Ewingite: Earth's most complex mineral

Travis A. Olds[1], Jakub Plášil[2], Anthony R. Kampf[3], Antonio Simonetti[1], Luke R. Sadergaski[1], Yu-Sheng Chen[4] and Peter C. Burns[1,5*]

[1.] Department of Civil and Environmental Engineering and Earth Sciences, University of Notre Dame, Notre Dame, IN 46556, USA
[2.] Institute of Physics, Academy of Sciences of the Czech Republic, v.v.i., Na Slovance 1999/2, 18221 Praha 8, Czech Republic
[3.] Mineral Sciences Department, Natural History Museum of Los Angeles County, 900 Exposition Boulevard, Los Angeles, CA 90007, USA
[4.] Center for Advanced Radiation Sources, University of Chicago, Chicago, IL 60632, USA.
[5.] Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN 46556, USA

*E-mail: pburns@nd.edu

Supplementary Materials

Materials and Methods:

Deposited Material

The new mineral and its name were approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA2015-128). The description is based on one holotype specimen, housed at the Natural History Museum of Los Angeles County, 900 Exposition Boulevard, Los Angeles, CA 90007, USA, catalogue number 65686.

Raman and Infrared spectroscopy

Raman spectroscopy was conducted using a Bruker Instruments Sentinel-785 laser head mounted on a Nikon Optiphot-2 microscope. A Peltier cooled integrated diode laser was calibrated internally with polystyrene and NIST SRM 2065 standards, operated at 400 mW, 785 nm, with a 100-micron beam size and 5 cm^{-1} resolution. Attenuated total reflectance (ATR) Fourier transform infrared (FTIR) spectra were obtained using a liquid N_2 cooled SENSIR Technologies IlluminatIR mounted to an Olympus BX51 microscope. An ATR objective was pressed into crystals of ewingite and measured from 4000 to 650 cm^{-1}. The Raman spectrum of ewingite is shown in Fig. DR1, and the infrared spectrum in Fig DR2. The broad infrared band observed around 3200 cm^{-1}, with shoulders at 3350 and 3500 cm^{-1} are attributed to ν O–H stretching vibrations of structurally unique hydrogen bonded water molecules. Using the correlation function given by Libowitzky (1999), the approximate O-H···O hydrogen bond-lengths calculated from the observed stretching frequencies lie within the range ~2.9 to 2.6 Å. A weak IR band centered at 1630 cm^{-1} may be assigned to the ν_2 (δ) bending vibration of water, though it is not observed in the Raman spectrum since it may be too weak. Assignments become complicated in the region between 1300 and 1600 cm^{-1} due to overlap with the ν_3 $(CO_3)^{2-}$ antisymmetric stretching vibrations, which in Raman are observed at 1379, 1344, and 1250 cm^{-1}. The same assignment is given to the following bands in IR, 1494 cm^{-1} (shoulder at 1505 cm^{-1}), and 1332 cm^{-1} (shoulder at 1440 cm^{-1}). Splitting of the ν_3 $(CO_3)^{2-}$ antisymmetric stretching vibrations indicate the presence of bidentately bonded carbonate groups about uranium(Čejka, 1999; Jolivet et al., 1980). The split ν_1 $(CO_3)^{2-}$ symmetric stretching vibrations are observed at 1095, (shoulders at 1107 and 1087 cm^{-1}) in Raman. A very weak band of the same assignment is found at 1108 cm^{-1} in IR and though should be forbidden, its activation is due to non-symmetric $(CO_3)^{2-}$ units(Urbanec and J., 1979). The number of Raman bands in this region (~1100 cm^{-1}) proves that multiple symmetrically distinct $(CO_3)^{2-}$ groups are present in the structure.

A very strong Raman band at 832 cm^{-1} is assigned as the ν_1 $(UO_2)^{2+}$ symmetric stretching vibration. In the IR spectrum the ν_3 $(UO_2)^{2+}$ antisymmetric stretching vibration is present as a very strong band at 918 cm^{-1}. Bartlett and Cooney(Bartlett and Cooney, 1989) provide an empirical relationship to derive the approximate U–O_{yl} bond lengths from the band position assigned to the $(UO_2)^{2+}$ stretching vibrations, which gives 1.779 Å (Raman ν_1), and 1.772 (IR ν_3); lengths on par with U–O_{yl} bond lengths(Burns et al., 1997). There are no ν_2 (δ) $(CO_3)^{2-}$ bending modes found in the Raman or IR spectra, however, they may be weak and obscured by the intense ν_1 or ν_3 $(UO_2)^{2+}$ stretch. The ν_4 (δ) $(CO_3)^{2-}$ in-plane bending vibrations manifest in Raman at 761 cm^{-1} (shoulder at 751 cm^{-1}), 687, 668, and 636 cm^{-1} and in the IR spectrum as a single band at 771 cm^{-1}. Weak

Raman bands, assigned to ν_2 (δ) $(UO_2)^{2+}$ bending modes, are found at 340, 329, 317, 243, and 203 cm^{-1}. Remaining bands <200 cm^{-1} are assigned to external lattice vibrational modes.

Chemical Analysis: HR-ICP-MS

Microprobe data were obtained, but difficulty in analysis and preparation of the weak and heavily hydrated crystals gave poor data. In light of this, high resolution Inductively Coupled Mass Spectrometry (HR-ICP-MS) was utilized to empirically determine the formula for ewingite. Approximately forty small crystals, weighing roughly ~250 µg, were hand-picked with the aid of a microscope and then placed in two separate micro-centrifuge tubes. The crystals were digested in 1 mL of high purity, double distilled 2% HNO_3 acid and subsequently diluted 200-fold. Solution-mode ICP-MS analyses were conducted using the AttoM HR-ICP-MS (by Nu Instruments) in medium mass resolution (Δm/m ~3300). An external calibration method was used to determine the concentrations of U, Mg, Mn, and Ca. A five-point calibration curve was adopted for each element ranging in concentrations from 0.2 ppb to 50 ppb. The ion signals for the following isotopes were measured: ^{238}U, ^{235}U, ^{24}Mg, ^{25}Mg, ^{55}Mn, and ^{44}Ca. Dissolved mineral samples were run in triplicate and average elemental ratios were calculated (Table S1) along with their respective standard deviation and relative standard deviation (%). Obtaining an accurate mass of dissolved crystals was impossible due to limited material, which prevents back-calculation to true weight percent oxide values; thus the reported elemental concentrations are reported as a ratio relative to uranium. For convenience, the mean *apfu* values were converted to calculated weight percent oxide based on 292 O, 24 U, and 30 CO_3 *pfu*.

