

NEW MINERALS FROM THE REDMOND MINE, NORTH CAROLINA, USA: III. CHEROKEEITE AND CUPROCHEROKEEITE, TWO NEW MINERALS CONTAINING $[\text{Pb}_2(\text{Zn}, \text{Cu}^{2+})(\text{OH})_4]^{2+}$ CHAINS

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ABSTRACT

The new minerals cherokeeite, $[\text{Pb}_2\text{Zn}(\text{OH})_4](\text{SO}_4) \cdot \text{H}_2\text{O}$ (IMA2022-016), and cuprocherokeeite, $[\text{Pb}_8\text{Zn}_3\text{Cu}^{2+}(\text{OH})_{16}](\text{SO}_4)_4 \cdot 4\text{H}_2\text{O}$ (IMA2022-086), 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. Cherokeeite has the following properties: colorless to pale pink prisms or blades to about 1 mm; white streak; vitreous luster; brittle; Mohs hardness 2½; splintery fracture; at least two perfect cleavages; 5.011 g/cm³ calculated density; biaxial (+) with $\alpha = 1.745(5)$, $\beta = 1.770(5)$, $\gamma = 1.805(5)$, and $2V = 85(2)^\circ$. Cuprocherokeeite has the following properties: light blue prisms or blades to about 1 mm; very pale bluish-white streak; vitreous luster; brittle; Mohs hardness 2½; irregular, curved fracture; probably two good cleavages; 5.032 g/cm³ calculated density; biaxial (+) with $\alpha = 1.760(5)$, $\beta = 1.770(5)$, $\gamma = 1.800(5)$, and $2V$ (meas.) = 65(3)°. Electron probe microanalyses provided the empirical formulae $[\text{Pb}_{2.00}\text{Zn}_{1.00}(\text{OH})_4](\text{SO}_4)_{0.85}(\text{S}_2\text{O}_3)_{0.15} \cdot \text{H}_2\text{O}$ and $[\text{Pb}_{8.14}(\text{Zn}_{2.52}\text{Cu}^{2+}_{1.34})(\text{OH})_{16}][(\text{SO}_4)_{3.07}(\text{S}_2\text{O}_3)_{0.93}] \cdot 4\text{H}_2\text{O}$ for cherokeeite and cuprocherokeeite, respectively. Cherokeeite is monoclinic, $P2_1/n$, $a = 17.1697(7)$, $b = 6.47173(19)$, $c = 17.5304(12)$ Å, $\beta = 115.440(8)^\circ$, $V = 1759.06(19)$ Å³, and $Z = 8$. Cuprocherokeeite is monoclinic, $P2_1/n$, $a = 12.6828(5)$, $b = 9.4629(5)$, $c = 14.7876(8)$ Å, $\beta = 94.798(4)^\circ$, $V = 1768.53(15)$ Å³, and $Z = 2$. The structures of cherokeeite ($R_1 = 0.0425$ for 2681 $I > 2\sigma I$) and cuprocherokeeite ($R_1 = 0.0741$ for 2411 $I > 2\sigma I$) both contain edge-sharing chains of octahedra decorated by Pb^{2+} cations, which are strongly bonded to the chains *via* short Pb–O bonds. In cherokeeite, the octahedral cations are all Zn, whereas in cuprocherokeeite, one in every four cations is Cu^{2+} .

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

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INTRODUCTION

This is the third 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, clusters assembled by short $\text{Pb}^{2+}\text{-O}$ bonds. In the first paper in this series, the new mineral species redmondite, hydroredmondite, and sulfatoredmondite (Kampf *et al.* 2023a) were described and, in the second, the new species cubothioplumbite and hexathioplumbite were described (Kampf *et al.* 2023b). The two new minerals described herein, cherokeeite (IMA2022-016; symbol: Chr) and cuprocherokeeite (IMA2022-086; symbol: Cch), contain novel $[\text{Pb}_2(\text{Zn,Cu}^{2+})(\text{OH})_4]^{2+}$ chains in which edge-sharing chains of (Zn,Cu^{2+}) octahedra are decorated by Pb^{2+} cations.

The name cherokeeite is for the Cherokee, an indigenous people that, prior to the 18th century, were concentrated in the region surrounding the Redmond mine (southwestern North Carolina, southeastern Tennessee, the edges of western South Carolina, northern Georgia, and northeastern Alabama). Most of the Cherokee were forcibly removed to a reservation in Oklahoma in 1838–1839, although the Eastern Band of Cherokee Indians (EBCI) still owns and occupies a reservation in western North Carolina known as the Qualla Boundary. The Redmond mine is about 36 km NE of the town of Cherokee, the headquarters of the EBCI. The name cuprocherokeeite is based on the fact that the mineral contains the same distinctive chains found in the structure of cherokeeite but with one in every four Zn sites occupied by Cu^{2+} .

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 cherokeeite have catalogue numbers 76216, 76217, and 76218. Three cotype specimens of cuprocherokeeite have catalogue numbers 76272, 76273, and 76274.

OCCURRENCE

Cherokeeite and cuprocherokeeite 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



Fig. 1. Cherokeeite crystals on cotype specimen #76216. The field of view is 0.68 mm across.

of galena and sphalerite with lesser chalcopyrite, occurs in an epithermal vein system consisting of disconnected sulfide-bearing quartz lenses near the contact between a granite gneiss and a mica schist (Espenshade *et al.* 1947). The new minerals occur in an unusual, localized, secondary mineral assemblage that has been discussed in detail in the first paper in this series (Kampf *et al.* 2023a). Cherokeeite and cuprocherokeeite occur together in vugs in massive galena-sphalerite-chalcopyrite-quartz. Cherokeeite also occurs with anglesite, bechererite, chenite, elyite, haywoodite (Kampf *et al.* 2022), hydroredmondite, lanarkite, redmondite, steverustite, sulfatoredmondite, susannite, and several other potentially new minerals. Cuprocherokeeite also occurs with chenite, elyite, and several other potentially new minerals.

PHYSICAL AND OPTICAL PROPERTIES

Cherokeeite

Cherokeeite crystals are short to long prisms or blades with wedge-like pyramidal terminations up to about 1 mm in length. Crystals occur in subparallel to divergent intergrowths (Fig. 1). Crystals exhibit the forms $\{100\}$, $\{001\}$, $\{110\}$ and $\{10\bar{1}\}$ (Fig. 2). No twinning was observed. 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 splintery, and there are at least two perfect cleavages in the $[010]$ zone; probably $\{100\}$, $\{001\}$ and/or $\{10\bar{1}\}$. The density could not be measured because crystals exceed the density of available density fluids. The calculated density is 5.011 g/cm^3 for the empirical formula and

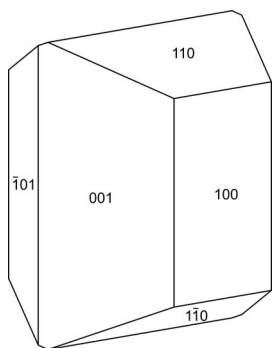


FIG. 2. Crystal drawing of cherokeeite (clinographic projection in nonstandard orientation, **b** vertical). Note that habits of cherokeeite crystals vary considerably, depending on the relative development of the crystal forms.

