotation modes of $(\text{S}_2\text{O}_3)^{2-}$ (see Gabelica 1980, Bindi *et al.* 2011), whereas those in the sulfatoredmondite spectrum are likely due mostly to various stretching, bending, and rotation modes of $(\text{SO}_4)^{2-}$ and, to a lesser extent, $(\text{S}_2\text{O}_3)^{2-}$. In particular, the strong band at 975 cm^{-1} in the sulfatoredmondite spectrum is assignable to ν_1 $(\text{SO}_4)^{2-}$ symmetric stretching. In all three spectra, at least some of the bands between 400 and 100 cm^{-1} are related to various Pb–O stretching and bending modes (see Jensen 2002, Welch *et al.* 2016), although various bands in the 400 to 200 cm^{-1} range have been ascribed to Zn–O stretching and bending (see Frost *et al.* 2008).

CHEMICAL COMPOSITION

Analyses were performed at Caltech on a JEOL 8200 electron microprobe in WDS mode. Analytical conditions were 15 kV accelerating voltage and 10 nA beam current. A 2 μm beam diameter was used for redmondite and a 5 μm beam diameter was used for hydroredmondite and sulfatoredmondite. Redmondite and hydroredmondite crystals did not polish well, possibly contributing to the low analytical totals obtained. There was an insufficient amount of material

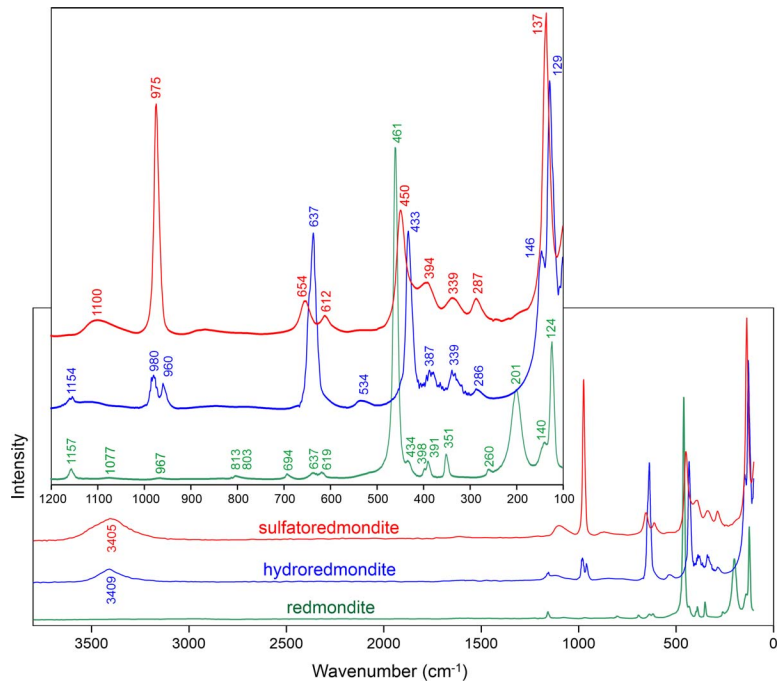


FIG. 8. Raman spectra of redmondite, hydroredmondite, and sulfatoredmondite recorded with a 532 nm laser.

for the determination of H₂O for all three minerals, so it was calculated based on results derived from their refined crystal structures.

For nearly all minerals analyzed in this assemblage analytical data indicated lower-than-expected values for S for the thiosulfates and somewhat higher-than-expected values for S for the sulfates. 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 substitution is clearly demonstrated in

results for the refined crystal structure refinement of sulfatoredmondite (see below). To adjust for this substitution, total analyzed S, reported as SO₃, is allotted into SO₃ and S, so as to provide total (SO₄) + (S₂O₃) in accord with the ideal formulae as indicated by the crystal-structure determinations. Analytical data and the empirical, simplified, and ideal formulae are given in Tables 1, 2, and 3 for redmondite, hydroredmondite, and sulfatoredmondite, respectively.

TABLE 1. ANALYTICAL DATA (6 POINTS) IN wt.% FOR REDMONDITE

Constituent	Mean	Range	S.D.	Standard	Norm.	Ideal
PbO	73.60	73.17–73.91	0.26	PbS	77.94	77.45
ZnO	3.40	3.30–3.50	0.09	ZnO	3.48	3.53
SO ₃	(25.39)	25.07–25.68	0.20	anhydrite		
SO ₃ *	13.22				13.61	13.89
S*	4.87				5.45	5.56
H ₂ O [§]	2.23				2.23	2.34
O=S	–2.43				–2.72	–2.78
Total	94.43				99.99	99.99

* Allocated based on the structure (SO₄ + S₂O₃ = 4 and Pb + Zn = 9).

