

Putnisite, $\text{SrCa}_4\text{Cr}_8^{3+}(\text{CO}_3)_8\text{SO}_4(\text{OH})_{16}\cdot 25\text{H}_2\text{O}$, a new mineral from Western Australia: description and crystal structure

Dedicated to the memory of Dr Ernest H. Nickel, who died in July 2009

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ABSTRACT

Putnisite, $\text{SrCa}_4\text{Cr}_8^{3+}(\text{CO}_3)_8\text{SO}_4(\text{OH})_{16}\cdot 25\text{H}_2\text{O}$, is a new mineral from the Polar Bear peninsula, Southern Lake Cowan, Western Australia, Australia. The mineral forms isolated pseudocubic crystals up to 0.5 mm in size in a matrix composed of quartz and a near amorphous Cr silicate. Putnisite is translucent, with a pink streak and vitreous lustre. It is brittle and shows one excellent and two good cleavages parallel to {100}, {010} and {001}. The fracture is uneven and the Mohs hardness $1\frac{1}{2}$ –2. The measured density is 2.20(3) g/cm³ and the calculated density based on the empirical formula is 2.23 g/cm³. Optically, putnisite is biaxial negative, with $\alpha = 1.552(3)$, $\beta = 1.583(3)$ and $\gamma = 1.599(3)$ (measured in white light). The optical orientation is uncertain and pleochroism is distinct: X pale bluish grey, Y pale purple, Z pale purple. Putnisite is orthorhombic, space group *Pnma*, with $a = 15.351(3)$, $b = 20.421(4)$ Å, $c = 18.270(4)$ Å, $V = 5727(2)$ Å³ (single-crystal data), and $Z = 4$. The strongest five lines in the X-ray powder diffraction pattern are [$d(\text{Å})/I(hkl)$]: 13.577 (100) (011), 7.659 (80) (200), 6.667 (43) (211), 5.084 (19) (222, 230), 3.689 (16) (411). Electron microprobe analysis (EMPA) gave (wt.%): Na₂O 0.17, MgO 0.08, CaO 10.81, SrO 5.72, BaO 0.12, CuO 0.29, Cr₂O₃ 31.13, SO₃ 3.95, SiO₂ 0.08, Cl[−] 0.28, CO_{2calc} 17.94, H₂O_{calc} 30.30, O=Cl −0.06, total 100.81. The empirical formula, based on O + Cl = 69, is: $\text{Cr}_{8.02}^{3+}\text{Ca}_{3.78}\text{Sr}_{1.08}\text{Na}_{0.11}\text{Cu}_{0.07}^{2+}\text{Mg}_{0.04}\text{Ba}_{0.02}[(\text{SO}_4)_{0.96}(\text{SiO}_4)_{0.03}]_{0.99}(\text{CO}_3)_{7.98}(\text{OH})_{16.19}\text{Cl}_{0.15}\cdot 24.84\text{H}_2\text{O}$. The crystal structure was determined from single-crystal X-ray diffraction data (MoK α , CCD area detector and refined to $R1 = 5.84\%$ for 3181 reflections with $F_0 > 4\sigma F$. Cr(OH)₄O₂ octahedra link by edge-sharing to form an eight-membered ring. A 10-coordinated Sr²⁺ cation lies at the centre of each ring. The rings are decorated by CO₃ triangles, each of which links by corner-sharing to two Cr(OH)₄O₂ octahedra. Rings are linked by Ca(H₂O)₄O₄ polyhedra to form a sheet parallel to (100). Adjacent sheets are joined along [100] by corner-sharing SO₄ tetrahedra. H₂O molecules occupy channels that run along [100] and interstices between slabs. Moderate to weak hydrogen bonding provides additional linkage between slabs.

KEYWORDS: putnisite, new mineral species, crystal structure, strontium calcium chromium sulfate carbonate, Polar Bear peninsula, Western Australia.

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Introduction

IN mid 2007, specimens of an unidentified mineral forming purple pseudocubic crystals collected by Perth mineral collector David Vaughn, were given to the late Ernie Nickel, who was for 14 years chief research scientist at the CSIRO Division of Mineralogy in Perth, Western Australia. Preliminary analysis using powder X-ray diffraction (XRD) and energy-dispersive X-ray spectrometry (EDS) showed it to be a probable new species and the specimens were forwarded to one of the authors (P.E.) for characterization. The new mineral has been named putnisite in honour of Australian mineralogists Christine and Andrew Putnis of the Institut für Mineralogie, Universität Münster, Germany, in recognition of their outstanding contributions to mineralogy. Cotype material is preserved in the collections of South Australian Museum, Adelaide, South Australia, (registration number G33429) and the Canadian Museum of Nature, Ottawa, Canada (catalogue number CMNMC 86133).

Occurrence

Specimens containing the mineral were collected from the Halls Knoll gossan, Polar Bear peninsula, Southern Lake Cowan, 40 km north of Norseman, Western Australia, Australia. The area is located within the southern section of the Norseman-Wiluna Greenstone Belt of the Yilgarn Craton, Western Australia, which is composed of volcanic and sedimentary rocks that were deposited around 2.7 Ga (Swager *et al.*, 1992). Extensive folding was followed by metamorphism to middle amphibolite facies, extensive intrusion by granitoids and major faulting along northerly to north-northwesterly trends. Ultramafic rocks to the north host the world-class nickel sulfide deposits at Kambalda and Widgiemooltha (Marston *et al.*, 1981; McQueen, 1981). The local stratigraphy comprises strongly-sheared and altered mafic rocks with gossanous quartz stringers, which are largely obscured by overlying granite and the sediments of Lake Cowan. The Halls Knoll gossan has formed by the oxidation of massive nickel sulfides and the gossan contains extremely high levels of Ni, Cu and platinum group metals. Putnisite formed during the oxidation of the sulfide-bearing komatiite/diorite rocks.