A direct determination of H_2O and CO_2 content was not done due to the paucity of material. In the absence of a direct determination of CO_2, the empirical formula is calculated for 24 U and 292 O, with 30 CO_3 *pfu* as obtained from the X-ray data, and charge is balanced by adding hydrogen. Infrared spectroscopy confirmed the presence of $(CO_3)^{2-}$ and H_2O, and $(CO_3)^{2-}$ was also observed in the Raman spectrum.

Physical Properties

The mineral occurs as aggregates of equant golden yellow crystals to 0.2 mm (Fig. DR3, S5). No twinning was observed. Crystals are transparent with a vitreous luster. The mineral has a pale yellow streak, and is non-fluorescent under LW and SW UV. The Mohs hardness is about 2, estimated by the behavior of crystals when broken. Crystals of ewingite are brittle with no discernable cleavage and uneven fracture. The density could not be measured due to the limited availability of material. The calculated density is 2.543 g·cm^{-3} based on the empirical formula.

Optical Properties:

Uniaxial +/–, $\omega = \varepsilon = 1.537(1)$ (white light)

Crystals of ewingite are so weakly anisotropic that, for practical purposes, they can be considered isotropic. The apparent isotropism is interesting because the optics appear to be dominated by the cubic symmetry of the U cage (T_d), where the packing of multiple cage-clusters is only slightly twisted (~14°) from cubic symmetry along the $\bar{4}$ axes (Fig. DR4).

Single Crystal X-ray Diffraction

A yellow crystal with dimensions 66 x 44 x 11 μm was mounted on the tip of a glass fiber with glue. The X-ray diffraction experiment was performed with a Bruker D8 diffractometer and an APEX II detector using synchrotron radiation, 30 keV (0.41328Å), at 100(2) K with an Oxford Cyrojet. A total of 2160 frames (0.5°/ϕ scans) were collected at a 2θ angle of -8° and -15°. At each 2θ angle, the ω are at values of -180°, -160°, 140°. The distance between the detector and the crystal was 12 cm with an exposure time of 0.2s.

The Apex 3 software package was used for processing collected diffraction data, including corrections for background, polarization and Lorentz effects. A multi-scan empirical absorption correction was done using SADABS, and an initial model was obtained by the charge-flipping method using SHELXT(Sheldrick, 2015). Refinement proceeded by full-matrix least-squares on F^2 using SHELX-2014/7(Sheldrick, 2008), and refined to an R_1 of 15.15% for 1394 reflections with $I_{obs} > 4\sigma(I)$. The space-group $I4_1/acd$ was confirmed as the most well converged refinement, details for which are given in Table S2. Crystals of ewingite have pseudo-symmetric diffraction patterns, and refinement was initially attempted in the orthorhombic space group *Ibca,* with an applied pseudo-tetragonal twin law that gave a marginally similar model (R_1 = ~15.5%), but also an unrealistic coordination environment about several U atoms. Placement in the orthorhombic space group effectively doubles the number of refined parameters, which provides an artificially better model by numbers, though there is no improvement in the estimated standard deviations or R_w values relative to $I4_1/acd$. Atomic coordinates, displacement parameters, and bond valence sums are given in Data table S1. The anisotropic displacement parameters are given in Data table S2, and selected bond distances in Data table S3.

Powder Diffraction

Powder diffraction data were recorded using a Rigaku R-Axis Rapid II curved imaging plate microdiffractometer with monochromated MoKα radiation. A Gandolfi-like motion on the φ and ω axes was used to randomize the sample. Observed d-spacings and intensities were derived by profile fitting using JADE 2010 software (Materials Data, Inc.). A table comparing the experimentally observed and calculated peak positions (in Å for MoKα) is given in Data Table S4. Unit cell parameters refined from the powder data using JADE 2010 with whole pattern fitting are given below.

Tetragonal Space group: $I4_1/acd$
a = 35.624(10) Å c = 48.449(13) Å
V = 61485(38) Å^3 Z = 8

Table 1. Element ratios from ICP-MS with standard deviation (SD) and relative standard deviation (RSD, %), average of six analyses.

Element	**Mean Ratio (U/cation)**	**Range**	**SD**	**RSD**	**Mean *apfu***	**Calculated wt% oxide (total = 100%)**
Mg	3.042	2.857-3.158	0.121	3.96	7.889	2.75
Ca	3.122	2.915-3.507	0.231	7.40	7.687	3.73
Mn	70.240	61.731-79.446	6.35	9.04	0.342	0.21
U*	1.000	-	-	-	24	59.41
CO_2*	-	-	-	-	30	11.43
H_2O**	-	-	-	-	144.09	22.47

*Calculated with respect to the ideal formula where U = 24 and CO_3 = 30 *pfu* and charge is balanced by adding H

* *From the structure model

The empirical formula is: $(Mg_{7.89}Ca_{7.69}Mn_{0.34})_{\Sigma=15.92}(UO_2)_{24}(CO_3)_{30}O_4(OH)_{11.84}(H_2O)_{138.16}$

The ideal formula is: $Mg_8Ca_8(UO_2)_{24}(CO_3)_{30}O_4(OH)_{12}(H_2O)_{138}$ which requires, MgO 2.79, CaO 3.88, UO3 59.43, CO2 11.43, H2O 22.46 (100 wt. %)

Table S2. Data collection and structure refinement details for ewingite.

Diffractometer	Bruker D8, Apex II detector
X-ray radiation/power	λ = 0.41328 Å/30 keV
Temperature	100(2) K
Structural Formula	$Mg_8Ca_8(UO_2)_{24}(CO_3)_{30}O_4(OH)_{12}(H_2O)_{138}$
Space group	$I4_1/acd$
Unit cell dimensions	*a* = 35.142(2) Å
	c = 47.974(3) Å
V	59245(8) Å^3
Z	8
Density (for above formula)	2.525 g cm^{-3}
Absorption coefficient	13.350 mm^{-1}
F(000)	39840
Crystal size	66 x 44 x 11 μm

θ_{range}	1.363-23.266°
Index ranges	$-36 \le h \le 24$, $-34 \le k \le 39$, $-38 \le l \le 53$
Reflections collected/unique	194306/10598; R_{int} = 0.0907
Reflections with $I_{obs} > 2\sigma(I)$	7707
Completeness to θ_{max}	99.3%
Refinement method	Full-matrix least-squares on F^2
Parameters refined (restraints)	509 (82)
GoF (obs/all)	1.097/1.094
R (obs), *wR* (obs)	0.1515/0.3894
R (all), *wR* (all)	0.1969/0.4324
Largest diff. peak/hole	+3.27/–4.07 e Å^{-3}

