

NEW MINERALS FROM THE REDMOND MINE, NORTH CAROLINA, USA: V. FINESCREEKITE AND HAYELASDIITE, TWO NEW THIOSULFATE MINERALS CONTAINING CUBANE-LIKE Pb_4O_4 STRUCTURAL UNITS

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, 180 Colchester Ave., 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 finescreekite, $[\text{Pb}_4(\text{OH})_4](\text{S}_2\text{O}_3)_2$ (IMA2022–030), and hayelasdiite, $[\text{Pb}_4\text{O}_{1.5}(\text{OH})_{2.5}]_2[\text{Cu}^+(\text{S}_2\text{O}_3)_4(\text{S}_2\text{O}_2\text{OH})_2(\text{H}_2\text{O})] \cdot 4\text{H}_2\text{O}$ (IMA2022–021), were found in the Redmond mine, Haywood County, North Carolina, USA, where they occur in a highly unusual secondary assemblage that comprises a variety of rare Pb–Zn–Cu sulfates, thiosulfates, and carbonates. Finescreekite was found in close association with anglesite, cubothioplumbite, redmondite, and steverustite. Hayelasdiite was found in close association with anglesite and steverustite. Finescreekite properties: colorless tablets to about 1.5 mm across; white streak; resinous to adamantine luster; brittle; Mohs hardness $\sim 2\frac{1}{2}$; curved, stepped fracture; excellent cleavage on {001}, fair on {100}, {010}, and {110}; 5.675 g/cm³ calculated density; biaxial (–) with $\alpha = 2.00(1)$, $\beta = 2.04(\text{calc})$, $\gamma = 2.065(\text{calc})$, $2V = 75.9(5)^\circ$. Hayelasdiite properties: colorless prisms and blades to about 0.5 mm in length; white streak; vitreous to subadamantine luster; brittle; Mohs hardness $\sim 2\frac{1}{2}$; curved fracture; perfect cleavage on {010}; 4.909 g/cm³ calculated density; biaxial (–) with $\alpha = 1.89(1)$, $\beta = 1.95(\text{calc})$, $\gamma = 1.97(\text{calc})$, $2V = 58(5)^\circ$. Electron probe microanalyses provided the empirical formulae $[\text{Pb}_4(\text{OH})_4](\text{S}_2\text{O}_3)_{1.76}(\text{SO}_4)_{0.24}$ and $[\text{Pb}_{4.00}\text{O}_{1.5}(\text{OH})_{2.5}]_2[\text{Cu}^{+}_{5.00}(\text{S}_2\text{O}_3)_{3.24}(\text{SO}_4)_{0.76}(\text{S}_2\text{O}_2\text{OH})_2(\text{H}_2\text{O})] \cdot 4\text{H}_2\text{O}$ for finescreekite and hayelasdiite, respectively. Finescreekite is Orthorhombic, $P2_12_12_1$, $a = 8.2330(9)$, $b = 10.7128(13)$, $c = 14.8256(13)$ Å, $V = 1307.6(2)$ Å³, and $Z = 4$. Hayelasdiite is triclinic, $P\bar{1}$, $a = 7.52089(15)$, $b = 14.9345(3)$, $c = 17.9895(13)$ Å, $\alpha = 106.727(8)$, $\beta = 90.966(6)$, $\gamma = 90.031(6)^\circ$, $V = 1934.79(16)$ Å³, and $Z = 2$. The structures of finescreekite ($R_1 = 0.061$ for $1440\ I > 2\sigma I$) and hayelasdiite ($R_1 = 0.055$ for $5636\ I > 2\sigma I$) both contain cubane-like Pb_4O_4 clusters, $[\text{Pb}_4(\text{OH})_4]^{4+}$ in finescreekite and $[\text{Pb}_4\text{O}_{1.5}(\text{OH})_{2.5}]^{2.5+}$ in hayelasdiite. The structure of hayelasdiite also contains a decorated double chain with the formula $[\text{Cu}^{+}_5(\text{S}_2\text{O}_3)_4(\text{S}_2\text{O}_2\text{OH})_2(\text{H}_2\text{O})]^{5-}$.

Keywords: finescreekite, hayelasdiite, 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

This is the fifth in a series of papers describing the new minerals recently discovered at the Redmond mine, a very small and long-inactive lead-zinc mine in western North Carolina, USA. The highly unusual secondary assemblage of Pb-Zn-Cu sulfates, thiosulfates, and carbonates found at the Redmond mine is particularly noteworthy for yielding phases with structures containing rare, and in some cases novel, structural units based on short $\text{Pb}^{2+}\text{-O}$ bonds. In the second paper in this series, the dimorphous minerals cubothioplumbite and hexathioplumbite, $[\text{Pb}_4(\text{OH})_4]\text{Pb}(\text{S}_2\text{O}_3)_3$, were described (Kampf *et al.* 2023a). The structures of these minerals contain the cubane-like $[\text{Pb}_4(\text{OH})_4]^{4+}$ cluster. Herein are described the new minerals finescreekite and hayelasdiite that contain the same type of cluster.

The name finescreekite is for Fines Creek, the nearest town to the mine (5.5 km due east), and for the creek itself, which runs through the town and comes within about 2.5 km of the mine. It is worthy of note that light reflecting off the ridged faces of finescreekite crystals (Fig. 1) looks much like light reflecting off ripples in a stream. Furthermore, the original name of Fines Creek (prior to the late 1700s) was Crystal Creek.

The name hayelasdiite (/har:'jer:'la:z:'di: ait/) is based on the Cherokee word *hayelasdi* (ᏍᏊᏩᏍᏏ in the Tsalagi language) meaning short blade or knife, in reference to the blade-like habit of the mineral. The Cherokee are an indigenous people that, prior to the 18th century, were concentrated in the region surrounding the Redmond mine. The Eastern Band of Cherokee Indians (EBCI) still own and occupy a reservation that is headquartered in the town of Cherokee, North Carolina, about 36 km SW of the Redmond mine.