Appearance, physical and optical properties

Putnisite occurs as isolated pseudocubic crystals up to 0.5 mm in size (Fig. 1) in a matrix composed of quartz and masses of a near-amorphous dark green mineral, which chemical analysis shows is a Cr silicate with minor amounts of Ca, Mg, Na, Ni, S and Cl. Putnisite is translucent and the colour ranges from pale to dark purple, with a pink streak. Crystals are brittle, have an uneven fracture, and one excellent and two good cleavages parallel to {100}, {010} and {001}. The lustre is vitreous and the Mohs hardness is 1½–2. The density, measured by suspension in a mixture of Clerici solution and water, is 2.20(3) g/cm³ and the calculated density is 2.23 g/cm³ based on the chemical formula from the chemical analysis. Optically, putnisite is biaxial negative, with $\alpha = 1.552(3)$, $\beta = 1.583(3)$ and $\gamma = 1.599(3)$ (measured in white light). The optical orientation is uncertain and pleochroism is distinct: X pale bluish grey, Y pale purple, Z pale purple. The Gladstone-Dale compatibility index (Mandarino, 1981) is 0.038, categorized as excellent.

Chemical and spectroscopic data

Putnisite was analysed using a Cameca SX51 electron microprobe, using an operating voltage of 15 kV, a beam current of 10 nA, and a beam diameter of 20 µm. Analytical difficulties due to

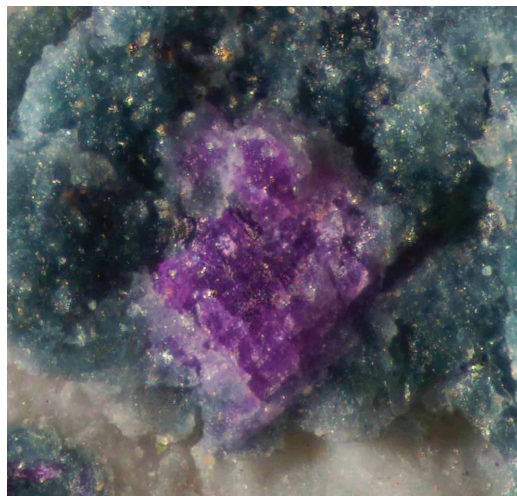


FIG. 1. A crystal of putnisite, 0.25 mm across, in a matrix composed of a green, near-amorphous Cr silicate mineral and quartz.

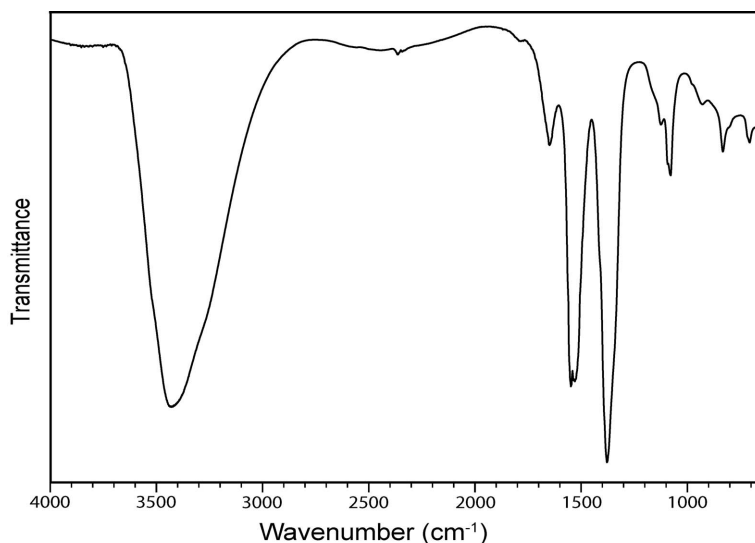


FIG. 2. Fourier transform-infrared spectrum of powdered putnisite.

the instability of the crystals were overcome by defocusing the electron beam and moving it slowly during the analysis. Data were reduced using the $\phi(\rho Z)$ method of Pouchou and Pichoir (1985). Elements present in minor amounts (<0.05 wt.% oxide) are Al and K. As only a small amount of material was available, a direct water and carbonate determination was not carried out, but the presence of H_2O and CO_2 was confirmed by the crystal-structure solution and infrared spectroscopy (Fig. 2). The results of 13 analyses are given in Table 2. The empirical formula, based on $\text{O} + \text{Cl} = 69$, with the OH content derived from charge balance is: $\text{Cr}_{8.02}\text{Ca}_{3.78}\text{Sr}_{1.08}\text{Na}_{0.11}\text{Cu}_{0.07}^{2+}\text{Mg}_{0.04}\text{Ba}_{0.02}[(\text{SO}_4)_{0.96}(\text{SiO}_4)_{0.03}]_{0.99}(\text{CO}_3)_{7.98}(\text{OH})_{16.19}\text{Cl}_{0.15} \cdot 24.84\text{H}_2\text{O}$ and the ideal simplified formula is $\text{SrCa}_4\text{Cr}_8^{3+}(\text{CO}_3)_8\text{SO}_4(\text{OH})_{16} \cdot 25\text{H}_2\text{O}$. The large total cations in the empirical formula, 13.12 as opposed to the ideal of 13.00, is attributed to the instability of putnisite under the electron beam.

An infrared-absorption spectrum of powdered putnisite (Fig. 2) shows bands due to OH-stretching vibrations (broad band ~ 3680 to ~ 2280 cm^{-1} , centred on 3420 cm^{-1}), H—O—H bending of H_2O groups (at 1645 cm^{-1}), ν_3 vibration of CO_3^{2-} groups (1375 cm^{-1} and a split band at 1544 and 1525 cm^{-1}), overlapping bands of the ν_3 vibration of the SO_4 tetrahedra and ν_3 vibration of CO_3^{2-} groups (at 1122 and 1076 cm^{-1}), ν_1 vibration of the SO_4 tetrahedra (at 922 cm^{-1}), ν_2 vibration of CO_3^{2-} groups (at

830 cm^{-1}), ν_4 vibration of CO_3^{2-} groups (at 702 cm^{-1}).

