

NEW MINERALS FROM THE REDMOND MINE, NORTH CAROLINA, USA: IV. HAYWOODITE AND HANAHANITE, TWO NEW MINERALS CONTAINING GORDAITE-LIKE SHEETS

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ABSTRACT

The new minerals haywoodite, $[\text{Pb}(\text{H}_2\text{O})_{10}][\text{Zn}_{12}(\text{OH})_{20}(\text{H}_2\text{O})(\text{SO}_4)_3]$ (IMA2021-115), and hanahanite, $[\text{Zn}_8(\text{OH})_{14}(\text{SO}_4)] \cdot 3\text{H}_2\text{O}$ (IMA2022-012), 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. Haywoodite has the following properties: colorless to pale pink pseudohexagonal tablets and barrel-like prisms up to about 0.5 mm in diameter; white streak; vitreous luster; brittle; Mohs hardness $2\frac{1}{2}$; curved and stepped fracture; one perfect cleavage on $\{011\}$; $3.27(2) \text{ g/cm}^3$ measured density; biaxial (–) with $1.588(2)$, $\beta = 1.600(2)$, $\gamma = 1.607(2)$, and $2V(\text{meas.}) = 76(2)^\circ$. Hanahanite has the following properties: light blue prisms up to 0.3 mm in length; white streak; vitreous luster; brittle; Mohs hardness 3; curved fracture; one very good cleavage on $\{001\}$; $3.28(2) \text{ g/cm}^3$ measured density; uniaxial (–) with $\omega = 1.636(3)$ and $\varepsilon = 1.620(3)$. Electron probe microanalyses provided the empirical formulae $\text{Pb}_{1.36}\text{Zn}_{11.97}\text{S}_{3.00}\text{O}_{43}\text{H}_{41.33}$ and $(\text{Zn}_{6.69}\text{Cu}_{1.27}\text{Co}_{0.01})_{\Sigma 7.97}\text{S}_{1.00}\text{O}_{21}\text{H}_{20.04}$ for haywoodite and hanahanite, respectively. Haywoodite is triclinic, $P1$, $a = 8.35298(19)$, $b = 13.2769(7)$, $c = 18.2744(13) \text{ \AA}$, $\alpha = 92.427(8)$, $\beta = 90.419(6)$, $\gamma = 108.214(4)^\circ$, $V = 1922.94(18) \text{ \AA}^3$, and $Z = 2$. Hanahanite is hexagonal, $P6_3$, $a = 8.312(2)$, $c = 15.295(2) \text{ \AA}$, $V = 915.2(5) \text{ \AA}^3$, and $Z = 2$. The structures of haywoodite ($R_1 = 0.037$ for $6876 I > 2\sigma I$) and hanahanite ($R_1 = 0.065$ for $772 I > 2\sigma I$) both contain gordaite-like sheets. In the haywoodite structure, a disordered interlayer region contains approximately one Pb and ten H_2O *pfu*. In the hanahanite structure, ZnO_4 tetrahedra in adjacent sheets are linked by sharing corners and the interlayer region only contains an H_2O group.

Keywords: haywoodite, hanahanite, new mineral, crystal structure, gordaite-like sheet, layered hydroxide, sulfate, Pb^{2+} lone-pair electrons, Redmond mine, North Carolina, USA.

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INTRODUCTION

This is the fourth 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 Pb^{2+} -O bonds. The first three papers in this series described new mineral species with structures based on such unusual structural units: redmondite, hydroredmondite, and sulfatoredmondite contain the novel $[\text{Pb}_8\text{O}_2\text{Zn}(\text{OH})_6]^{8+}$ cluster (Kampf *et al.* 2023a); cubothioplumbite and hexathioplumbite contain the cubane-like $[\text{Pb}_4(\text{OH})_4]^{4+}$ cluster (Kampf *et al.* 2023b); and cherokeeite and cuprocherokeeite contain novel $[\text{Pb}_2(\text{Zn}, \text{Cu}^{2+})(\text{OH})_4]^{2+}$ chains (Kampf *et al.* 2023c). The two new minerals described herein, haywoodite (IMA2021-115; symbol: Hyw) and hanahanite (IMA2022-012; symbol: Hnh), have structures based on heteropolyhedral, gordaite-like sheets that are assembled from ZnO_6 octahedra, ZnO_4 tetrahedra, and SO_4 tetrahedra.

It is worth noting that haywoodite and hanahanite belong to a class of compounds referred to as layered hydroxides. Such phases have been shown to have a variety of technological uses, generally related to their abilities to host ions (in most cases anions) between their layers (Nakagaki *et al.* 2021, Leal *et al.* 2022). Besides haywoodite and hanahanite, the minerals bechererite, lahnsteinite, namuwite, and osakaite, which also have structures based on gordaite-like sheets, occur in the unusual Redmond mine assemblage. The only one of these minerals with potential for hosting ions in its interlayer is haywoodite. Like gordaite, haywoodite has sheets with a net negative charge and hosts Pb^{2+} , as well as H_2O , in its interlayer, whereas the sheets in hanahanite, bechererite, lahnsteinite, namuwite, and osakaite do not have net charges; hanahanite, lahnsteinite, namuwite, and osakaite only host H_2O between their layers, and bechererite is without interlayer content.

The name haywoodite is for Haywood County, North Carolina, in which the mine is located. Hanahanite is named in honor of American geoscience educator and mineral collector John (Jack) Hanahan (1924–2001). Mr. Hanahan was on the faculty of Belmont Abbey College in North Carolina from 1952 to 1987, teaching geology, geography, and Spanish and ultimately serving as chair of the Geosciences Division. He was highly regarded as a dedicated and effective educator. After his retirement, he continued as professor emeritus. Mr. Hanahan built a fine personal mineral collection with a particular specialty in North Carolina specimens, but he

is best known as a strong proponent of the mineral collecting hobby. He served as a leader in numerous amateur mineralogical organizations, he generously supported museum mineral collections both as a specimen donor and in volunteer curatorial roles, and he fostered collector-oriented magazines, including serving as an executive editor of *Rocks & Minerals* for many years. A more detailed compilation of Jack Hanahan's contributions to the mineralogical community was provided by Cook (2002).

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 haywoodite have catalogue numbers 76205, 76206, and 76207. Three cotype specimens of hanahanite have catalogue numbers 76212, 76213, and 76214.