§ Based on the structure (O + S = 28 apfu)

Empirical formula: [Pb_{7.99}O₂Zn_{1.01}(OH)₆](S₂O₃)_{3.68}(SO₄)_{0.32}

Simplified formula: [Pb₈O₂Zn(OH)₆](S₂O₃)_{4–x}(SO₄)_x

Ideal formula: [Pb₈O₂Zn(OH)₆](S₂O₃)₄

TABLE 2. ANALYTICAL DATA (6 POINTS) IN wt.% FOR HYDROREDMONDITE

Constituent	Mean	Range	S.D.	Standard	Norm.	Ideal
PbO	73.66	73.24–74.22	0.32	PbS	76.34	76.26
ZnO	3.33	3.18–3.56	0.14	ZnO	3.45	3.48
SO ₃	(26.10)	25.88–26.39	0.19	anhydrite		
SO ₃ [*]	13.19				13.67	13.68
S [*]	5.17				5.36	5.48
H ₂ O [§]	3.72				3.86	3.85
O=S	–2.58				–2.67	–2.73
Total	96.49				100.01	100.02

* Allocated based on the structure (SO₄ + S₂O₃ = 4 and Pb + Zn = 9).

§ Based on the structure (O + S = 30 *apfu*)

Empirical formula: [Pb_{8.07}O₂Zn_{0.99}(OH)₆](S₂O₃)_{3.91}(SO₄)_{0.09}·2H₂O

Simplified formula: [Pb₈O₂Zn(OH)₆](S₂O₃)_{4–x}(SO₄)_x·2H₂O

Ideal formula: [Pb₈O₂Zn(OH)₆](S₂O₃)₄·2H₂O

TABLE 3. ANALYTICAL DATA (5 POINTS) IN wt.% FOR SULFATOREDMONDITE

Constituent	Mean	Range	S.D.	Standard	Ideal
PbO	75.02	74.46–75.83	0.65	PbS	76.00
ZnO	3.40	3.34–3.47	0.06	ZnO	3.46
SO ₃	(16.45)	16.10–16.80	0.26	anhydrite	
SO ₃ [*]	13.46				13.63
S [*]	1.20				
H ₂ O [§]	6.82				6.90
O=S	–0.60				–0.60
Total	99.30				99.99

* Allocated based on the structure (SO₄ + S₂O₃ = 4 and Pb + Zn = 9).

§ Based on the structure (O + S = 34 *apfu*)

Empirical formula: [Pb_{8.009}O₂Zn_{0.99}(OH)₆](SO₄)_{3.11}(S₂O₃)_{0.89}·6H₂O

Simplified formula: [Pb₈O₂Zn(OH)₆](SO₄)_{4–x}(S₂O₃)_x·6H₂O

Ideal formula: [Pb₈O₂Zn(OH)₆](SO₄)₄·6H₂O

X-RAY CRYSTALLOGRAPHY

Powder X-ray studies were done using a Rigaku R-Axis Rapid II curved imaging plate microdiffractometer, with monochromatized MoK α radiation (λ = 0.71075 Å). A Gandolfi-like motion on the ϕ and ω axes was used to randomize 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, S2, and S3.

Single-crystal data were collected using the same diffractometer and radiation as noted above. The Rigaku CrystalClear software package was used for processing the structure data, including the application of empirical absorption corrections using the multi-scan method with ABSCOR (Higashi 2001). The structures were solved using SHELXT (Sheldrick 2015a). SHELXL-2016 (Sheldrick 2015b) was used for the refinements of the structures. Data collection and refinement details are given in Table 4, selected

bond distances in Tables 5 through 7, and bond-valence analyses in Tables 8 through 10. CIF files that contain the atom coordinates and displacement parameters, as well as the observed and calculated structure factors, have been deposited and are available from the Depository of Unpublished Data on the MAC website¹.

ATOMIC ARRANGEMENT

Structural unit

The structures of redmondite, hydroredmondite, and sulfatoredmondite each contain the same strongly bonded [Pb₈O₂Zn(OH)₆]⁸⁺ structural unit (Fig. 9).

¹ Supplementary Data are available from the Depository of Unpublished Data on the MAC website (<http://mineralogicalassociation.ca/>), document “Redmondite, hydroredmondite, sulfatoredmondite, CM60, 22-00059”.