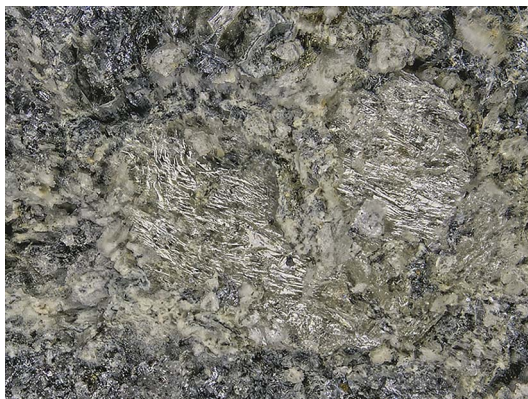


FIG. 1. Finescreekite crystals on holotype specimen #76227. The field of view is 3 mm across.



FIG. 2. Hayelasdiite crystals associated with steverustite needles on the holotype specimen, #76219. The field of view is 0.6 mm across

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. The holotype specimen of finescreekite has catalogue number 76227. The holotype specimen of hayelasdiite has catalogue number 76219.

OCCURRENCE

Finescreekite and hayelasdiite 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 chalcocopyrite, 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.* 2023b). The hallmark of this assemblage is its apparent formation at near-neutral pH conditions, as evidenced by the occurrence of minerals containing the cubane-like $[\text{Pb}_4(\text{OH})_4]^{4+}$ cluster (or variants thereof), including the new minerals finescreekite and hayelasdiite described herein.

Finescreekite and hayelasdiite were both found in vugs in massive galena-sphalerite-chalcocopyrite-quartz. Finescreekite was found in close association with

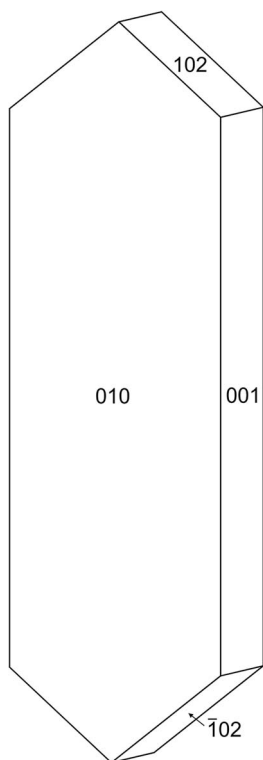


FIG. 3. A crystal drawing of hayelasdiite (clinographic projection in nonstandard orientation, **a** vertical).

anglesite, cubothioplumbite (Kampf *et al.* 2023a), redmondite (Kampf *et al.* 2023b), and steverustite. Hayelasdiite was found in a single vug in close association with anglesite and steverustite.

PHYSICAL AND OPTICAL PROPERTIES

Finescreekite

Finescreekite crystals are colorless tablets, up to about 1.5 mm across, with ridged faces and irregular outlines, flattened on {001} with stepped ridges parallel to [100] (Fig. 1). Steps on the prominent {001} faces are consistent with the forms {100}, {010}, and {110}. No twinning was observed. The streak is white and the luster is resinous to adamantine. The mineral does not fluoresce under long- or short-wave ultraviolet light. The Mohs hardness is $\sim 2\frac{1}{2}$ based on scratch tests. The tenacity is brittle, the fracture is curved and stepped. Cleavage is excellent on {001} and fair on {100}, {010}, and {110}. The density could not be measured because it exceeds that of available density fluids. The calculated density is 5.675 g/cm³ for the empirical formula and 5.694 g/cm³ for the ideal formula. In room-temperature dilute HCl, finescreekite immediately becomes cloudy and then slowly dissolves.

Finescreekite is optically biaxial (–), $\alpha = 2.00(1)$ measured in white light. The $2V$ was determined from extinction data using EXCALIBUR (Gunter *et al.* 2004). The $\beta - \alpha$ birefringence measured with a Berek compensator is 0.04, allowing the calculation of β ($= 2.04$). The

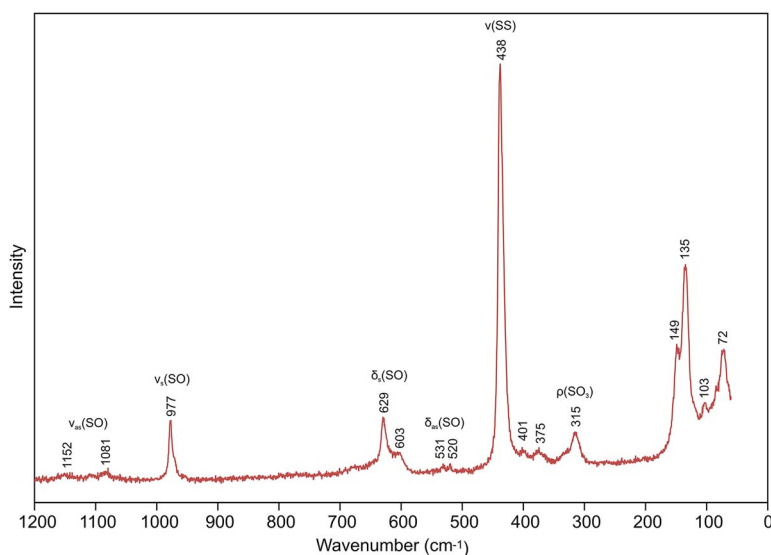


FIG. 4. The Raman spectrum of finescreekite recorded with a 785 nm laser.

