

SHINKOLOBWEITE, FROM THE SHINKOLOBWE MINE, DEMOCRATIC REPUBLIC OF CONGO: A NEW MINERAL CONTAINING URANIUM IN THE RARE PENTAVALENT OXIDATION STATE

TRAVIS A. OLDS[§]

Section of Minerals and Earth Sciences, Carnegie Museum of Natural History, 4400 Forbes Avenue, Pittsburgh, Pennsylvania 15213, USA

AARON J. LUSSIER

Canadian Museum of Nature, P.O. Box 3443, Station D, Ottawa, Ontario K1P 6P4, Canada

VÁCLAV PETŘÍČEK AND JAKUB PLÁŠIL

Institute of Physics, Academy of Sciences of the Czech Republic, v.v.i., Na Slovance 1999/2, 18221 Praha 8, Czech Republic

ANTHONY R. KAMPF

Mineral Sciences Department, Natural History Museum of Los Angeles County, 900 Exposition Boulevard, Los Angeles, California 90007, USA

ALLEN G. OLIVER, PETER C. BURNS, AND MATEUSZ DEMBOWSKI

Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556, USA

Department of Civil and Environmental Engineering and Earth Sciences, University of Notre Dame, Notre Dame, Indiana 46556, USA

IAN M. STEELE

Notre Dame Integrated Imaging Facility, University of Notre Dame, Notre Dame, Indiana 46556, USA

ABSTRACT

Shinkolobweite, $\text{Pb}_{1.333}[\text{U}^{5+}\text{O}(\text{OH})(\text{UO}_2)_5\text{O}_{4.67}(\text{OH})_{5.33}](\text{H}_2\text{O})_5$, is a new lead uranyl oxide-hydroxide hydrate mineral containing hexavalent and pentavalent uranium from the Shinkolobwe mine, Democratic Republic of Congo. Crystals of shinkolobweite are dark reddish-brown prisms up to 0.5 mm in length, occurring on a matrix of massive uraninite associated with fourmarierite, rutherfordine, soddyite, and sklodowskite. Crystals are translucent with subadamantine luster and light bronze-yellow streak, are flattened on {010}, are elongated on [001], and exhibit the forms {100}, {010}, {101}, and {10 $\bar{1}$ }. The mineral is non-fluorescent under both longwave and shortwave ultraviolet illumination. It has a Mohs hardness of ~2 and exhibits brittle tenacity with perfect cleavage on {010}, imperfect cleavage on {100}, and even fracture. The calculated density is 5.853 g/cm³ based on the empirical formula. Electron probe microanalysis provided the empirical formula $\text{Pb}_{1.290}\text{U}^{6+}_{4.876}\text{U}^{5+}_{1.166}\text{O}_{27}\text{H}_{16.633}$ based on 27 O *apfu* and U^{5+} · U^{6+} determined by X-ray photoelectron spectroscopy. Shinkolobweite is orthorhombic, superspace group *Pnnm*(0b0)000, $a = 14.4808(4)$, $b = 7.0681(8)$, $c = 11.9423(3)$ Å, $V = 1222.32(15)$ Å³, modulation wave vector [0 1/3 0], and $Z = 2$. The structure was refined from 8959 reflections to a final $R_1 = 0.0736$ for all reflections. Uranyl oxide-hydroxide sheets in shinkolobweite adopt the β - U_3O_8 topology and possess (3 + 1) commensurately modulated ordering that results from the long-range ordering of U^{5+} and U^{6+} in the sheet, as well as the position and occupancy of interlayer Pb^{2+} cations. Observations of a topological transition between α - U_3O_8 and β - U_3O_8 type sheets in shinkolobweite supplements our understanding of U^{5+} mineral oxidation and stability.

Keywords: shinkolobweite, crystal structure, new mineral, pentavalent uranium, modulation, uraninite.

[§] Corresponding author e-mail address: oldst@carnegiemnh.org

INTRODUCTION

Uranium in Earth's crust is primarily present in the U^{4+} and U^{6+} oxidation states; the former occurs abundantly in the oxide mineral uraninite, UO_2 , and constitutes much of the crustal uranium inventory. Janeczek & Ewing (1992) noted that uraninite is inherently oxidized beyond its ideal stoichiometry, UO_{2+x} , and it is well-known that further oxidation produces the stable and soluble hexavalent uranyl ion $(U^{6+}O_2)^{2+}$, found in more than 250 minerals (Lussier *et al.* 2016). The rare pentavalent oxidation state is also accessible by the one-electron oxidation of U^{4+} , but at standard conditions, U^{5+} is unstable to disproportionation, forming U^{4+} and U^{6+} . Significant synthetic efforts to stabilize U^{5+} have been made (Arnold *et al.* 2009, Graves & Kiplinger 2009) and bioremediation strategies designed to reduce U^{6+} -bearing solutions are known to depend on the intermediate U^{5+} valence state (Suzuki *et al.* 2002, Renshaw *et al.* 2005). When adsorbed to the surface of mica (Ilton *et al.* 2005), U^{5+} is stable for only short periods (~ 20 h), and in most geochemical systems, it is considered metastable with respect to the significantly more stable U^{6+} and U^{4+} valence states. The metastability of U^{5+} observed in laboratory experiments is reflected in its mineralogy as well: all known uranium minerals containing essential U^{5+} are found as mixed-valence U species (U^{5+} and U^{6+}), and, with the description of shinkolobweite, there are now five minerals known to contain essential U^{5+} , all possessing sheet-like structures. These include wyartite (Burns & Finch 1999), dehydrated wyartite "wyartite-II" (Hawthorne *et al.* 2006), richetite (Plášil 2017), and nollmotzite (Plášil *et al.* 2018a). In addition, the mixed-valence uranium mineral, ianthinite, may contain U^{5+} , resulting from the oxidation of U^{4+} in its structure (Table 1).

Ianthinite and wyartite are susceptible to oxidation under typical storage conditions and do so at seemingly different rates on exposure to air and, allegedly, on exposure to light, suggesting an underlying complexity to the crystal chemistry and stability of mixed-valence U minerals (Burns *et al.* 1997b). Over time, both minerals develop micrometer-sized oxidized domains that are difficult to characterize, but on a crystal-structure basis, the oxidation products are found to closely resemble schoepite or metaschoepite (ianthinite) and urancalcrite (wyartite). The understanding of the oxidation and stability of minerals containing U^{5+} remains underdeveloped; however, that U^{5+} has persisted in these minerals on a geological time scale, possibly more than 100,000 years, reinforces the concept that crystallization is the most effective method for long-term stabilization of this rarely encountered oxidation state. Herein, U^{5+} is investigated in the crystal structure of

the new mineral shinkolobweite, documenting the first known case of modulated ordering that arises due to differences in the oxidation state of uranium.

The name shinkolobweite is for its type locality, the Shinkolobwe mine, Democratic Republic of Congo. Although it has been sealed for over 40 years, specimens recovered from the Shinkolobwe mine remain a prolific source for knowledge of uranium mineralogy and continue to serve as a natural analogue for the advancement of nuclear science. Interestingly, the name "chinkolobwite" was first penned by Schoep (1923) in his description of the (then) newly discovered U-Si phase that was later defined as sklodowskite (Schoep 1926). The name shinkolobweite and its status as a new mineral were approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA2016-095). The holotype specimen is deposited in the collections of the Canadian Museum of Nature with the catalogue number CMNMC 86897. Several crystals from the holotype specimen are also deposited in the Natural History Museum of Los Angeles County under catalogue number 65618.

OCCURRENCE AND ASSOCIATED MINERALS

Shinkolobweite occurs on a specimen of massive uraninite from the Shinkolobwe mine, Democratic Republic of Congo, housed at the Canadian Museum of Nature in Ottawa, Canada. The specimen was part of the personal collection of the late collector William W. Pinch, who in turn may have obtained the specimen from Belgian geologist and mineralogist Gilbert Gauthier. The specimen was originally labeled as "richetite & sayrite, Shinkolobwe, Zaire" and consists of massive uraninite that is richly mineralized with other secondary U minerals, including fourmarierite, rutherfordine, soddyite, and sklodowskite. Neither richetite nor sayrite were identified on the sample; nevertheless, additional specimens of shinkolobweite from the type locality have been confirmed from private collections, and it is suspected that other misidentified or incorrectly labeled specimens may exist.

Uranium deposition at the Shinkolobwe mine is known to have followed the emplacement of Cu and Co ores, and U-bearing heterogenite from the region has been dated to 623 ± 23 Ma (Deliens 1974) and between ~ 650 Ma and 850 Ma (Decree *et al.* 2014). Though a radiometric age range was not determined for crystals of shinkolobweite in this study, the new mineral may be among the secondary minerals that first crystallized in the assemblage and is likely to be no younger than $\sim 100,000$ years, based on U-series activity dating of paragenetically related minerals (Finch *et al.* 1996). Shinkolobweite was likely formed

TABLE 1. STRUCTURAL AND COMPOSITIONAL DETAILS FOR SHINKOLOBWEITE AND RELATED MINERALS

Mineral	Formula	$Me^{(a)}:U$	Topology	Ref.
Mixed valence				
Shinkolobweite	$Pb_{1.333}[U^VO(OH)(UO_2)_5O_{4.67}(OH)_{5.33}](H_2O)_5$	1:4.5	$\beta/\alpha-U_3O_8$	1
richetite	$(Fe^{2+},Mg)_{0.5}Pb_{4.5}[(U^V(UO_2)_{17}O_{18}(OH)_{14})(H_2O)_{\sim 19.5}]$	1:3.6	$\alpha-U_3O_8$	2, 3
wyartite	$Ca[U^V(UO_2)_2(CO_3)O_4(OH)](H_2O)_7$	1:3	$\beta-U_3O_8$	4
wyartite-II	$Ca[U^V(UO_2)_2(CO_3)O_4(OH)](H_2O)_3$	1:3	$\beta-U_3O_8$	5
nollmotzite	$Mg[U^V(UO_2)_2O_4F_3](H_2O)_4$	1:3	$\beta-U_3O_8$	6
ianthinite	$[U^{IV}_2(UO_2)_4O_6(OH)_4(H_2O)_4](H_2O)_5$	0	$\beta-U_3O_8$	7
U^{6+} only				
fourmarierite	$Pb[(UO_2)_4O_3(OH)_4](H_2O)_4$	1:4	fourmarierite	8, 9
compreignacite	$K_2[(UO_2)_3O_2(OH)_3]_2(H_2O)_7$	1:3	$\alpha-U_3O_8$	10
masuyite	$Pb[(UO_2)_3O_3(OH)_2](H_2O)_3$	1:3	$\alpha-U_3O_8$	11
protasite	$Ba(UO_2)_3O_3(OH)_2 \cdot 3H_2O$	1:3	$\alpha-U_3O_8$	12
sayrite	$Pb_2[(UO_2)_5O_6(OH)_2](H_2O)_4$	1:2.5	sayrite	13
rameauite	$K_2Ca(UO_2)_6O_6(OH)_4 \cdot 6H_2O$	1:2	$\beta-U_3O_8$	14
spriggite	$Pb_3[(UO_2)_6O_8(OH)_2](H_2O)_3$	1:2	$\beta-U_3O_8$	15

(a) Me = cation (Ca, Fe, Mg, K, Ba, Pb).