TABLE 1. X-ray powder diffraction data for putnisite.

I_{obs}	d_{obs}	I_{calc}	d_{calc}	h	k	l
100	13.58	100	13.583	0	1	1*
80	7.66	73	7.663	2	0	0*
10	7.09	6	7.063	2	0	1
43	6.67	38	6.674	2	1	1*
6	5.775	7	5.807	2	2	1
19	5.084	{ 9	5.083	2	2	2*
		{ 15	5.086	2	3	0*
13	4.901	13	4.899	2	3	1*
6	4.649	6	4.633	2	1	3
7	3.385	6	3.831	4	0	0
16	3.689	13	3.687	4	1	1*
7	3.594	{ 4	3.587	4	2	0
		{ 2	3.585	0	1	5
		{ 2	3.400	0	6	0
7	3.402	{ 2	3.396	0	4	4
		{ 3	3.386	0	5	3
6	2.824	3	2.817	4	2	4*
7	2.765	5	2.761	4	5	1
5	2.459	3	2.449	4	6	2
4	2.223	3	2.220	4	6	4
4	2.174	3	2.168	4	7	3
4	2.046	2	2.042	6	6	0
4	1.999	2	1.999	6	3	5
4	1.959	1	1.961	2	9	4

* lines used for unit-cell refinement

TABLE 2. Compositional data for putnisite.

Constituent	Wt. %	Range	Stand. Dev.	Probe standard
Na ₂ O	0.17	0.09–0.34	0.08	albite
MgO	0.08	0.00–0.16	0.05	almandine
CaO	10.81	19.48–12.63	0.99	hydroxylapatite
SrO	5.72	4.66–6.19	0.47	celestite
BaO	0.12	0.00–0.44	0.17	baryte
CuO	0.29	0.00–0.74	0.27	chalcopyrite
Cr ₂ O ₃	31.13	28.90–32.66	1.21	crocoite
CO ₂ *	17.94			
SO ₃	3.95	3.07–4.55	0.50	chalcopyrite
SiO ₂	0.08	0.01–0.20	0.05	almandine
Cl [−]	0.28	0.16–0.57	0.12	tugtupite
H ₂ O [†]	30.30			
O=Cl	−0.06			
Total	100.81			

Number of analyses = 11.

* CO₂ calculated from structure solution.

† H₂O calculated from structure solution.

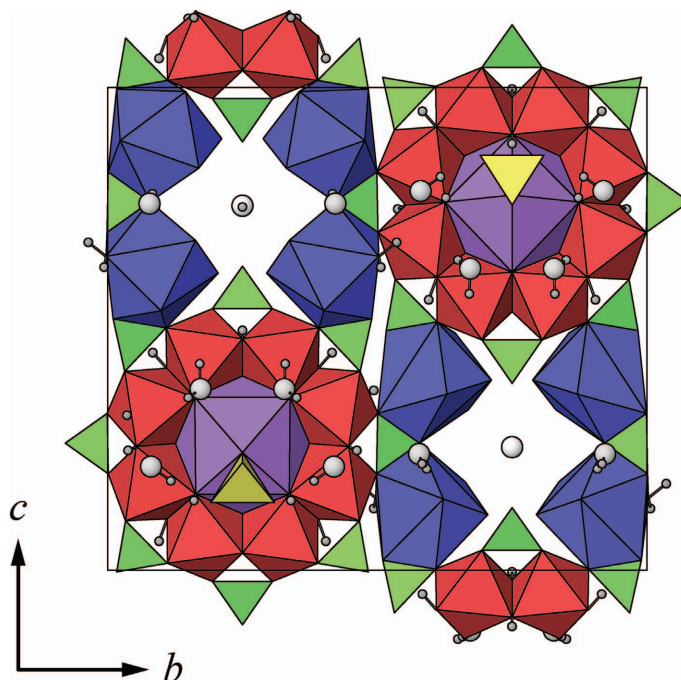


FIG. 3. The crystal structure of putnisite viewed along [100]. Sr₁₀ polyhedra are purple; Ca₈ polyhedra are blue; Cr₆ octahedra are red; CO₃ triangles are green; SO₄ tetrahedra are yellow; H₂O molecules are large grey spheres; hydrogen atoms are small grey spheres. The unit cell is outlined. All structure drawings were completed using *ATOMS* (Shape Software 1997).

X-ray powder diffraction data

X-ray powder diffraction data (Table 1) were collected using a Bruker AXS Discover 8 microdiffractometer using a Hi-Star 2-dimensional area detector operated with a GA DDS system. The measurement was made using $\text{CuK}\alpha$ (1.5418 Å) radiation at 40 kV and 40 mA with a sample to detector distance of 12 cm. The instrument was calibrated with a corundum standard using a refined statistical calibration (Rowe, 2009). The unit-cell parameters, refined using *CELREF* (Laugier and Bochu, 2003), are $a = 15.325(6)$, $b = 20.40(2)$, $c = 18.21(3)$ Å, $V = 5692(8)$ Å³, which are in excellent agreement with those obtained from the single-crystal study.

Structure determination

Single-crystal X-ray data collection

Data were collected at room temperature from a crystal fragment using an Oxford Diffraction Xcalibur E diffractometer equipped with an Eos CCD detector using $\text{MoK}\alpha$ X-radiation ($\lambda = 0.71073$ Å) and a detector distance of 46 mm. Data collection conditions are given in Table 3. The data were processed using the *CrysAlisPro* program (Oxford Diffraction, 2009) and corrected for Lorentz and polarization effects. An empirical absorption correction was applied using the SCALE3 ABSPACK algorithm, as implemented in *CrysAlisPro*.

TABLE 3. Crystal data, data collection and refinement details.