4.998 g/cm³ for the ideal formula. In room-temperature dilute HCl, cherokeeite immediately turns opaque and slowly dissolves. Cherokeeite is optically biaxial (+) with $\alpha = 1.745(5)$, $\beta = 1.770(5)$, and $\gamma = 1.805(5)$, determined in white light. Note that γ was observed to be slightly higher than the index of refraction of the 1.80 liquid, based on very low relief and the appearance of a colored Becke line. The mineral could not be tested using the 1.81 liquid because it rapidly decomposes in that liquid. The $2V$ measured directly on a spindle stage is $85(2)^\circ$. The calculated $2V$ is 81.8° . Slight $r > v$ dispersion was observed. The optical orientation is $X = \mathbf{b}$, $Y \wedge c = 56^\circ$ in the obtuse angle β . No pleochroism was observed. The Gladstone-Dale compatibility $1 - (K_p/K_c)$ is 0.046 (good) for the empirical formula and 0.023 (excellent) for the ideal formula (Mandarino 2007).



FIG. 3. Cuprocherokeeite crystals on cotype specimen #76273. The field of view is 1 mm across.

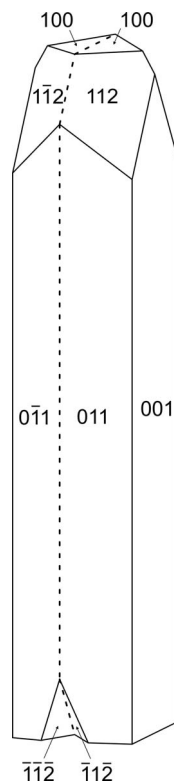


FIG. 4. Crystal drawing of cuprocherokeeite twin (clinographic projection in nonstandard orientation, **a** vertical). The trace of the twin plane is shown by dashed line.

Cuprocherokeeite

Cuprocherokeeite crystals are short to long prisms or blades, elongated on [100] and more or less flattened on {001}, up to about 1 mm in length. Crystals occur in subparallel to divergent intergrowths (Fig. 3). Crystals exhibit the forms {100}, {001}, {011}, and {112}; they are twinned by 180° rotation around [100] (Fig. 4). Note that the {112} form could not be measured and is only surmised from the visual appearance of crystals. The mineral is light blue and transparent with vitreous luster and very pale bluish-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 irregular and curved. Two good cleavages in the [100] zone are likely based on the crystal structure; however, no distinct cleavages were observed. The density could not be measured because crystals exceed the density of available density fluids. The calculated density is 5.032 g/cm³.

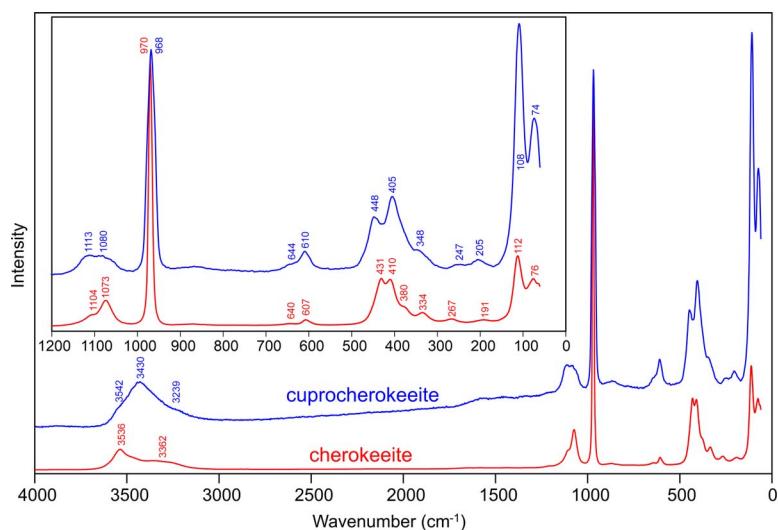


FIG. 5. Raman spectra of cherookeite and cuprocherookeite recorded with a 532 nm laser.

for the empirical formula and 4.986 g/cm^3 for the ideal formula. In room-temperature dilute HCl, cuprocherookeite immediately turns opaque and slowly dissolves. Cuprocherookeite is optically biaxial (+) with $\alpha = 1.760(5)$, $\beta = 1.770(5)$, $\gamma = 1.800(5)$, determined in white light. The $2V$ measured directly on a spindle stage is $65(3)^\circ$. The calculated $2V$ is 60.8° . No dispersion was observed. The optical orientation is $Y = \mathbf{b}$, $X \approx \mathbf{a}$. No pleochroism was observed. The Gladstone-Dale compatibility $1 - (K_p/K_c)$ is 0.057 (good) for the empirical formula and 0.015 (superior) for the ideal formula (Mandarino 2007).

RAMAN SPECTROSCOPY

Raman spectroscopy was conducted on a Horiba XploRA PLUS using a 532 nm diode laser, 200 μm slit, 1800 gr/mm diffraction grating, and a $100\times$ (0.9 NA) objective. The spectra for cherookeite and cuprocherookeite from 4000 to 60 cm^{-1} are shown in Figure 5. The two spectra are very similar.

Bands in the 3700 to 3100 cm^{-1} range are clearly assignable to O–H stretching vibrations. A poorly defined hump in the cuprocherookeite spectrum from about 1150 to 1050 cm^{-1} composed of at least two bands at approximately 1113 and 1080 cm^{-1} is assigned to split $\nu_3 \text{ SO}_4$ vibrations. The very strong band at $970/968 \text{ cm}^{-1}$ (for cherookeite/cuprocherookeite) corresponds to the $\nu_1 \text{ SO}_4$ symmetric stretching vibration. The bands at $640/644$ and $607/610 \text{ cm}^{-1}$ can be assigned to the $\nu_4 \text{ SO}_4$ bending modes and those at $432/448$ and $410/405 \text{ cm}^{-1}$ can be assigned to $\nu_2 \text{ SO}_4$

bending modes. Bands at lower wavenumbers are related to low-energy lattice modes including Pb–O (see Jensen 2002, Welch *et al.* 2016) and Zn–O (see Frost *et al.* 2008) stretching and bending vibrations.