(1) This work, (2) Burns (1998a), (3) Plášil (2017), (4) Burns & Finch (1999), (5) Hawthorne *et al.* (2006), (6) Plášil *et al.* (2018a), (7) Burns *et al.* (1997b), (8) Piret (1984), (9) Li & Burns (2000), (10) Burns (1998b), (11) Burns & Hanchar (1999), (12) Pagoaga *et al.* (1987), (13) Piret *et al.* (1983), (14) Plášil *et al.* (2016), (15) Brugger *et al.* (2004).

during the initial alteration stages of uraninite when the system exhausted available O_2 , leading to an incomplete oxidation of uraninite, or partial reduction of U^{6+} , these favoring the persistence of appreciable concentrations of U^{5+} in solution. In agreement with inferences given by Burns *et al.* (1997b) made in relation to the formation of ianthinite, coatings of the uranyl carbonate rutherfordine, which is found in close association with shinkolobweite, may suggest that bacterial respiration or decomposition produced locally reducing conditions that favored formation of U^{5+} . Additionally, a recent re-examination of richetite reveals that it contains U^{5+} , so it may be posited that the redox coupling of U with $Fe^{2+} \leftrightarrow Fe^{3+}$ may have produced the reducing conditions necessary for its crystallization (Plášil 2017). The presence of Fe-bearing minerals in association with shinkolobweite was not observed in this study, although direct contact with the surface of uraninite, where the activity of U^{5+} and radiogenic Pb were highest, appears to have been essential for the formation of the shinkolobweite.

PHYSICAL AND OPTICAL PROPERTIES

Shinkolobweite occurs as deep reddish-brown prismatic and bladed crystals measuring up to 0.5 mm in length (Figs. 1, 2). Crystals are flattened on {010}, elongated on [001], and exhibit the forms {100}, {010}, {101}, and {10 $\bar{1}$ }. Shinkolobweite crystals are translucent with a subadamantine luster and a light

bronze-yellow streak and are non-fluorescent under both longwave and shortwave ultraviolet illumination. The mineral slowly dissolves in dilute HCl, initially turning yellowish orange, possibly due to the oxidation of U^{5+} . The Mohs hardness is estimated to be about 2 based on scratch tests. Crystals of shinkolobweite have a brittle tenacity with perfect cleavage on {100} and imperfect cleavage on {010} and exhibit an even fracture. The density could not be measured because it exceeds that of known heavy

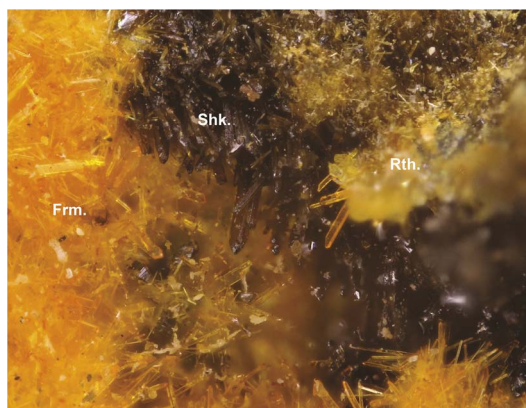


FIG. 1. Dark reddish-brown prisms of shinkolobweite (Shk.), orange fourmarierite (Frm.), and pale rutherfordine (Rth.) atop massive uraninite (not visible). Horizontal field of view is 1.0 mm.

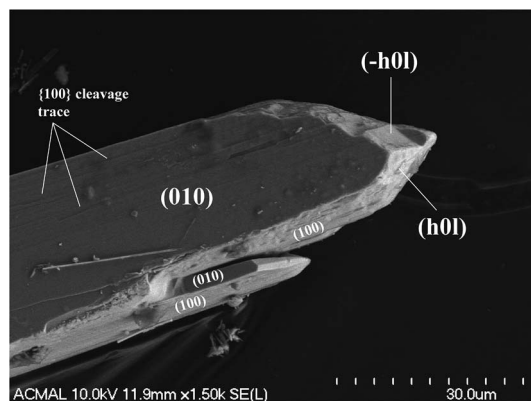


FIG. 2. Secondary electron image of an aggregate of shinkolobweite showing complex termination. Use of general Miller index notation for some faces is due to the fact that interfacial angles were not precisely determined for this sample.

liquids. The calculated density is 5.853 g/cm^3 based on the empirical formula and 5.850 g/cm^3 for the ideal formula.

Optically, shinkolobweite is biaxial (+), with $\alpha = 1.865(5)$, $\beta = 1.875(5)$, and $\gamma = 1.890(5)$ (measured in white light). The measured $2V$ is $77(1)^\circ$, based on extinction data collected using a spindle stage and analyzed by EXCALIBUR (Gunter *et al.* 2004), and the calculated $2V$ is 79° . Dispersion is extreme, $r \gg v$. The mineral is pleochroic with X = orange yellow, Y = yellow brown, and Z = dark olive green; $X < Y \ll Z$. The optical orientation is $X = c$, $Y = a$, $Z = b$. The Gladstone-Dale compatibility (Mandarino 2007), $1 - (K_p/K_c)$, is -0.009 (superior) for the ideal formula, and -0.003 (superior) for the empirical formula using $k(\text{UO}_3) = 0.134$, as given by Larsen (1921).

INFRARED SPECTROSCOPY

The attenuated total reflectance (ATR) Fourier transform infrared (FTIR) spectrum was obtained using a liquid N_2 cooled SENSIR Technologies IlluminatIR mounted to an Olympus BX51 microscope. An ATR objective was pressed into crystals of shinkolobweite and its spectrum, shown in Figure 3, was measured from 4000 to 650 cm^{-1} . The following spectral assignments are based primarily upon those summarized by Čejka (1999) for uranyl oxide hydrates. The broad and moderately intense band centered near 3050 cm^{-1} with a shoulder at 3570 cm^{-1} is assigned to the $\nu \text{ O-H}$ stretching vibrations of hydrogen-bonded water molecules and hydroxide groups. Approximate $\text{O-H}\cdots\text{O}$ hydrogen bond lengths calculated from the

observed stretching frequencies lie within the range ~ 3.0 to $2.6 \text{ \AA}$ using the empirical correlation derived by Libowitzky (1999). Several broad, weak intensity bands found between 2280 and 1980 cm^{-1} may correspond to combination bands (*i.e.*, vibrations excited simultaneously). The broad band observed at 1597 cm^{-1} is assigned to the $\nu_2(\delta)$ bending vibration of H_2O groups. A weak shoulder at 1423 cm^{-1} can be assigned to either $\delta \text{ U-OH}$ bending or a combination band.

The antisymmetric stretch $\nu_3 (\text{UO}_2)^{2+}$ occurs at 957 cm^{-1} . This band is composed of a broadened tail at higher wavenumbers that is formed from several overlapping $\delta \text{ UOH}$ (in-plane) bending modes with fitted centers at 1123 , 1070 , and 1020 cm^{-1} (Fig. 3 inset). Several weak bands were fitted to the region from 850 to 650 cm^{-1} , including one centered at 841 cm^{-1} and assigned to the $\nu_1 (\text{UO}_2)^{2+}$ symmetric stretch. A coincidence between $\nu_1 (\text{UO}_2)^{2+}$ and $\nu_3 (\text{UO}_2)^{2+}$ stretching modes complicates assignment in this region, along with overlap of modes related to the long modulated axial $\text{U}^{5+}\text{-O}$ bonds. Belai *et al.* (2008) report the IR spectrum of a synthetic mixed-valence U^{5+} and U^{6+} compound that is chemically and structurally closely related to shinkolobweite and assign a band centered at 790 cm^{-1} in its spectrum to the stretching $\nu_3 \text{ U}^{5+}\text{-O}_{yl}$ mode. Several similar bands occur in this region in the spectrum of shinkolobweite; the fitted bands at 770 , 710 , and 670 cm^{-1} are assigned as either $\nu_3 \text{ U}^{5+}\text{-O}$, $\gamma \text{ U-OH}$ (out-of-plane bending), or H_2O libration modes. The bond lengths for the uranyl cations calculated using the empirical relation given by Bartlett & Cooney (1989) are $1.77 \text{ \AA}$ (ν_1) and $1.75 \text{ \AA}$ (ν_3).

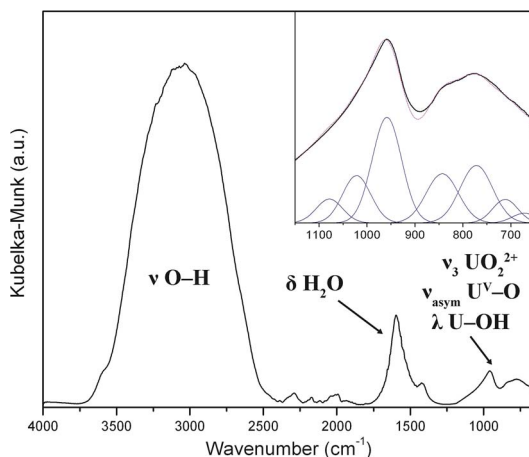


FIG. 3. The infrared (ATR) spectrum of shinkolobweite from 4000 to 650 cm^{-1} .

RAMAN SPECTROSCOPY

The Raman spectrum of shinkolobweite was measured using a Bruker Instruments Sentinel-785 laser head mounted on a Nikon Optiphot-2 microscope with Peltier-cooled integrated 785 nm diode laser, operated at 200 mW, with 100 μm spot size and $\sim 5\text{ cm}^{-1}$ resolution. The spectrometer was calibrated using software-controlled procedures (Opus software) from neon emission lines (wavelength calibration), and Tylenol[®] Raman bands (frequency calibration). A background correction was applied using the Opus software.

The Raman spectrum of shinkolobweite, collected from 1900 to 100 cm^{-1} , is shown in Figure 4. The $\nu_1(\text{UO}_2)^{2+}$ symmetric stretching vibration is present as a strong band at 823 cm^{-1} . Bartlett & Cooney (1989) provide an empirical relationship to derive the approximate U–O_{yl} bond lengths from the band positions assigned to the $(\text{UO}_2)^{2+}$ stretching vibrations, which gives 1.79 Å, in accordance with U–O_{yl} bond lengths given by others (Burns *et al.* 1997a, Lussier *et al.* 2016) for the uranyl cation in pentagonal bipyramidal coordination and agreeing well with the average U1–O_{yl} bond length of 1.78 Å from the structural data. The apical U(2)–O_{yl} ($\text{U}^{6+}/^{5+}$ –O) bond lengths from the structural data are variable due to modulation and range between ~ 1.79 and ~ 2.10 Å. A set of strong bands shouldering $\nu_1(\text{UO}_2)^{2+}$ at 779 and 751 and a separate strong band at 685 cm^{-1} may be connected to $\nu_1\text{U}^{5+}$ –O modes. The empirically calculated U–O_{yl} bond lengths for these bands are 1.83 Å (779), 1.86 Å (751), and 1.95 Å (685). We cannot, however, rule out coincidences of these three bands with out-of-plane γ U–OH bending vibrations or H₂O libration modes. The bands occurring at 562, 433, and 350 cm^{-1} are assigned as $\nu(\text{U–O}_{\text{ligand}})$ stretches and the doubly degenerate $\nu_2(\delta)(\text{UO}_2)^{2+}$ bending mode is found at 258 cm^{-1} . Remaining bands below 200 cm^{-1} are assigned to lattice vibration modes.