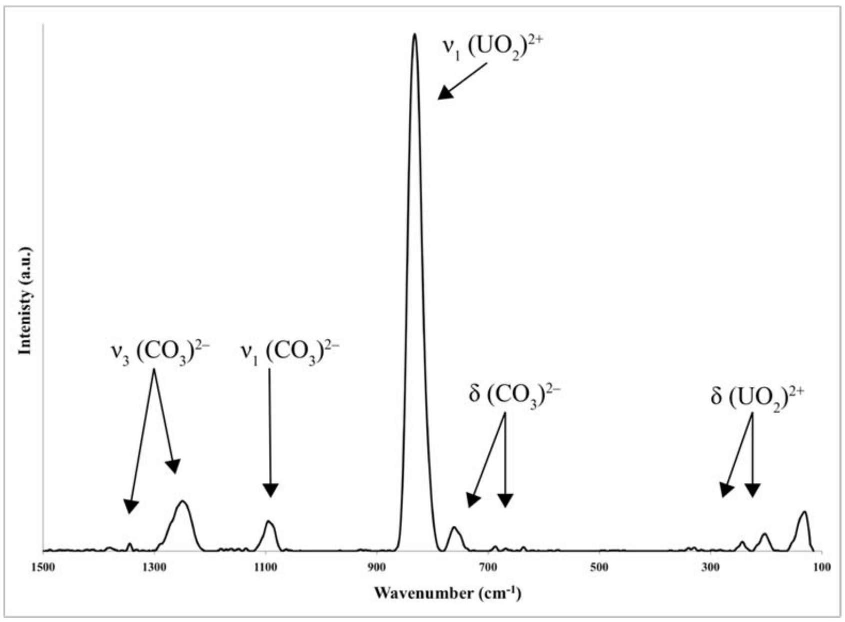

Figure DR1. The Raman spectrum of ewingite collected with a 785 nm laser, from 1500 to 100 cm^{-1}.

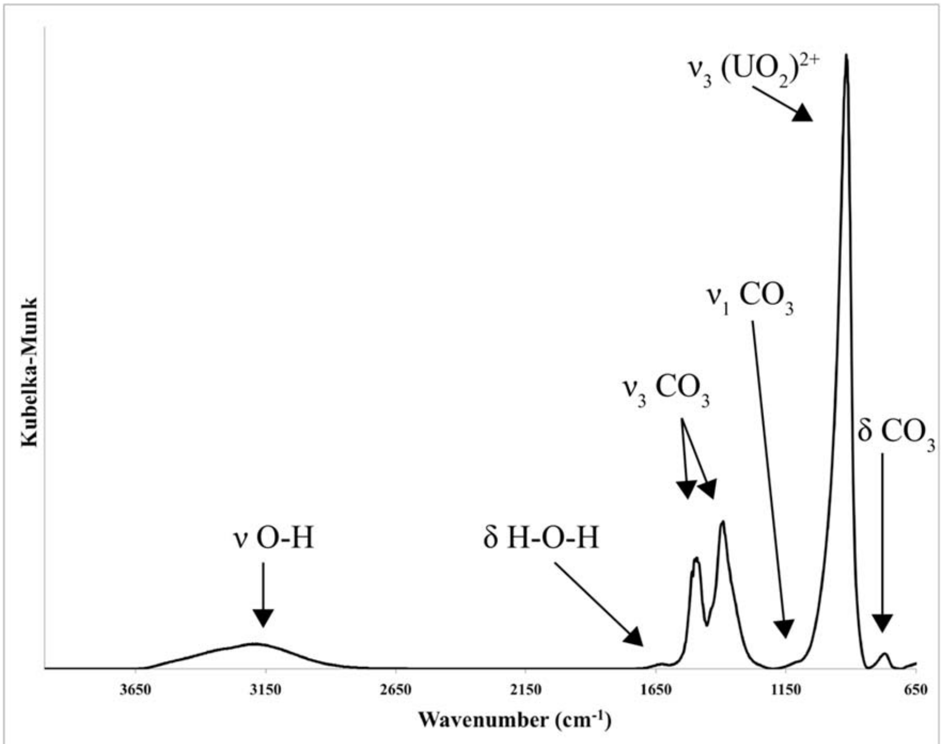

Figure DR2. The FTIR spectrum of ewingite, from 4000 to 650 cm^{-1}.

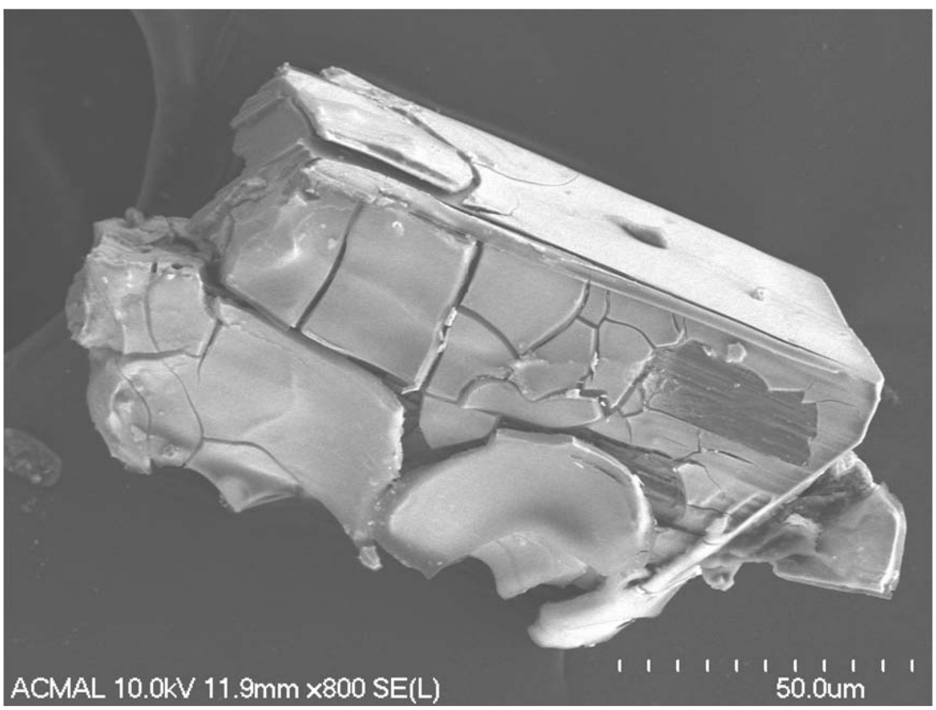

Figure DR3. SEM secondary electron image of a crystal of ewingite, which rapidly dehydrated and cracked when exposed to vacuum.