Crystal data

Space group	<i>Pnma</i>
a, b, c (Å)	15.351(3), 20.421(4), 18.270(4)
V (Å ³), Z	5727(2), 4
$F(000)$	3828
Absorption correction; multi-scan	$\mu = 2.925$ (mm ⁻¹), $T_{\min}$, $T_{\max} = 0.72, 1.00$
Crystal dimensions (mm)	$0.06 \times 0.04 \times 0.03$

Data collection

Diffractometer	Oxford Diffraction Xcalibur E
Temperature (K)	293
Radiation, wavelength (Å)	$\text{MoK}\alpha$, $\lambda = 0.71073$
θ range (°)	2.59 to 27.88
Detector distance (mm)	46
Rotation axes	ω
Rotation width (°)	1
Total no. of frames	321
Collection time per frame (s)	20
h, k, l ranges	$-19 \rightarrow 19, -26 \rightarrow 26, -23 \rightarrow 21$
Total reflections measured	34220
Data completeness (%)	97.7
Unique reflections	6850 ($R_{\text{int}} = 0.0983$)

Refinement

Refinement on	F^2
R_1^* for $F_o > 4\sigma F_o$	5.84%
$wR_2^\dagger$ for all F_o^2	14.81%
Reflections used $F_o > 4\sigma F_o$	3181
Number of parameters refined	499
Extinction factor	0.00018(11)
$\Delta\rho_{\min}$, $\Delta\rho_{\max}$ (e/Å ³)	1.421, -1.679
Goof	0.981

* $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$
 $\dagger wR_2 = \sum w(|F_o|^2 - |F_c|^2)^2 / \sum w|F_o|^2)^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.042 P)^2 + 12.60 P]$;
 $P = ([\max \text{ of } (0 \text{ or } F_o^2)] + 2F_c^2)/3$

TABLE 4. Fractional coordinates and displacement parameters ($\text{\AA}^2$) for atoms for putnisite.

	x	y	z	U_{eq}	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Sr	0.26100(7)	0.25	0.26070(5)	0.0177(4)	0.0220(7)	0.0160(5)	0.0150(6)	0	-0.0003(5)	0
Ca(1)	0.89408(11)	0.59583(8)	0.10255(8)	0.0211(6)	0.0244(10)	0.0217(9)	0.0172(10)	-0.0005(7)	-0.0006(7)	-0.0009(7)
Ca(2)	0.90849(11)	0.58505(8)	0.37485(8)	0.0213(6)	0.0222(10)	0.0252(10)	0.0164(9)	-0.0007(7)	-0.0015(7)	-0.0029(8)
Cr(1)	0.74757(8)	0.32260(6)	0.04790(6)	0.0163(5)	0.0201(8)	0.0145(7)	0.0143(8)	-0.0025(5)	0.0003(6)	0.0001(6)
Cr(2)	0.75157(8)	0.42178(6)	0.16020(6)	0.0138(4)	0.0158(8)	0.0131(7)	0.0124(7)	-0.0003(5)	-0.0003(5)	0.0010(6)
Cr(3)	0.76176(8)	0.42059(6)	0.32013(6)	0.0131(4)	0.0139(7)	0.0125(7)	0.0131(7)	-0.0019(5)	-0.0001(5)	-0.0010(5)
Cr(4)	0.76802(8)	0.32169(6)	0.43427(6)	0.0135(4)	0.0166(8)	0.0109(7)	0.0130(8)	0.0011(5)	-0.0010(5)	-0.0007(5)
S	0.5192(2)	0.25	0.31235(16)	0.0184(11)	0.0147(19)	0.0185(17)	0.022(2)	0	-0.0006(13)	0
C(1)	0.8378(8)	0.25	-0.0738(6)	0.024(3)	0.021(7)	0.022(7)	0.029(7)	0	0.000(6)	0
C(2)	0.6597(5)	0.4509(4)	0.0222(4)	0.0239(19)	0.021(5)	0.021(5)	0.030(5)	0.006(4)	0.004(4)	-0.003(4)
C(3)	0.8488(5)	0.5258(4)	0.2372(4)	0.0223(18)	0.014(4)	0.032(5)	0.021(4)	0.006(4)	0.004(4)	0.012(4)
C(4)	0.6787(5)	0.4469(4)	0.4622(4)	0.0238(19)	0.019(5)	0.028(5)	0.025(5)	-0.006(4)	-0.003(4)	-0.002(4)
C(5)	0.8611(7)	0.25	0.5549(6)	0.023(3)	0.014(6)	0.021(6)	0.033(7)	0	-0.005(5)	0
O(1)	0.5872(6)	0.25	0.2561(4)	0.038(2)	0.030(5)	0.041(5)	0.041(5)	0	0.008(4)	0
O(2)	0.4333(6)	0.25	0.2769(5)	0.046(2)	0.025(5)	0.042(6)	0.071(6)	0	-0.005(5)	0
O(3)	0.5291(4)	0.3093(3)	0.3598(3)	0.0492(19)	0.057(5)	0.050(5)	0.040(4)	-0.011(3)	-0.005(3)	0.007(4)
O(4)	0.8793(5)	0.25	-0.1295(4)	0.033(2)	0.034(5)	0.032(5)	0.034(5)	0	0.026(4)	0
O(5)	0.8155(4)	0.3056(3)	-0.0415(3)	0.0253(14)	0.035(4)	0.020(3)	0.021(3)	-0.002(2)	0.004(3)	0.002(3)
O(6)	0.6219(4)	0.4897(3)	-0.0205(2)	0.0266(14)	0.040(4)	0.026(3)	0.014(3)	0.002(2)	-0.005(3)	-0.003(3)
O(7)	0.6773(4)	0.4682(3)	0.0883(3)	0.0240(13)	0.029(4)	0.026(3)	0.017(3)	-0.006(2)	-0.004(2)	0.003(3)
O(8)	0.6778(4)	0.3917(3)	-0.0021(3)	0.0270(14)	0.025(3)	0.025(3)	0.031(3)	-0.010(3)	-0.003(3)	0.003(3)
O(9)	0.8931(4)	0.5785(2)	0.2369(3)	0.0265(13)	0.032(3)	0.022(3)	0.025(3)	0.002(2)	-0.001(3)	-0.015(3)
O(10)	0.8297(3)	0.4988(2)	0.3004(2)	0.0214(13)	0.031(3)	0.018(3)	0.015(3)	0.004(2)	0.000(2)	-0.004(3)
O(11)	0.8224(3)	0.5008(3)	0.1751(3)	0.0232(13)	0.026(3)	0.027(3)	0.017(3)	-0.011(2)	-0.008(2)	-0.005(3)
O(12)	0.6336(4)	0.4834(3)	0.5036(3)	0.0332(16)	0.054(4)	0.028(4)	0.017(3)	-0.006(2)	0.015(3)	0.013(3)
O(13)	0.6977(4)	0.4668(2)	0.3977(3)	0.0226(13)	0.036(4)	0.020(3)	0.012(3)	0.000(2)	-0.001(2)	0.007(3)
O(14)	0.6996(4)	0.3891(3)	0.4855(3)	0.0247(13)	0.026(3)	0.017(3)	0.031(3)	0.003(2)	0.000(3)	-0.002(3)
O(15)	0.8985(6)	0.25	0.6131(4)	0.038(2)	0.056(6)	0.027(5)	0.030(5)	0	-0.030(5)	0
O(16)	0.8388(4)	0.3056(3)	0.5230(3)	0.0249(14)	0.033(4)	0.024(3)	0.018(3)	0.002(2)	-0.005(3)	-0.001(3)
OH(17)	0.8284(4)	0.3904(3)	0.0817(3)	0.0231(13)	0.027(3)	0.020(3)	0.023(3)	0.002(2)	0.000(2)	-0.002(3)
OH(18)	0.6897(3)	0.3384(3)	0.1419(3)	0.0199(13)	0.022(3)	0.024(3)	0.014(3)	-0.003(2)	0.003(2)	-0.005(3)
OH(19)	0.8104(5)	0.25	0.0977(4)	0.0214(18)	0.013(4)	0.030(5)	0.022(4)	0	-0.010(3)	0
OH(20)	0.6659(5)	0.25	0.0204(4)	0.0224(18)	0.019(5)	0.021(4)	0.027(4)	0	-0.009(4)	0
OH(21)	0.6767(3)	0.4470(3)	0.2438(3)	0.0222(12)	0.021(3)	0.026(3)	0.020(3)	-0.004(2)	-0.003(2)	0.006(2)
OH(22)	0.8176(3)	0.3744(3)	0.2374(3)	0.0203(12)	0.013(3)	0.023(3)	0.026(3)	-0.002(2)	0.000(2)	0.003(2)
OH(23)	0.7049(3)	0.3368(2)	0.3428(3)	0.0176(12)	0.017(3)	0.016(3)	0.019(3)	0.001(2)	-0.002(2)	-0.003(2)
OH(24)	0.8470(3)	0.3897(2)	0.3936(3)	0.0221(13)	0.019(3)	0.019(3)	0.029(3)	0.002(2)	-0.001(2)	-0.001(2)