X-RAY PHOTOELECTRON SPECTROSCOPY

X-ray photoelectron spectroscopy (XPS) was used to determine the valence proportions of U in shinkolobweite by measuring U4f photoemission spectra with a PHI VersaProbe II X-Ray Photoelectron Spectrometer. Several crystals ($\sim 500 \times 100 \times 50\text{ }\mu\text{m}$) were selected and mounted onto carbon tape, cleaved on {100} to reveal a fresh surface, and immediately transferred to the vacuum chamber of the XPS. Spectra were collected at high resolution with monochromatic AlK α radiation using a pass energy of 93.9 eV and a 100 μm spot size. Surface charge neutralization was performed automatically, and spectra were collected for U4f and C1s photoelectrons. No measurable beam-

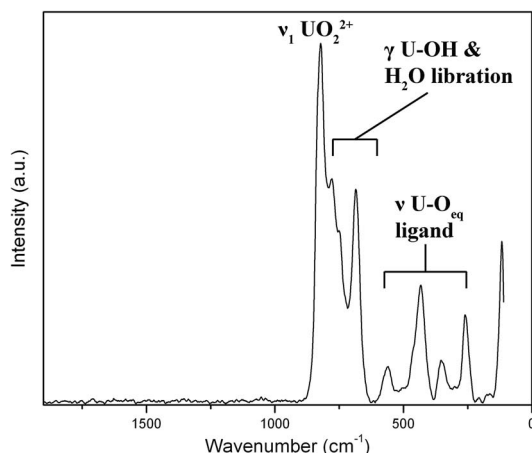


FIG. 4. The Raman spectrum of shinkolobweite taken with a 532 nm laser collected from 1900 to 100 cm^{-1} .

induced reduction of U^{6+} was observed for freshly cleaved crystals of fourmarierite measured alongside shinkolobweite.

The measured binding energies were referenced by fixing the position of adventitious C1s to 285.0 eV. A Shirley background (Shirley 1972) and asymmetric peak shape profile were used to model fitted bands under the envelopes of U4f electrons (376–407 eV) and their corresponding satellite peaks (400–420 eV). Satellite peak positions are best used to determine the oxidation state of uranium, as shown by Ilton *et al.* (2007) and Schindler *et al.* (2009). The satellite peak these authors attribute to the presence of U^{5+} occurs near ~ 400 eV, approximately ~ 8 eV upfield from the U4f_{5/2} peak that occurs near 382 eV. This satellite peak is readily evident in the spectrum of shinkolobweite and confirms the presence of mixed-valence states of uranium (Fig. 5). Peak fittings give an average $\text{U}^{5+}:\text{U}^{6+}$ ratio of $\sim 24\%$ based on area ratios.

CHEMICAL DATA

Chemical analyses ($n = 5$) were performed using a Cameca SX50 electron microprobe operated at 15 kV, 30 nA, with a 1 μm beam diameter (Table 2). Matrix effects were accounted for using the PAP correction routine (Pouchou & Pichoir 1985). Due to the limited amount of material available, the H₂O content was not measured and is instead calculated by stoichiometry (27 O *apfu*) with OH adjusted to achieve charge balance. No other elements were present above detection limits. The empirical formula, calculated on the basis of $\text{UO}_{2.5}/\text{UO}_3 = 0.24$ set by the XPS fitting, with 27 O *apfu* is $\text{Pb}_{1.29}\text{U}^{6+}_{4.88}\text{U}^{5+}_{1.17}\text{O}_{27}\text{H}_{16.63}$.

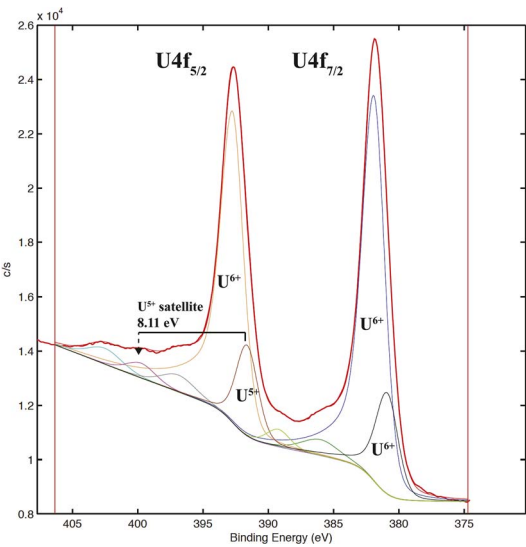


FIG. 5. X-ray photoelectron spectrum of the U4f electron region for shinkolobweite.

The ideal formula, based on the structural and spectroscopic considerations presented above, is $\text{Pb}_{1.333}[\text{U}^{5+}\text{O}(\text{OH})(\text{UO}_2)_5\text{O}_{4.67}(\text{OH})_{5.33}](\text{H}_2\text{O})_5$, which requires, ideally, UO_3 66.43, $\text{UO}_{2.5}$ 12.92 (RUO_3 79.72), PbO 13.82, H_2O 6.83, for a total 100.00 wt.%. Table 2 shows the final formula calculations based on 27 anions. For comparison, formula calculations are given for two relevant ratios of $[\text{U}^{5+}/\text{U}^{6+}]$: (1) 0.20, which corresponds to the ideal structural formula, and (2) 0.24, which corresponds to the ratio derived from XPS analyses. We note the differences between these results to be of little significance.

POWDER X-RAY DIFFRACTION

Powder X-ray diffraction data were recorded using a Rigaku R-Axis Rapid II curved imaging plate microdiffractometer with monochromatized $\text{MoK}\alpha$ radiation. A Gandolfi-like motion on the φ and ω axes was used to randomize the sample orientation. Observed d values and intensities were derived by profile fitting using JADE 2010 software (Materials Data, Inc.). The data are provided in the Supplementary material¹. The space group $Pn\bar{m}m$ was chosen to index the powder diffraction data by fitting to the average structure obtained from single-

crystal X-ray data. This led to a slightly larger indexed cell and the omission of several weak satellite peaks. Unit-cell parameters refined from the powder data using whole pattern fitting in JADE 2010 are as follows: $a = 14.551(6)$ Å, $b = 7.083(3)$ Å, $c = 11.988(5)$ Å, $V = 1235.6(9)$ Å³.

SINGLE-CRYSTAL X-RAY DIFFRACTION

Data were collected from a small crystal fragment ($25 \times 30 \times 160$ μm) mounted to a glass fiber using a Rigaku SuperNova diffractometer equipped with an Atlas S2 CCD detector and microfocus source utilizing monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073$ Å) at room temperature. Corrections for background, Lorentz, and polarization effects were applied using the *CrysAlis* package (Rigaku Oxford Diffraction Ltd, Oxfordshire, UK). An absorption correction was made using empirical scaling in the Jana2020 program. Initial attempts to solve the average structure were made in the orthorhombic space group *Immm* with a tripled c parameter using data obtained from a $\text{MoK}\alpha$ X-ray microfocus source and an Apex II CCD-based detector mounted to a Bruker Apex II Quazar three-circle diffractometer, but this route led to a poor refinement ($R_1 = 0.15$) and

TABLE 2. ELECTRON MICROPROBE DATA AND *apfu* CALCULATIONS FOR SHINKOLOBWEITE

	U ⁵⁺ /U ⁶⁺	0.20	0.24	
		wt.% Ox.		± ^(b)
	UO ₃	67.47	65.30	
	U ₂ O ₅	13.07	15.18	
	ΣUO ₃	80.91(26)		0.30
	PbO	13.48(45)		0.42
(a)	H ₂ O <i>h</i>	2.68	2.67	
(a)	H ₂ O <i>w</i>	4.24	4.22	
	ΣH ₂ O	6.92	6.89	
	Σ	100.94	100.85	0.72
		<i>apfu</i> ^(c)		±
	ΣU	6.016	6.042	0.023
	U(1)			
	U ⁶⁺	4.016	4.042	
	U(2)			
	U ⁵⁺	1	1.166	
	U ⁶⁺	1	0.834	
	Pb(1) b(1) Pb(1)			
	Pb	1.284	1.290	0.042
	(OH)	6.333		
	H ₂ O	5.000		
	Pb _{SREF}	1.284(2)		

(a) calculated by stoichiometry: (*h*, OH) and (*w*, H₂O); (b) indicates observed range of 5 EMP analyses; (c) normalized on 27 anions. Analytical standards: UO_{2(syn.)}; PbS.

¹ Supplementary Data are available from the Depository of Unpublished Data on the MAC website (<http://mineralogical.association.ca/>), document “Shinkolobweite, CM61, 23-00003”.

TABLE 3. DATA COLLECTION AND STRUCTURE REFINEMENT DETAILS FOR SHINKOLOBWEITE

Diffractionmeter	Rigaku SuperNova w/Atlas S2 CCD
X-ray radiation/power	MoK α (λ = 0.71073 Å)/50 kV, 60 mA
Temperature	298(2) K
Structural Formula	Pb _{1.284} U ₆ O _{27.392}
Superspace group	<i>Pnnm</i> (0 <i>b</i> 0)000
Unit-cell dimensions	<i>a</i> = 14.4808(4) Å <i>b</i> = 7.0681(8) Å <i>c</i> = 11.9423(3) Å
Modulation wave vector (q ₁)	1/3 b *
<i>V</i>	1222.32(15) Å ³
<i>Z</i>	2
Density (for above formula)	5.801 g/cm ³
Absorption coefficient	48.521 mm ⁻¹
<i>F</i> (000)	1759
Crystal size	25 × 30 × 160 μm
θ range	2.38 to 28.18°
Index ranges (up to 1 st order satellites)	−19 ≤ <i>h</i> ≤ 19, −9 ≤ <i>k</i> ≤ 9, −15 ≤ <i>l</i> ≤ 15, −1 ≤ <i>m</i> ≤ 1
Reflections independent/observed	8959/6963; <i>R</i> _{int} = 0.0502
Reflections with <i>I</i> _{obs} > 3σ(<i>I</i>)	3936
Completeness to θ_{max} = 28.18°	98%
Refinement method	Full-matrix least-squares on <i>F</i> ²
Parameters refined (restraints/constraints)	313 (0/0)
GoF(obs/all)	2.67/2.46
<i>R</i> factors for all reflections (8959)	
<i>R</i> _{obs} , <i>wR</i> _{obs}	0.0736, 0.1685
<i>R</i> _{all} , <i>wR</i> _{all}	0.0930, 0.1773
<i>R</i> factors for main reflections (2981)	
<i>R</i> _{obs} , <i>wR</i> _{obs}	0.0570, 0.1447
<i>R</i> _{all} , <i>wR</i> _{all}	0.0665, 0.1507
<i>R</i> factors for satellites (5978)	
<i>R</i> _{obs} , <i>wR</i> _{obs}	0.0985, 0.1956
<i>R</i> _{all} , <i>wR</i> _{all}	0.1304, 0.2071
Twin fraction	0.46(3)/0.54(3)
Largest diff. peak/hole	+16.32/−9.84 e Å ⁻³