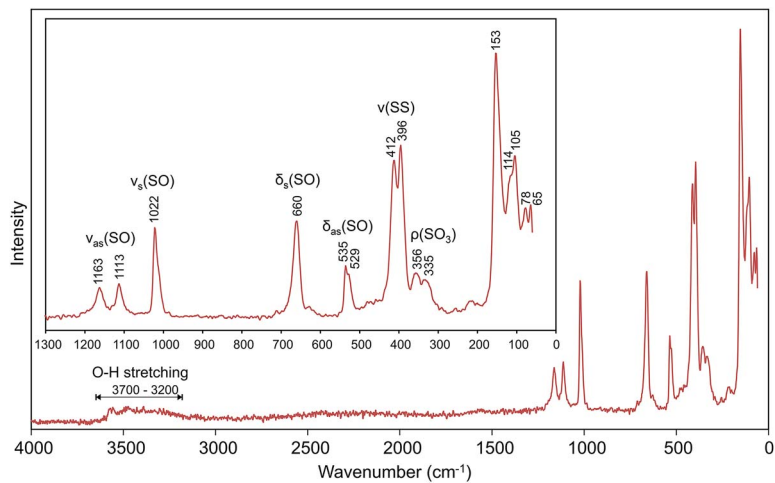


FIG. 5. The Raman spectrum of hayelasdiite recorded with a 532 nm laser.

measured $2V$ then permits the calculation of γ ($= 2.065$). Dispersion is $r > v$ strong and the optical orientation is $X = \mathbf{b}$, $Y = \mathbf{a}$, $Z = \mathbf{c}$. Finescreekite is nonpleochroic. The Gladstone-Dale compatibility, $1 - (K_p/K_c)$, is -0.073 (fair) for the empirical formula and -0.050 (good) for the ideal formula (Mandarino 2007).

Hayelasdiite

Hayelasdiite crystals are prisms and blades with wedge-like pyramidal terminations, elongated on $[100]$ and flattened on $\{010\}$, up to about 0.5 mm in length (Fig. 2). The crystal forms are $\{010\}$, $\{001\}$, $\{102\}$, and $\{10\bar{2}\}$ (Fig. 3). No twinning was observed. The mineral is intrinsically colorless, but sometimes appears pale orange-brown. The streak is white and the luster is vitreous to subadamantine. The mineral does not fluoresce under long- or short-wave ultraviolet light.

The Mohs hardness is $\sim 2\frac{1}{2}$ based on scratch tests. The tenacity is brittle, the fracture is curved, and there is a perfect cleavage on $\{010\}$. The density could not be measured because it exceeds that of available density fluids. The calculated density is 4.909 g/cm^3 for the empirical formula and 4.931 g/cm^3 for the ideal formula. The mineral immediately turns opaque white and slowly dissolves in room-temperature dilute HCl.

Hayelasdiite is optically biaxial ($-$) with $\alpha = 1.89(1)$ determined in white light. The $2V$ measured directly on a spindle stage is $58(5)^\circ$. The $\beta - \alpha$ birefringence measured with a Berek compensator is 0.06 allowing the calculation of β ($= 1.95$). The measured $2V$ then permits the calculation of γ ($= 1.97$). The Gladstone-Dale compatibility, $1 - (K_p/K_c)$, is 0.004 (superior) for the empirical formula and 0.026 (excellent) for the ideal formula (Mandarino 2007).

TABLE 1. ANALYTICAL DATA IN wt.% FOR FINESCREEKITE AND HAYELASDIITE

Constituent	Finescreekite (4 points)			Hayelasdiite (8 points)			Standard
	Mean	Range	S.D.	Mean	Range	S.D.	
Cu ₂ O	n.d.			12.02	12.02–12.67	0.22	Cu metal
PbO	77.98	77.74–78.24	0.21	59.97	59.47–60.74	0.45	PbS
SO ₃	(26.29)	26.10–26.38	0.13	(30.22)	29.69–30.52	0.28	anhydrite
SO ₃ *	13.98			16.14			
S*	4.93			5.65			
H ₂ O [§]	3.15			5.15			
O=S	−2.46			−2.82			
Total	97.58			96.11			

* Allocated based on the refined crystal structure.

§ Based on the refined crystal structure.

TABLE 2. DATA COLLECTION AND STRUCTURE REFINEMENT DETAILS FOR FINESCREEKITE AND HAYELASDIITE

Mineral	Finescreekite	Hayelasdiite
Diffractometer	Rigaku R-Axis Rapid II	Rigaku R-Axis Rapid II
X-ray radiation	MoK α (λ = 0.71075 Å)	MoK α (λ = 0.71075 Å)
Temperature	293(2) K	293(2) K
Structural formulas (incl. unlocated H)	[Pb ₄ (OH) ₄](S ₂ O ₃) ₂	[Pb ₄ O _{1.5} (OH) _{2.5}] ₂ [Cu ⁺ ₅ (S ₂ O ₃) ₄ (S ₂ O ₂ OH) ₂ (H ₂ O)]·4H ₂ O
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁ (#19)	<i>P</i> $\bar{1}$ (#2)
Unit-cell dimensions	<i>a</i> = 8.2330(9) Å <i>b</i> = 10.7128(13) Å <i>c</i> = 14.8256(13) Å	<i>a</i> = 7.52089(15) Å <i>b</i> = 14.9345(3) Å <i>c</i> = 17.9895(13) Å α = 106.727(8)° β = 90.965(6)° γ = 90.031(6)°
<i>V</i>	1307.6(2) Å ³	1934.79(16) Å ³
<i>Z</i>	4	2
Density (calc.)	5.694 g/cm ³	4.932 g/cm ³
Absorption coefficient	52.021 mm ⁻¹	38.092 mm ⁻¹
<i>F</i> (000)	1904	2516
Crystal size	130 × 60 × 20 μm	260 × 80 × 40 μm
θ range	3.12 to 22.21°	3.05 to 27.47°
Index ranges	$\bar{8} \leq h \leq 6$ $\bar{11} \leq k \leq 11$ $\bar{15} \leq l \leq 13$	$\bar{9} \leq h \leq 9$ $\bar{19} \leq k \leq 19$ $\bar{23} \leq l \leq 23$
Refl. collected	4466	43611
Independent reflections	1588; <i>R</i> _{int} = 0.183	8835; <i>R</i> _{int} = 0.125
Refl. with <i>I</i> > 2σ <i>I</i>	1440	5636
Completeness to $\theta_{\max}$	96.8%	99.8%
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Parameters/restraints	158/0	505/0
Goodness-of-fit	1.062	1.098
Final <i>R</i> indices [<i>I</i> > 2σ <i>I</i>]	<i>R</i> ₁ = 0.0611 <i>wR</i> ₂ = 0.1436	<i>R</i> ₁ = 0.0550 <i>wR</i> ₂ = 0.1561
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0669 <i>wR</i> ₂ = 0.1491	<i>R</i> ₁ = 0.0785 <i>wR</i> ₂ = 0.1741
Absolute structure parameter	−0.05	
Largest diff. peak/hole	+2.30/−2.98 e Å ⁻³	+6.63/−2.72 e Å ⁻³

$R_{\text{int}} = \Sigma |F_o^2 - F_c^2| / \Sigma [F_o^2]$. 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 finescreekite, *a* is 0.0644 and *b* is 0 and for hayelasdiite, *a* is 0.0662 and *b* is 33.34.