CHEMICAL COMPOSITION

Chemical analyses for cherookeite (5 points) and cuprocherookeite (3 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. A $10 \mu\text{m}$ beam diameter was used for the cherookeite analyses and a $15 \mu\text{m}$ beam diameter was used for the cuprocherookeite analyses. For these and several other new minerals in this assemblage, it has been generally observed that analyses for S are somewhat lower than expected for thiosulfate phases and somewhat higher than expected for sulfate phases. This appears to be due to the substitution of a small amount of sulfate for thiosulfate or thiosulfate for sulfate in their crystal structures, an observation made during refinement of the crystal structure of sulfatoredmondite (Kampf *et al.* 2023a). To adjust for this substitution, total analyzed S reported as SO_3 is then allotted into SO_3 and S such that for cherookeite $\text{SO}_4 + \text{S}_2\text{O}_3 = 1$ and $\text{Zn} = 1$ and for cuprocherookeite $\text{Pb} + \text{Zn} + \text{Cu} = 12$, $\text{SO}_4 + \text{S}_2\text{O}_3 = 4$, and $\text{O} + \text{S} = 40 \text{ apfu}$. Crystals did not take a good polish and the low analytical totals may be attributed to the irregular surfaces of the crystals. Insufficient material is available for the determination of H_2O , so it is calculated based on the structures. Analytical data are given in Table 1.

TABLE 1. ANALYTICAL DATA IN wt.% FOR CHEROKEEITE AND CUPROCHEROKEEITE

Const.	cherokeeite				cuprocherokeeite				Standard
	Mean	Range	S.D.	Norm.	Mean	Range	S.D.	Norm.	
PbO	63.58	62.93–63.81	0.37	67.16	60.12	59.46–60.70	0.62	67.80	PbS
ZnO	11.60	11.51–11.75	0.09	12.25	6.77	6.70–6.83	0.06	7.64	ZnO
CuO	n.d.				3.51	3.45–3.57	0.06	3.99	Cu metal
SO ₃	(13.16)	13.09–13.25	0.07		(13.04)	12.85–13.16	0.16		anhydrite
SO ₃ *	11.44			12.08	10.60			11.95	
S*	0.69			0.73	0.98			1.11	
H ₂ O [§]				8.14				8.06	
O=S				−0.36				−0.55	
Total				100.00				100.00	

* Allocated based on the structure.

§ Based on the structure.

For cherokeeite, the empirical formula based on O + S = 10 *apfu* is Pb_{2.00}Zn_{1.00}S⁶⁺_{1.00}S^{2−}_{0.15}O_{8.85}H_{6.00} or, in structural format, [Pb_{2.00}Zn_{1.00}(OH)₄](SO₄)_{0.85}(S₂O₃)_{0.15}·H₂O. The simplified formula is [Pb₂Zn(OH)₄](SO₄)_{1−x}(S₂O₃)_x·H₂O, where *x* < 0.5. The ideal formula is [Pb₂Zn(OH)₄](SO₄)·H₂O, which requires PbO 67.44, ZnO 12.30, SO₃ 12.10, H₂O 8.17, total 100 wt.%.

For cuprocherokeeite, the empirical formula based on O + S = 40 *apfu* is Pb_{8.14}Zn_{2.52}Cu²⁺_{1.34}S⁶⁺_{4.00}S^{2−}_{0.93}O_{35.07}H_{23.99} or, in structural format, [Pb_{8.14}(Zn_{2.52}Cu²⁺_{1.34})(OH)₁₆](SO₄)_{3.07}(S₂O₃)_{0.93}·4H₂O. The simplified formula is [Pb₈(Zn,Cu²⁺)₃Cu²⁺(OH)₁₆](SO₄)_{4−x}(S₂O₃)_x·H₂O, where *x* < 2. The ideal formula is [Pb₈Zn₃Cu²⁺(OH)₁₆](SO₄)₄·4H₂O, which requires PbO 67.49, ZnO 9.23, CuO 3.01, SO₃ 12.10, H₂O 8.17, 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 MoK α radiation (λ = 0.71075 Å). A Gandolfi-like motion on the ϕ and ω axes was used to randomize the orientations of the samples. Observed *d* values and intensities were derived by profile fitting using JADE Pro software (Materials Data, Inc.). Data are deposited as Supplementary Tables S1 and 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 ABCOR (Higashi 2001). The structures were solved using SHELXT (Sheldrick 2015a), and SHELXL-2016 (Sheldrick 2015b) was used for the refinements of the structures. Crystals of cuprocherokeeite are of relatively poor quality and ubiquitously twinned. The best quality crystal found measured only 110 × 20 × 20 μ m. Beyond 40° 2 θ , the reflections became too weak and diffuse to be useful. The crystal that was analyzed was found to be twinned by 180° rotation around [100], as indicated by the TwinSolve program within the Rigaku CrystalClear software package. TwinSolve was used to integrate the data, providing a data set from one twin component with no twin overlaps for structure solution and a combined HKLF5 data set for refinement of the structure. It should be noted that the deficiencies in the cuprocherokeeite refinement noted below are most like due to the relatively limited data set, the difficulty in integrating the twinned reflections, and the inability of the ABCOR program to completely correct for the absorption by the twinned crystal.

For the cherokeeite structure, all non-hydrogen atoms were successfully refined at full occupancies and with anisotropic displacement parameters. One of the two SO₄ groups exhibited two anomalously short S–O bonds, S2–O5 (1.412 Å) and S2–O6 (1.430 Å); to compensate, all four S–O bonds associated with this group were restrained to 1.47(1) Å, resulting in a slight improvement in the final *R*₁. Difference Fourier mapping failed to locate possible H atom sites.

For the cuprocherokeeite structure, all cation sites were successfully refined with anisotropic displacement parameters; however, many of the O sites

¹ Supplementary Data are available from the Depository of Unpublished Data on the MAC website (<http://mineralogicalassociation.ca/>), document “Cherokeeite and cuprocherokeeite, CM61, 23-00001”.