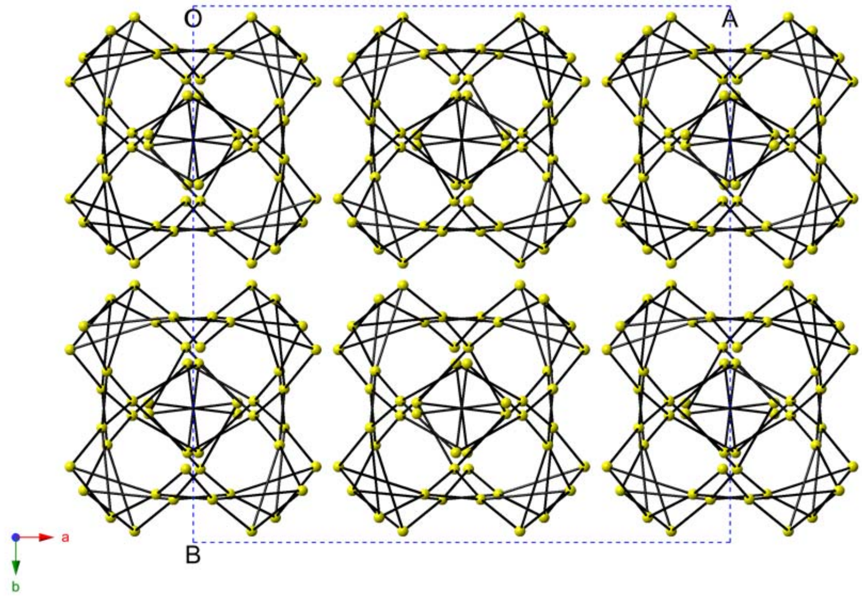

Figure DR4. The crystal packing of multiple clusters as viewed down *c*. Clusters are drawn showing the connectivity of uranium atoms in order to make the slight twist of the $\bar{4}$ axis apparent.

Figure DR5. Near the center of the image lies a small golden yellow aggregate of ewingite. It crystallized on yellow green liebigite, coated by masses of powdery pale-yellow metazellerite, with the whole assemblage sitting atop massive black uraninite. Horizontal field of view is 2 mm.

Crystallographic Supplementary Data Tables

Data table DR1. Atomic coordinates, displacement parameters (Å^2), and bond valence sums for ewingite