reflections responsible for tripling the *c*-axis were found to result from commensurate modulation. A 1D *q*-vector (*q* = 1/3**b***) was derived from the data obtained on the Rigaku SuperNova, and an initial model in the (3 + 1)-dimensional superspace group *Pnnm*(0*b*0)000 was produced using the charge-flipping method *Superflip* (Palatinus & Chapuis 2007) and subsequently refined within Jana2020, the successor of the Jana2006 program (Petríček *et al.* 2014). Displacive (positional) modulation was applied to all atoms, modulation involving anisotropic displacement parameters were used for the U and Pb atoms, and occupancy modulation was applied to all atoms except O5, O6, O7, O8, and O9. Twinning by inversion was refined using the matrix [$\bar{1}$ 0 0/0 $\bar{1}$ 0/0 0 $\bar{1}$; 0.46(3) : 0.54(3)]. Other details regarding the data collection and refinement results are given in Table 3, average atomic coordinates and anisotropic displacement parameters are in Table 4, selected interatomic distances are in Table 5, and a bond-

valence analysis is in Table 6. Bond-valence analysis was performed with the DIST calculation in the Jana2020 program, using the parameters of Gagné & Hawthorne (2015) for U⁶⁺–O, U⁵⁺–O, and Pb²⁺–O. Hydrogen atoms could not be located; therefore, no discussion regarding hydrogen bonding is presented.

THE AVERAGE CRYSTAL STRUCTURE

The basic structural elements of shinkolobweite consist of sheets of edge- and vertex-sharing uranyl polyhedra, adopting the configuration observed in minerals with either α- or β-U₃O₈ sheets (Table 1). These sheets are separated by an interlayer consisting of Pb²⁺ cations and H₂O groups. The complete average structure is illustrated in Figure 6, and the individual structural components are illustrated in Figure 7, with details discussed below.

TABLE 4. ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS ($\text{\AA}^2$) FOR THE AVERAGE STRUCTURE OF SHINKOLOBWEITE

Atoms	SOF	x	y	z	$U_{\text{eq}}/U_{\text{iso}}$	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
U1		0.74059(2)	0.50060(3)	0.18919(3)	0.01496(12)	0.0247(2)	0.0088(2)	0.0114(2)	-0.00081(11)	-0.00001(10)	-0.00055(8)
U2		0.26695(4)	0.01315(8)	0	0.0301(2)	0.0274(3)	0.0560(4)	0.0069(2)	0.0086(3)	0	0
Pb1	0.321(2)	0.0003(2)	0.1658(5)	0.1288(4)	0.098(3)	0.054(3)	0.084(3)	0.157(8)	-0.011(2)	0.035(4)	-0.027(4)
O2		0.5102(6)	0.1722(17)	0.1691(9)	0.066(5)						
O2'	0.49(2)	0.5	0	0.0902(19)	0.015(4)						
O3		0.3996(9)	0.0360(14)	0	0.057(3)						
O4		0.6203(5)	0.5171(7)	0.2223(6)	0.0341(16)						
O5		0.2788(5)	-0.1821(9)	0.1446(5)	0.0306(15)						
O6		0.2567(4)	0.1863(9)	0.1500(5)	0.0331(16)						
O7		0.6966(7)	0.5153(10)	0	0.030(2)						
O8		0.8588(5)	0.4848(7)	0.1541(6)	0.0333(16)						
O9		0.1357(8)	-0.0111(14)	0	0.051(3)						
O10		0	0	0.5	0.172(14)						

TABLE 5. SELECTED INTERATOMIC DISTANCES ($\text{\AA}$) IN THE COMMENSURATE STRUCTURE OF SHINKOLOBWEITE

Distance	Average	Minimum	Maximum
U1–O4	1.82(5)	1.79(5)	1.85(5)
U1–O5 ⁱ	2.46(2)	2.44(2)	2.51(2)
U1–O6 ^j	2.34(2)	2.27(2)	2.43(2)
U1–O7	2.35(2)	2.31(2)	2.38(2)
U1–O8	1.77(5)	1.77(5)	1.79(5)
U1–O5 ⁱⁱ	2.35(2)	2.26(2)	2.45(2)
U1–O6 ⁱⁱⁱ	2.31(2)	2.21(2)	2.41(2)
U2–O3	1.92(8)	1.81(8)	2.01(8)
U2–O5	2.21(2)	2.05(2)	2.36(2)
U2–O5 ^{iv}	2.21(2)	2.05(2)	2.36(2)
U2–O6	2.20(2)	2.13(2)	2.26(2)
U2–O6 ^{iv}	2.20(2)	2.13(2)	2.26(2)
U2–O9	1.94(7)	1.83(7)	2.11(7)
*U2–O7 ^v	3.46(4)	2.85(4)	3.80(4)
*U2–O7 ^{vi}	3.68(4)	3.03(4)	4.07(4)
Pb1–O2 ^{vii}	2.60(4)	2.58(4)	2.61(4)
Pb1–O4 ^{viii}	2.74(4)	2.56(4)	2.83(4)
Pb1–O8 ^{vi}	3.06(4)	2.87(5)	3.29(4)
Pb1–O9	2.78(5)	2.54(6)	2.92(6)
Pb1–O4 ^{viii}	2.69(4)	2.56(4)	2.78(4)
Pb1–O8 ⁱⁱⁱ	3.28(4)	2.96(4)	3.66(4)
Pb1–O9	2.81(6)	2.47(6)	3.08(6)
Pb1–Pb1 ^{iv}	3.21(2)	2.85(3)	3.58(3)
Pb1–Pb1	2.38(2)	2.25(2)	2.49(2)
Pb1–Pb1 ^{iv}	3.87(2)	3.77(2)	3.96(2)
Pb1–Pb1 ^{ix}	4.74(2)	4.37(2)	5.12(2)

Symmetry transformations used to generate equivalent atoms: (i) $x + 1/2, -y + 1/2, -z + 1/2$; (ii) $x + 1, y, z$; (iii) $x + 1, y + 1, z$; (iv) $x, y, -z$; (v) $x - 1, y - 1, z$; (vi) $x - 1, y, z$; (vii) $x - 1/2, -y + 1/2, -z + 1/2$; (viii) $x + 1/2, -y - 1/2, -z + 1/2$; (ix) $x, y + 1, z$.

* The bond between U2–O7 is only formed periodically.

α - U_3O_8 and β - U_3O_8 sheets

The cation-anion arrangement observed in the uranyl sheets of shinkolobweite is illustrated in Figure 7a [where apical uranyl ($-y/$) oxygen anions are omitted for clarity]. From this configuration, either α - U_3O_8 or β - U_3O_8 sheets may form (see minerals listed in Table 1). In the structure of shinkolobweite, the distribution of U–O bond lengths indicates β - U_3O_8 to be the dominant sheet topology. However, localized regions of the α - U_3O_8 sheet topology also appear to occur, a feature discussed in greater detail below.

In both α - and β -sheets, infinite, parallel chains of edge-sharing pentagonal bipyramids are linked by common vertices, resulting in the formation of elongated hexagonal voids. In each void, an additional uranium cation occurs in either pentagonal (in α -sheets; Fig. 7b)

TABLE 6. AVERAGE, MINIMUM, AND MAXIMUM BOND-VALENCE SUMS FOR ATOMS IN THE COMMENSURATELY MODULATED STRUCTURE OF SHINKOLOBWEITE

Atom	Average	Minimum	Maximum	Valence/type
U1	6.00(8)	5.91(8)	6.09(8)	U ⁶⁺
U2	5.51(4)	5.40(5)	5.59(5)	U ^{5+/6+}
Pb1	1.27(1)	1.03(1)	1.43(1)	Pb ²⁺
O2	0.09(1)	0.06(1)	0.15(1)	H ₂ O group
O2'	0.07(1)	0.06(1)	0.09(1)	H ₂ O group
O3	1.43(6)	1.13(9)	1.78(9)	O/OH _{yl} -U2
O4	1.76(3)	1.70(4)	1.84(4)	O _{yl} -U1
O5	1.73(1)	1.51(1)	2.04(1)	O/OH
O6	1.97(1)	1.89(1)	2.07(1)	O
O7	1.12(1)	0.99(1)	1.19(1)	OH
O8	1.82(4)	1.81(4)	1.85(4)	O _{yl} -U1
O9	1.65(5)	1.36(7)	1.85(7)	O/OH _{yl} -U2
O10	-	-	-	non-bonding H ₂ O group

or square (in β -sheets; Fig. 7c) bipyramidal coordination. Thus, two crystallographically distinct cation positions occur in the shinkolobweite uranyl sheet: chain-forming and hexagonal-void-occupying polyhedra coordinate the $U(1)$ and $U(2)$ sites, respectively.

Interlayer

In the interlayer (Fig. 7d), a single symmetrically unique cation position, $Pb(1)$, is arranged at the vertices of a rectangle. A [7]-coordinated, irregular polyhedron occurs around the $Pb(1)$ site. The interlayer also contains several disordered [$O(2)$, $O(10)$] and partially occupied [$O(2')$] anion positions; these sites constitute H₂O groups that periodically form bonds with Pb²⁺ as well as hydrogen bonds with O atoms of adjacent sheets.

CATION SITE OCCUPANCIES

The assignment of cations to the three cation sites, $U(1)$, $U(2)$, and $Pb(1)$, in shinkolobweite is generally straightforward, as U^{5+/6+} and Pb²⁺ can only be accommodated by the $U(1,2)$ and $Pb(1)$ sites, respectively, consistent with their observed geometries (Fig. 8). However, the distribution of U^{5+/6+} between $U(1,2)$ as well as the partial occupancy of Pb²⁺ at $Pb(1)$ requires more detailed consideration.

$U(1)$ and $U(2)$ sites

The calculated sum of U in shinkolobweite ranges from 6.016 to 6.042 *apfu* (Table 2), which is in accord with the sum of $U(1)$ - and $U(2)$ -positions in the crystal structure (*i.e.*, 6 *pfu*) and with both of these sites being fully occupied by U. Results from refinement of the crystal structure (Table 4) show no evidence supporting

fractional site occupancies for either position. For the $U(1)$ site, the incident bond-valence sum is 6.00(8) *vu* (Table 5), suggesting that all U is present as U⁶⁺. For the $U(2)$ site, the incident bond-valence sum is 5.51(4), suggesting an approximately equivalent distribution of U⁵⁺ and U⁶⁺. Such a distribution would yield [$^{U(2)}U^{5+}/^{U(1,2)}U^{6+}$] = [1/5] = 0.2, which is in good agreement with the value of 0.24 determined by XPS analysis. The assignment of U⁵⁺ to this site is consistent with its location in other phases containing uranium of mixed valence: *i.e.*, wyartite (Burns & Finch 1999), dehydrated wyartite ('wyartite-II'; Hawthorne *et al.* 2006), richetite (Burns 1998a, Plášil 2017), nollmotzite (Plášil *et al.* 2018a), and ianthinite (Burns *et al.* 1997b).