TABLE 2. DATA COLLECTION AND STRUCTURE REFINEMENT DETAILS FOR CHEROKEEITE AND CUPROCHEROKEEITE

Mineral	cherokeeite	cuprocherokeeite
Diffractionmeter	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 ₂ Zn(OH) ₄](SO ₄)·H ₂ O	[Pb ₈ Zn ₃ Cu ²⁺ (OH) ₁₆](SO ₄) ₄ ·4H ₂ O
Space group	<i>P</i> 2 ₁ / <i>n</i> (#14)	<i>P</i> 2 ₁ / <i>n</i> (#14)
Unit cell dimensions	<i>a</i> = 17.1697(7) Å <i>b</i> = 6.47173(19) Å <i>c</i> = 17.5304(12) Å β = 115.440(8)° 1759.06(19) Å ³	<i>a</i> = 12.6828(5) Å <i>b</i> = 9.4629(5) Å <i>c</i> = 14.7876(8) Å β = 94.798(4)° 1768.53(15) Å ³
<i>V</i>	8	2
<i>Z</i>	8	2
Density (calc.)	4.998 g/cm	4.945 g/cm
Absorption coefficient	41.153 mm ⁻¹	40.855 mm ⁻¹
F(000)	2304	2278
Crystal size	120 × 100 × 60 μm	110 × 20 × 20 μm
θ range	3.40 to 25.03°	2.03 to 20.02°
Index ranges	-20 ≤ <i>h</i> ≤ 20 -6 ≤ <i>k</i> ≤ 7 -20 ≤ <i>l</i> ≤ 20	0 ≤ <i>h</i> ≤ 12 0 ≤ <i>k</i> ≤ 9 -14 ≤ <i>l</i> ≤ 14
Refl. collected	12455	26053
Independent reflections	3091; <i>R</i> _{int} = 0.088	3226
Refl. with <i>I</i> > 2σ/ <i>I</i>	2681	2411
Completeness to $\theta_{\max}$	99.5%	98.3%
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Parameters/restraints	236/4	150/10
Goodness-of-fit	1.098	1.153
Final <i>R</i> indices	<i>R</i> ₁ = 0.0425	<i>R</i> ₁ = 0.0746
[<i>I</i> > 2σ/ <i>I</i>]	<i>wR</i> ₂ = 0.1068	<i>wR</i> ₂ = 0.1966
<i>R</i> indices	<i>R</i> ₁ = 0.0495	<i>R</i> ₁ = 0.1022
(all data)	<i>wR</i> ₂ = 0.1107	<i>wR</i> ₂ = 0.2072
Extinction coefficient	0.00013(4)	0.00025(16)
Largest diff. peak/hole	+4.90/-2.98 e Å ⁻³	+2.70/-2.89 e Å ⁻³

$R_{\text{int}} = \Sigma |F_o^2 - F_o^2(\text{mean})| / \Sigma [F_o^2]$. GoF = $S = \{\Sigma [w(F_o^2 - F_c^2)] / (n-p)\}^{1/2}$. $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. $wR_2 = \{\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]\}^{1/2}$; $w = 1/(\sigma^2(F_o^2) + (aP)^2 + bP)$ where P is $[2F_c^2 + \text{Max}(F_o^2, 0)]/3$; for cherokeeite, *a* is 0.0514 and *b* is 23.35 and for cuprocherokeeite, *a* is 0.1127 and *b* is 37.9627.

became non-positive definite when refined anisotropically. Ultimately, it was decided to refine all of the O sites on an isotropic basis. Other problems encountered were anomalously short S–O distances ($\langle \text{S1–O} \rangle = 1.40$ Å, $\langle \text{S2–O} \rangle = 1.43$ Å) and anomalously long equatorial Cu–O distances ($\langle \text{Cu–O}_{\text{eq}} \rangle = 2.05$ Å). To compensate for these, bond length restraints of 1.47(2) Å for the S–O bonds and 1.97(2) Å for the Cu–O_{eq} bonds were applied. The application of these restraints resulted in a very small increase in the final *R*₁ from 0.0741 to 0.0746. Difference Fourier mapping failed to locate possible H atom sites.

Data collection and refinement details are given in Table 2, atom coordinates and displacement parameters in Tables 3 and 4, selected bond distances in Tables 5 and 6, and bond-valence analyses in Tables 7 and 8. CIF files for both structures have been deposited and are available from the Depository of Unpublished Data on the MAC website².

² Supplementary Data are available from the Depository of Unpublished Data on the MAC website (<http://mineralogicalassociation.ca/>), document “Cherokeeite and cuprocherokeeite, CM61, 23-00001”.

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

	x/a	y/b	z/c	U_{eq}		
Pb1	0.38558(3)	0.70026(8)	0.93592(3)	0.02297(19)		
Pb2	0.56051(3)	0.77873(8)	0.61112(4)	0.02151(18)		
Pb3	0.42432(4)	0.70696(8)	0.74237(4)	0.02660(19)		
Pb4	0.73476(4)	0.30026(9)	0.91615(4)	0.02841(19)		
Zn1	0.74598(9)	0.0445(2)	0.74927(9)	0.0186(4)		
Zn2	0.25102(9)	0.9575(2)	0.75148(9)	0.0202(4)		
S1	0.4568(2)	0.2383(5)	0.6232(2)	0.0234(8)		
S2	0.1251(2)	0.7366(6)	0.4592(2)	0.0264(8)		
O1	0.5093(8)	0.4118(19)	0.6692(8)	0.058(4)		
O2	0.4812(10)	0.179(2)	0.5564(10)	0.068(4)		
O3	0.3665(8)	0.2998(19)	0.5876(11)	0.061(4)		
O4	0.4761(9)	0.0651(18)	0.6827(7)	0.053(3)		
O5	0.0990(11)	0.796(3)	0.3743(11)	0.091(6)		
O6	0.1506(13)	0.525(2)	0.4734(15)	0.125(8)		
O7	0.1981(8)	0.8649(18)	0.5097(9)	0.052(3)		
O8	0.0565(9)	0.777(3)	0.4851(10)	0.078(5)		
OH1	0.6830(6)	0.2994(12)	0.7723(6)	0.018(2)		
OH2	0.8314(6)	0.2868(14)	0.7499(7)	0.025(2)		
OH3	0.8203(6)	0.0684(14)	0.8837(6)	0.021(2)		
OH4	0.6709(6)	0.0099(14)	0.6147(6)	0.025(2)		
OH5	0.2747(6)	0.7077(13)	0.6858(6)	0.022(2)		
OH6	0.2552(6)	0.2063(13)	0.6733(6)	0.023(2)		
OH7	0.3856(5)	0.9223(13)	0.8278(6)	0.020(2)		
OH8	0.1154(6)	0.9882(13)	0.6741(6)	0.0200(19)		
OW1	0.3543(7)	0.7022(15)	0.5251(7)	0.033(3)		
OW2	0.5221(8)	0.2139(17)	0.8469(8)	0.045(3)		
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pb1	0.0218(3)	0.0267(3)	0.0191(3)	0.0006(2)	0.0075(3)	0.0011(2)
Pb2	0.0156(3)	0.0241(3)	0.0219(3)	−0.0006(2)	0.0052(2)	0.00002(19)
Pb3	0.0250(3)	0.0283(3)	0.0340(4)	−0.0005(2)	0.0199(3)	−0.0004(2)
Pb4	0.0317(4)	0.0341(4)	0.0256(4)	−0.0031(2)	0.0182(3)	−0.0025(2)
Zn1	0.0188(8)	0.0165(8)	0.0183(9)	−0.0017(6)	0.0059(7)	−0.0004(6)
Zn2	0.0197(8)	0.0178(8)	0.0221(9)	0.0029(6)	0.0079(7)	0.0032(6)
S1	0.0214(18)	0.0225(16)	0.025(2)	0.0011(14)	0.0083(16)	0.0028(14)
S2	0.0210(19)	0.0295(18)	0.026(2)	−0.0058(16)	0.0073(17)	−0.0040(15)
O1	0.044(7)	0.043(7)	0.057(9)	−0.008(6)	−0.006(6)	0.010(6)
O2	0.083(11)	0.082(11)	0.054(10)	0.012(8)	0.045(9)	0.023(8)
O3	0.027(7)	0.060(9)	0.094(12)	0.029(8)	0.024(7)	0.015(6)
O4	0.082(9)	0.039(7)	0.029(7)	0.015(5)	0.014(6)	0.014(7)
O5	0.076(12)	0.151(19)	0.050(11)	0.002(10)	0.029(9)	0.000(11)
O6	0.128(16)	0.021(8)	0.24(3)	0.033(11)	0.090(17)	0.021(9)
O7	0.033(6)	0.036(6)	0.085(10)	−0.024(7)	0.022(7)	−0.015(6)
O8	0.031(8)	0.143(15)	0.064(11)	−0.023(10)	0.024(8)	−0.012(8)
OH1	0.016(5)	0.018(5)	0.019(6)	−0.001(4)	0.006(4)	0.002(3)
OH2	0.018(5)	0.032(6)	0.021(6)	−0.003(4)	0.006(4)	0.001(4)
OH3	0.022(5)	0.021(5)	0.018(5)	−0.001(4)	0.006(4)	−0.005(4)
OH4	0.018(5)	0.025(5)	0.026(6)	−0.001(4)	0.005(4)	−0.003(4)
OH5	0.031(6)	0.023(5)	0.014(5)	0.001(4)	0.013(5)	0.002(4)
OH6	0.020(5)	0.023(5)	0.024(6)	−0.005(4)	0.008(5)	−0.004(4)
OH7	0.014(4)	0.020(5)	0.023(5)	0.002(4)	0.004(4)	0.003(4)
OH8	0.025(5)	0.013(4)	0.023(5)	−0.002(4)	0.010(4)	−0.003(4)
OW1	0.023(6)	0.039(7)	0.034(7)	0.000(5)	0.008(5)	−0.001(4)
OW2	0.047(8)	0.045(7)	0.040(8)	0.004(5)	0.017(6)	0.008(6)