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OH(25)	0.6881(5)	0.25	0.4647(4)	0.0252(19)	0.032(5)	0.010(4)	0.034(5)	0	0.003(4)	0
OH(26)	0.8310(5)	0.25	0.3828(3)	0.0182(17)	0.022(4)	0.017(4)	0.016(4)	0	0.002(3)	0
H ₂ O(27)	1.0164(5)	0.5231(4)	0.1100(3)	0.064(2)	0.059(5)	0.092(6)	0.042(4)	0.024(4)	0.012(4)	0.041(5)
H ₂ O(28)	0.7474(6)	0.6292(7)	0.1353(4)	0.163(6)	0.111(8)	0.331(17)	0.048(5)	0.068(7)	0.028(5)	0.163(10)
H ₂ O(29)	0.9922(8)	0.6690(6)	0.1674(4)	0.184(7)	0.285(15)	0.229(13)	0.039(5)	-0.051(6)	0.050(7)	-0.236(12)
H ₂ O(30)	0.9950(5)	0.6446(5)	0.0086(4)	0.078(3)	0.041(5)	0.147(9)	0.046(4)	0.016(5)	0.000(4)	-0.020(5)
H ₂ O(31)	1.0020(8)	0.6632(5)	0.3171(4)	0.186(8)	0.319(17)	0.174(11)	0.064(6)	0.081(7)	-0.107(8)	-0.218(12)
H ₂ O(32)	0.7615(7)	0.6225(7)	0.3525(5)	0.187(7)	0.154(10)	0.332(17)	0.075(6)	-0.131(9)	-0.083(6)	0.201(11)
H ₂ O(33)	1.0104(4)	0.4971(4)	0.3501(3)	0.0467(19)	0.032(4)	0.061(5)	0.047(4)	-0.013(4)	0.000(3)	0.015(4)
H ₂ O(34)	1.0277(4)	0.5988(3)	0.4627(3)	0.0461(18)	0.053(5)	0.041(4)	0.044(4)	-0.009(3)	-0.018(3)	-0.010(3)
H ₂ O(35)	0.5137(5)	0.3277(5)	0.1247(5)	0.084(3)	0.037(5)	0.112(8)	0.103(6)	-0.011(6)	-0.008(5)	0.026(5)
H ₂ O(36)	0.4984(4)	0.4196(3)	0.2854(3)	0.0476(18)	0.049(5)	0.050(4)	0.044(4)	0.002(3)	0.008(3)	-0.001(4)
H ₂ O(37)	1.1438(6)	0.5776(4)	0.2407(6)	0.113(4)	0.053(6)	0.042(5)	0.243(13)	0.052(7)	0.056(7)	0.022(5)
H ₂ O(38)	0.7483(8)	0.75	0.2451(6)	0.088(4)	0.090(10)	0.112(11)	0.061(8)	0	0.004(8)	0
H ₂ O(39)*	0.8819(10)	0.7049(6)	0.3850(6)	0.053(6)	0.084(12)	0.045(9)	0.029(8)	0.005(6)	0.017(7)	0.017(8)
H ₂ O(40)*	0.8601(9)	0.7116(6)	0.1061(6)	0.040(5)	0.055(11)	0.037(9)	0.029(8)	-0.006(6)	-0.022(7)	-0.003(7)
H1	0.856(5)	0.416(4)	0.049(4)	0.043(7)						
H2	0.627(3)	0.342(4)	0.138(4)	0.043(7)						
H3	0.866(4)	0.25	0.117(6)	0.043(7)						
H4	0.607(4)	0.25	0.003(6)	0.043(7)						
H5	0.621(3)	0.462(4)	0.252(4)	0.043(7)						
H6	0.878(3)	0.373(4)	0.228(4)	0.043(7)						
H7	0.646(3)	0.340(4)	0.356(4)	0.043(7)						
H8	0.861(5)	0.402(4)	0.441(3)	0.043(7)						
H18	0.992(5)	0.654(4)	-0.046(3)	0.043(7)						
H23	0.968(4)	0.516(4)	0.380(4)	0.043(7)						
H24	1.065(3)	0.493(4)	0.372(4)	0.043(7)						
H27	0.508(5)	0.329(4)	0.072(2)	0.043(7)						
H28	0.466(4)	0.350(4)	0.142(4)	0.043(7)						
H29	0.495(6)	0.383(3)	0.315(4)	0.043(7)						
H31	1.091(3)	0.583(5)	0.220(4)	0.043(7)						
H32	1.188(4)	0.592(4)	0.210(4)	0.043(7)						
H34	0.807(3)	0.75	0.248(7)	0.043(7)						