$Pb(1)$ site

In the shinkolobweite structure, the interlayer $Pb(1)$ site is the only one capable of accommodating Pb²⁺ cations. Results from SREF indicate incomplete occupancy at this site (Table 4). Good agreement is observed between the abundance of Pb at $Pb(1)$ determined by SREF and by EMP, *i.e.*, 1.284(8) and 1.29(4) *apfu*, respectively (Table 2), in accord with all Pb occurring at $Pb(1)$. The local bonding configuration about the $Pb(1)$ site is illustrated in Figure 8c. Each $Pb(1)$ site is [7]-coordinated, with five of the Pb–O bond lengths being short, at 2.62 Å [$O(2)$], 2.67 & 2.75 Å [$O(4)$], and 2.78 & 2.81 Å [$O(9)$], and two being long, at 3.04 [$O(8)$] and 3.24 Å [$O(8)$]. This distribution of bond lengths is consistent with Pb²⁺ cations having a stereochemically active lone pair of 6s² electrons, likely extending into the [$Pb(1)_4$] rectangle, approximately along the direction indicated by the blue arrow in Figure 8c.

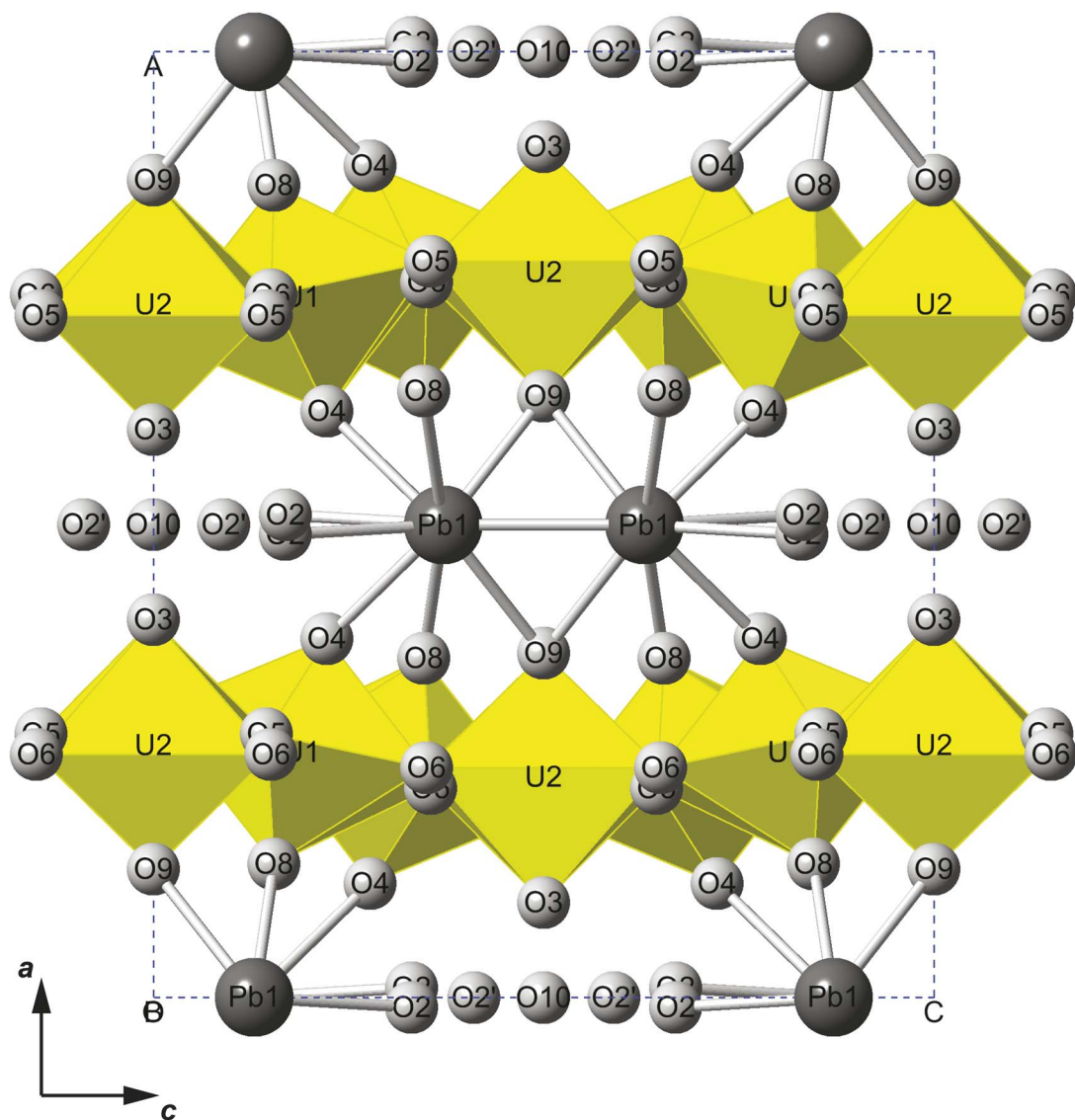


FIG. 6. The average shinkolobweite structure viewed along [010].

Similarities between interlayer cations in shinkolobweite and compreignacite

The crystal structures of compreignacite $[K_2[(UO_2)_3O_2(OH)_2](H_2O)_7]$ (Burns 1998b) and shinkolobweite are based on sheets of uranyl polyhedra with identical anion topologies (α - and β - U_3O_8 sheets, respectively). In both structures, interlayer cation sites define approximate rectangles of similar dimension, 3.1×2.1 and 3.1×2.2 Å, respectively. Crystal-structure refinements show these interlayer cation sites to be only

partially occupied by the respective cations, with $K(1) = (K_x \square_{4-x})$, $x \approx 0.49$ in compreignacite and $Pb(1) = (Pb_x \square_{4-x})$, $x = 1.284(8)$ in shinkolobweite. However, in compreignacite, where $K(1) = \square$, (H_2O) is observed to occupy an additional site, $O(10)$, located very close (~ 0.9 Å) to $K(1)$. This results in the rectangular cluster of the interlayer having the average composition $K_{0.5}(H_2O)_{0.5}$.

The structural similarities suggest a possibly analogous situation in the structure of shinkolobweite, where the occupancy of the $Pb(1)$ site may, in reality, be $[Pb_x$

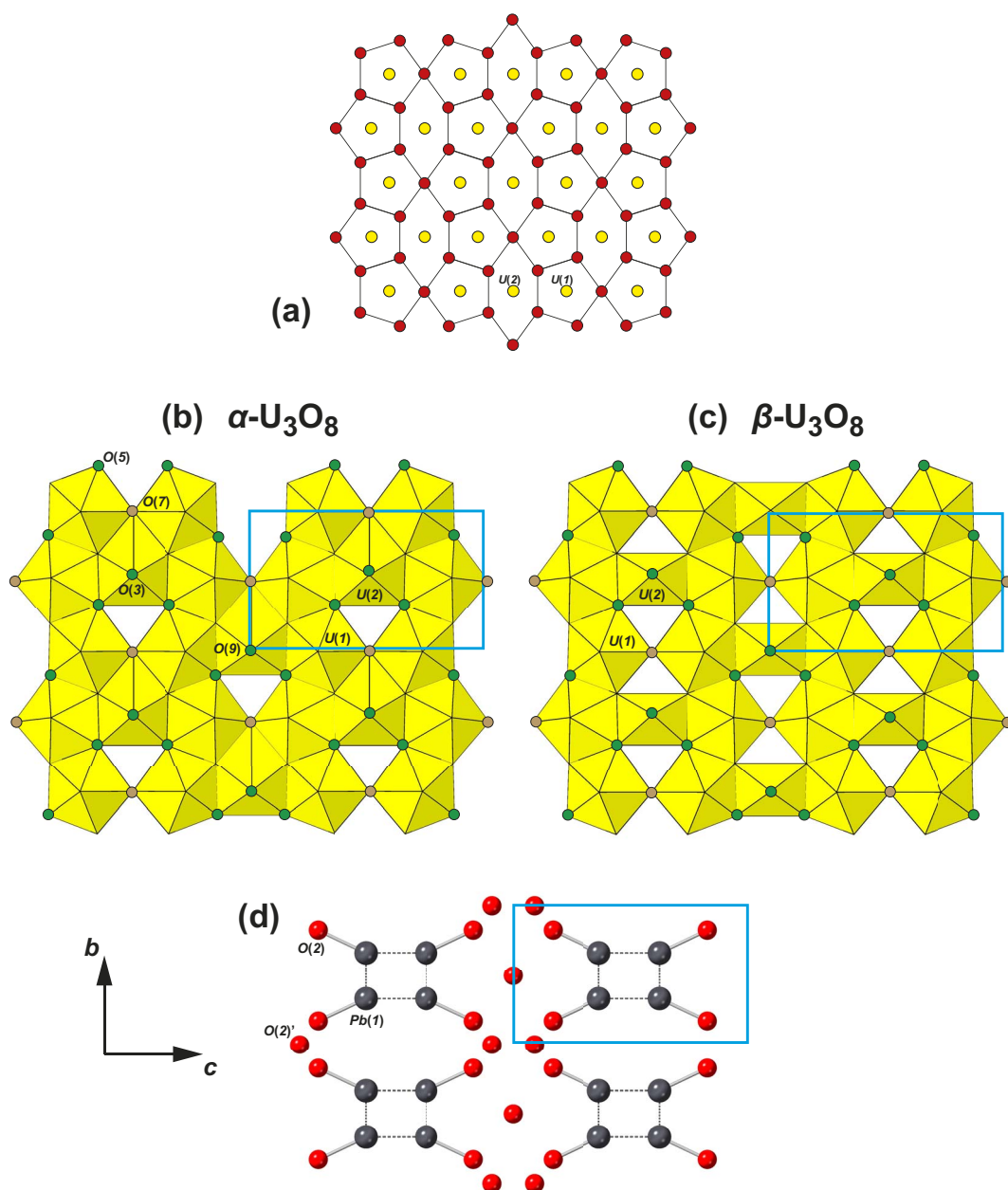


FIG. 7. Sheet components of the shinkolobweite structure projected along (001): (a–c) U_3O_8 layer, (d) interlayer. (a) A graphical representation of the sheet-anion topology of U_3O_8 sheets in shinkolobweite. Here, red and yellow nodes indicate anion and cation positions, respectively, while edges linking the anions occurring in $U(1)$ polyhedra [$U(2)$ polyhedra are not depicted]. (b) and (c) Polyhedral representations of α - and β - U_3O_8 sheets. Anion positions with (OH) and mixed $[(OH)_xO_{1-x}]$ occupancy are highlighted in green and brown, respectively (note: the dashed green circle indicates the position of an anion on the opposing side of the sheet and anions with complete O^{2-} occupancy are not highlighted). In (d), the configuration of the $Pb-(H_2O)$ interlayer is shown, emphasizing the occurrence of $\{Pb(1)_4\}$ rectangular clusters; the position of the fractionally occupied $O(2)'$ position is also indicated. The unit cell is outlined in blue.