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

	x/a	y/b	z/c	U_{eq}		
Pb1	0.35511(18)	0.8125(3)	0.46251(17)	0.0287(9)		
Pb2	0.62187(19)	0.3774(3)	0.31479(17)	0.0320(9)		
Pb3	0.88586(19)	0.8354(2)	0.45616(17)	0.0287(9)		
Pb4	0.0962(2)	0.3200(3)	0.31316(18)	0.0334(9)		
Cu	0	0.5	0.5	0.022(3)		
Zn1	0.5	0.5	0.5	0.019(2)		
Zn2	0.7519(5)	0.5216(7)	0.5087(5)	0.0213(18)		
S1	0.8793(11)	0.0988(17)	0.6734(11)	0.030(4)		
S2	0.6221(12)	0.9268(16)	0.3342(11)	0.031(4)		
O1	0.955(4)	0.214(5)	0.679(4)	0.081(18)		
O2	0.922(3)	-0.006(4)	0.738(3)	0.051(13)		
O3	0.786(4)	0.169(7)	0.704(5)	0.13(3)		
O4	0.867(3)	0.047(5)	0.580(2)	0.050(13)		
O5	0.698(4)	0.815(5)	0.324(4)	0.073(16)		
O6	0.534(3)	0.872(6)	0.382(4)	0.083(18)		
O7	0.675(4)	1.051(4)	0.377(3)	0.065(15)		
O8	0.571(4)	0.966(6)	0.244(2)	0.069(16)		
OH1	-0.105(2)	0.479(4)	0.593(2)	0.022(9)		
OH2	0.120(2)	0.404(4)	0.572(2)	0.029(10)		
OH3	0.996(3)	0.254(4)	0.428(3)	0.036(11)		
OH4	0.635(3)	0.425(4)	0.584(2)	0.019(9)		
OH5	0.620(2)	0.566(3)	0.418(2)	0.012(8)		
OH6	0.477(3)	0.698(4)	0.568(3)	0.031(10)		
OH7	0.749(3)	0.327(4)	0.446(3)	0.031(10)		
OH8	0.780(3)	0.726(4)	0.559(3)	0.028(10)		
OW1	0.852(3)	0.116(5)	0.300(3)	0.039(11)		
OW2	0.865(3)	0.370(5)	0.837(3)	0.056(14)		
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pb1	0.0360(16)	0.0194(14)	0.0307(18)	0.0033(12)	0.0031(12)	0.0024(12)
Pb2	0.0416(16)	0.0327(17)	0.0223(17)	-0.0054(12)	0.0059(12)	-0.0032(12)
Pb3	0.0348(16)	0.0188(15)	0.0322(18)	0.0041(12)	0.0018(12)	0.0034(12)
Pb4	0.0393(16)	0.0365(16)	0.0242(17)	-0.0046(13)	0.0006(12)	-0.0022(13)
Cu	0.013(5)	0.027(6)	0.026(7)	0.000(5)	-0.001(4)	-0.001(5)
Zn1	0.019(5)	0.019(5)	0.021(6)	-0.003(5)	0.006(4)	0.000(4)
Zn2	0.017(4)	0.020(4)	0.026(5)	-0.002(3)	-0.001(3)	-0.005(3)
S1	0.027(9)	0.022(9)	0.043(12)	0.005(8)	0.018(8)	0.005(7)
S2	0.036(9)	0.023(10)	0.035(12)	0.012(8)	0.008(8)	0.005(7)