The anisotropic displacement factors (U_{ij}) are defined as $\exp[-2\pi^2 \sum_{i,j=1}^3 \sum_{k=1}^3 U_{ij} a_i^* a_j^* h_i h_j]$
 * half occupied

TABLE 5. Selected interatomic distances (Å), angles (°) for putnisite.

Sr1	O2	2.661(9)	Ca1	OW27	2.398(7)	Ca2	OW31	2.392(8)
	OH22	2.685(5)		OW40	2.423(13)		OW32	2.417(8)
	OH22	2.685(5)		OW28	2.427(8)		OW33	2.424(7)
	O1	2.686(9)		OW29	2.430(8)		OW34	2.451(6)
	OH19	2.697(7)		O12	2.462(5)		OW34	2.451(6)
	OH23	2.731(5)		O9	2.481(5)		OW39	2.488(13)
	OH23	2.731(5)		OW30	2.518(7)		O6	2.489(5)
	OH18	2.762(5)		O14	2.595(5)		O11	2.533(5)
	OH18	2.762(5)		O10	<u>2.595(5)</u>		O9	2.534(5)
	OH26	<u>2.833(7)</u>		<Ca-O>	2.481		O8	<u>2.652(5)</u>
	<Sr-O>	2.723					<Ca-O>	2.483
Cr1	OH17	1.960(5)	Cr2	O10	1.964(5)	Cr3	OH23	1.955(5)
	OH18	1.960(5)		OH17	1.965(5)		O14	1.969(5)
	O5	1.969(5)		OH18	1.978(5)		O16	1.979(5)
	OH19	1.989(5)		OH21	1.980(5)		OH24	1.988(5)
	O8	1.994(6)		O7	1.981(5)		OH25	1.989(5)
	OH20	<u>2.006(5)</u>		OH22	<u>1.989(5)</u>		OH26	<u>1.991(5)</u>
	<Cr-O>	1.980		<Cr-O>	1.976		<Cr-O>	1.979
Cr3	O11	1.941(5)	Cr4	OH23	1.955(5)	S1	O4	1.201(12)
	OH23	1.965(5)		O14	1.969(5)		O5	<u>1.325(7) × 2</u>
	O13	1.967(5)		O16	1.979(5)		<C-O>	1.284
	OH22	1.977(5)		OH24	1.988(5)			
	OH24	1.979(5)		OH25	1.989(5)			
	OH21	<u>1.986(5)</u>		OH26	<u>1.991(5)</u>			
	<Cr-O>	1.969		<Cr-O>	1.979			
S1	O1	1.465(8)	C1	O9	1.273(9)	C2	O6	1.254(9)
	O2	1.469(9)		O10	1.308(9)		O7	1.287(9)
	O3 × 2	<u>1.497(6)</u>		O11	<u>1.313(8)</u>		O8	<u>1.317(9)</u>
	<S-O>	1.482		<C-O>	1.298		<C-O>	1.286
C2	O6	1.254(9)	C3	O9	1.273(9)	C4	O12	1.267(9)
	O7	1.287(9)		O10	1.308(9)		O13	1.280(9)
	O8	<u>1.317(9)</u>		O11	<u>1.313(8)</u>		O14	<u>1.296(9)</u>
	<C-O>	1.286		<C-O>	1.298		<C-O>	1.281
C4	O12	1.267(9)	C5	O15	1.208(12)	C5	O15	1.208(12)
	O13	1.280(9)		O16	<u>1.322(7) × 2</u>		O16	<u>1.322(7) × 2</u>
	O14	<u>1.296(9)</u>		<C-O>	1.284		<C-O>	1.284
	<C-O>	1.281						

Table 5 (*contd.*)

O1–S–O2	109.3(5)	O9–C3–O11	119.5(7)
O1–S–O3	109.5(3)	O9–C3–O10	118.5(7)
O2–S–O3	110.3(3)	O11–C3–O10	<u>122.0(7)</u>
O1–S–O3	109.5(3)	O<O–C–O>	120.0
O2–S–O3	110.3(3)		
O3–S–O3	<u>108.0(5)</u>	O12–C4–O13	119.2(8)
<O–S–O>	<u>109.5</u>	O12–C4–O14	118.3(7)
		O13–C4–O14	<u>122.4(7)</u>
O4–C1–O5	121.0(5)	O<O–C–O>	120.0
O4–C1–O5	121.0(5)		
O5–C1–O5	<u>118.1(10)</u>	O15–C5–O16	120.7(5)
<O–C–O>	<u>120.0</u>	O15–C5–O16	120.7(5)
		O16–C5–O16	<u>118.6(9)</u>
O6–C2–O7	120.5(8)	O<O–C–O>	120.0
O6–C2–O8	117.8(7)		
O7–C2–O8	<u>121.6(7)</u>		
<O–C–O>	<u>120.0</u>		