Atoms	Occ.	*x*	*y*	*z*	U_{eq}/U_{iso}	B.V. (O type)	Atoms	Occ.	*x*	*y*	*z*	U_{eq}/U_{iso}	B.V. (O type)
U1	1	0.48371(6)	0.13609(5)	0.00616(3)	0.0426(5)	5.96	O27	1	0.5971(13)	0.0671(15)	0.0483(11)	0.097(16)	1.80 (O)
U2	1	0.41713(7)	0.26286(6)	-0.06235(4)	0.0530(6)	6.26	O28	1	0.7324	0.0586	0.0454	0.23(5)	1.64 (O)
U3	1	0.53365(6)	0.07913(6)	0.06148(4)	0.0440(5)	6.11	O29	1	0.4333(14)	0.0482(14)	0.0402(10)	0.083(13)	1.57 (O)
U4	1	0.70174(7)	0.09024(10)	0.08238(6)	0.0855(10)	6.46	O30	1	0.700(2)	0.0462(12)	0.1010(14)	0.14(2)	1.66 (O)
U5	1	0.42766(6)	0.08977(6)	0.06385(4)	0.0442(5)	5.83	O31	1	0.4904(13)	0.1830(7)	0.0200(9)	0.076(12)	1.82 (O)
U6	1	0.60131(10)	0.01849(7)	0.16671(4)	0.0786(9)	6.11	O32	1	0.5189(12)	0.0441(10)	0.0365(7)	0.074(12)	1.85 (O)
Ca1	1	0.5	0.25	-0.0027(3)	0.052(4)	2.18	O33	1	0.770(2)	0.0851(19)	0.0783(14)	0.13(2)	1.77 (O)
Ca2	1	0.6041(3)	0.1196(3)	0.1239(2)	0.050(2)	2.27	O34	1	0.7348(14)	0.1168(15)	0.1192(11)	0.095(15)	2.03 (O)
Ca3	0.5	0.3657(4)	0.1668(4)	-0.0918(3)	0.018(3)	1.99	O35	1	0.3000(17)	0.1132(16)	0.0478(12)	0.103(17)	1.61 (O)
Mg1	0.5	0.5	0.25	0.0757(15)	0.080(18)	1.15	O36	1	0.5586(9)	0.0343(14)	0.1838(10)	0.091(15)	1.63 (O)
Mg2	0.75	0.3114(9)	0.3020(9)	-0.1517(7)	0.078(8)	2.27	O37	1	0.6462(8)	0.0066(14)	0.1518(10)	0.086(14)	1.68 (O)
Mg3	0.25	0.505(5)	0.264(4)	0.103(3)	0.12(5)	1.45	O38	1	0.5546(11)	0.0281(11)	0.0877(8)	0.062(10)	2.11 (O)
Mg4	0.75	0.4768(11)	0.0260(10)	0.0032(8)	0.095(10)	1.10	O39	1	0.3624(12)	0.0917(12)	0.0533(9)	0.070(11)	1.77 (O)
O1	1	0.5869(14)	-0.0488(14)	0.1714(10)	0.084(13)	0.76 (H_2O)	O40	0.5	0.794(3)	0.049(3)	0.041(2)	0.11(4)	1.35 (O)
O2	1	0.3786(13)	0.2977(13)	-0.0986(10)	0.081(13)	1.65 (O)	O41	1	0.2574(14)	0.1821(14)	-0.1242(10)	0.083(13)	1.38 (O)
O3	1	0.3684(13)	0.2343(13)	-0.0922(9)	0.077(12)	2.14 (O)	Ow1	0.5	0.604(2)	0.025(2)	0.2910(18)	0.07(2)	0.39 (H_2O)
O4	1	0.4537(8)	0.2565(11)	-0.0876(6)	0.056(9)	1.69 (O)	Ow2	1	0.4528(13)	0.2543(13)	0.0322(9)	0.074(12)	0.42 (H_2O)
O5	1	0.4610(11)	0.2942(11)	-0.0307(8)	0.057(9)	2.24 (O)	Ow3	1	0.4039(13)	0.1125(13)	-0.0718(9)	0.078(12)	0.22 (H_2O)
O6	1	0.4788(12)	0.0605(12)	0.0896(9)	0.067(11)	0.97 (OH)	Ow4	1	0.4833(12)	0.0811(12)	0.1473(9)	0.069(11)	0.00 (H_2O)
O7	1	0.3358(10)	0.1307(10)	0.0847(7)	0.049(8)	1.97 (O)	Ow5	1	0.3309(12)	0.1893(12)	-0.1336(9)	0.068(11)	0.25 (H_2O)
O8	1	0.5820(12)	0.0549(12)	0.1262(9)	0.072(12)	2.14 (O)	Ow6	0.5	0.414(4)	-0.029(4)	0.072(3)	0.12(4)	0.35 (H_2O)
O9	1	0.4451(11)	0.1592(10)	-0.0290(8)	0.059(10)	2.03 (O)	Ow7	0.5	0.468(4)	-0.029(4)	0.152(3)	0.14(5)	0.00 (H_2O)
O10	1	0.6335(10)	0.0961(10)	0.0817(7)	0.053(9)	2.15 (O)	Ow8	0.25	0.745(5)	0.031(5)	0.164(4)	0.07(5)	0.00 (H_2O)
O11	1	0.4229(10)	0.1274(10)	0.0905(7)	0.054(9)	1.65 (O)	Ow9	1	0.3576(14)	0.1076(14)	-0.125	0.082(18)	0.16 (H_2O)
O12	1	0.6723(11)	0.1265(11)	0.1218(8)	0.057(9)	1.83 (O)	Ow10	1	0.4267(17)	0.2407(16)	-0.1514(12)	0.103(17)	0.00 (H_2O)
O13	1	0.4293(11)	0.3297(11)	-0.0601(8)	0.055(9)	1.99 (O)	Ow11	0.5	0.3278(19)	0.277(2)	-0.1913(14)	0.048(17)	0.36 (H_2O)
O14	1	0.4828(12)	0.1152(12)	0.0520(9)	0.070(11)	2.03 (O)	Ow12	1	0.5879(15)	0.1801(15)	0.0409(11)	0.094(15)	0.00 (H_2O)
O15	1	0.4110(13)	0.1935(14)	-0.0596(10)	0.087(14)	2.15 (O)	Ow13	0.5	0.372(3)	0.090(3)	-0.018(2)	0.11(3)	0.00 (H_2O)
O16	1	0.4516(12)	0.2212(12)	-0.0307(8)	0.064(10)	2.01 (O)	Ow14	0.25	0.512(4)	0.088(4)	0.294(3)	0.06(4)	0.00 (H_2O)
O17	1	0.7059(17)	0.1335(10)	0.0639(11)	0.106(17)	1.73 (O)	Ow15	0.5	0.268(4)	0.052(4)	-0.167(3)	0.12(4)	0.00 (H_2O)
O18	1	0.4005(12)	0.0447(12)	0.0941(8)	0.065(11)	1.74 (O)	Ow16	0.5	0.75	0.001(5)	0	0.11(5)	0.00 (H_2O)
O19	1	0.4234(12)	0.1302(12)	0.0244(9)	0.068(11)	1.16 (OH)	Ow17	0.5	0.377(3)	-0.083(3)	0.163(2)	0.10(3)	0.00 (H_2O)
O20	1	0.5497(10)	0.1189(10)	0.0219(7)	0.052(9)	0.90 (OH)	Ow18	0.25	0.682(6)	0.036(6)	-0.005(4)	0.08(5)	0.00 (H_2O)
O21	1	0.5242(12)	0.1437(13)	-0.0342(9)	0.071(12)	1.58 (O)	Ow19	0.5	0.540(2)	0.188(2)	0.0639(15)	0.055(18)	0.00 (H_2O)
O22	1	0.3821(12)	0.2705(16)	-0.0363(9)	0.102(17)	1.70 (O)	Ow20	1	0.4206(11)	0.1706(11)	-0.125	0.057(13)	0.23 (H_2O)
O23	1	0.3374(15)	0.2659(16)	-0.1258(11)	0.100(16)	1.68 (O)	Ow21	1	0.5485(12)	0.1463(12)	0.2082(8)	0.064(10)	0.00 (H_2O)
O24	1	0.6599(15)	0.0648(16)	0.0467(12)	0.109(18)	1.79 (O)	Ow22	1	0.5499(13)	0.1343(13)	0.1485(9)	0.078(12)	0.41 (H_2O)
O25	1	0.4768(10)	0.0895(6)	-0.0090(7)	0.053(9)	1.79 (O)	Ow23	0.5	0.681(2)	-0.044(2)	0.0198(15)	0.052(18)	0.00 (H_2O)
O26	1	0.5483(11)	0.1128(9)	0.0873(6)	0.059(10)	1.82 (O)	Ow24	0.5	0.467(2)	-0.0258(16)	0.0225(15)	0.06(2)	0.54 (H_2O)

Data table DR1 (cont). Atomic coordinates, displacement parameters (Å^2), and bond valence sums for ewingite.