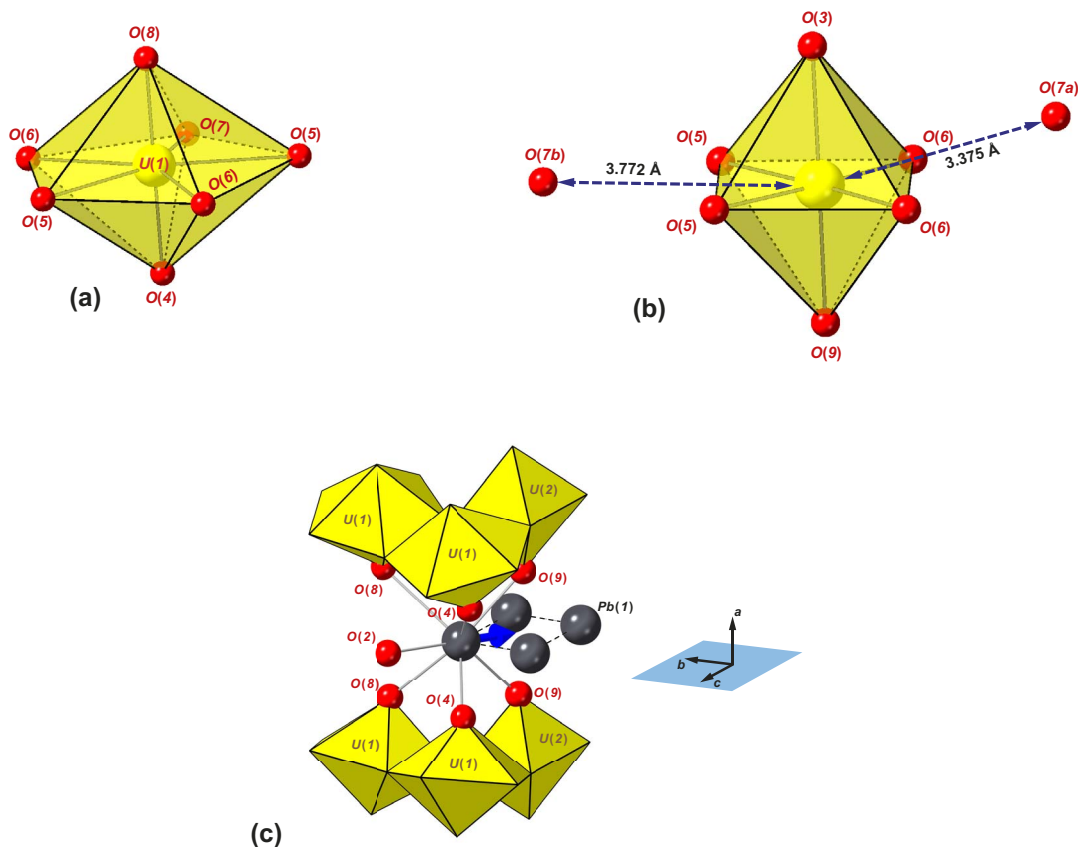


FIG. 8. Coordination polyhedra at the (a) $U(1)$, (b) $U(2)$, and (c) $Pb(1)$ sites. (b) Relative position of the $O(7a,b)$ sites: distances of the average structure are shown. In (c) the $\{Pb(1)_4\}$ cluster is shown, and the blue arrow indicates the probable orientation of the stereochemically active lone electron emanating from Pb^{2+} at $Pb(1)$.

$\Phi_{4-x}]$, where Φ indicates a generalized anion site occupancy [O^{2-} , $(OH)^-$, and O of H_2O groups]. However, as indicated above, the assignment of all Pb^{2+} to the $Pb(1)$ site accommodates the totality of observed scattering at this site. This is in accord with Pb being the only occupant of the $Pb(1)$ site and with remaining positions being vacant, *i.e.*, $Pb(1) = (Pb_x \square_{4-x})$. Further, no proximal (H_2O) positions, analogous to $O(10)$ in comignacite, are observed in shinkolobweite.

ANION SITE OCCUPANCIES IN THE U_3O_8 SHEETS

An investigation of incident bond-valence sums (Table 6) suggests variability in anion occupancy in the U_3O_8 sheets of the structural unit. Assuming an average O–H bond strength of ~ 0.8 *vu* (Hawthorne 1992), expected bond-valence sums at anion positions are 2.0, 1.2, and 0.4 *vu*, for full site occupancy by O^{2-} , $(OH)^-$, and (H_2O) , respectively. Seven crystallographically unique anion positions occur in the

shinkolobweite U_3O_8 sheet. At positions $O(4)$, $O(6)$, and $O(8)$, incident sums are here considered as reasonably close to 2.0 *vu* (>1.75 *vu*), in accord with complete O^{2-} occupancy. For positions, $O(3)$, $O(5)$, and $O(9)$, incident sums are between 1.2 and 2.0 *vu*, in accord with a mixed occupancy, *i.e.*, $(OH)_x O_{1-x}$. For the position $O(7)$, the incident sum is 1.12 *vu*, in accord with dominant (OH) occupancy. The location of these anion sites in the U_3O_8 sheets in shinkolobweite is shown in Figures 7b and c, with green and brown circles highlighting sites occupied by $[(OH)_x O_{1-x}]$ and $(OH)^-$, respectively (note: anion positions occupied solely by O^{2-} are not highlighted). For anion sites of composition $[(OH)_x O_{1-x}]$, the value of x could theoretically be calculated through linear combination of ideal valence sums, *i.e.*, $1.2x + 2.0(1 - x) = \Sigma'_{bv}$ (where Σ'_{bv} corresponds to the incident bond-valence sum at the i^{th} site). However, this approach is not pursued here, as accounting for strain in the modulated

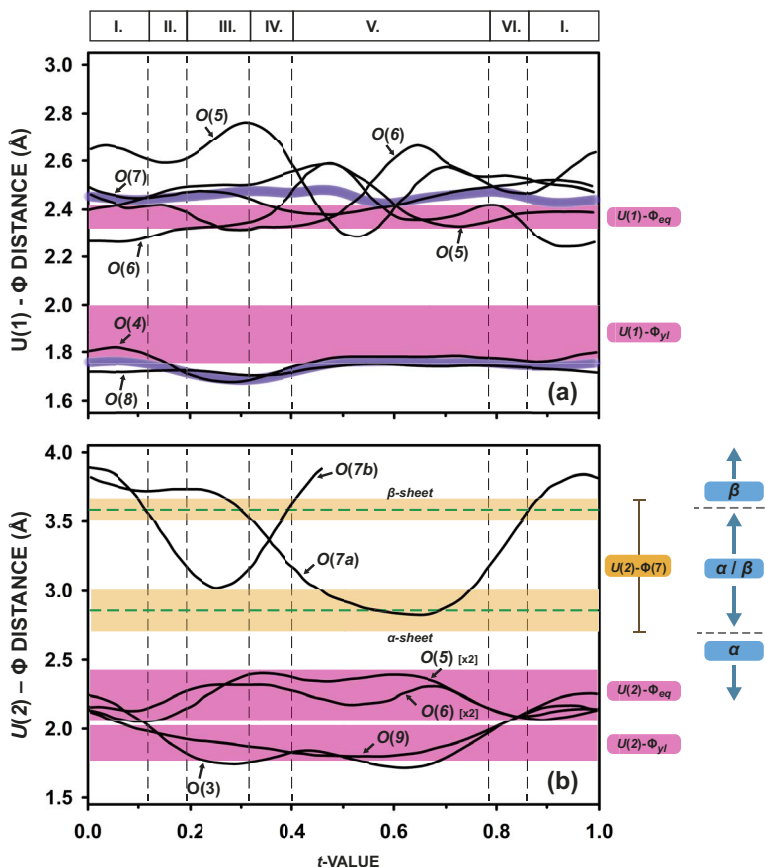


FIG. 9. Bond length variation as a function of structure modulation (t -value) for uranium positions in shinkolobweite: (a) $U(1)$ and (b) $U(2)$. Anion positions correspond to those illustrated in Figure 8. Shaded regions indicate mean values for bond lengths observed in other structures based on α - U_3O_8 and β - U_3O_8 sheets (taken from Lussier *et al.* 2017); pink shading – bond lengths for $-eq$ and $-yl$ bonds; orange shading – $U(2)-\Phi(7)$ distances. Averaged structures are given in Supplementary Table S2.

structure, which would affect both the ideal lengths and strengths of bonds, is not possible.

The disordered $O(2)'$ position

A highly disordered and low occupancy O atom of an H_2O group is located very near the $O(3)$ and $O(2)$ anions. The former is the $-yl$ anion position of the $U(2)$ site, whereas the latter is OH_2 and bonded to the $\text{Pb}(1)\text{Pb}^{2+}$. The $O(2)'$ site is located only 1.5 and ~ 1.8 Å from the $O(2)$ [x2] and $O(3)$ [x2] sites, respectively, which clearly precludes simultaneous occupancies. Structure refinement shows that both $O(2)$ and $O(3)$ sites are fully occupied by O^{2-} , and it is therefore suggested the $O(2)'$ site may represent highly disordered electron density associated with unresolved H atoms surrounding $O(2)$ and $O(3)$.

EFFECT OF MODULATION: U_3O_8 SHEETS

Uranium coordination polyhedra in shinkolobweite

Figure 9 shows the observed variation in U–O bond distances as a function of structure modulation in both $U(1)$ and $U(2)$ polyhedra. Figures 8a and b show a magnified region of the $U(1)$ and $U(2)$ coordination environments, respectively. In the U_3O_8 sheets, displacive modulation amplitudes are largest for the $U(2)$ site and its coordinated O atoms; along **a**, $U(2)$ and its equatorial anions $O(5)$ and $O(6)$ and the apical anion $O(9)$ show the largest displacements of all atoms in the structure as a function of the internal modulation parameter, t , which is also reflected in their respective bond distances (in Å) to one another [$-0.5 < O(5)_{da} < -0.4$; $-0.1 < O(6)_{da} < 0.5$; $-0.66 < O(9)_{da} < 0.46$]. Likewise, the atoms at the $O(9)$, $O(3)$, $U(2)$, and $O(7)$

sites have large displacements along the **b** axis as a function of *t*.