Structure solution and refinement

Scattering curves for neutral atoms were taken from the *International Tables for Crystallography* (Wilson, 1992). Systematic absences in the single-crystal XRD data are consistent with space group *Pnma*, and the structure was solved by direct methods using *SHELXS-97* (Sheldrick, 2008) and refined by full-matrix least-squares (*SHELXL-97*, Sheldrick, 2008). With all non-hydrogen atoms located and refined with anisotropic displacement parameters, the refinement converged to $R_1 = 6.04\%$ and $wR_2 = 17.41\%$ for 3181 reflections with $F_o > 4\sigma F$. Difference Fourier syntheses located the H atom sites associated with the OH sites and eight H atoms associated with the H₂O sites. The remaining H atoms associated with H₂O sites could not be located. The O (donor)–H distances were restrained to be close to 0.95(5) Å, and the H–H distances of H₂O groups were restrained to be close to 1.5(5) Å during refinement. In the final refinement, R_1 converged to 5.84% and wR_2 to 14.81%. The refined coordinates and displacement parameters of the atoms are listed in Table 4, selected interatomic distances and angles are given in Table 5, bond valences are given in Table 6 and suggested hydrogen bonds are listed in Table 7.

Structure description

Putnisite has a complex framework structure that is unique among minerals and synthetic compounds. A polyhedral representation of the

structure, viewed in projection along the *a* axis, is shown in Fig. 3. It consists of eight-membered rings of edge-sharing Cr(OH)₄O₂ octahedra, which are decorated by CO₃ triangles, each of which links by corner-sharing to two Cr(OH)₄O₂ octahedra. The Sr²⁺ cation lies at the centre of each ring and rings are linked in the *b* and *c* directions by Ca1 and Ca2 cations and by hydrogen bonds to form a sheet parallel to (100). Adjacent sheets are joined along [100] by corner-sharing SO₄ tetrahedra via the O1 and O2 anions (Fig. 4). H₂O molecules occupy channels that run along [100] and interstices between sheets.

The asymmetric unit contains one Sr, two Ca, four Cr, one S, five C, 38 O and 34 H sites, although not all of the H sites could be located. The Sr cation is [10]-coordinated by eight OH groups and two O atoms (Fig. 5). The observed mean Sr–O bond length of 2.723 Å is in accord with the calculated $\langle M-\phi \rangle$ distance of 2.710 Å (Shannon, 1976) for complete occupancy by Sr. The occupancy factor of 1.022(2) from site-occupancy refinement also supports the occupancy of the site by Sr, plus minor Ba. Each Ca site is coordinated by four O atoms, six fully occupied H₂O groups and one half-occupied H₂O group. The average bond lengths for the polyhedra are 2.484 and 2.490 Å for Ca1 and Ca2, respectively, and the site occupancy factors are 0.992(2) and 0.988(2), suggesting that the minor Na detected in the EMPA is located at these sites.

Each of the four Cr positions is coordinated by two O atoms and four OH groups in a distorted-

TABLE 6. Bond-valence* analysis for putnisite.

	Sr	Ca1	Ca2	Cr1	Cr2	Cr3	Cr4	S	C1	C2	C3	C4	C5	Sum
O1	0.22							1.54						1.76
O2	0.23							1.52						1.75
O3								1.41 $\times 2 \downarrow$						1.41
O4									1.67 $\times 2 \downarrow$					1.67
O5				0.52					1.19 $\times 2 \downarrow$					1.71
O6			0.24							1.44				1.68
O7					0.50					1.32				1.82
O8			0.16	0.48						1.22				1.86
O9		0.25	0.22								1.37			1.84
O10			0.22			0.56					1.25			2.03
O11		0.18			0.52						1.23			1.93
O12		0.26										1.39		1.65
O13						0.52						1.35		1.87
O14		0.19					0.52					1.29		1.99
O15													1.64 $\times 2 \downarrow$	1.64
O16													1.20 $\times 2 \downarrow$	1.70
OH17				0.53	0.52									1.05
OH18	0.18 $\times 2 \downarrow$			0.53	0.50									1.21
OH19	0.21			0.49										1.20
OH20				0.47 $\times 2 \rightarrow$										0.94
OH21					0.50	0.49								0.99
OH22	0.22 $\times 2 \downarrow$				0.49	0.50								1.21
OH23	0.19 $\times 2 \downarrow$					0.52	0.54							1.25
OH24						0.50	0.49							0.99
OH25							0.49 $\times 2 \rightarrow$							0.98
OH26	0.14						0.49 $\times 2 \rightarrow$							1.12
H ₂ O27		0.31												0.31
H ₂ O28		0.29												0.29
H ₂ O29		0.29												0.29
H ₂ O30		0.23												0.23
H ₂ O31			0.32											0.32
H ₂ O32			0.30											0.30
H ₂ O33			0.29											0.29
H ₂ O34			0.27											0.27
H ₂ O35														0.00