TABLE 4. DATA COLLECTION AND STRUCTURE REFINEMENT DETAILS FOR REDMONDITE, HYDROREDMONDITE, AND SULFATOREDMONDITE

Mineral	Redmondite	Hydroredmondite	Sulfatoredmondite
Diffraction	Rigaku R-Axis Rapid II		
X-ray rad. / power	MoK α (λ = 0.71075 Å) / 50 kV, 40 mA		
Temperature	293(2) K		
Structural formula (incl. unlocated H)	[Pb ₈ O ₂ Zn(OH) ₆] (S ₂ O ₃) ₄	[Pb ₈ O ₂ Zn(OH) ₆] (S ₂ O ₃) ₄ ·2H ₂ O	[Pb ₈ O ₂ Zn(OH) ₆](SO ₄) _{3.39} (S ₂ O ₃) _{0.61} ·5.31H ₂ O
Space group	<i>P</i> 2 ₁ / <i>c</i> (#14)	<i>P</i> 2 ₁ / <i>n</i> (#14)	<i>C</i> 2/ <i>m</i> (#12)
Unit cell dimensions	<i>a</i> = 9.1672(4) Å <i>b</i> = 10.6576(4) Å <i>c</i> = 14.0620(10) Å β = 101.173(7)°	<i>a</i> = 12.5991(9) Å <i>b</i> = 9.2819(4) Å <i>c</i> = 12.9774(9) Å β = 90.443(6)°	<i>a</i> = 17.294(2) Å <i>b</i> = 7.3668(9) Å <i>c</i> = 12.7271(18) Å β = 110.622(9)°
<i>V</i>	1347.83(12) Å ³	1517.57(16) Å ³	1517.5(4) Å ³
<i>Z</i>	2	2	2
Density (calc.)	5.681 g/cm ³	5.124 g/cm ³	5.136 g/cm ³
Absorption coeff.	51.337 mm ⁻¹	45.604 mm ⁻¹	45.397 mm ⁻¹
<i>F</i> (000)	1960	2000	2012
Crystal size	110 × 100 × 90 μm	200 × 25 × 20 μm	90 × 90 × 60 μm
θ range	3.11 to 25.03°	3.14 to 27.48°	3.04 to 27.48°
Index ranges	-10 ≤ <i>h</i> ≤ 10 -12 ≤ <i>k</i> ≤ 11 -14 ≤ <i>l</i> ≤ 16	-16 ≤ <i>h</i> ≤ 16 -12 ≤ <i>k</i> ≤ 10 -16 ≤ <i>l</i> ≤ 16	-22 ≤ <i>h</i> ≤ 22 -7 ≤ <i>k</i> ≤ 9 -16 ≤ <i>l</i> ≤ 16
Refl. collected	9871	14486	14253
Independent refl.	2372 [<i>R</i> _{int} = 0.096]	3463 [<i>R</i> _{int} = 0.121]	1871 [<i>R</i> _{int} = 0.101]
Refl. with <i>I</i> > 2σ/ <i>I</i>	2061	3022	1661
Completeness to $\theta_{\max}$	99.6 %	99.4 %	99.5 %
Refinement method	Full-matrix least-squares on <i>F</i> ²		
Parameters/restraints	170/0	170/0	125/2
Goodness-of-fit	1.079	1.096	1.103
Final <i>R</i> indices [<i>I</i> > 2σ/ <i>I</i>]	<i>R</i> ₁ = 0.0346 <i>wR</i> ₂ = 0.0810	<i>R</i> ₁ = 0.0473 <i>wR</i> ₂ = 0.1041	<i>R</i> ₁ = 0.0344 <i>wR</i> ₂ = 0.0782
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0420 <i>wR</i> ₂ = 0.0850	<i>R</i> ₁ = 0.0545 <i>wR</i> ₂ = 0.1082	<i>R</i> ₁ = 0.0398 <i>wR</i> ₂ = 0.0813
Extinction coefficient	0.00061(6)	—	—
Largest diff. peak/hole	+2.12/-1.75 e Å ⁻³	+3.29/-2.26 e Å ⁻³	+1.92/-2.15 e Å ⁻³

$R_{\text{int}} = \sum |F_o^2 - F_c^2| / \sum F_o^2$; $\text{GoF} = S = \{ \sum [w(F_o^2 - F_c^2)^2] / (n - p) \}^{1/2}$; $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$; $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ where P is $[2F_c^2 + \text{Max}(F_o^2, 0)]/3$; for redmondite, *a* is 0.0303 and *b* is 7.4268, for hydroredmondite, *a* is 0.0166 and *b* is 33.03, and for sulfatoredmondite, *a* is 0.0241 and *b* is 40.7468.

Strong Pb–O bonding within the structural units is facilitated by the stereoactive 6s² lone-pair electrons evident for all Pb²⁺ cations in these structures. The structural unit is centered by a Zn cation located on a center of symmetry and octahedrally coordinated by 6 OH groups. Each of the three OH groups on *trans* faces of the Zn(OH)₆ octahedron forms two short (strong) bonds to two different Pb sites, which belong to oxygen-centered OPb₄ tetrahedra. Conversely, each of the three Pb sites composing one face of an OPb₄ tetrahedron forms strong bonds to two OH groups of the Zn(OH)₆ octahedron and one strong bond to the O atom at the center of the OPb₄ tetrahedron. The remaining Pb atom in each OPb₄ tetrahedron forms

only one strong bond, that being to the O atom at the center of the OPb₄ tetrahedron. The [Pb₈O₂Zn(OH)₆]⁸⁺ structural unit appears to be unique among minerals and synthetic phases (see Siidra *et al.* 2008).