ATOMIC ARRANGEMENTS

In the structure of cherokeeite, each of two crystallographically unique sites assigned to Zn (Zn1 and Zn2) are octahedrally coordinated by six OH groups. The $\text{Zn}(\text{OH})_6$ octahedra link by sharing *trans* edges to form chains along [010]. The octahedra in one chain are centered by Zn1 atoms, and those in an essentially identical chain are centered by Zn2 atoms. In the structure of cuprocherokeeite, two Zn sites (Zn1 and Zn2) and one Cu site are each octahedrally coordinated by six OH groups. The octahedra link by

sharing *trans* edges to form straight chains along [100]. The $\text{Cu}(\text{OH})_6$ octahedron exhibits strong Jahn-Teller distortion (Table 6). There are four distinct sites assigned to Pb in both structures (Pb1, Pb2, Pb3, and Pb4), all of which exhibit markedly off-center coordinations typical of Pb^{2+} with stereoactive $6s^2$ lone-pair electrons. The Pb atoms each form three very short (strong) bonds to OH sites of the $\text{Zn}(\text{OH})_6$ and $\text{Cu}(\text{OH})_6$ octahedra. The Pb atoms decorate the edge-sharing octahedral chains and form additional strong linkages, resulting in a chain of formula $[\text{Pb}_2\text{Zn}(\text{OH})_4]^{2+}$ (or $[\text{Pb}_8\text{Zn}_4(\text{OH})_{16}]^{8+}$) in cherokeeite

TABLE 5. SELECTED BOND LENGTHS (IN Å) FOR CHEROKEEITE

Pb1–OH6	2.353(10)	Pb2–OH2	2.344(10)	Zn1–OH1	2.105(8)	Zn2–OH5	2.109(9)
Pb1–OH8	2.361(9)	Pb2–OH4	2.395(9)	Zn1–OH1	2.132(8)	Zn2–OH5	2.123(9)
Pb1–OH7	2.379(9)	Pb2–OH3	2.427(8)	Zn1–OH2	2.137(9)	Zn2–OH6	2.125(9)
Pb1–O8	2.676(11)	Pb2–O2	2.723(15)	Zn1–OH2	2.145(10)	Zn2–OH7	2.128(9)
Pb1–O6	2.843(16)	Pb2–O1	2.865(14)	Zn1–OH3	2.149(9)	Zn2–OH6	2.137(10)
Pb1–O7	2.973(12)	Pb2–O2	2.890(14)	Zn1–OH4	2.160(10)	Zn2–OH8	2.142(9)
Pb1–O8	3.036(17)	Pb2–O4	2.943(13)	<Zn1–O>	2.138	<Zn2–O>	2.127
Pb1–OW2	3.483(13)	Pb2–OW1	3.236(11)				
<Pb1–O _{sh} >	2.364	<Pb2–O _{sh} >	2.389	S1–O1	1.449(13)	<i>Hydrogen bonds</i>	
<Pb1–O _{lg} >	3.002	<Pb2–O _{lg} >	2.931	S1–O2	1.453(14)	OH1...O1	2.839(15)
				S1–O3	1.455(12)	OH2...O5	2.921(18)
Pb3–OH5	2.322(10)	Pb4–OH1	2.285(9)	S1–O4	1.470(11)	OH3...OW1	2.882(14)
Pb3–OH8	2.341(8)	Pb4–OH3	2.335(9)	<S1–O>	1.457	OH4...OW1	2.957(15)
Pb3–OH7	2.343(9)	Pb4–OH4	2.348(9)			OH5...O7	2.962(17)
Pb3–O4	2.837(12)	Pb4–O6	2.936(16)	S2–O5	1.455(9)	OH6...O3	2.956(17)
Pb3–O5	2.870(16)	Pb4–O7	2.939(13)	S2–O6	1.456(8)	OH7...OW2	2.915(15)
Pb3–O1	3.006(13)	Pb4–O3	2.954(16)	S2–O7	1.459(8)	OH8...OW2	2.848(14)
Pb3–OW1	3.468(11)	Pb4–O5	3.360(19)	S2–O8	1.464(8)	OW1...O3	2.797(16)
Pb3–O3	3.603(16)	Pb4–OW2	3.362(13)	<S2–O>	1.459	OW1...O7	2.781(15)
Pb3–OW2	3.702(12)	<Pb4–O _{sh} >	2.323			OW2...O4	2.811(18)
Pb3–OW2	3.783(12)	<Pb4–O _{lg} >	3.110			OW2...O6	2.82(2)
<Pb3–O _{sh} >	2.335						
<Pb3–O _{lg} >	3.324						

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

Pb1–OH4	2.36(3)	Pb3–OH2	2.31(4)	Cu–OH1(×2)	1.99(2)	S1–O1	1.45(3)
Pb1–OH6	2.37(4)	Pb3–OH3	2.34(4)	Cu–OH2(×2)	2.00(2)	S1–O2	1.45(3)
Pb1–OH7	2.37(4)	Pb3–OH8	2.36(4)	Cu–OH3(×2)	2.55(4)	S1–O3	1.47(3)
Pb1–O6	2.71(5)	Pb3–O4	2.74(3)	<Cu–O _{eq} >	2.00	S1–O4	1.47(3)
Pb1–O7	2.76(5)	Pb3–O5	2.96(5)	<Cu–O _{ap} >	2.55	<S1–O>	1.46
Pb1–O3	2.93(8)	Pb3–O1	3.00(6)				
Pb1–O4	3.13(4)	Pb3–O4	3.41(4)	Zn1–OH5(×2)	2.12(3)	S2–O5	1.45(3)
Pb1–OW2	3.54(5)	Pb3–O7	3.48(5)	Zn1–OH4(×2)	2.15(3)	S2–O6	1.47(3)
<Pb1–O _{sh} >	2.37	Pb3–OW1	3.52(4)	Zn1–OH6(×2)	2.16(4)	S2–O7	1.47(3)
<Pb1–O _{lg} >	3.01	Pb3–O _{sh} >	2.34	<Zn1–O>	2.16	S2–O8	1.47(3)
		Pb3–O _{lg} >	3.19			<S2–O>	1.46
Pb2–OH6	2.33(4)			Zn2–OH7	2.06(4)		
Pb2–OH5	2.35(3)	Pb4–OH3	2.30(4)	Zn2–OH8	2.09(4)	<i>Hydrogen bonds*</i>	
Pb2–OH7	2.47(4)	Pb4–OH1	2.36(4)	Zn2–OH5	2.09(3)	OH1...O1	2.89(5)
Pb2–OW1	2.86(4)	Pb4–OH8	2.39(4)	Zn2–OH4	2.13(3)	OH2...O8	2.94(5)
Pb2–O1	2.93(6)	Pb4–O8	2.62(5)	Zn2–OH1	2.15(4)	OH4...O2	2.86(5)
Pb2–O2	2.95(4)	Pb4–O3	3.00(4)	Zn2–OH2	2.21(4)	OH5...O6	3.14(5)
Pb2–O5	3.24(5)	Pb4–O2	3.07(4)	<Zn2–O>	2.16	OH8...O4	3.25(5)
Pb2–O7	3.28(5)	Pb4–O6	3.24(6)			OW1...O5	2.67(5)
<Pb2–O _{sh} >	2.38	<Pb4–O _{sh} >	2.35			OW1...O7	2.66(5)
<Pb2–O _{lg} >	3.05	<Pb4–O _{lg} >	2.98			OW2...O3	2.85(5)

* Only hydrogen bonds received by O1 through O8 are listed.