RAMAN SPECTROSCOPY

Raman spectroscopy for both minerals was conducted on a Horiba XploRA PLUS using a 200 μm slit, a 1800 grooves/mm diffraction grating, and a 100× (0.9 NA) objective. For finescreekite, use of a 532 nm diode laser operated at 1% power was unsuccessful owing to sample burn up. Alternatively, a 785 nm laser operated at 10% power was used, leading to a relatively noisy spectrum. The spectrum was recorded from 2000 to 60 cm⁻¹ but showed no features between 2000 and 1200 cm⁻¹, so only the spectrum from 1200

to 60 cm⁻¹ is shown in Figure 4. Hayelasdiite was also very sensitive to the laser, but it was possible to obtain a spectrum using the 532 nm laser at 1% power. The spectrum for hayelasdiite from 4000 to 60 cm⁻¹ is shown in Figure 5.

The spectra of both hayelasdiite and finescreekite exhibit numerous bands attributable to the various stretching, bending, and rotation modes of (S₂O₃)²⁻ (see Gabelica 1980, Bindi *et al.* 2011). These are labeled in Figures 4 and 5 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, δ_{as}

TABLE 3. SELECTED BOND LENGTHS (IN Å) FOR FINESCREEKITE

Pb1–OH9	2.45(3)	Pb2–OH7	2.23(4)	Pb3–OH8	2.35(3)
Pb1–OH7	2.46(4)	Pb2–OH10	2.36(3)	Pb3–OH9	2.38(4)
Pb1–OH8	2.53(4)	Pb2–OH8	2.42(4)	Pb3–OH10	2.46(3)
Pb1–O4	2.81(3)	Pb2–O5	2.69(4)	Pb3–O2	2.60(4)
Pb1–O5	2.85(4)	Pb2–O3	2.83(4)	Pb3–O6	3.11(5)
Pb1–O1	2.96(4)	Pb2–S2A	3.172(16)	Pb3–S1A	3.351(12)
Pb1–O6	3.14(6)	Pb2–O1	3.20(3)	Pb3–O1	3.35(4)
Pb1–S2A	3.195(16)	Pb2–S1A	3.836(14)	Pb3–O4	3.42(3)
Pb1–S1A	3.234(13)	<Pb2–O _{sh} >	2.34	Pb3–O3	3.66(4)
Pb1–O2	3.65(4)	<Pb2–O _{lg} >	3.15	<Pb3–O _{sh} >	2.45
<Pb1–O _{sh} >	2.48			<Pb3–O _{lg} >	3.38
<Pb1–O _{lg} >	3.12				
Pb4–OH10	2.36(3)	S1–O1	1.46(4)	Hydrogen bond	
Pb4–OH9	2.42(4)	S1–O2	1.46(4)	OH7...O3	2.92(6)
Pb4–OH7	2.58(3)	S1–O3	1.50(4)	OH8...O3	2.93(6)
Pb4–O6	2.84(4)	S1–S1A	2.022(18)	OH9...O2	2.87(4)
Pb4–S2A	3.015(15)	<S1–O>	1.47	OH10...O1	3.30(6)
Pb4–O4	3.18(3)				
Pb4–O3	3.31(4)	S2–O4	1.41(4)		
Pb4–S1A	3.332(14)	S2–O5	1.45(5)		
Pb4–O2	3.49(5)	S2–O6	1.51(4)		
Pb4–O2	3.54(4)	S2–S2A	2.04(2)		
<Pb4–O _{sh} >	2.45	<S2–O>	1.46		
<Pb4–O _{lg} >	3.24				

(SO) = S–O asymmetric deformation, $\nu(\text{SS})$ = S–S stretching, and $\rho(\text{SO}_3)$ = SO_3 rotation. Some of the bands between 420 and 300 cm^{-1} may also be due to Pb–O stretching, whereas those below 160 cm^{-1} are probably related to Pb–O–Pb bending (see Jensen 2002, Welch *et al.* 2016).

CHEMICAL COMPOSITION

Chemical analyses for finescreekite (4 points) and hayelasdiite (8 points) 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, with 15 μm beam diameter for finescreekite and 10 μm for hayelasdiite. For these and several other new phases in this assemblage, we have generally observed S analyses that 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.* 2023b). To adjust for this substitution, total analyzed S, reported as SO_3 , is allotted into SO_3 and S to provide total $(\text{SO}_4) + (\text{S}_2\text{O}_3) = 2$ and $\text{Pb} = 4$ for finescreekite and total $(\text{SO}_4) + (\text{S}_2\text{O}_3) + (\text{S}_2\text{O}_2\text{OH}) = 6$ and $\text{Cu} = 5$ for hayelasdiite, in accord with the ideal

formulae as indicated by the structure determinations. We attribute the low analytical totals 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 ($\text{O} + \text{S} = 14$ *apfu* for finescreekite and $\text{O} + \text{S} = 43$ *apfu* for hayelasdiite). Analytical data are given in Table 1.

The empirical formula for finescreekite based on $\text{O} + \text{S} = 14$ *apfu* is $[\text{Pb}_4(\text{OH})_4](\text{S}_2\text{O}_3)_{1.76}(\text{SO}_4)_{0.24}$. The ideal formula is $[\text{Pb}_4(\text{OH})_4](\text{S}_2\text{O}_3)_2$, which requires PbO 79.64, SO_3 14.28, S 5.72, H_2O 3.21, $\text{O}=\text{S} -2.85$, total 100 wt.%.