OCCURRENCE

Haywoodite and hanahanite were found by one of the authors (JBS) underground at the Redmond mine, Haywood County, North Carolina, USA ($35^\circ40'55''\text{N}$, $83^\circ0'56''\text{W}$). The ore, composed mainly of galena and sphalerite with lesser chalcopryrite, 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 an unusual, localized, secondary mineral assemblage that has been discussed in detail in the first paper in this series (Kampf *et al.* 2023a). Haywoodite and hanahanite both occur in vugs in massive galena-sphalerite-chalcopryrite-quartz. Haywoodite occurs with chenite, cherokeeite, elyite, lanarkite, redmondite, and sulfatoredmondite. Hanahanite occurs with bechererite, cale-donite, hydrocerussite, lanarkite, and steverustite.

PHYSICAL AND OPTICAL PROPERTIES

Haywoodite

Haywoodite crystals (Fig. 1) occur as pseudo-hexagonal tablets, flattened on $\{01\bar{1}\}$, and as barrel-like prisms, probably resulting from the stacking of polysynthetically twinned tablets. Crystals are up to about 0.5 mm in diameter. Crystals exhibit the forms $\{01\bar{1}\}$, $\{101\}$, $\{011\}$, and $\{\bar{1}11\}$ and are commonly twinned, probably by reflection on $\{01\bar{1}\}$ (Fig. 2). The mineral is colorless to pale pink and transparent with vitreous luster and white streak. The mineral does not fluoresce under long- or short-wave ultraviolet light. The Mohs hardness is about $2\frac{1}{2}$ based on scratch tests. The tenacity is brittle, the fracture is curved and stepped. There is



FIG. 1. Haywoodite tablets with lanarkite needles on a matrix of galena, sphalerite, chalcopyrite, and quartz. Cotype specimen #76205. The field of view is 0.84 mm across.



FIG. 3. Hanahanite prisms with hydrocerussite (white) and quartz on a matrix of galena, sphalerite, chalcopyrite, and quartz. Cotype specimen #76212. The field of view is 0.84 mm across.

one perfect cleavage on $\{011\}$. The density measured by flotation in a mixture of methylene iodide and toluene is $3.27(2) \text{ g/cm}^3$. The calculated density is 3.265 g/cm^3 for the empirical formula. In room-temperature, dilute HCl, crystals immediately turn opaque and slowly dissolve. Haywoodite is optically biaxial (–), with $\alpha = 1.588(2)$, $\beta = 1.600(2)$, and $\gamma = 1.607(2)$, determined in white light. The $2V$ measured directly on a spindle stage is $76(2)^\circ$. The calculated $2V$ is 74.2° . Slight $r > v$ dispersion was observed. The optical orientation is $X \wedge \mathbf{b} = 35^\circ$, $Y \wedge \mathbf{c} = 45^\circ$, $Z \wedge \mathbf{a} = 13^\circ$. No pleochroism was observed. The Gladstone-Dale compatibility $1 - (K_p/K_c)$ is 0.047 (good) for the empirical formula and 0.024 (excellent) for the ideal formula (Mandarino 2007).

Hanahanite

Hanahanite crystals occur as hexagonal prisms with flat terminations up to about 0.3 mm in length (Fig. 3).

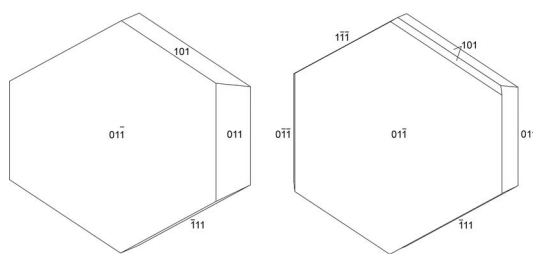


FIG. 2. Crystal drawings (clinographic projections in nonstandard orientations, $\mathbf{a}$ vertical) of haywoodite: untwinned (left) and twinned by reflection on (011) (right).

Crystals exhibit the $\{100\}$ prism and the $\{001\}$ basal pinacoid. Racemic twinning is indicated by crystal structure refinement. The mineral is light blue and transparent with vitreous luster and white streak. The mineral does not fluoresce under long- or short-wave ultraviolet light. The Mohs hardness is about 3 based on behavior when broken. The tenacity is brittle, the fracture is curved, and there is one very good cleavage on $\{001\}$. The density measured by flotation in a mixture of methylene iodide and toluene is $3.28(2) \text{ g/cm}^3$. The calculated density is 3.293 g/cm^3 for the empirical formula. Hanahanite dissolves easily in room-temperature dilute HCl. Hanahanite is optically uniaxial (–), with $\omega = 1.636(3)$ and $\epsilon = 1.620(3)$, determined in white light. No pleochroism was observed. The Gladstone-Dale compatibility $1 - (K_p/K_c)$ is 0.029 (excellent) for the empirical formula (Mandarino 2007).

RAMAN SPECTROSCOPY

Raman spectroscopy was conducted on a Horiba XploRA PLUS system using a 532 nm diode laser, 100 μm slit, 1800 gr/mm diffraction grating, and a $100\times$ (0.9 NA) objective. The spectra for haywoodite and hanahanite are compared with that for gordaite, $[\text{Na}(\text{H}_2\text{O})_6][\text{Zn}_4(\text{OH})_6\text{Cl}(\text{SO}_4)]$, from the Blue Lizard mine (Red Canyon, Utah, USA) in Figure 4. The spectra are similar to one another and to those reported previously for gordaite (Nasdala *et al.* 1998) and its Co analogue, thérèsemanaganite (Kasatkin *et al.* 2018). Bands in the 3700 to 3000 cm^{-1} range are clearly assignable to O–H stretching vibrations. Very weak bands at 1625 cm^{-1} in the haywoodite spectrum and 1603 cm^{-1} in the hanahanite spectrum are