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

	Pb1	Pb2	Pb3	Pb4	Zn1	Zn2	S1	S2	Hydrogen bonds		sum
									donated	accepted	
O1		0.15	0.11				1.63			0.17	2.06
O2		0.21					1.61				1.96
		0.14									
O3			0.03	0.12			1.60			0.14	2.09
O4		0.13	0.16				1.54			0.18	2.00
O5			0.15	0.05				1.60		0.15	1.95
O6	0.16			0.13				1.60		0.18	2.07
O7	0.12			0.13				1.59		0.14	2.18
O8	0.23							1.57			1.90
	0.10										
OH1				0.56	0.33				−0.17		1.03
					0.31						
OH2		0.49			0.31				−0.15		0.95
					0.30						
OH3		0.41		0.50	0.30				−0.16		1.05
OH4		0.44		0.49	0.29				−0.14		1.08
OH5			0.52			0.33			−0.14		1.03
						0.32					
OH6	0.48					0.32			−0.14		0.97
						0.31					
OH7	0.46		0.49			0.31			−0.15		1.11
OH8	0.48		0.50			0.30			−0.17		1.11
OW1		0.07	0.04						−0.18	0.16	0.04
									−0.19	0.14	
OW2	0.04		0.02	0.05					−0.18	0.15	0.09
			0.02						−0.18	0.17	
sum	2.07	2.04	2.04	2.03	1.84	1.89	6.38	6.36			

Bond-valence parameters are from Gagné & Hawthorne (2015). Hydrogen bond contributions estimated from $O_D \dots O_A$ distances using Ferraris & Ivaldi (1988).

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

	Pb1	Pb2	Pb3	Pb4	Cu	Zn1	Zn2	S1	S2	H bonds	sum
O1		0.13	0.11					1.62		0.16	2.02
O2		0.13		0.10				1.62		0.16	2.01
O3	0.13							1.54		0.17	1.84
O4			0.20, 0.04	0.11				1.54		0.10	1.99
O5		0.07	0.12						1.62	0.24	2.05
O6	0.22			0.07					1.54	0.11	1.94
O7	0.19	0.06	0.04						1.54	0.25	2.08
O8				0.27					1.54	0.14	1.95
OH1				0.48	$0.43 \times 2 \downarrow$		0.30				1.21
OH2			0.53		$0.41 \times 2 \downarrow$		0.25				1.19
OH3			0.50	0.55	$0.09 \times 2 \downarrow$						1.14
OH4	0.48					$0.30 \times 2 \downarrow$	0.31				1.09
OH5		0.49				$0.32 \times 2 \downarrow$	0.35				1.16
OH6	0.47	0.51				$0.29 \times 2 \downarrow$					1.27
OH7	0.47	0.37					0.37				1.21
OH8			0.48	0.44			0.35				1.27
OW1		0.15	0.03								0.18
OW2	0.03										0.03
sum	2.09	1.91	2.05	2.02	1.86	1.92	1.93	6.32	6.24		

Bond-valence parameters are from Gagné & Hawthorne (2015). Hydrogen bond contributions estimated from $O_D \dots O_A$ distances using Ferraris & Ivaldi (1988). Only hydrogen bonds contributions received by O1 through O8 are included.

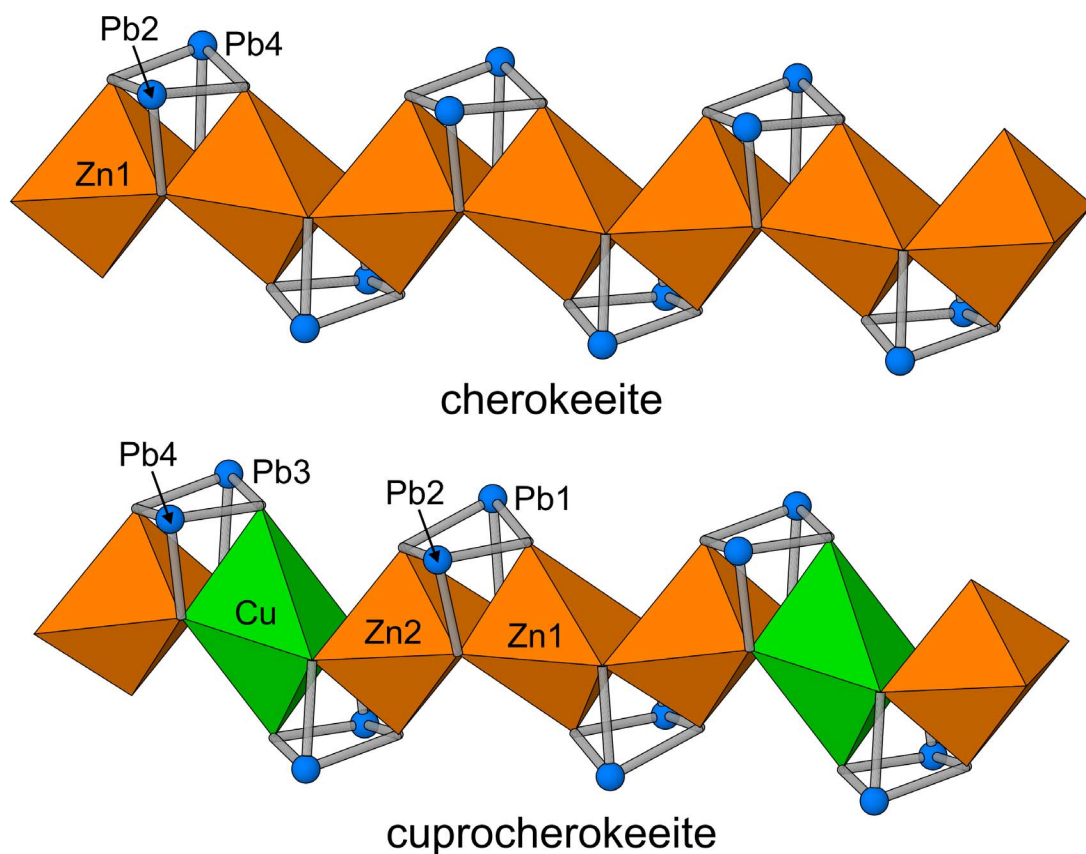


FIG. 6. $[\text{Pb}_2\text{Zn}(\text{OH})_4]^{2+}$ chain along **b** in the structure of cherokeeite compared with the $[\text{Pb}_8\text{Zn}_3\text{Cu}^{2+}(\text{OH})_{16}]^{8+}$ chain along **a** in the structure of cuprocherokeeite. Short (strong) Pb–OH bonds are shown as thick gray sticks.

and a chain of formula $[\text{Pb}_8\text{Zn}_3\text{Cu}^{2+}(\text{OH})_{16}]^{8+}$ in cuprocherokeeite (Fig. 6). The chains in cherokeeite and cuprocherokeeite are topologically identical.