Interstitial complexes

The crystal structures of the three minerals (Figs. 10 and 11) differ with respect to their interstitial complexes, which are nonetheless similar. In redmondite, there are two independent thiosulfate groups [(S⁶⁺O₃S²⁻)²⁻ or (S₂O₃)²⁻] (four S₂O₃ *pfu*). In hydroredmondite, there are two independent thiosulfate groups (four S₂O₃ *pfu*) and an H₂O group (two H₂O *pfu*). In sulfatoredmondite, there are two independent

TABLE 5. SELECTED BOND LENGTHS (IN Å) IN REDMONDITE

Pb1–OH10	2.322(9)	Pb3–O7	2.342(8)	Zn–OH8 (×2)	2.045(9)
Pb1–O7	2.330(8)	Pb3–OH9	2.355(9)	Zn–OH9 (×2)	2.141(9)
Pb1–OH8	2.333(9)	Pb3–OH8	2.419(9)	Zn–OH10 (×2)	2.157(9)
Pb1–O4	2.788(11)	Pb3–O1	2.708(9)	<Zn–O>	2.157
Pb1–O6	2.940(11)	Pb3–O6	2.936(10)		
Pb1–O3	3.007(12)	Pb3–O6	3.247(10)	S1–O1	1.451(10)
Pb1–O2	3.015(11)	Pb3–S2A	3.290(4)	S1–O2	1.465(10)
Pb1–O5	3.379(11)	Pb3–S1A	3.558(4)	S1–O3	1.493(11)
Pb1–S1A	3.583(4)	<Pb3–O _{sh} >	2.372	S1–S1A	1.999(5)
<Pb1–O _{sh} >	2.328	<Pb3–O _{lg} >	3.148	<S1–O>	1.470
<Pb1–O _{lg} >	3.119				
		Pb4–O7	2.286(9)	S2–O4	1.448(11)
Pb2–O7	2.347(8)	Pb4–O5	2.563(10)	S2–O5	1.454(11)
Pb2–OH10	2.379(9)	Pb4–O2	2.690(10)	S2–O6	1.497(11)
Pb2–OH9	2.385(9)	Pb4–S2A	2.869(4)	S2–S2A	2.033(5)
Pb2–O2	2.839(10)	Pb4–O3	2.924(12)	<S2–O>	1.466
Pb2–O3	3.075(12)	Pb4–S1A	3.285(4)		
Pb2–S1A	3.161(4)	Pb4–O5	3.349(11)	<i>Hydrogen bonds (bifurcated)</i>	
Pb2–O5	3.355(10)	Pb4–O4	3.487(12)	OH8...O1	2.705(13)
Pb2–S2A	3.388(4)	Pb4–S2A	3.543(4)	OH8...O6	2.884(14)
Pb2–O1	3.730(11)	Pb4–O2	3.673(10)	OH9...O4	2.989(15)
<Pb2–O _{sh} >	2.370	Pb4–O1	3.764(11)	OH9...O6	3.143(13)
<Pb2–O _{lg} >	3.258	<Pb4–O _{sh} >	2.286	OH10...O3	3.208(15)
		<Pb4–O _{lg} >	3.215	OH10...O4	3.036(14)

TABLE 6. SELECTED BOND LENGTHS (IN Å) IN HYDROREDMONDITE

Pb1–OH8	2.370(10)	Pb3–O7	2.311(9)	Zn–OH9 (×2)	2.079(9)
Pb1–OH10	2.379(10)	Pb3–OH9	2.330(11)	Zn–OH10 (×2)	2.095(10)
Pb1–O7	2.418(9)	Pb3–OH8	2.338(9)	Zn–OH8 (×2)	2.149(10)
Pb1–O4	2.828(12)	Pb3–OW11	2.886(12)	<Zn–O>	2.157
Pb1–O1	2.864(11)	Pb3–O3	3.016(15)		
Pb1–O6	2.908(10)	Pb3–O4	3.566(13)	S1–O1	1.432(11)
Pb1–O1	2.938(11)	Pb3–S2A	3.668(5)	S1–O2	1.446(14)
Pb1–S1A	3.401(7)	Pb3–O2	3.786(14)	S1–O3	1.464(12)
<Pb1–O _{sh} >	2.389	<Pb3–O _{sh} >	2.326	S1–S1A	1.987(8)
<Pb1–φ _{lg} >	2.988	<Pb3–φ _{lg} >	3.384	<S1–O>	1.447
Pb2–O7	2.284(9)	Pb4–O7	2.272(9)	S2–O4	1.437(11)
Pb2–OH10	2.346(9)	Pb4–O6	2.708(10)	S2–O5	1.459(11)
Pb2–OH9	2.426(10)	Pb4–S2A	2.763(4)	S2–O6	1.476(12)
Pb2–O2	2.857(13)	Pb4–S1A	2.872(6)	S2–S2A	2.026(5)
Pb2–O3	2.894(14)	Pb4–O2	3.091(16)	<S2–O>	1.457
Pb2–O5	2.947(12)	Pb4–O5	3.143(11)		
Pb2–O3	3.238(13)	Pb4–O3	3.144(17)	<i>Hydrogen bonds</i>	
Pb2–O1	3.239(15)	Pb4–OH9	3.692(10)	OH8...O5	2.811(14)
Pb2–S2A	3.620(4)	Pb4–S2A	3.816(5)	OH9...O2	2.779(16)
<Pb2–O _{sh} >	2.352	<Pb4–O _{sh} >	2.272	OH10...OW11	2.812(15)
<Pb2–φ _{lg} >	3.133	<Pb4–φ _{lg} >	3.154	OW11...O4	2.863(17)
				OW11...O6	2.832(15)