The empirical formula for hayelasdiite based on $\text{O} + \text{S} = 43$ *apfu* is $[\text{Pb}_{4.00}\text{O}_{1.5}(\text{OH})_{2.5}]_2[\text{Cu}^{+5.00}(\text{S}_2\text{O}_3)_{3.24}(\text{SO}_4)_{0.76}(\text{S}_2\text{O}_2\text{OH})_2(\text{H}_2\text{O})] \cdot 4\text{H}_2\text{O}$. Note that for simplicity, this formula assumes that the sulfate $\leftrightarrow$ thiosulfate substitution occurs only for the (S_2O_3) groups and not for the $(\text{S}_2\text{O}_2\text{OH})$ groups. The ideal formula is $[\text{Pb}_4\text{O}_{1.5}(\text{OH})_{2.5}]_2[\text{Cu}^{+5}(\text{S}_2\text{O}_3)_4(\text{S}_2\text{O}_2\text{OH})_2(\text{H}_2\text{O})] \cdot 4\text{H}_2\text{O}$, which requires PbO 62.15, Cu_2O 12.45, SO_3 16.72, S 6.70, H_2O 5.33, $\text{O}=\text{S} -3.34$, total 100 wt.%.

X-RAY CRYSTALLOGRAPHY

Powder X-ray studies were done using a Rigaku R-Axis Rapid II curved imaging plate microdiffractometer, with monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71075$ Å). A Gandolphi-like motion on the ϕ

TABLE 4. SELECTED BOND LENGTHS (IN Å) FOR HAYELASDIITE

Pb1–O19	2.261(9)	Pb2–O19	2.265(9)	Pb3–OH20	2.347(10)	Pb4–O19	2.274(8)
Pb1–OH21	2.355(9)	Pb2–OH20	2.373(10)	Pb3–OH22	2.354(9)	Pb4–OH21	2.346(9)
Pb1–OH20	2.393(10)	Pb2–OH22	2.392(9)	Pb3–OH21	2.362(10)	Pb4–OH22	2.386(9)
Pb1–O1	2.836(10)	Pb2–O9	2.919(10)	Pb3–O13	2.855(13)	Pb4–O3	2.854(11)
Pb1–O5	2.850(10)	Pb2–O5	2.921(10)	Pb3–O3	3.036(11)	Pb4–O9	2.901(10)
Pb1–O8	2.853(10)	Pb2–O8	2.927(11)	Pb3–O10	3.118(10)	Pb4–O5	2.957(10)
Pb1–O7	3.052(10)	Pb2–O14	3.119(16)	Pb3–O1	3.130(11)	Pb4–O7	3.127(10)
Pb1–O9	3.291(12)	Pb2–S2A	3.644(4)	Pb3–S4A	3.796(4)	Pb4–O8	3.144(11)
Pb1–O4	3.636(11)	<Pb2–O _{sh} >	2.343	<Pb3–O _{sh} >	2.354	Pb4–O6	3.175(11)
Pb1–O4	3.636(11)	<Pb2–O _{sh} >	2.343	<Pb3–O _{sh} >	2.354	Pb4–O6	3.175(11)
<Pb1–O _{sh} >	2.336	<Pb2–O _{lg} >	3.106	<Pb3–O _{lg} >	3.187	<Pb4–O _{sh} >	2.335
<Pb1–O _{lg} >	3.086					<Pb4–O _{lg} >	3.026
Pb5–O23	2.286(9)	Pb6–OH25	2.332(9)	Pb7–O23	2.265(9)	Pb8–O23	2.258(8)
Pb5–OH24	2.396(10)	Pb6–OH24	2.341(9)	Pb7–OH26	2.365(9)	Pb8–OH26	2.335(9)
Pb5–OH25	2.403(9)	Pb6–OH26	2.389(10)	Pb7–OH24	2.377(10)	Pb8–OH25	2.399(9)
Pb5–O12	2.855(10)	Pb6–OW28	2.800(18)	Pb7–O11	2.854(10)	Pb8–O6	2.855(11)
Pb5–O2	2.896(10)	Pb6–O16	2.947(17)	Pb7–O4	2.867(11)	Pb8–O2	2.954(10)
Pb5–OW29	2.951(18)	Pb6–O6	3.049(10)	Pb7–O2	2.899(9)	Pb8–O12	2.974(10)
Pb5–O11	2.957(10)	Pb6–O7	3.119(10)	Pb7–O10	3.037(10)	Pb8–O10	3.121(10)
Pb5–O17	3.297(16)	Pb6–O4	3.131(12)	Pb7–O12	3.239(11)	Pb8–O3	3.149(11)
Pb5–S1A	3.705(4)	<Pb6–O _{sh} >	2.354	Pb7–O1	3.717(11)	Pb8–O11	3.151(11)
<Pb5–O _{sh} >	2.362	<Pb6–O _{lg} >	3.006	<Pb7–O _{sh} >	2.336	<Pb8–O _{sh} >	2.331
<Pb5–O _{lg} >	3.110			<Pb7–O _{lg} >	3.102	<Pb8–O _{lg} >	3.034
Cu1–S1A	2.264(4)	Cu2–S4A	2.227(4)	S1–O1	1.459(10)	S2–O4	1.445(11)
Cu1–S4A	2.266(4)	Cu2–S1A	2.231(4)	S1–O2	1.462(10)	S2–O5	1.464(9)
Cu1–S5A	2.367(5)	Cu2–S6A	2.425(4)	S1–O3	1.463(11)	S2–O6	1.478(11)
<Cu1– φ >	2.299	<Cu2– φ >	2.294	S1–S1A	2.061(5)	S2–S2A	2.069(5)
				<S1–O>	1.461	<S2–O>	1.462
Cu3–S2A	2.248(4)	Cu4–S3A	2.234(4)				
Cu3–S3A	2.251(4)	Cu4–S2A	2.251(4)	S3–O7	1.449(10)	S4–O10	1.466(10)
Cu3–S5A	2.324(5)	Cu4–S6A	2.439(4)	S3–O8	1.460(10)	S4–O11	1.476(10)
<Cu3– φ >	2.274	<Cu4– φ >	2.308	S3–O9	1.475(10)	S4–O12	1.481(10)
				S3–S3A	2.062(5)	S4–S4A	2.069(5)
Cu5–OW27	2.126(12)			<S3–O>	1.461	<S4–O>	1.474
Cu5–S5A	2.227(5)						
Cu5–S6A	2.311(6)			S5–O13	1.424(13)	S6–O16	1.441(18)
<Cu5– φ >	2.221			S5–O14	1.462(15)	S6–O17	1.462(15)
				S5–OH15	1.510(14)	S6–OH18	1.540(16)
				S5–S5A	2.097(6)	S6–S6A	2.130(6)
				<S5–O>	1.465	<S6–O>	1.481