Atoms	Occ.	*x*	*y*	*z*	U_{eq}/U_{iso}	B.V. (O type)	Atoms	Occ.	*x*	*y*	*z*	U_{eq}/U_{iso}	B.V. (O type)
Ow25	0.5	0.560(3)	0.033(3)	0.254(2)	0.10(3)	0.00 (H_2O)	Ow53	1	0.5546(15)	0.1825(15)	0.1835(10)	0.089(14)	0.00 (H_2O)
Ow26	0.5	0.559(3)	0.247(3)	0.110(3)	0.11(4)	0.86 (H_2O)	Ow54	0.25	0.566(4)	0.213(4)	0.088(3)	0.06(4)	0.00 (H_2O)
Ow27	0.5	0.298(3)	0.329(3)	-0.1144(17)	0.10(4)	0.55 (H_2O)	Ow55	0.25	0.663(8)	0.007(8)	0.034(6)	0.14(9)	0.00 (H_2O)
Ow28	1	0.6028(13)	0.1797(13)	0.0994(9)	0.075(12)	0.45 (H_2O)	Ow56	0.5	0.538(2)	0.111(2)	0.2573(17)	0.07(2)	0.00 (H_2O)
Ow29	0.5	0.411(2)	-0.024(2)	-0.0026(16)	0.058(19)	0.06 (H_2O)	Ow57	0.25	0.440(5)	0.047(5)	0.190(4)	0.07(5)	0.00 (H_2O)
Ow30	1	0.6004(17)	0.0862(17)	0.2953(12)	0.107(17)	0.21 (H_2O)	Ow58	1	0.4803(18)	-0.0153(18)	0.1020(13)	0.117(19)	0.45 (H_2O)
Ow31	0.5	0.3573(18)	0.337(2)	-0.1652(16)	0.06(2)	0.31 (H_2O)	Ow59	0.5	0.6066(18)	0.2319(18)	0.1286(13)	0.040(15)	0.00 (H_2O)
Ow32	0.5	0.410(2)	-0.049(2)	0.1241(19)	0.06(2)	0.00 (H_2O)	C1	1	0.4546(18)	0.3255(18)	-0.0416(13)	0.064(16)	4.01
Ow33	0.5	0.538(4)	0.050(4)	0.248(3)	0.12(4)	0.00 (H_2O)	C2	1	0.6298(11)	0.0768(9)	0.0593(7)	0.037(11)	3.90
Ow34	0.5	0.292(2)	0.102(2)	-0.1503(17)	0.07(2)	0.00 (H_2O)	C3	0.5	0.7678(15)	0.0647(16)	0.0557(13)	0.045	3.71
Ow35	0.5	0.452(4)	-0.036(4)	0.249(3)	0.12(4)	0.00 (H_2O)	C4	1	0.7072(16)	0.1283(18)	0.1336(12)	0.065(16)	3.71
Ow36	0.5	0.418(3)	-0.100(3)	0.262(2)	0.09(3)	0.00 (H_2O)	C5	1	0.4366(12)	0.1898(12)	-0.0410(9)	0.038(11)	4.01
Ow37	0.5	0.442(3)	0.033(3)	-0.0517(19)	0.08(3)	0.00 (H_2O)	C6	1	0.3619(12)	0.2655(14)	-0.1051(10)	0.09(2)	3.83
Ow38	0.25	0.784(4)	-0.045(4)	-0.013(3)	0.06(4)	0.00 (H_2O)	C7	1	0.5657(18)	0.0285(17)	0.1122(10)	0.072(17)	3.77
Ow39	0.5	0.439(4)	-0.039(4)	0.227(3)	0.13(5)	0.00 (H_2O)	C8	1	0.331(2)	0.106(3)	0.064(2)	0.14(4)	3.47
Ow40	0.5	0.414(3)	0.336(3)	-0.125	0.10(5)	0.00 (H_2O)							
Ow41	0.5	0.839(3)	0.130(3)	0.153(2)	0.09(3)	0.00 (H_2O)							
Ow42	0.5	0.583(4)	0.107(4)	0.242(3)	0.13(5)	0.00 (H_2O)							
Ow43	0.25	0.465(6)	0.032(6)	0.233(5)	0.09(6)	0.00 (H_2O)							
Ow44	1	0.5	0.25	-0.125	0.16(6)	0.00 (H_2O)							
Ow45	0.5	0.675(3)	-0.035(3)	0.249(2)	0.09(3)	0.00 (H_2O)							
Ow46	0.5	0.343(4)	-0.077(4)	0.084(3)	0.12(4)	0.00 (H_2O)							
Ow47	0.5	0.660(3)	-0.032(3)	-0.019(2)	0.09(3)	0.00 (H_2O)							
Ow48	0.25	0.661(4)	-0.051(4)	0.184(3)	0.05(4)	0.00 (H_2O)							
Ow49	0.25	0.664(4)	0.052(4)	0.002(3)	0.05(3)	0.00 (H_2O)							
Ow50	0.25	0.368(5)	0.408(5)	-0.070(4)	0.08(5)	0.00 (H_2O)							
Ow51	0.5	0.305(4)	0.089(4)	-0.243(3)	0.13(4)	0.00 (H_2O)							
Ow52	1	0.4981(17)	0.1931(17)	0.0798(13)	0.109(18)	0.66 (H_2O)							

Ca^{2+}–O,Mg^{2+}–O, and C^{4+}–O bond strengths taken from Brown and Altermatt (Brown and Altermatt, 1985); U^{6+}–O bond strength from Burns *et al.* (Burns et al., 1997).

Data table DR2. Anisotropic displacement parameters (Å^2) for ewingite.

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
U1	0.0626(13)	0.0401(11)	0.0250(9)	0.0025(7)	0.0026(8)	0.0001(9)
U2	0.0672(14)	0.0493(12)	0.0423(11)	0.0030(9)	-0.0178(10)	-0.0038(10)
U3	0.0507(12)	0.0452(11)	0.0361(10)	0.0012(8)	-0.0054(8)	0.0013(9)
U4	0.0535(15)	0.121(2)	0.0815(18)	-0.0498(17)	0.0024(13)	0.0016(15)
U5	0.0495(12)	0.0491(12)	0.0341(10)	-0.0017(8)	0.0025(8)	-0.0022(9)
U6	0.152(3)	0.0465(13)	0.0371(12)	0.0069(10)	-0.0203(14)	-0.0186(15)
Ca1	0.064(10)	0.045(7)	0.046(8)	0	0	0.000(6)
Ca2	0.055(6)	0.052(6)	0.043(5)	0.005(4)	0.001(4)	-0.006(5)
Ca3	0.024(8)	0.025(7)	0.006(6)	0.001(5)	-0.011(6)	-0.002(6)

Data table DR3. Selected bond distances (in Å) for ewingite.