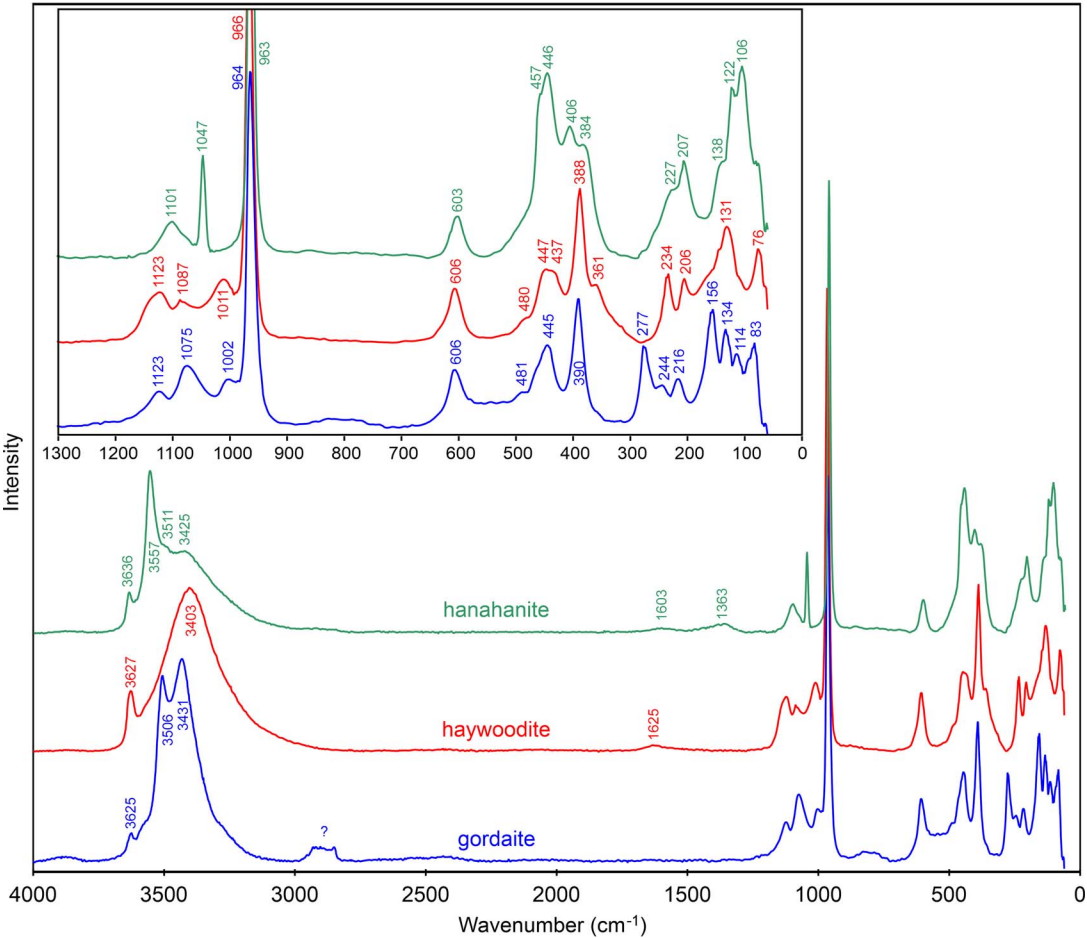


FIG. 4. Raman spectra of gordaite, haywoodite, and hanahanite recorded with a 532 nm laser. Expanded portions of the spectra from 1300 to 0 cm^{-1} are shown in the inset.

assignable to the H–O–H bending of H_2O groups. Split $\nu_3\text{SO}_4$ vibrations occur between 1125 and 1000 cm^{-1} . The very strong bands at 964, 966, and 963 cm^{-1} in the gordaite, haywoodite, and hanahanite

spectra, respectively, correspond to the $\nu_1\text{SO}_4$ symmetric stretching vibration. The bands at 606 cm^{-1} for gordaite and haywoodite and 603 cm^{-1} for hanahanite can be assigned to the $\nu_4\text{SO}_4$ bending modes and those

TABLE 1. ANALYTICAL DATA IN wt.% FOR HANAHANITE AND HAYWOODITE

Const.	Hanahanite			Haywoodite			Standard
	Mean	Range	S.D.	Mean	Range	S.D.	
PbO	16.81	16.67–16.93	0.13	n.d.			PbS
ZnO	53.90	53.41–54.47	0.47	61.91	61.28–62.30	0.55	ZnO
CuO	n.d.			11.51	11.06–12.01	0.48	Cu metal
CoO	n.d.			0.12	0.11–0.13	0.01	Co metal
SO ₃	13.29	13.17–13.48	0.13	9.10	9.00–9.16	0.09	anhydrite
H ₂ O*	20.60			20.52			
Total	104.60			103.16			

* Based on the structure.

TABLE 2. DATA COLLECTION AND STRUCTURE REFINEMENT DETAILS FOR HANAHANITE AND HAYWOODITE

Mineral	Haywoodite	Hanahanite
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 _{1.08} Zn ₁₂ S ₃ O _{42.89} H ₂₀	Zn _{7.82} S ₁ O ₂₁ H ₂₀
Space group	<i>P</i> 1 (#2)	<i>P</i> 6 ₃ (#173)
Unit-cell dimensions	<i>a</i> = 8.35298(19) Å <i>b</i> = 13.2769(7) Å <i>c</i> = 18.2744(13) Å α = 92.427(8)° β = 90.419(6)° γ = 108.214(4)° 1922.94(18) Å ³	<i>a</i> = 8.312(2) Å <i>c</i> = 15.295(2) Å
<i>V</i>		915.2(5) Å ³
<i>Z</i>	2	2
Density (calc.)	3.128 g cm ⁻³	3.263 g cm ⁻³
Absorption coefficient	12.333 mm ⁻¹	10.276 mm ⁻¹
<i>F</i> (000)	1719.4	1719.4
Crystal size	120 × 90 × 60 μm	100 × 30 × 30 μm
θ range	3.23 to 27.45°	3.13 to 24.99°
Index ranges	-10 ≤ <i>h</i> ≤ 10 -17 ≤ <i>k</i> ≤ 17 -23 ≤ <i>l</i> ≤ 23	-9 ≤ <i>h</i> ≤ 9 -9 ≤ <i>k</i> ≤ 9 -18 ≤ <i>l</i> ≤ 18
Refl. collected	45031	5789
Independent reflections	8748; <i>R</i> _{int} = 0.065	1074; <i>R</i> _{int} = 0.093
Refl. with <i>I</i> > 2σ/ <i>I</i>	6880	2411
Completeness to $\theta_{\max}$	99.6 %	99.6 %
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Parameters/restraints	641/20	94/1
Goodness-of-fit	1.098	1.043
Final <i>R</i> indices	<i>R</i> ₁ = 0.0372	<i>R</i> ₁ = 0.0650
[<i>I</i> > 2σ/ <i>I</i>]	<i>wR</i> ₂ = 0.0907	<i>wR</i> ₂ = 0.1794
<i>R</i> indices	<i>R</i> ₁ = 0.0518	<i>R</i> ₁ = 0.0854
(all data)	<i>wR</i> ₂ = 0.1002	<i>wR</i> ₂ = 0.2007
Absolute structure parameter		0.27(18)
Largest diff. peak/hole	+2.55/-2.95 e Å ⁻³	+2.74/-1.12 e Å ⁻³

$R_{\text{int}} = \Sigma |F_o^2 - F_o^2(\text{mean})| / \Sigma [F_o^2]$. GoF = $S = \{\Sigma [w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$. $R_1 = \Sigma |F_o| - |F_c| / \Sigma |F_o|$. $wR_2 = \{\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]\}^{1/2}$; $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ where P is $[2F_c^2 + \text{Max}(F_o^2, 0)]/3$; for haywoodite a is 0.0479 and b is 4.6924 and for hanahanite a is 0.123 and b is 0.

between 460 and 380 cm⁻¹ can be assigned to ν₂SO₄ bending modes. Bands at wavenumbers less than 300 cm⁻¹ are related to low-energy lattice modes, including Zn–O stretching vibrations.