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 S2.¹

¹ Supplementary Data are available from the Depository of Unpublished Data on the MAC website (<http://mineralogicalassociation.ca/>), document “Finescreekite and Hayelasdiite, CM62, 23-00044”.

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 ABCOR (Higashi 2001). The structures were solved using SHELXT (Sheldrick 2015a) and SHELXL-2016 (Sheldrick 2015b) was used for the refinements of the crystal structures.

For finescreekite, all crystals examined were multiple subparallel intergrowths. The best crystal fragment found included at least one satellite crystal and

TABLE 5. BOND-VALENCE SUMS (IN VALENCE UNITS) FOR FINESCREEKITE

	Pb1	Pb2	Pb3	Pb4	S1	S2	H bonds	sum
O1	0.12	0.07	0.05		1.58		0.09	1.91
O2	0.03		0.28	0.04, 0.03	1.58		0.16	2.12
O3		0.16	0.03	0.06	1.43		0.15, 0.15	1.98
O4	0.17		0.04	0.07		1.79		2.07
O5	0.16	0.23				1.62		2.01
O6	0.08		0.09	0.16		1.40		1.73
OH7	0.38	0.64		0.29			−0.15	1.16
OH8	0.32	0.42	0.49				−0.15	1.08
OH9	0.39		0.46	0.42			−0.16	1.11
OH10		0.48	0.38	0.48			−0.09	1.25
S1A	0.15	0.03	0.11	0.12	1.14			1.55
S2A	0.17	0.18		0.28		1.08		1.71
sum	1.97	2.21	1.93	1.95	5.73	5.89		

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 donated hydrogen-bond valences.

exhibited moderately high mosaicity, which became more problematic at higher angles. This limited the usable data and is responsible for the high R_{int} (0.183), for several O sites being markedly prolate or oblate, and for our inability to refine the OH10 site anisotropically. For hayelasdiite, all non-hydrogen atoms were successfully refined at full occupancies and with anisotropic displacement parameters, although OW27 was strongly prolate, suggestive of some positional disorder. For both structures, difference Fourier mapping failed to locate possible H atom sites.

Data collection and refinement details are given in Table 2, selected bond distances in Tables 3 and 4, and bond-valence analyses in Tables 5 and 6. Atom coordinates and displacement parameters can be found in their respective CIF files, which have been deposited and are available from the Depository of Unpublished Data on the MAC website [document Finescreekite and Hayelasdiite, CM62, 23-00044].

ATOMIC ARRANGEMENTS

Finescreekite

The crystal structure of finescreekite contains four independent Pb^{2+} cation sites (Pb1, Pb2, Pb3, and Pb4). Each Pb^{2+} forms three short (strong) bonds ($<2.59 \text{ \AA}$) with O atoms of OH groups to form a cubane-like $[Pb_4(OH)_4]^{4+}$ cluster. The Pb^{2+} atoms each have a stereoactive $6s^2$ lone electron pair, which is oriented opposite from their short bonds. Pb3 also forms a short bond (2.60 $\text{\AA}$) with the O2 atom of a thiosulfate group $[(S^{6+}O_3S^{2-})^{2-}$ or $(S_2O_3)^{2-}]$ centered by the S1 site, and Pb2 also forms a moderately short bond (2.69 $\text{\AA}$) with the O5 atom of a thiosulfate group centered by

the S2 site. The $[Pb_4(OH)_4]^{4+}$ cluster and thiosulfate groups are linked together by longer Pb–O and Pb– S^{2-} bonds and by hydrogen bonds (Fig. 6).

Hayelasdiite

The crystal structure of hayelasdiite contains eight independent Pb^{2+} cation sites. Each Pb^{2+} forms three short (strong) bonds with O atoms to form two different cubane-like $[Pb_4O(OH)_3]^{3+}$ clusters, with Pb1, Pb2, Pb3, and Pb4 participating in one cluster and Pb5, Pb6, Pb7, and Pb8 participating in the other. The Pb^{2+} atoms each have a stereoactive $6s^2$ lone electron pair, which is oriented opposite from their three short bonds. Based upon the bond-valence sums (BVS) for the O atoms in each cluster, one is assigned as O^{2-} and three are assigned as OH^- . However, the OH^- sites exhibit BVS values higher than are typical for OH^- groups (1.38–1.44 *vu*), suggesting they may have a partial O^{2-} character and that the formulae for the clusters can better be expressed as $[Pb_4O_{1.5}(OH)_{2.5}]^{2.5+}$.