TABLE 7. SELECTED BOND LENGTHS (IN Å) IN SULFATOREDMONDITE

Pb1–O7	2.305(5)	Pb2–OH8 (×2)	2.351(8)	Pb3–O7	2.265(9)
Pb1–OH9	2.328(6)	Pb2–O7	2.441(9)	Pb3–O4	2.520(14)
Pb1–OH8	2.400(7)	Pb2–OW11 (×2)	2.76(3)	Pb3–O5 (×2)	2.575(10)
Pb1–O3	2.604(10)	Pb2–OW10	2.768(11)	Pb3–O1	2.638(17)
Pb1–O3	3.004(12)	Pb2–O4	2.820(12)	Pb3–OW11 (×2)	3.21(3)
Pb1–O5	3.082(12)	Pb2–OW12 (×2)	3.413(10)	Pb3–OW13 (×2)	3.41(5)
Pb1–O6	3.24(3)	Pb2–S2A (×2)	3.864(4)	Pb3–S2A	3.43(2)
Pb1–S2A	3.369(16)	<Pb2–O _{sh} >	2.381	Pb3–O6	3.50(3)
Pb1–O2	3.382(10)	<Pb2–φ _{lg} >	3.285	<Pb3–O _{sh} >	2.265
<Pb1–O _{sh} >	2.344			<Pb3–φ _{lg} >	3.084
<Pb1–φ _{lg} >	3.114				
		S1–O1	1.451(17)	S2–O4	1.435(12)
Zn–OH8 (×4)	2.106(7)	S1–O2	1.458(10)	S2–O5 (×2)	1.435(10)
Zn–OH9 (×2)	2.120(9)	S1–O3 (×2)	1.463(10)	S2–O6	1.470(18)
<Zn–O>	2.157	<S1–O>	1.457	S2–S2A	1.967(13)
				<S2–O>	1.435

sulfate groups (four SO₄ *pfu*), one fully occupied H₂O group, and three partially occupied H₂O groups (~six H₂O *pfu*).

In the redmondite structure, all of the long (weak) bonds from the Pb sites are to the O²⁻ and S²⁻ vertices of the S₂O₃ groups. In addition, each of the OH groups of the Zn(OH)₆ octahedron form bifurcated hydrogen bonds to thiosulfate O vertices. The three-dimensional linkage of the redmondite structure is *via* these weak bonds between the [Pb₈O₂Zn(OH)₆]⁸⁺ clusters and the S₂O₃²⁻ groups. The same type of bonding occurs in the hydroredmondite structure; however, hydrogen bonding from the interstitial H₂O group to thiosulfate O atoms also contributes to the three-dimensional

linkage. In the sulfatoredmondite structure, the SiO₄ group forms moderately strong bonds to the [Pb₈O₂Zn(OH)₆]⁸⁺ structural unit [Pb3–O1 = 2.638 Å and Pb1–O3 = 2.604 Å (×2)], thereby forming a triple bridge between the O1–O3–O3 face of the SiO₄ tetrahedron and the Pb1–Pb1–Pb3 face of the OPb₄ tetrahedron. The S₂O₄ group forms moderately strong bonds to Pb3 atoms in three different [Pb₈O₂Zn(OH)₆]⁸⁺ units [Pb3–O4 = 2.638 Å and Pb3–O5 = 2.604 Å (×2)], thereby linking the structural units into a relatively loosely bonded irregular sheet parallel to (20 $\bar{1}$). All other Pb–O bonds are longer than 2.75 Å.