U1−O31	1.793(28)	U6−O37	1.782(34)	Ca3−Ow3	2.523(48)
U1−O25	1.808(24)	U6−O36	1.798(38)	Ca3−O3	2.374(48)
U1−O14	2.319(43)	U6−O8	2.424(43)	Ca3−Ow5	2.478(45)
U1−O19	2.302(42)	U6−O35	2.383(58)	Ca3−Ow20	2.505(33)
U1−O21	2.418(43)	U6−O7	2.449(35)	Ca3−O1	2.438(51)
U1−O9	2.312(38)	U6−O41	2.461(49)	Ca3−O15	2.409(49)
U1−O20	2.513(35)	U6−Ow1	2.542(81)	Ca3−Ow9	2.636(42)
<U1−O$_{Ur}$>	1.801	U6−O1	2.429(49)	Ca3−Ow30	2.533(60)
<U1−O$_{Eq}$>	2.373	<U6−O$_{Ur}$>	1.790	<Ca3−O>	2.487
		<U6−O$_{Eq}$>	2.448		
U2−O2	2.521(47)			C1−O21	1.36(7)
U2−O3	2.448(45)	Mg1−Ow26 (x2)	2.64(13)	C1−O5	1.24(8)
U2−O4	1.780(29)	Mg1−Ow52 (x2)	2.010(60)	C1−O13	1.26(7)
U2−O5	2.428(39)	Mg1−Ow2 (x2)	2.669(72)	<C1−O>	1.29
U2−O16	2.432(41)	<Mg1−O>	2.439		
U2−O22	1.775(43)			C2−O27	1.31(6)
U2−O13	2.340(39)	Mg2−Ow31	2.129(74)	C2−O24	1.29(6)
U2−O15	2.451(49)	Mg2−Ow6	2.08(15)	C2−O10	1.28(5)
<U2−O$_{Ur}$>	1.778	Mg2−Ow27	2.08(9)	<C2−O>	1.29
<U2−O$_{Eq}$>	2.437	Mg2−O23	1.996(63)		
		Mg2−Ow11	2.0670(4)	C3−O40	1.28(12)
U3−O26	1.789(31)	Mg2−Ow58	1.986(71)	C3−O33	1.30(9)
U3−O32	1.795(35)	<Mg2−O>	2.056	C3−O28	1.36(5)
U3−O27	2.356(47)			<C3−O>	1.31
U3−O14	2.238(42)	Mg3−Ow26	2.02(20)		
U3−O38	2.311(39)	Mg3−Ow26	2.30(20)	C4−O34	1.26(8)
U3−O20	2.424(34)	Mg3−Ow26	2.38(19)	C4−O18	1.33(7)
U3−O6	2.442(43)	Mg3−Ow26	3.13(19)	C4−O12	1.35(7)
<U3−O$_{Ur}$>	1.792	Mg3−Ow52	1.88(15)	<C4−O>	1.31
<U3−O$_{Eq}$>	2.354	Mg3−Ow52	2.74(15)		
		<Mg3−O>	2.41	C5−O16	1.32(6)
U4−O17	1.766(41)			C5−O15	1.27(6)
U4−O30	1.788(50)	Mg4−Ow24	2.070(70)	C5−O9	1.26(6)
U4−O24	2.427(56)	Mg4−Ow24	2.328(81)	<C5−O>	1.28
U4−O34	2.311(52)	Mg4−O25	2.307(42)		
U4−O28	2.355(3)	Mg4−O32	2.268(54)	C6−O2	1.31(7)
U4−O10	2.407(35)	Mg4−Ow29	2.917(80)	C6−O3	1.28(7)
U4−O12	2.504(39)	Mg4−O29	2.469(82)	C6−O23	1.31(7)
U4−O33	2.414(70)	<Mg4−O>	2.393	<C6−O>	1.30
<U4−O$_{Ur}$>	1.777				
<U4−O$_{Eq}$>	2.403	Ca1−O16 (x2)	2.392(42)	C7−O8	1.28(7)
		Ca1−Ow2(x2)	2.362(46)	C7−O38	1.24(6)
U5−O11	1.847(35)	Ca1−O5 (x2)	2.469(39)	C7−O41	1.42(8)
U5−O29	1.860(49)	Ca1−O31 (x2)	2.616(30)	<C7−O>	1.377
U5−O14	2.208(43)	<Ca1−O>	2.460		
U5−O19	2.371(43)			C8−O35	1.36(10)
U5−O18	2.351(41)	Ca2−Ow28	2.418(46)	C8−O7	1.33(11)
U5−O39	2.350(42)	Ca2−O7	2.375(36)	C8−O39	1.32(9)
U5−O6	2.411(43)	Ca2−O12	2.411(40)	<C8−O>	1.34
<U5−O$_{Ur}$>	1.854	Ca2−O8	2.405(44)		
<U5−O$_{Eq}$>	2.338	Ca2−O10	2.418(36)		
		Ca2−O26	2.643(36)		
		Ca2−Ow22	2.300(46)		
		Ca2−O11	2.617(36)		
		<Ca2−O>	2.448		

Data Table DR4. Powder X-ray data for ewingite (*d* values in Å).