Ranges of observed bond lengths in analogous structures (*i.e.*, also based on α - and β -type sheets: Supplementary Table S2) are also indicated in Figure 9. In pink: averages (denoted by $\langle \rangle$) for both $\langle U-\Phi_{yl} \rangle$ and $\langle U-\Phi_{eq} \rangle$; in orange: averages for specific bond lengths for (those topologically equivalent to) $U-O(7a)$ and $U-O(7b)$. Comparing the bond lengths in shinkolobweite to the observed ranges in analogous structures allows for an improved understanding of variation in $U(1,2)$ site coordination states through structure modulation.

U(1) coordination. Figure 9a shows that, throughout superspace, the $U(1)$ position consistently occurs in pentagonal bipyramidal coordination. A total of seven cation–anion distances are observed to fall within a range consistent with bonding. Specifically, two distances [$U(1)-O(4)$ and $U(1)-O(8)$] show lengths consistent with those expected for $-yl$ bonds (*i.e.*, 1.7 to 1.8 Å), and five distances [$U(1)-O(7) \times 2$, $U(1)-O(5)$, and $2 \times U(1)-O(6)$] show lengths consistent with those expected for $-eq$ bonds (*i.e.*, 2.25 to 2.75 Å). The $U(1)$ pentagonal bipyramid is slightly distorted for all values of *t*, with $\langle U(1)-\Phi_{yl} \rangle$ and $\langle U(1)-\Phi_{eq} \rangle$ for shinkolobweite (thick blue lines: Fig. 9) being consistently larger and smaller than average values, respectively.

U(2) coordination. For the $U(2)$ polyhedron, bond length variation with modulation (Fig. 9b) shows a more complicated situation than in $U(1)$ polyhedra. In shinkolobweite, two [$U(2)-O(3)$ and $U(2)-O(9)$] and four [$2 \times U(2)-O(3)$, $2 \times U(2)-O(6)$] distances are consistent with $-yl$ and $-eq$ bonds, respectively. Conversely, the $U(2)-O(7a,b)$ distances remain significantly above expected mean values.

In shinkolobweite, $U(2)-O(7a,b)$ distances range continuously between ~ 2.8 and 3.7 Å, values that are generally in accord with the minima and maxima observed for α - and β - U_3O_8 sheets of other phases. As $U(2)-O(7)$ distances approach ~ 2.8 Å, it can be concluded that $U(2)$ occurs in pentagonal bipyramid coordination and that the sheet has α - U_3O_8 topology. Conversely, as $U(2)-O(7)$ distances approach ~ 3.6 Å, it can be concluded that $U(2)$ occurs in square bipyramid coordination and that the sheet has β - U_3O_8 topology. At intermediate values, $U(2)-O(7)$ distances may correspond to an averaging of bonding and non-bonding distances, suggesting the possible occurrence of both sheet topologies.

α_1 - and α_2 - U_3O_8 sheets. From the schematic depiction of the proximal $U(2)$ sheet environment in Figure 10, it is possible to see how bonds may develop between $^{U(2)}U$ and anions at either $O(7a)$ or $O(7b)$ sites, as the $U(2)$ site modulates within the hexagonal void.

These maximal modulated positions are schematically illustrated in Figure 10a. The occurrence of U at $U(2)_{\alpha 1}$ or $U(2)_{\alpha 2}$ results in the formation of $^{U(2)\alpha 1}U(2)-O(7a)$ and $^{U(2)\alpha 2}U-O(7b)$ bonds, respectively. Although both situations result in sheets with the α - U_3O_8 topology, they are effectively rotated 180° (about an axis perpendicular to the sheet) with respect to each other. In shinkolobweite, both $U(2)-O(7a)$ and $U(2)-O(7b)$ distances approach similar minimal values of 2.9 ($t \sim 0.6$) to 3.0 Å ($t \sim 0.25$; Fig. 9b), suggesting that the occurrence of both α_1 - and α_2 - U_3O_8 sheet orientations is possible.

$\alpha_{1,2}$ - and β -sheet distribution. Figure 9 may be divided into six (labeled I through VI) distinct regions based on the combination of occurring sheet types. Table 7 shows the general, qualitative abundances of each sheet using the following criteria:

- (1) Where $U(2)-O(7)$ approaches a minimum value (~ 2.9 Å);
 α - U_3O_8 sheet high abundance; β - U_3O_8 sheet topology low abundance.
 This situation occurs in Regions III (α_2 topology) and V (α_1 topology).
- (2) Where $2.7 < U(2)-O(7) < 3.6$ Å;
 α - and β - U_3O_8 sheet topologies of intermediate abundances. This situation occurs in Regions II (α_2 topology) and VI (α_1 topology). Region IV is the only one in which both the $U(2)-O(7a)$ and $U(2)-O(7b)$ are between the minimal and maximal values, indicating the simultaneous occurrence of sheet with α_1 and α_1 orientations.
- (3) Where $U(2)-O(7) > 3.6$ Å;
 α - U_3O_8 sheet low abundance; β - U_3O_8 sheet topology high abundance. This situation occurs in Region I.

EFFECT OF MODULATION: INTERLAYER

Modulation at the $Pb(1)$ site

Interlayer Pb^{2+} cations exhibit both positional and occupational modulation (Fig. 11). In the average structure, the cluster has the appearance of a nearly perfect rectangle (Figs. 7, 12a). However, with respect to modulation along the **c** axis, $Pb(1)$ exhibits the largest displacement of all atoms in the structure, $-0.5 < Pb(1)_{dc} < \sim 0.3$ (in Å), which results in significant changes in the $Pb(1)-Pb(1)$ distances within individual clusters (Fig. 11). The schematic illustrations in Figure 12 show the nature of $\{Pb(1)\}_4$ rectangle distortion with modulation. The changes in $Pb(1)-Pb(1)$ distances are such that the geometric configuration of the cluster becomes a trapezoid, constrained by the occurrence of a mirror

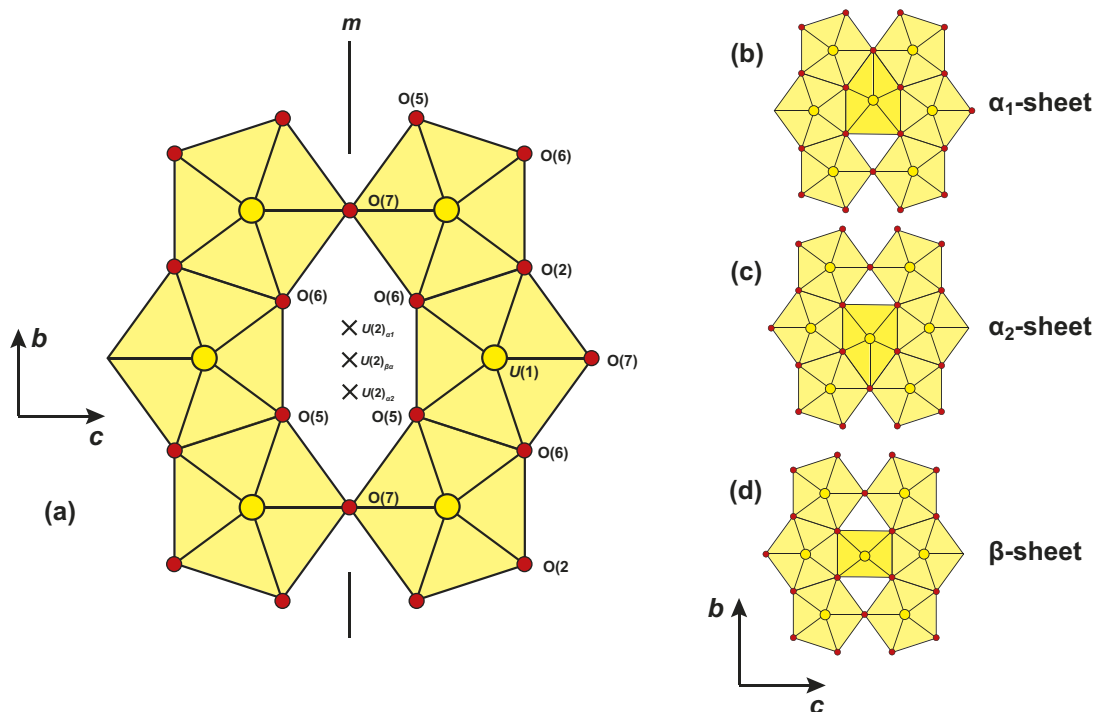


FIG. 10. Aspects of U_3O_8 sheet topology in shinkolobweite. (a) Chains of edge-sharing pentagonal bipyramids connect by common vertices to form voids in the shape of elongated hexagons. Three possible positions within the hexagonal void that may accommodate U are given by X: $U(2)_{\alpha 1}$, $U(2)_{\alpha 2}$, and $U(2)_{\beta}$. The occurrence of U at either of these sites results in the formation of sheets labeled as: (b) α_1 , (c) α_2 , and (d) β . For reference, uranium coordination polyhedra are also shown: (e) $U(1)$ and (f) $U(2)$. Selected distances from the averaged structure are shown.

plane perpendicular to (001). Particularly noteworthy is the large difference observed in the $Pb(1)^2-Pb(1)^3$ distance, the shortest being 2.1 Å (at $t \approx 0.2$) and the longest being 3.6 Å (at $t \approx 0.8$).

TABLE 7. DISTRIBUTION OF U_3O_8 SHEET TOPOLOGIES IN SHINKOLOBWEITE

Region (Fig. 9)	Rel. Ab.		
	α_1	α_2	β
I.	Red	Red	Green
II.	Purple	Red	Purple
III.	Green	Red	Purple
IV.	Purple	Purple	Purple
V.	Red	Green	Purple
VI.	Red	Purple	Purple

Ordering of Pb^{2+} ions in $\{Pb_x\Box_{4-x}\}$ clusters

In other sheet-type, Pb-bearing uranyl-oxide hydroxide-hydrate phases, such as gauthierite ($\{KPb(H_2O)_8\}[(UO_2)_7O_5(OH)_7]$; Olds *et al.* 2016), kroupaite ($\{KPb_{0.5}(H_2O)_{10}\}[(UO_2)_8O_4(OH)_{10}]$; Plášil *et al.* 2020), and fourmarierite ($\{Pb(H_2O)_4\}[(UO_2)_4O_3(OH)_4]$; Li & Burns 2000), the shortest distances between Pb atoms in the interlayer are 3.82, 3.95, and 4.15 Å, respectively. On this basis, it may be considered that in shinkolobweite, $Pb(1)-Pb(1)$ distances of ~ 4 Å are required for adjacent positions to be occupied by Pb^{2+} ions within a single $\{Pb_x\Box_{4-x}\}$ cluster.