There are five independent Cu^+ cation sites. Each Cu^+ forms three bonds to form approximately planar triangular coordination; Cu1, Cu2, Cu3, and Cu4 each bond to three S^{2-} atoms, whereas Cu5 bonds to two S^{2-} atoms and a H_2O group (OW27). The S^{2-} atoms participating in the Cu coordinations are vertices of thiosulfate $[(S^{6+}O_3S^{2-})^{2-}$ or $(S_2O_3)^{2-}]$ or hydrogen-thiosulfate $[(S^{6+}O_2(OH)S^{2-})^-$ or $(S_2O_2OH)^-]$ groups. There are four different thiosulfate groups (centered by S1, S2, S3, and S4) and two hydrogen-thiosulfate groups (centered by S5 and S6). Each of the S^{2-} vertices of the CuS_3 and $CuS_2(H_2O)$ triangles is shared with another Cu coordination triangle, resulting in a decorated double

TABLE 6. BOND-VALENCE SUMS (IN VALENCE UNITS) FOR HAYELASDIITE

	Pb1	Pb2	Pb3	Pb4	Pb5	Pb6	Pb7	Pb8	Cu1	Cu2	Cu3	Cu4	Cu5	S1	S2	S3	S4	S5	S6	sum
O1	0.16		0.08				0.02							1.59						1.85
O2					0.14		0.14	0.12						1.57						1.97
O3			0.10	0.16				0.08						1.57						1.91
O4	0.03														1.64					1.90
O5	0.16	0.13		0.12			0.15								1.57					1.98
O6				0.08		0.10									1.51					1.85
O7	0.10			0.08		0.09										1.63				1.90
O8	0.16	0.13		0.08												1.58				1.95
O9	0.06	0.13		0.14												1.52				1.85
O10			0.09				0.10	0.09									1.56			1.84
O11					0.12		0.16	0.08									1.52			1.88
O12					0.16		0.07	0.12									1.50			1.85
O13			0.16															1.73		1.89
O14		0.09																1.57		1.66
OH15																		1.40		1.40
O16																			1.66	1.79
O17						0.13													1.57	1.63
OH18					0.06														1.29	1.29
O19	0.60	0.59		0.58																1.77
OH20	0.44	0.46	0.49																	1.39
OH21	0.48		0.47	0.49																1.44
OH22		0.44	0.48	0.45																1.37
O23					0.56		0.59	0.60												1.75
OH24					0.44	0.50	0.46													1.40
OH25					0.43	0.51		0.44												1.38
OH26						0.45	0.47	0.50												1.42
OW27													0.21							0.21
OW28						0.18														0.18
OW29																				0.13
OW30					0.13															0.00
OW31																				0.00
S1A					0.04				0.37	0.41				1.02						1.84
S2A		0.05									0.39	0.39			1.00					1.83
S3A											0.39	0.40				1.02				1.81
S4A			0.03						0.37	0.41							1.00			1.81
S5A									0.28		0.32		0.41					0.93		1.94
S6A										0.24		0.23	0.33						0.85	1.65
sum	2.19	2.02	1.90	2.18	2.08	2.04	2.16	2.19	1.02	1.06	1.10	1.02	0.95	5.75	5.72	5.75	5.58	5.63	5.37	

Pb²⁺-O, Cu²⁺-O, and S⁶⁺-O bond-valence parameters are from Gagné & Hawthorne (2015). Pb²⁺-S²⁻, Cu²⁺-S²⁻, and S⁶⁺-S²⁻ bond-valence parameters are from Brese & O'Keeffe (1991). Hydrogen-bond contributions are not included.

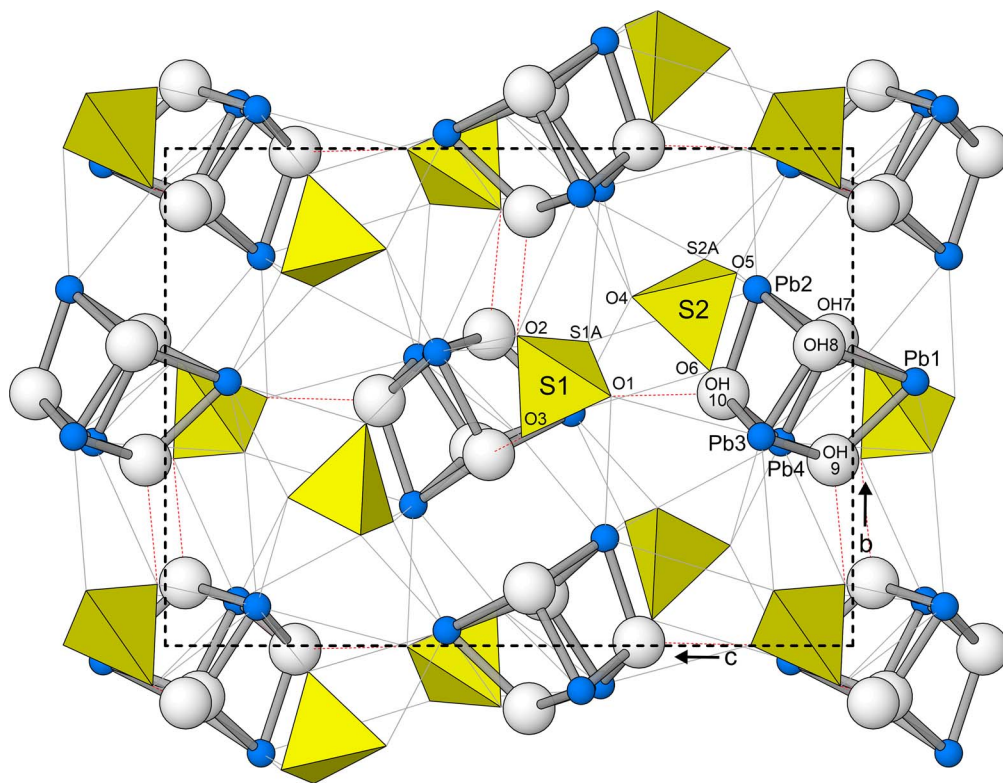


FIG. 6. The crystal structure of finescreekite. Short (strong) Pb–O bonds ($<2.59 \text{ \AA}$) are shown as thick gray sticks, longer (weaker) Pb–O and Pb– S^{2-} bonds are shown as thin gray lines, and hydrogen bonds are shown as dashed red lines. The outline of the unit cell is shown by dashed black lines.