Both structures also include two independent SO_4 groups, centered by S1 and S2, and two independent H_2O groups (OW1 and OW2). The vertices of the SO_4 groups and the O atoms of the H_2O groups participate in long (weak) bonds to the Pb sites. In the cherokeeite structure, each of OH groups of the $\text{Zn}(\text{OH})_6$ octahedra forms a hydrogen bond to either an O atom of a SO_4 group or an O atom of a H_2O group and the H_2O groups donate hydrogen bonds to O atoms of SO_4 groups. In the cuprocherokeeite structure, each O atom in the SO_4 groups receives one hydrogen bond from either an OH group or an H_2O group. The three-dimensional linkages in both structures are *via* these weak bonds between the chains, the SO_4^{2-} groups, and the H_2O groups.

Although cherokeeite and cuprocherokeeite are not isostructural, they share topologically identical

chain structural units and the linkages between the chains and the interstitial SO_4^{2-} and H_2O groups are very similar. Even the placements of the structural components are very similar (Figs. 7 and 8). The differences between the cuprocherokeeite and cherokeeite structures are clearly attributable to the replacement of one in four Zn^{2+} atoms by Cu^{2+} and the realignment of the more weakly bonded structural components induced by the Jahn-Teller distortion of the Cu^{2+} coordination. It is interesting to note that the two structures have the same space group, identical cell contents (except for Cu replacing one in every four Zn in cuprocherokeeite), and approximately the same cell volumes; nevertheless, the unit cells are very different geometrically (Figs. 7 and 8). In the chain direction (**b** in cherokeeite and **a** in cuprocherokeeite), the cuprocherokeeite cell is approximately double that of cherokeeite ($a_{\text{chkr}} = 2 \times b_{\text{chkr}}$), whereas in the projection along the chains (Fig. 8), the cherokeeite cell is approximately twice the area of

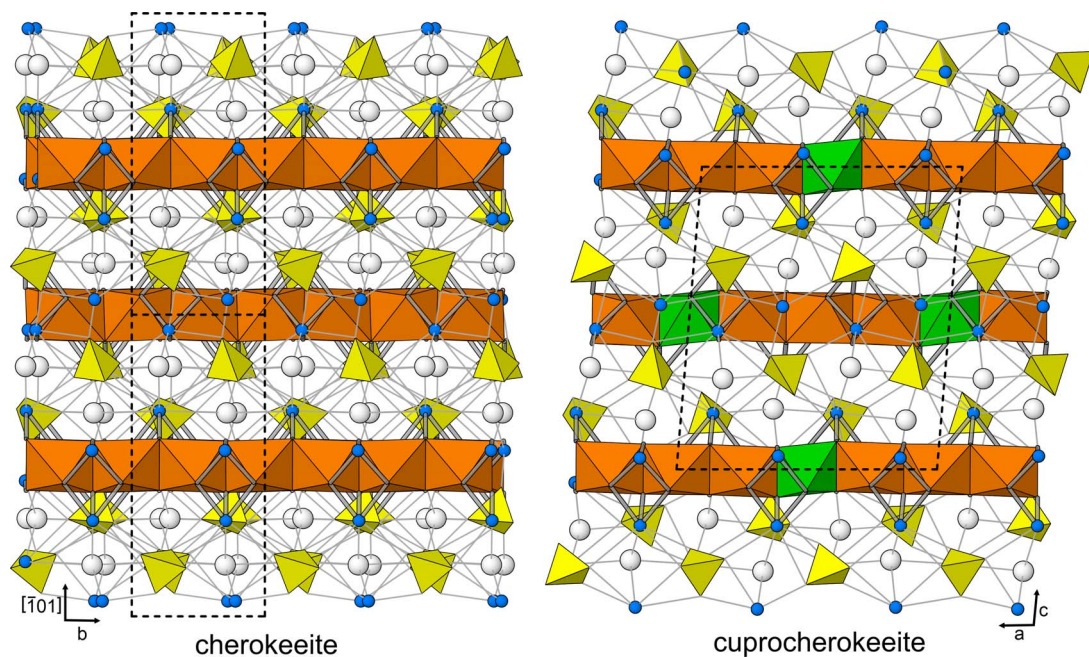


FIG. 7. The structures of cherokeite and cuprocherokeite viewed with chain directions horizontal. SO_4 tetrahedra are yellow; H_2O groups are white balls. Long (weak) Pb–O bonds are shown as gray lines. The unit cell outline is shown by dashed black lines.

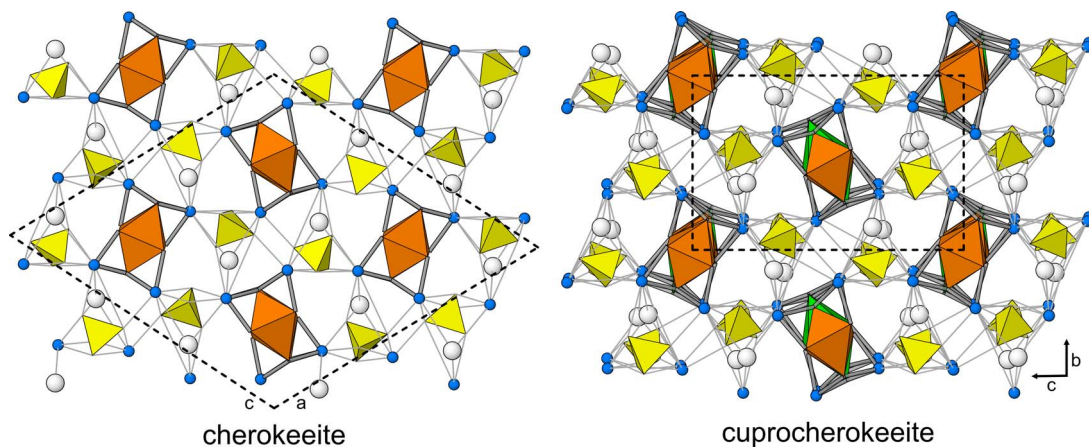


FIG. 8. The structures of cherokeite and cuprocherokeite viewed along the chain directions.

the cuprocherokeite cell ($a_{\text{chrk}} \times c_{\text{chrk}} \sin \beta = 2 \times b_{\text{cchk}} \times c_{\text{cchk}} \sin \beta$).

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