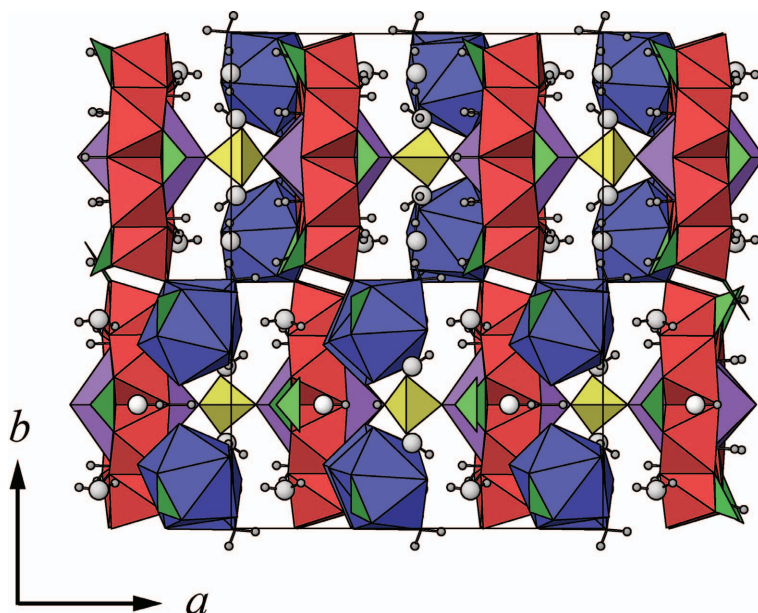


FIG. 4. The crystal structure of putnisite viewed along [001]. Legend as in Fig. 3. The unit cell is outlined.

octahedral arrangement with $\langle \text{Cr}-\text{O} \rangle$ distances of 1.980, 1.976, 1.970 and 1.975 Å for Cr1, Cr2, Cr3 and Cr4, respectively (Table 5). The bond-valence sums of 3.02–3.09 vu (Table 6) confirm that Cr is present in trivalent form. Site occupancy

factors for Cr1, Cr2, Cr3 and Cr4 are 0.992(2), 0.980(2), 0.985(2) and 0.992(2), respectively, suggesting minor occupancy by Mg and Cu. The CrO_6 octahedra are regular in geometry; the largest deviations are for the OH19–Cr1–OH20 and OH23–Cr3–OH21 angles which are 82.4(2) and 95.4(2)°, respectively. The S site is tetrahedrally coordinated by four O atoms with a mean distance of 1.482 Å, which is in accord with literature values (Baur, 1972; Hawthorne *et al.*, 2000). Bond-valence calculations (Table 6) are in accord with complete occupancy of the site by S. The SO_4 tetrahedron is quite regular; the largest deviations from ideal tetrahedral bond-angles are 110.2(4) and 108.2(6)°.

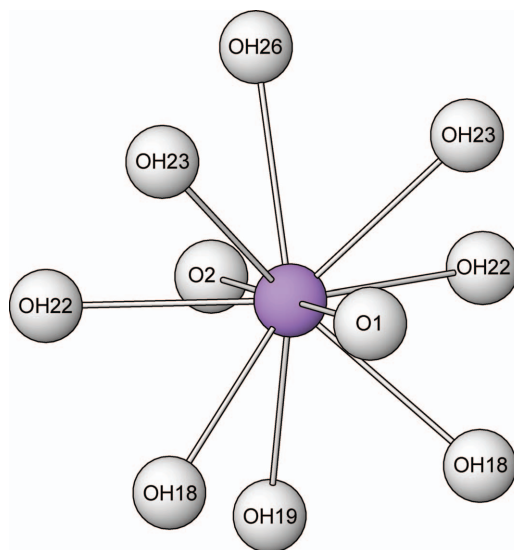


FIG. 5. Coordination of the Sr site in the structure of putnisite.

H₂O and OH groups and hydrogen bonding

The bond-valence analysis (Table 6) indicates that there are ten OH groups and eight H_2O groups in the putnisite structure. There are 16 sites occupied by O^{2-} anions, with incident bond-valences from 1.41 to 2.03 vu. Many of the H_2O groups, in particular the OW28, OW29, OW31, OW32 and OW37 atoms, and to a lesser extent the OW30, OW35 and OW38 atoms, have relatively high anisotropic displacement parameters. This may be an indication of slight positional disorder. Occupancy refinements show

that OW28, OW29, OW31, OW36 and OW38 have occupancies of 1.10 to 1.20 suggesting partial occupancy by heavier elements such as Na or Cl. The OW39 and OW40 sites are situated close to a mirror plane, resulting in O–O distances of ~1.82 and 1.57 Å respectively, and thus the sites are unlikely to be fully occupied. The refined occupancies of the sites are 0.483(15) and 0.446(14). Difference Fourier syntheses located the H atom sites associated with the OH groups and nine H atom sites associated with the H₂O groups. The hydrogen bonds associated with these H atoms are shown in Table 7. Possible hydrogen bonds from the remaining OH and H₂O groups based on O...O bond distances are as follows: OW30–O3 2.901, OW29–O4 2.662, OW29–O4 2.662, OW32–O5 2.704, OW34–O6 2.862, OW31–O15 2.665, OW31–O15 2.665, OW28–O16 2.778, OW34–O16 2.842, OW36–OW27 3.019, OW27–OW36 2.867, OW33–OW37 2.947, OW32–OW37 2.648, OH25–OW40 2.821 Å. The O1, O2, O3, O4, O5, O6, O12, O15 and O16 anions with bond-valence sums of 1.41 to 1.76 vu are undersaturated so are likely hydrogen-bond acceptors. These anions, except O1 and O2, receive bond-valence contributions via hydrogen bonding that satisfies their incident bond-valence requirements. There are no possible hydrogen-bond donors in the vicinity of O1 and O2 so these anions remain undersaturated. The OW29, OW31, OW33 and OW34 anions, which bond to Ca1 and Ca2, provide hydrogen bonds directed towards oxygen atoms coordinated to C cations in adjacent sheets thus providing additional linkage between sheets. Hydrogen bonding via H₂O molecules OW35, OW36 and OW37, which are not bonded to cations and act as both hydrogen-bond donors and acceptors, also provided links between sheets. OH23 and OW30 direct hydrogen bonds to the O3 anion which is coordinated to the S cation. The remaining hydrogen bonds are within the sheets. The hydrogen bonds can be classified as strong to weak, with O...O distances in the range of 2.648 to 3.003 Å.

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