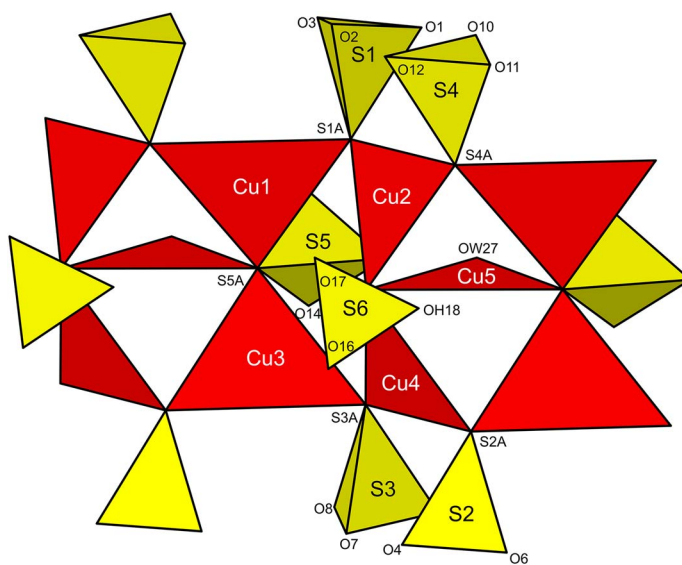


FIG. 7. The $[\text{Cu}^{+5}(\text{S}_2\text{O}_3)_4(\text{S}_2\text{O}_2\text{OH})_2(\text{H}_2\text{O})]^{5-}$ chain along **a** in the structure of hayelasiite.

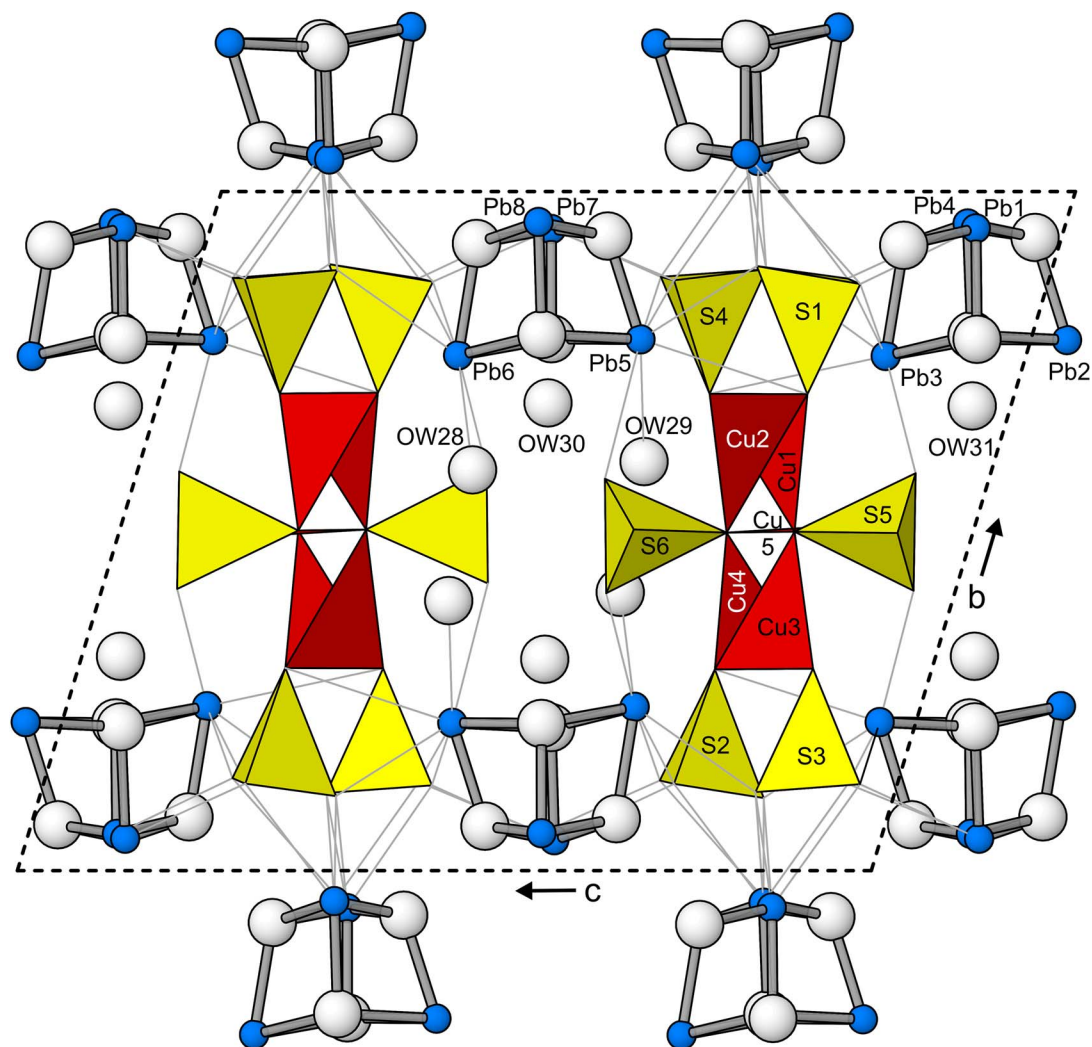


FIG. 8. The crystal structure of hayelasdiite viewed along *a*. Short (strong) Pb–O bonds are shown as thick gray sticks and long (weak) Pb–O bonds are shown as thin gray lines. The unit-cell outline is shown by dashed black lines.

chain along *a* with the formula $[\text{Cu}^+_5(\text{S}_2\text{O}_3)_4(\text{S}_2\text{O}_2\text{OH})_2(\text{H}_2\text{O})]^{5-}$ (Fig. 7).

The Pb^{2+} atoms in the two $[\text{Pb}_4\text{O}_{1.5}(\text{OH})_{2.5}]^{2.5+}$ clusters form long (weak) bonds to the O atoms of the $[\text{Cu}^+_5(\text{S}_2\text{O}_3)_4(\text{S}_2\text{O}_2\text{OH})_2(\text{H}_2\text{O})]^{5-}$ chains and to two additional H_2O groups (OW28 and OW29). There are also two H_2O groups (OW30 and OW31) that only bond to the other structural components *via* hydrogen bonds. Our inability to locate H atom positions in the structure of hayelasdiite made it impossible to propose an unambiguous hydrogen-bonding scheme. The entire structure is shown in Figure 8.

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