CHEMICAL COMPOSITION

Chemical analyses for haywoodite (four points) and hanahanite (three points) were performed at the California Institute of Technology on a JEOL 8200 electron microprobe in WDS mode. Analytical conditions were 15 kV accelerating voltage and 10 nA beam current. A 15 μm beam diameter was used for

the haywoodite analyses and a 10 μm beam diameter was used for the hanahanite analyses. Insufficient material is available for the determination of H₂O, so it is calculated based on the structures: O = 43 *apfu* for haywoodite and O = 21 *apfu* for hanahanite. The high analytical totals are attributed to H₂O loss under vacuum, which resulted in higher concentrations for the remaining constituents than are to be expected for the fully hydrated phases. Analytical data are given in Table 1.

For haywoodite, the empirical formula based on 43 O *apfu* is Pb_{1.36}Zn_{11.97}S_{3.00}O₄₃H_{41.33}. The simplified formula is [Pb(H₂O)₁₀][Zn₁₂(OH)₂₀(H₂O)(SO₄)₃]

TABLE 3. SELECTED BOND LENGTHS (IN Å) AND Pb BOND-VALENCE SUMS (BVS IN VALENCE UNITS) FOR HAYWOODITE

Pb1–OH1	2.287(4)	Zn1–OH1	1.933(4)	Zn7–OH13	2.047(3)	Zn12–OH19	2.035(3)
Pb1–OH5	2.300(4)	Zn1–OH2	1.966(3)	Zn7–OH16	2.052(3)	Zn12–OH13	2.061(3)
Pb1–W12	2.650(12)	Zn1–OH3	1.968(3)	Zn7–OH15	2.077(3)	Zn12–OH13	2.083(3)
Pb1–W9A	2.746(8)	Zn1–OH4	1.974(3)	Zn7–OH8	2.079(3)	Zn12–OH11	2.094(4)
Pb1–W3	2.784(9)	<Zn1–O>	1.960	Zn7–OH11	2.118(3)	Zn12–OH7	2.126(4)
Pb1–O3	2.828(4)			Zn7–O12	2.442(4)	Zn12–O12	2.374(4)
Pb1–O6	2.949(4)	Zn2–OH5	1.944(4)	<Zn7–O>	2.136	<Zn12–O>	2.129
Pb1–W2	2.999(7)	Zn2–OH6	1.961(3)				
Pb1–W9B	3.52(2)	Zn2–OH8	1.961(3)	Zn8–OH17	2.031(3)	S1–O1	1.466(4)
<Pb1–O _{sh} >	2.294	Zn2–OH7	1.970(3)	Zn8–OH12	2.057(3)	S1–O2	1.466(4)
<Pb1–O _{lg} >	2.925	<Zn2–O>	1.961	Zn8–OH14	2.075(3)	S1–O3	1.470(4)
BVS	2.17			Zn8–OH3	2.095(4)	S1–O4	1.507(4)
		Zn3–OH9	1.947(3)	Zn8–OH4	2.127(4)	<S1–O>	1.467
Pb2–W5	2.195(8)	Zn3–OH11	1.955(3)	Zn8–O4	2.414(3)		
Pb2–W1	2.277(5)	Zn3–OH10	1.956(3)	<Zn8–O>	2.133	S2–O5	1.464(4)
Pb2–W1	2.414(5)	Zn3–W1	1.997(4)			S2–O6	1.466(4)
Pb2–O9	2.841(5)	<Zn3–O>	1.964	Zn9–OH20	2.031(3)	S2–O7	1.468(4)
Pb2–O11	2.972(6)			Zn9–OH14	2.071(3)	S2–O8	1.502(4)
Pb2–W8	3.464(9)	Zn4–OH18	2.045(3)	Zn9–OH12	2.071(3)	<S2–O>	1.466
Pb2–W11	3.748(17)	Zn4–OH20	2.058(3)	Zn9–OH6	2.081(3)		
<Pb2–O _{sh} >	2.295	Zn4–OH17	2.073(3)	Zn9–OH10	2.137(3)	S3–O9	1.459(4)
<Pb2–O _{lg} >	3.256	Zn4–OH4	2.075(3)	Zn9–O8	2.349(3)	S3–O10	1.462(4)
BVS	2.03	Zn4–OH2	2.119(3)	<Zn9–O>	2.123	S3–O11	1.462(4)
		Zn4–O8	2.444(3)			S3–O12	1.500(4)
Pb3–W7	2.110(10)	<Zn4–O>	2.136	Zn10–OH12	2.031(3)	<S3–O>	1.461
Pb3–OH1	2.379(9)			Zn10–OH18	2.068(3)		
Pb3–OH5	2.402(9)	Zn5–OH15	2.053(3)	Zn10–OH18	2.087(3)	<i>Hydrogen bonds*</i>	
Pb3–O2	2.858(9)	Zn5–OH20	2.057(3)	Zn10–OH2	2.092(3)	OH2...O6	2.811(5)
Pb3–O5	3.011(9)	Zn5–OH17	2.078(3)	Zn10–OH3	2.123(3)	OH3...O5	2.838(6)
Pb3–W10A	3.491(15)	Zn5–OH10	2.095(3)	Zn10–O8	2.383(3)	OH4...O1	2.784(5)
Pb3–W12	3.588(15)	Zn5–OH8	2.122(3)	<Zn10–O>	2.131	OH6...O3	2.727(5)
Pb3–O6	3.710(9)	Zn5–O4	2.375(3)			OH7...O10	2.771(6)
Pb3–W2	3.774(10)	<Zn5–O>	2.130	Zn11–OH16	2.020(3)	OH8...O2	2.768(5)
<Pb3–O _{sh} >	2.297			Zn11–OH19	2.061(3)	OH9...O9	2.805(6)
<Pb3–O _{lg} >	3.405	Zn6–OH14	2.039(3)	Zn11–OH19	2.083(3)	OH10...O7	2.826(5)
BVS	2.10	Zn6–OH16	2.067(3)	Zn11–OH7	2.089(4)	OH11...O11	2.791(6)
		Zn6–OH15	2.072(3)	Zn11–OH9	2.148(3)		
		Zn6–OH9	2.101(3)	Zn11–O12	2.428(3)		
		Zn6–OH6	2.114(3)	<Zn11–O>	2.138		
		Zn6–O4	2.402(3)				
		<Zn6–O>	2.133				

* Only hydrogen bonds to O atoms in the structural unit are listed.

or $[\text{Pb}_{1+x}(\text{H}_2\text{O})_{10}][\text{Zn}_{12}(\text{OH})_{20+x}(\text{H}_2\text{O})_{1-x}(\text{SO}_4)_3]$, as discussed in the crystal structure section. The ideal formula is $[\text{Pb}(\text{H}_2\text{O})_{10}][\text{Zn}_{12}(\text{OH})_{20}(\text{H}_2\text{O})(\text{SO}_4)_3]$, which requires PbO 12.28, ZnO 53.71, SO_3 13.21, H_2O 20.81, total 100 wt.%.