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

	Pb1	Pb2	Pb3	Pb4	Zn	S1	S2	Hydrogen bonds		sum
								Accepted	Donated	
O1		0.02	0.22	0.02		1.62		0.11		1.99
O2	0.11	0.16		0.13, 0.02		1.56				1.98
O3	0.11	0.09		0.13		1.46		0.05		1.84
O4	0.18			0.04			1.63	0.07, 0.06		1.98
O5	0.05	0.05		0.30, 0.05			1.61			2.06
O6	0.13		0.13, 0.06				1.44	0.08, 0.05		1.89
O7	0.51	0.49		0.56, 0.50						2.06
OH8	0.51		0.42		0.39 ^{×2↓}				–0.11, –0.08	1.13
OH9		0.45	0.48		0.30 ^{×2↓}				–0.07, –0.05	1.11
OH10	0.52	0.46			0.29 ^{×2↓}				–0.05, –0.06	1.16
S1A	0.06	0.19	0.06	0.13		1.21				1.65
S2A		0.10	0.13	0.41, 0.07			1.11			1.82
sum	2.18	2.01	2.00	1.96	1.96	5.85	5.79			

Bond-valence parameters are from Gagné & Hawthorne (2015). Hydrogen bond contributions estimated from O_{Donor}...O_{Acceptor} distances using Ferraris & Ivaldi (1988). Negative values indicate amount of hydrogen bond valence donated.

TABLE 9. BOND-VALENCE SUMS (IN VALENCE UNITS) FOR HYDROREDMONDITE

	Pb1	Pb2	Pb3	Pb4	Zn	S1	S2	Hydrogen bonds		sum
								Accepted	Donated	
O1	0.15, 013	0.07				1.70				2.05
O2		0.15	0.02	0.09		1.64		0.19		2.09
O3		0.14, 0.07	0.11	0.08		1.57				1.97
O4	0.17		0.03				1.68	0.16		2.04
O5		0.13		0.08			1.59	0.18		1.98
O6	0.14			0.22			1.52	0.17		2.05
O7	0.42	0.57	0.53	0.58						2.10
OH8	0.47		0.50		0.30 $\times 2\downarrow$				-0.18	1.09
OH9		0.41	0.51	0.02	0.36 $\times 2\downarrow$				-0.19	1.11
OH10	0.46	0.49			0.34 $\times 2\downarrow$				-0.18	1.11
OW11			0.14					0.18	-0.16, -0.17	-0.01
S1A	0.10			0.41		1.25				1.76
S2A		0.05	0.05	0.55, 0.03			1.13			1.81
sum	2.04	2.08	1.89	2.06	2.00	6.16	5.92			

Bond-valence parameters are from Gagné & Hawthorne (2015). Hydrogen bond contributions estimated from $O_{\text{Donor}} \cdots O_{\text{Acceptor}}$ distances using Ferraris & Ivaldi (1988). Negative values indicate amount of hydrogen bond valence donated.

TABLE 10. BOND-VALENCE SUMS (IN VALENCE UNITS) FOR SULFATOREDMONDITE

	Pb1	Pb2	Pb3	Zn	S1	S2	sum
O1			0.25		1.62		1.87
O2	0.05 $\times 2 \rightarrow$				1.59		1.69
O3	0.27, 0.11				1.57 $\times 2\downarrow$		1.95
O4		0.17	0.33			1.68	2.18
O5	0.09		0.29 $\times 2\downarrow$			1.68 $\times 2\downarrow$	2.06
O6	0.07 $\times 0.69\downarrow \times 2 \rightarrow$		0.04 $\times 0.69\downarrow$			1.54 $\times 0.69\downarrow$	1.72
S2A	0.11 $\times 2 \rightarrow$	0.03 $\times 0.62\downarrow \times 2 \rightarrow$	0.09 $\times 0.31\downarrow$			1.32 $\times 0.31\downarrow$	1.69
O7	0.54 $\times 2 \rightarrow$	0.40	0.59				2.07
OH8	0.43	$\times 2\downarrow$ 0.49			0.33 $\times 4\downarrow$		1.25
OH9	0.51 $\times 2 \rightarrow$				0.32 $\times 2\downarrow$		1.34
OW10		0.19					0.19
OW11		0.19 $\times 0.64\downarrow$	$\times 0.66\downarrow$ 0.07				0.26
OW12		0.04 $\times 0.76\downarrow \times 2 \rightarrow$					0.08
OW13			0.04 $\times 1.24\downarrow \times 2 \rightarrow$				0.08
sum	2.09	1.90	1.92	1.96	6.35	6.53	

Bond-valence parameters are from Gagné & Hawthorne (2015). Site occupancies have been taken into consideration. Hydrogen bond contributions are not included because of ambiguities introduced by the disorder among the H_2O groups; however, likely hydrogen bonds are OH8 $\cdots$ O2 (2.88 Å), OW11 $\cdots$ O1 (2.70 Å), and OW11 $\cdots$ O6 (2.59 Å).