I_{obs}	d_{obs}	d_{calc}	I_{calc}	*hkl*
19	**17.8**	17.7005	27	2 0 0
		17.3535	9	1 1 2
		15.0399	4	2 1 1
31	**14.3**	14.2616	28	2 0 2
		12.0393	2	0 0 4
74	**10.1**	10.1513	74	3 1 2
		9.9548	26	2 0 4
		8.8502	2	4 0 0
		8.6767	3	2 2 4
		8.4527	3	4 1 1
		8.3759	2	3 2 3
100	**8.28**	8.3069	41	4 0 2
		8.1982	59	3 1 4
		7.8841	1	3 3 2
		7.5710	2	4 1 3
		7.3098	1	2 0 6
7	7.08	7.1308	5	4 0 4
		7.0049	4	4 3 1
24	**6.61**	6.6709	7	5 1 2
		6.6143	6	4 2 4
		6.5229	11	3 1 6
15	6.31	6.4091	5	4 1 5
		6.2581	15	4 4 0
		6.0834	1	5 2 3
30	**6.03**	6.0196	22	0 0 8
		5.9454	2	4 0 6
		5.9002	2	6 0 0
		5.8870	1	5 3 2
36	**5.69**	5.7845	5	3 3 6
		5.7306	6	6 0 2
		5.7047	1	4 3 5
		5.6360	26	4 2 6
		5.5974	1	6 2 0
		5.5527	1	4 4 4
		5.4926	2	5 4 1
10	5.40	5.4714	3	6 1 3
		5.4520	4	6 2 2
		5.3688	2	4 1 7
		5.3018	2	3 1 8
		5.2508	2	5 1 6
		5.2274	1	5 4 3
		5.0756	1	6 2 4
		4.9811	1	6 1 5
		4.9340	3	4 3 7
		4.9092	1	6 4 0
		4.8381	2	7 2 1
		4.8103	1	6 4 2
29	**4.774**	4.7539	25	6 0 6
13	4.596	4.6468	1	2 0 10
		4.6281	1	6 3 5
		4.6227	2	7 1 4
		4.5912	5	6 2 6
		4.5641	5	7 3 2
		4.5458	4	6 4 4
12	4.447	4.5127	3	6 5 1
		4.4432	1	6 1 7
		4.4238	6	3 1 10
		4.3728	3	8 1 1
16	4.322	4.3522	2	8 0 2
		4.3364	13	7 3 4
		4.2746	2	5 3 8
		4.2478	2	7 1 6
8	4.208	4.2354	3	7 4 3
		4.2300	3	4 0 10
		4.2136	1	6 0 8
		4.1720	1	6 6 0
		4.1499	1	5 2 9
		4.1281	1	8 3 1
9	4.066	4.0991	1	6 2 8
		4.0565	3	7 5 2
		4.0436	2	8 2 4
		4.0225	2	7 3 6
		4.0131	3	0 0 12
10	3.978	3.9953	7	8 1 5
		3.9709	5	7 2 7
		3.9570	4	5 1 10
		3.9421	1	6 6 4
		3.9138	1	2 0 12
		3.9055	1	8 4 2
7	3.863	3.8752	1	8 0 6
		3.8492	2	7 1 8
		3.8276	1	7 6 1
		3.8061	1	8 3 5
17	3.772	3.7855	4	8 2 6
		3.7777	4	3 1 12
		3.7344	2	7 6 3
		3.7308	7	6 0 10
11	3.695	3.7183	7	9 1 4
		3.7013	3	8 1 7
		3.6791	3	7 3 8
		3.6506	5	6 2 10
		3.6438	1	5 2 11
13	3.564	3.5987	1	7 2 9
		3.5654	6	8 0 8
		3.5498	3	8 4 6
		3.5401	3	8 6 0
		3.5146	3	9 1 6
		3.5076	3	9 4 3
		3.5024	1	8 6 2
6	3.479	3.4952	2	8 2 8
		3.4714	1	10 2 0
		3.4290	1	6 6 8
		3.4078	1	1 1 14
		3.3963	2	8 6 4
		3.3838	2	9 3 6
		3.3782	2	4 4 12
8	3.358	3.3676	1	9 4 5
		3.3529	1	9 2 7
		3.3445	1	7 3 10
		3.3062	3	9 5 4
		3.2881	1	3 1 14
		3.2760	1	8 3 9
		3.2608	1	8 7 3
		3.2567	1	10 4 2
5	3.218	3.2061	4	4 0 14
		3.1861	1	10 2 6
		3.1770	1	11 1 2
		3.1595	2	11 2 1
		3.1489	2	6 5 11
		3.1354	1	10 1 7
10	3.114	3.1286	2	7 5 10
		3.1196	3	9 2 9
		3.1065	2	10 5 3
		3.0972	1	11 1 4
		3.0794	1	11 3 2
		3.0577	2	8 4 10
13	3.044	3.0515	4	8 6 8
		3.0414	1	10 3 7
		3.0377	1	7 3 12
		3.0352	4	9 1 10
		3.0186	2	11 4 1
8	2.989	3.0098	4	0 0 16
		3.0065	3	9 7 4
		2.9975	1	8 7 7
		2.9928	3	5 3 14
		2.9727	3	8 0 12
		2.9501	1	12 0 0
		2.9344	1	9 8 1
		2.9306	2	6 2 14
4	2.910	2.9264	1	2 2 16
		2.9099	1	12 2 0
		2.8949	2	10 7 1
		2.8918	2	12 1 3
		2.8867	1	9 2 11
		2.8763	2	11 2 7
		2.8540	1	10 7 3
7	2.837	2.8393	1	10 6 6
		2.8351	1	5 5 14
		2.8314	2	8 1 13
		2.8160	2	10 2 10
		2.8133	1	4 2 16
10	2.788	2.8003	2	9 1 12
		2.7770	3	10 7 5
		2.7690	2	12 0 6
		2.7644	2	10 8 0
9	2.740	2.7615	2	5 1 16
		2.7444	2	10 1 11
		2.7327	3	9 3 12
		2.7250	2	11 2 9
		2.7148	2	10 4 10
7	2.684	2.7111	2	11 6 5
		2.6848	1	12 5 3
		2.6811	1	6 0 16
		2.6682	1	11 1 10
		2.6660	1	9 2 13
9	2.644	2.6544	1	13 2 3
		2.6509	1	6 2 16
		2.6486	2	11 7 4
		2.6453	1	2 0 18
		2.6425	3	12 3 7
		2.6330	2	11 4 9
		2.6274	2	10 9 1
		2.6199	3	12 2 8
		2.6135	1	11 6 7
7	2.597	2.6095	1	11 3 10
		2.5989	1	11 8 1
		2.5824	3	9 1 14
		2.5796	1	9 4 13
		2.5692	1	11 8 3
		2.5660	1	6 4 16
		2.5497	1	10 7 9
		2.5378	1	12 4 8
5	2.520	2.5264	1	7 3 16
		2.5188	1	14 1 1
		2.5156	1	12 0 10
		2.5044	1	11 1 12
		2.4959	1	6 3 17
		2.4906	1	12 2 10
		2.4868	1	13 5 4
		2.4766	1	8 7 13
		2.4630	1	7 6 15
6	2.449	2.4557	1	9 7 12
		2.4406	6	12 1 11
		2.4343	1	11 8 7
		2.4314	1	14 4 0
		2.4269	1	12 5 9
		2.4138	1	6 2 18
		2.4085	1	9 9 10
		2.3949	1	14 3 5
4	2.369	2.3863	1	4 3 19
		2.3596	1	7 1 18
		2.3556	1	11 10 3
		2.3540	2	3 1 20

Bartlett, J. R., and Cooney, R. P., 1989, On the determination of uranium-oxygen bond lengths in dioxouranium(VI) compounds by Raman spectroscopy: Journal of Molecular Structure, v. 193, p. 295-300.

Brown, I. D., and Altermatt, D., 1985, Bond-valence parameters obtained from a systematic analysis of the Inorganic Crystal Structure Database: Acta Crystallographica Section B, v. 41, no. 4, p. 244-247.

Burns, P. C., Ewing, R. C., and Hawthorne, F. C., 1997, The crystal chemistry of hexavalent uranium; polyhedron geometries, bond-valence parameters, and polymerization of polyhedra: The Canadian Mineralogist, v. 35, no. 6, p. 1551-1570.

Čejka, J., 1999, Infrared spectroscopy and thermal analysis of the uranyl minerals, *in* Burns, P. C., and Ewing, R. C., eds., Uranium: Mineralogy, Geochemistry and the Environment, Volume 38, Mineralogical Society of America, p. 521-622.

Jolivet, J. P., Thomas, Y., Taravel, B., and Lorenzelli, V., 1980, Vibrational study of coordinated $CO_3^{=}$ ions: Journal of Molecular Structure, v. 60, p. 93-98.

Sheldrick, G. M., 2008, A short history of SHELX: Acta Crystallographica Section A, v. 64, p. 112-122.

-, 2015, SHELXT - Integrated space-group and crystal-structure determination: Acta Crystallographica Section A, v. 71, p. 3-8.

Urbanec, Z., and J., Č., 1979, Chemistry of uranyl carbonates .3. Infrared-spectra of rutherfordine and sharpite: Collection of Czechoslovak Chemical Communications, v. 44, no. 1, p. 1-9.