For hanahanite, the empirical formula based on 21 O *apfu* is $(\text{Zn}_{6.69}\text{Cu}_{1.27}\text{Co}_{0.01})_{\Sigma 7.97}\text{S}_{1.00}\text{O}_{21}\text{H}_{20.04}$. The simplified formula is $[(\text{Zn,Cu})_8(\text{OH})_{14}(\text{SO}_4)] \cdot 3\text{H}_2\text{O}$ and the ideal formula is $[\text{Zn}_8(\text{OH})_{14}(\text{SO}_4)] \cdot$

$3\text{H}_2\text{O}$, which requires ZnO 71.44, SO_3 8.79, H_2O 19.77, total 100 wt.%.

X-RAY CRYSTALLOGRAPHY

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

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

Zn1–OH1	1.85(11)	Zn2–OH4(×3)	1.953(13)	S–O1(×3)	1.459(18)
Zn1–OH3(×3)	1.972(15)	Zn2–OH1	2.06(11)	S–O2	1.52(3)
<Zn1–O>	1.955	<Zn2–O>	1.966	<S–O>	1.459
Zn3–OH5	2.050(15)	Zn4–OH2	1.988(17)	<i>Hydrogen bonds</i>	
Zn3–OH2	2.067(15)	Zn4–OH5	2.038(16)	OH1...OW	3.25(2)*
Zn3–OH6	2.109(16)	Zn4–OH2	2.058(19)	OH2...OW	2.82(3)
Zn3–OH5	2.138(17)	Zn4–OH4	2.115(18)	OH3...O1	3.24(3)
Zn3–OH3	2.165(19)	Zn4–OH3	2.185(19)	OH4...O1	2.96(3)
Zn3–OH4	2.194(18)	Zn4–O2	2.443(19)	OH5...OW	2.99(3)
<Zn3–O>	2.121	<Zn4–O>	2.140	OH6...O1	3.27(4)
				OW...O1	2.92(3)
				OW...O1	3.10(2)*

* OH1 is interpreted as forming an average of $\frac{1}{3}$ H bond to each of three surrounding OW sites (at 3.25 Å), whereas OH1 receives a $\frac{1}{2}$ (bifurcated) H bond from two of the three OW sites (at 3.25 Å). The other $\frac{1}{2}$ of the bifurcated H bond from each OW is received by O1 (at 3.10 Å).

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 compared with the d values and intensities calculated from the structure studies are deposited as Supplementary Tables S1 and S2¹.

Single-crystal data were collected using the same diffractometer and radiation 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) and SHELXL-2016 (Sheldrick 2015b) was used for the refinements of the structures.

For the haywoodite crystal structure, all non-hydrogen atoms in the $[\text{Zn}_{12}(\text{OH})_{20}(\text{H}_2\text{O})(\text{SO}_4)_3]$ layer structural unit were successfully refined at full occupancies and with anisotropic displacement parameters. Three Pb sites located in the interlayer region refined to occupancies of Pb1: 0.9293(17), Pb2: 0.1273(13), and Pb3: 0.0296(12); see discussion below on the total occupancy of Pb in the haywoodite structure. The Pb1 and Pb2 sites were successfully refined with anisotropic displacement parameters. The interlayer region was also found to contain O sites representing H_2O groups comprising three fully occupied unsplit sites, two fully occupied split sites, and six partially occupied sites. Difference-Fourier maps located all H atom sites associated with the OH groups of the structural unit; these were then refined with soft restraints of 0.82(3) Å on the O–H distances and with the

U_{eq} of each H atom set to 1.5 times that of the corresponding OH O atom. No H atom sites associated with the H_2O groups were located.

For the hanahanite structure, the octahedrally coordinated Zn3 and Zn4 sites, both likely to be partially occupied by Cu, refined to 0.969(14) and 0.968(15) occupancy by Zn, respectively. Efforts to refine them with joint occupancy by Zn and Cu yielded unstable refinements, presumably due to the very similar scattering powers of Zn and Cu. The OH1 site, located on a three-fold axis at 0,0,0.337, exhibited strongly anisotropic displacement parameters in the (001) plane. This is similar to the behavior of the comparable O3 site in the structure of bechererite (Hoffmann *et al.* 1997). Difference-Fourier maps 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 Haywoodite and Hanahanite, CM61, 23-00027).

ATOMIC ARRANGEMENTS

Haywoodite

The crystal structure of haywoodite is based on a heteropolyhedral layer, the core of which is a brucite-like sheet of edge-sharing ZnO_6 octahedra in which one seventh of the Zn sites are empty. Above and below the empty octahedral sites are Zn-centered tetrahedra. The apical vertices (pointing into the interlayer) are either OH or H_2O groups. Single vertices of SO_4 tetrahedra also link to both sides of the

¹ Supplementary Data are available from the Depository of Unpublished Data on the MAC website (<http://mineralogical.association.ca/>), document “Haywoodite and Hanahanite, CM61, 23-00027”.