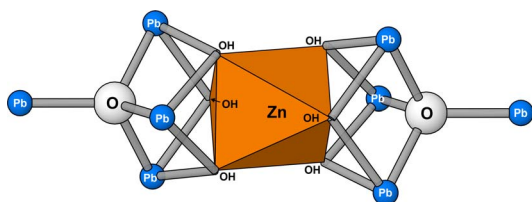
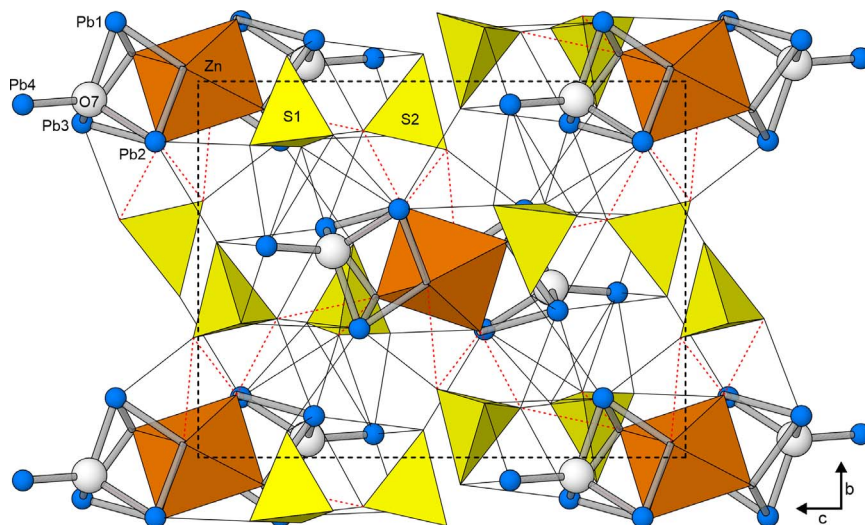


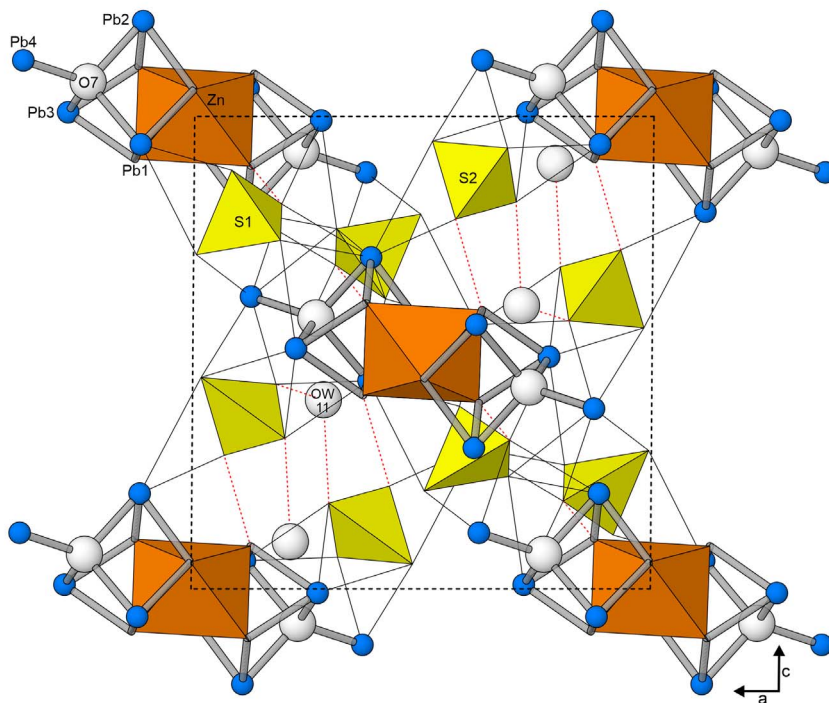
FIG. 9. $[Pb_8O_2Zn(OH)_6]^{8+}$ cluster in the structures of redmondite, hydroredmondite, and sulfatoredmondite.

Sulfate–thiosulfate substitution

As noted above, a common trend noted in the chemical analyses of the new minerals from the Redmond mine is that S contents are lower-than-expected for thiosulfate phases and 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



redmondite



hydroredmondite

FIG. 10. The structures of redmondite and hydroredmondite. Short (strong) Pb–O bonds are shown as thick gray sticks and long (weak) Pb–O and Pb–S bonds are shown as thin black lines. Hydrogen bonds are shown as red dashed lines. The outlines of the unit cells are shown by black dashed lines.