TABLE 5. BOND-VALENCE SUMS (IN VALENCE UNITS) FOR THE HAYWOODITE STRUCTURAL UNIT

	Pb1	Zn1	Zn2	Zn3	Zn4	Zn5	Zn6	Zn7	Zn8	Zn9	Zn10	Zn11	Zn12	S1	S2	S3	H	Sum
O1														1.56			0.19	1.75
O2														1.56			0.20	1.75
O3	0.17													1.54			0.21	1.92
O4						0.16	0.15		0.15					1.41				1.87
O5															1.57		0.17	1.74
O6	0.13														1.56		0.18	1.86
O7															1.55		0.19	1.75
O8					0.14					0.18	0.16				1.42			1.90
O9																1.59	0.18	1.77
O10																1.57	0.19	1.77
O11																1.57	0.19	1.76
O12								0.14				0.14	0.17			1.43		1.88
OH1	0.56	0.52																1.08
OH2		0.48			0.32						0.34							1.14
OH3		0.48							0.34		0.32							1.14
OH4		0.47			0.36				0.31									1.14
OH5	0.55		0.51															1.05
OH6			0.49				0.33			0.35								1.17
OH7			0.48									0.35	0.32					1.14
OH8			0.47			0.32		0.36										1.15
OH9				0.50			0.34					0.30						1.14
OH10				0.49		0.34				0.31								1.14
OH11				0.49				0.32					0.34					1.16
OH12									0.38	0.36	0.40							1.15
OH13								0.39					0.37					1.11
													0.35					
OH14							0.40		0.36	0.36								1.12
OH15						0.38	0.36	0.36										1.10
OH16							0.37	0.38				0.42						1.17
OH17					0.36	0.36			0.40									1.12
OH18					0.39						0.37							1.11
											0.35							
OH19												0.37	0.40					1.13
												0.35						
OH20					0.38	0.38				0.40								1.16
W1				0.44														0.44
	1.95	1.94	1.93	1.95	1.94	1.94	1.94	1.95	1.95	1.97	1.94	1.93	1.95	6.07	6.10	6.16		

Bond-valence parameters are from Gagné & Hawthorne (2015). Hydrogen bond contributions estimated from $O_D \cdots O_A$ distances using Ferraris & Ivaldi (1988). For simplicity, the low-occupancy Pb2 and Pb3 sites are not included and the Pb1 site is treated as fully occupied. Bond-valence sums for the three Pb sites are provided in Table 3.

octahedral sheet, yielding a $[Zn_{12}(OH)_{20}(H_2O)(SO_4)_3]^{2-}$ layer structural unit (Fig. 5). The interlayer region is occupied by Pb atoms and H_2O groups, which comprise the interstitial complex. The layers are joined by a complex system of Pb–O and hydrogen bonds. The entire structure is shown in Figure 6.

As noted above, there are three Pb sites and numerous H_2O groups [five fully occupied unsplit sites (W2, W3, W5), two fully occupied split sites (W9, W10), and six partially occupied sites (W4, W6,

W7, W8, W11, W12)] in the interlayer region. Based on a maximum Pb–O distance of 3.8 Å, the 0.9267-occupied Pb1 site is nine coordinated, the 0.1283-occupied Pb2 site is seven coordinated and the 0.0287-occupied Pb3 site is nine coordinated. The total refined occupancy of the three Pb sites indicates 1.08 Pb *apfu*, whereas electron probe microanalysis shows 1.36 Pb *apfu*. It is worth noting that the three Pb sites appear to be capable of accommodating greater Pb occupancy. The most obvious mechanism

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

	Zn1	Zn2	Zn3	Zn4	S1	Hydrogen bonds		Sum
						Donated	Accepted	
O1					1.59 ^{1×3}		0.10 0.14 0.03 0.15 0.06	2.06
O2				0.14 ^{→×3}	1.36			1.78
OH1	0.65	0.37				−0.10	0.10	1.02
OH2			0.37	0.45 0.38		−0.18		1.02
OH3	0.47 ^{1×3}		0.28	0.27		−0.10		0.92
OH4		0.50 ^{1×3}	0.26	0.32		−0.14		0.96
OH5			0.38 0.31	0.40		−0.13		0.96
OH6			0.33 ^{→×3}			−0.09		0.90
OW						−0.15 −0.05 −0.06	0.03 0.18 0.13	0.08
sum	2.06	1.87	1.93	1.96	6.13			

Bond-valence parameters are from Gagné & Hawthorne (2015). Hydrogen bond contributions estimated from $O_D \cdots O_A$ distances using Ferraris & Ivaldi (1988). The Zn3 and Zn4 sites are treated as fully occupied by Zn.

for maintaining charge balance with greater Pb content is by converting H_2O to OH at the W1 site. The formula could be written: $[Pb_{1+x}(H_2O)_{10}][Zn_{12}(OH)_{20+x}(H_2O)_{1-x}(SO_4)_3]$. Indeed, the W1 site is 2.277 and 2.414 Å from

Pb2 sites, so that increasing the occupancy of the Pb2 site would compensate for the bond-valence deficiency entailed in converting some of the H_2O to OH at the W1 site.

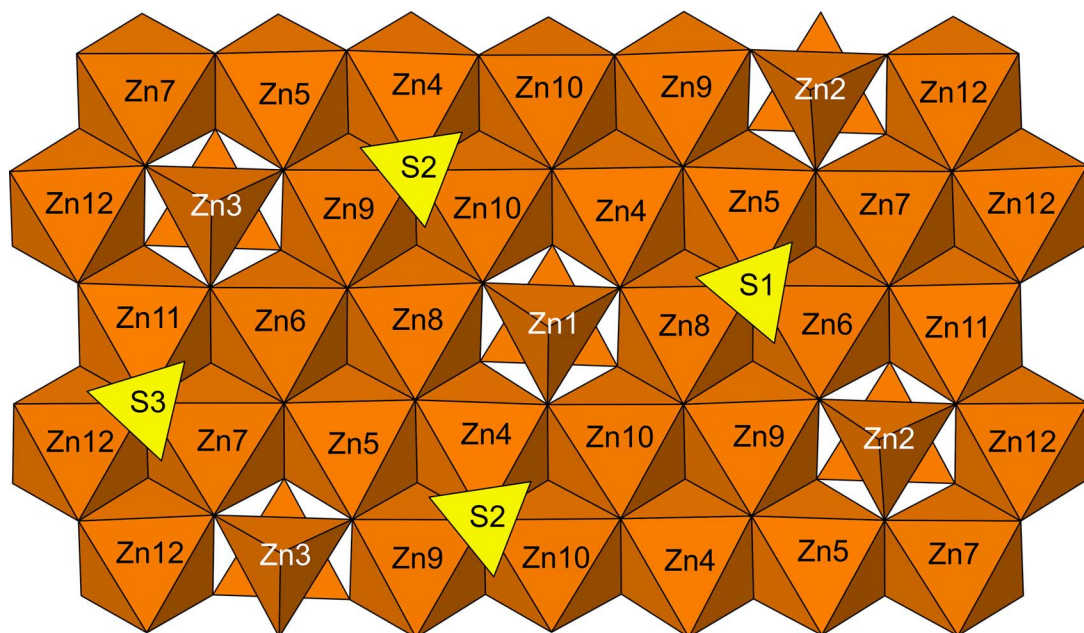


FIG. 5. The gordaite-like sheet in the structure of haywoodite viewed normal to $\{00\bar{1}\}$. The unit-cell outline is too complex to show.