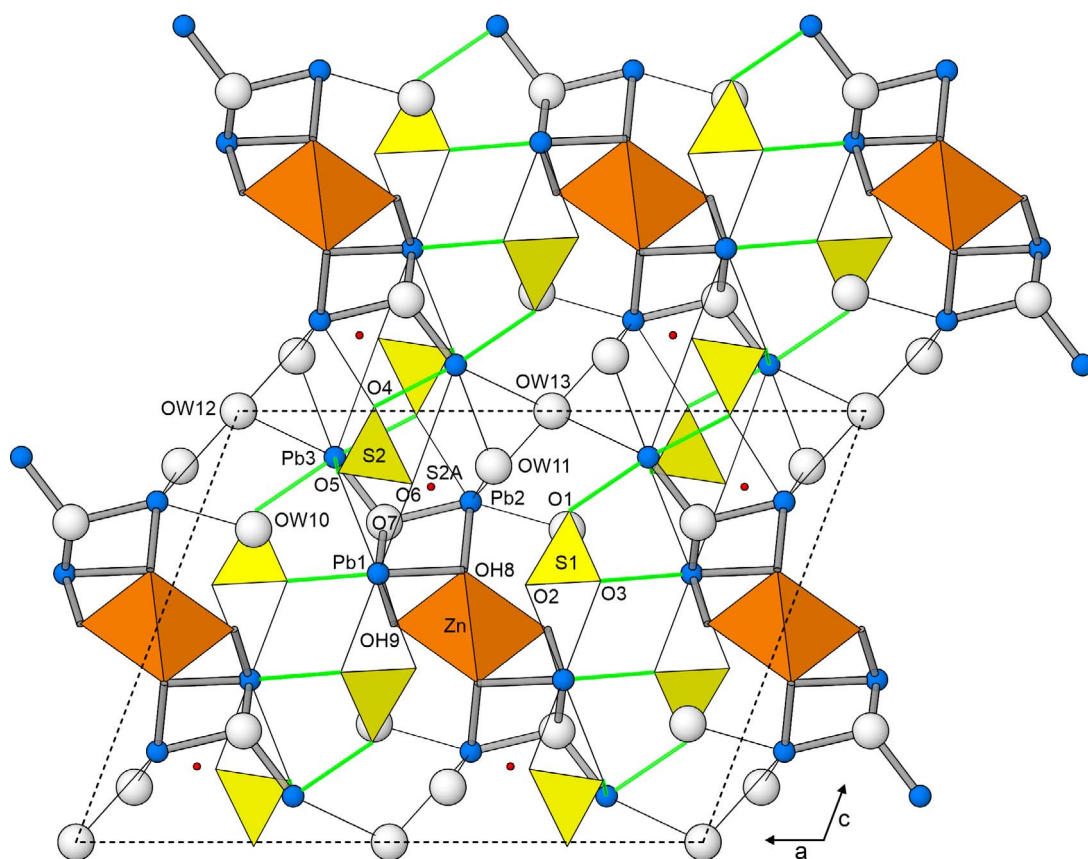


FIG. 11. The structure of sulfatoredmondite. Short (strong) Pb–O bonds are shown as thick gray sticks, medium length (moderately strong) Pb–O bonds are shown as green sticks and long (weak) Pb–O bonds are shown as thin black lines. The outline of the unit cell is shown by black dashed lines. Note that the partially occupied S2A (S^{2-}) site is shown as a small red ball.

structures. Two factors that may serve to enable this substitution: (1) both sulfate and thiosulfate phases are forming in this assemblage contemporaneously and in close proximity, indicating that both sulfate and thiosulfate anions are stable in the formational environment and (2) the sulfate and thiosulfate anions in most of the structures (including those of redmondite, hydroredmondite, and sulfatoredmondite) are interstitial components that are relatively weakly bonded to other structural components, thus allowing for some flexibility in the substitution of S^{2-} and O^{2-} .

In most cases, it was not impossible to directly observe structural evidence for the partial substitution of sulfate for thiosulfate or thiosulfate for sulfate. This is likely due to the low occupancies of the replacement S^{2-} or O^{2-} sites coupled with imperfect absorption corrections for the structure data, particularly given the presence of heavy Pb atoms. Thus far, only the refinement of the sulfatoredmondite structure has

provided such direct evidence. Initial refinements of this structure located one sulfate O site at about 1.8 Å from the S2 site. Based on the difference map, this site was split into O^{2-} (O6) and S^{2-} (S2A) sites with S2–O6 and S2–S2A distances restrained to 1.47(2) and 2.01(2) Å, respectively, and the total of the occupancies of the O6 (0.69) and S2A (0.31) sites constrained to 1. The partial thiosulfate character of the S2 sulfate group is consistent with the significant EPMA excess in S relative to the ideal formula. Significant anisotropies in the O sites of the sulfate groups suggest that these groups are relatively loosely held in the structure and are subject to some rotational disorder. Notably, the partially occupied O6 site in the S_2O_4 group forms only very long bonds with the Pb atoms (Pb1–O6 = 3.24 Å and Pb3–O6 = 3.50 Å), as does the associated partially occupied S2A site (Pb1–S2A = 3.369 Å, Pb2–S2A = 3.864, and Pb3–S2A = 3.43 Å).

ACKNOWLEDGMENTS

Reviewer Oleg Siidra is thanked for his 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.

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Received September 28, 2022. Revised manuscript accepted October 19, 2022.

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