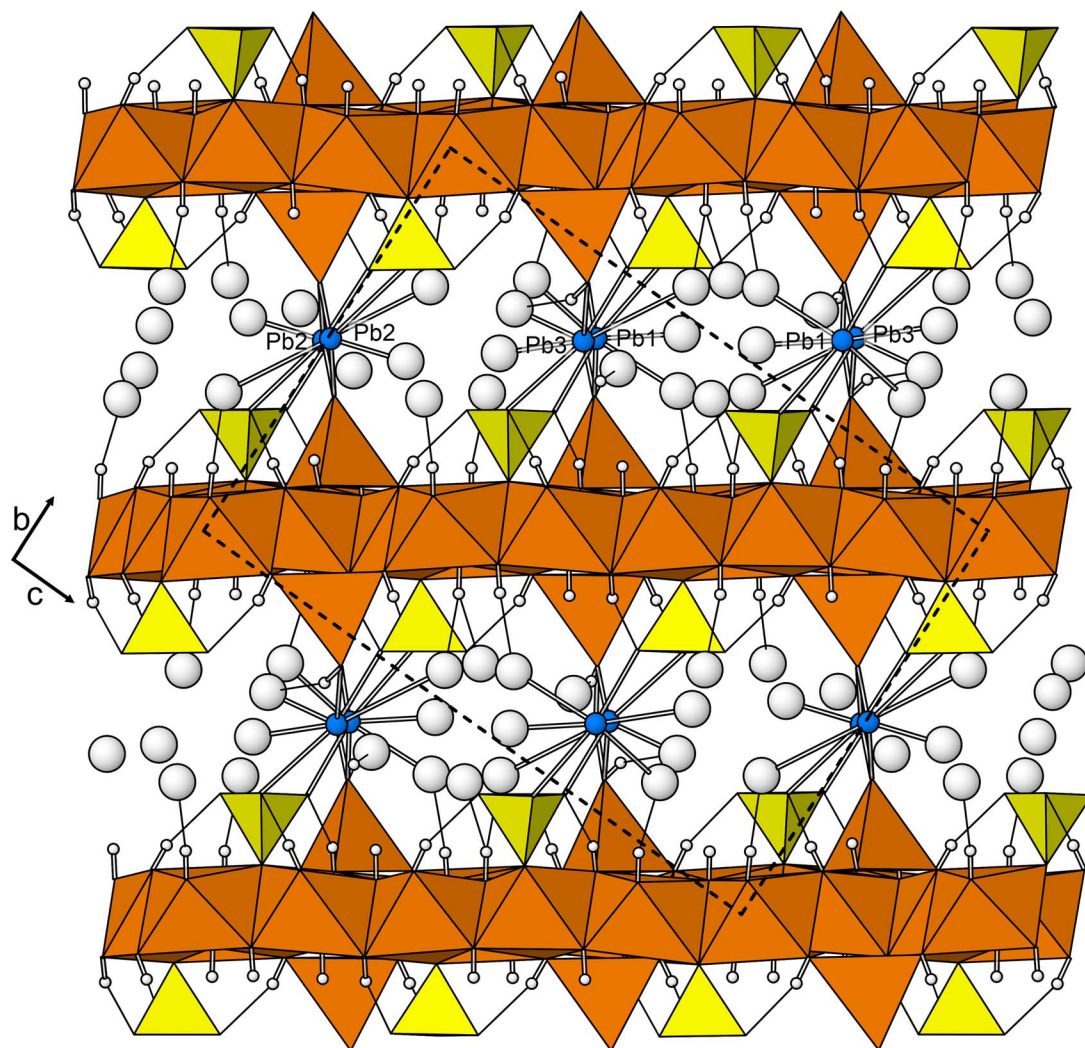


FIG. 6. The structure of haywoodite viewed along [100]. Polyhedra are as in Figure 4, Pb atoms are blue balls, O atoms of interlayer H_2O groups are large white balls, and H atoms of OH groups are small white balls. Pb–O and O–H bonds are white sticks; hydrogen bonds from OH groups are thin black lines. The unit-cell outline is shown by dashed black lines.

The topology of the $[\text{Zn}_{12}(\text{OH})_{20}(\text{H}_2\text{O})(\text{SO}_4)_3]^{2-}$ layer in the structure of haywoodite is the same as is found in the structures of gordaite, $[\text{Na}(\text{H}_2\text{O})_6][\text{Zn}_4(\text{OH})_6\text{Cl}(\text{SO}_4)]$ (Adiwidjaja *et al.* 1997); lahnsteinite, $[(\text{H}_2\text{O})_2][\text{Zn}_4(\text{OH})_6(\text{H}_2\text{O})(\text{SO}_4)]$ (Rastsvetaeva *et al.* 2012); namuwite, $[(\text{H}_2\text{O})_3][\text{Zn}_4(\text{OH})_6(\text{H}_2\text{O})(\text{SO}_4)]$ (Groat 1996); osakaite, $[(\text{H}_2\text{O})_4][\text{Zn}_4(\text{OH})_6(\text{H}_2\text{O})(\text{SO}_4)]$ (Bear *et al.* 1986); thérèsemanaganite, $[\text{Na}(\text{H}_2\text{O})_6][\text{Co}_4(\text{OH})_6\text{Cl}(\text{SO}_4)]$ (Kasatkin *et al.* 2018); and the slag-dump phase $[\text{Ca}(\text{H}_2\text{O})_9][\text{Zn}_4(\text{OH})_6\text{Cl}(\text{SO}_4)]_2$ (Burns *et al.* 1998). The above formulae have been arranged in brackets to show the interstitial complexes first, followed by the layer structural units.

Hanahanite

The crystal structure of hanahanite is based on the same heteropolyhedral layer as that of haywoodite and the other crystal structures noted above. In the hanahanite structure, single vertices of SO_4 tetrahedra link to only one side of the octahedral sheet (Fig. 7). The apical vertices of the Zn-centered tetrahedra in the layers are shared with the Zn-centered tetrahedra in the adjacent layers on either side, creating a $[\text{Zn}_8(\text{OH})_{14}(\text{SO}_4)]$ framework. One H_2O site (OW) is located in the open space between the layers of the framework (Fig. 8). Hydrogen bonds complete the linkage between

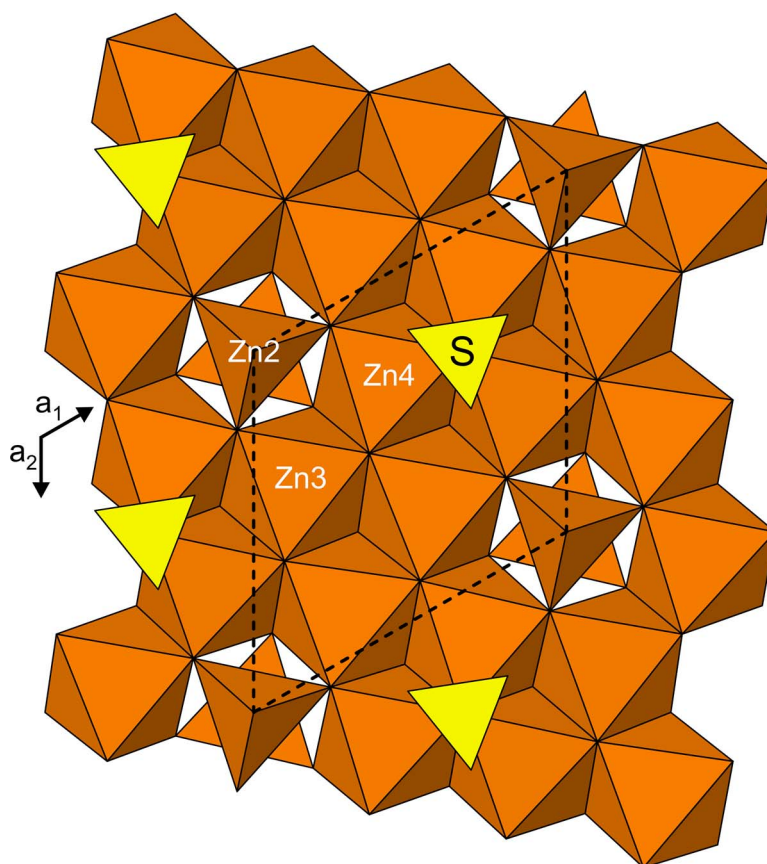


FIG. 7. The gordaite-like sheet in the structure of hanahanite viewed down [001]. The unit-cell outline is shown by dashed black lines.

the layers. The only H bond receptors are the free (unlinked) vertices of the SO_4 tetrahedra (O1) and the interlayer OW. The H bonds to and from OW require some discussion. The OH1 site, which is shared by the Zn-centered tetrahedra in adjacent layers, is on a three-fold axis and is 3.25 Å from three surrounding OW sites. OH1 is interpreted as forming an average of $\frac{1}{3}$ H bond to each of three surrounding OW sites (at 3.25 Å), whereas OH1 receives a $\frac{1}{2}$ (bifurcated) H bond from two of the three OW sites (at 3.25 Å). The other $\frac{1}{2}$ of the bifurcated H bond from each OW is received by O1 (at 3.10 Å).

It bears reiterating that the layer in the structure of hanahanite differs from that in the structures of haywoodite, gordaite, lahnsteinite, namuwite, osakaite, thérèsemaganite, and the slag-dump phase $[\text{Ca}(\text{H}_2\text{O})_9][\text{Zn}_4(\text{OH})_6\text{Cl}(\text{SO}_4)]_2$ in two respects: (1) The layer in hanahanite has SO_4 tetrahedra attached to only one side of the layer, whereas in the others, SO_4 tetrahedra are attached to both sides. (2) Adjacent layers in hanahanite

are linked together by a shared ZnO_4 vertex to form a framework, whereas in the others, the layers are not directly linked and are separated by an interlayer region containing the interstitial complex. Other minerals with structures containing layers that are linked together by shared tetrahedral vertices to form frameworks similar to that in hanahanite include bechererite, $\text{Zn}_7\text{Cu}(\text{OH})_{13}[(\text{SiO}(\text{OH})_3(\text{SO}_4)]$ (Hoffmann *et al.* 1997); hodge-smithite, $\text{Cu}_6\text{Zn}(\text{SO}_4)_2(\text{OH})_{10} \cdot 3\text{H}_2\text{O}$ (Elliott 2019); and ramsbeckite, $(\text{Cu},\text{Zn})_{15}(\text{OH})_{22}(\text{SO}_4)_4 \cdot 6\text{H}_2\text{O}$ (Effenberger 1988).

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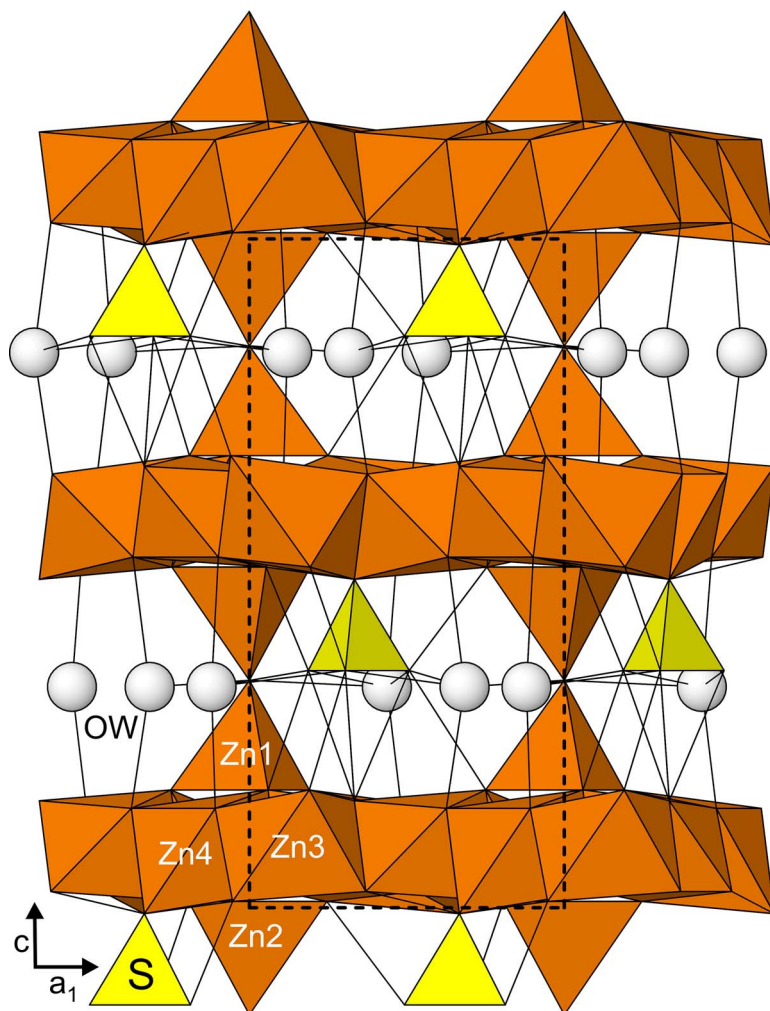


FIG. 8. The structure of hanahanite viewed down [010]. Hydrogen bonds are shown as black lines. The unit-cell outline is shown by dashed black lines.

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