With structure modulation, the configuration of each cluster in shinkolobweite departs from that of an ideal rectangle. Figure 11b shows the variation in individual $Pb(1)-Pb(1)$ distances over the entire range of modulations, $0 \leq t \leq 1$. Figure 12 shows a schematic representation of the average cluster configuration with individual positions differently

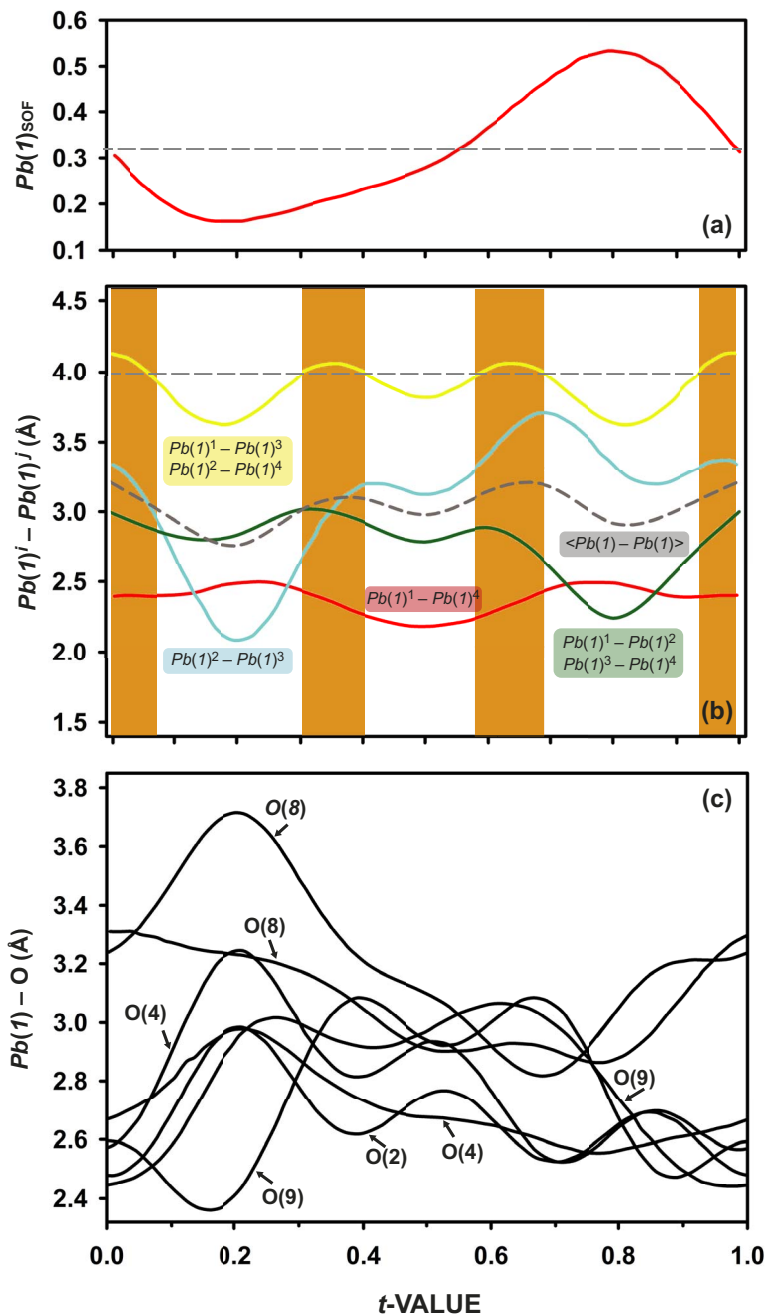


FIG. 11. The effect of modulation at the $Pb(1)$ site. Shown as a function of the modulation parameter, t : (a) the refined site-occupancy of the $Pb(1)$ site (note: the gray line indicates the average observed value of 0.32); (b) variation in distances between $Pb(1)$ sites in a rectangular tetramer; (c) variation in $Pb(1) - O(i)$ distances. In (b) dashed gray lines show mean values, and line-colors correspond to the schematic illustration in Figure 9; the orange highlighted regions correspond to those where $\{Pb_2\Box_2\}$ clusters are likely to occur. The coordination geometry about $Pb(1)$ is illustrated in Figures 6 and 10.

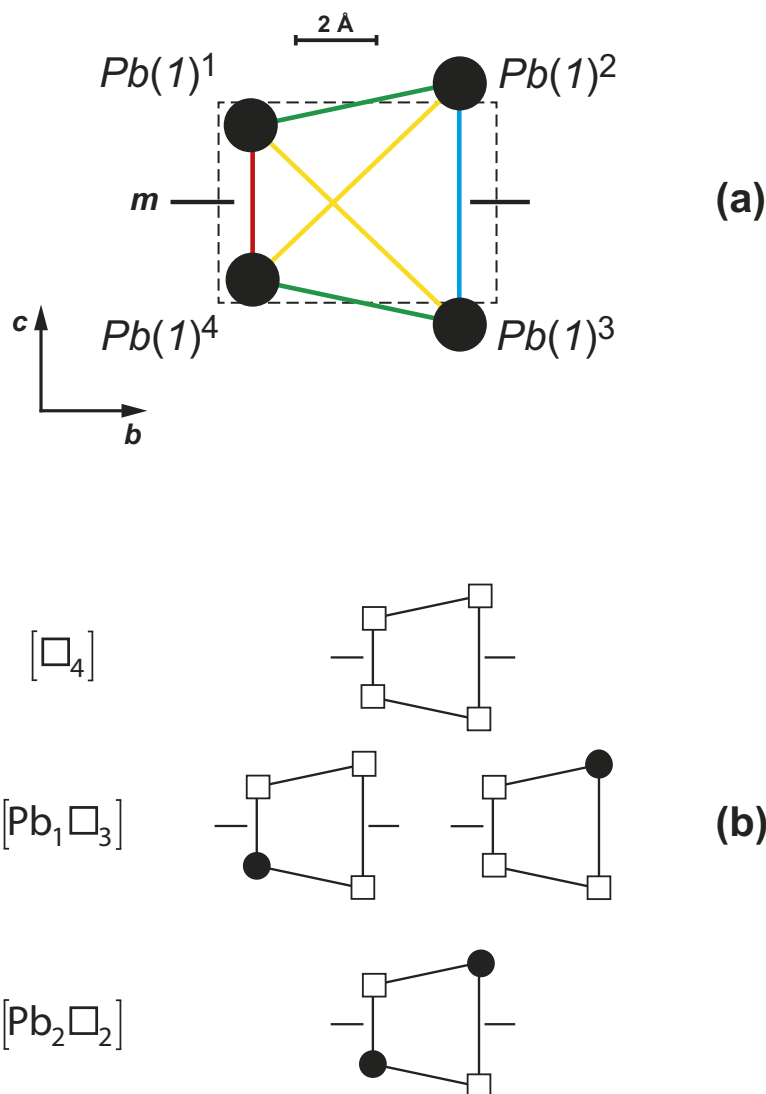


FIG. 12. Graphical representation of $\{Pb(1)_4\}$ clusters in the interlayer of shinkolobweite. In (a) the average geometric configuration is illustrated. Individual $Pb(1)-Pb(1)$ distances are colored as in Figure 8, and the length of each line corresponds to the average values. In (b) the four possible configurations of $\{Pb_x\Box_{4-x}\}$ cluster, where $x = 0, 1, 2$ are illustrated. Only clusters in which Pb-Pb adjacencies along outward edges do not occur (*i.e.*, on green, red, and blue lines) are considered here.

labeled. As the only $Pb(1)^i-Pb(1)^j$ distance to exceed ~ 4 Å corresponds to the diagonal distances (yellow lines in Fig. 11b), $Pb(1)^1-Pb(1)^3$ [$\equiv Pb(1)^2-Pb(1)^4$], the possible compositions of isolated clusters are restricted to those illustrated schematically in Figure 12b: (1) $\{\Box_4\}$; (2) $\{Pb_1\Box_3\}$, where a single Pb cation may occupy any position; and (3) $\{Pb_2\Box_2\}$, where two Pb cations occupy diagonally opposed positions. Clusters of types (1) and (2) may

occur over the entire range of t values; however, the occurrence of clusters of type (3) is restricted to the regions shaded in orange in Figure 11b.

The mean refined site-occupancy value of $Pb(1)$ over the averaged structure is 0.32(2) (Table 4), which arithmetically necessitates the occurrence of a mixture of these clusters in shinkolobweite. Over the averaged structure, the fraction of each cluster is constrained by

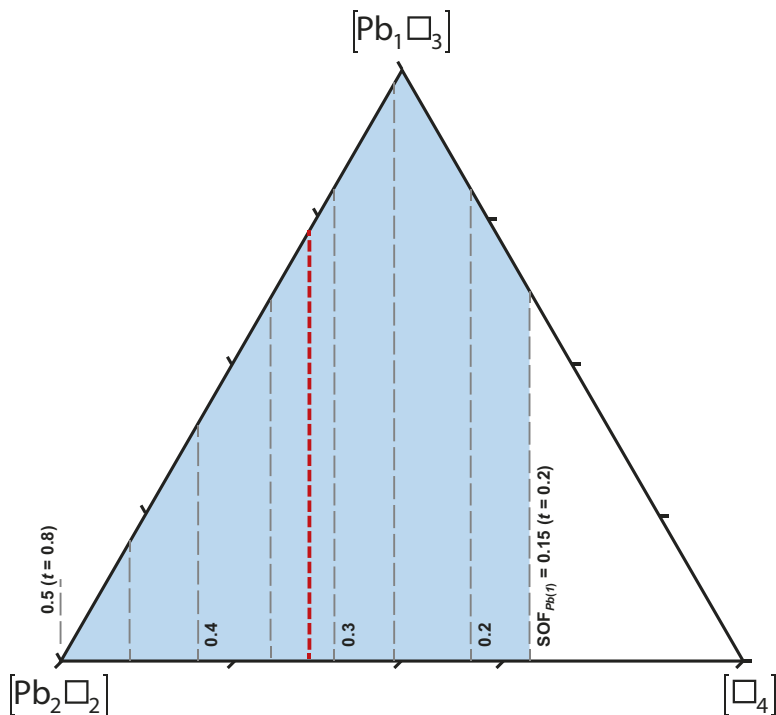


FIG. 13. Ternary diagram illustrating $Pb_x□_{4-x}$ cluster distribution in shinkolobweite. Constrained compositions, as calculated from chemical and site-scattering data, fall along the range indicated by blue shading; the mean composition is shown as the dashed red line.

$$\left[\frac{0}{4}\right]f_{\{\square_4\}} + \left[\frac{1}{4}\right]f_{\{Pb\square_3\}} + \left[\frac{2}{4}\right]f_{\{Pb_2\square_2\}} = Pb(1)_{SREF-SOF} = 0.32 \quad (1a)$$

$$f_{\{\square_4\}} + f_{\{Pb\square_3\}} + f_{\{Pb_2\square_2\}} = 1 \quad (1b)$$

where the coefficients of Equation 1a correspond to the occupied fractions $[x/4]$ of each cluster type. Lacking a third equation, the system can only be partially constrained, with all possible solutions occurring along the vector

$$(f_{\{\square_4\}}, f_{\{Pb\square_3\}}, f_{\{Pb_2\square_2\}}) = (0, 0.72, 0.28) + f_{\{\square_4\}}(1, -2, 1) \quad (2)$$

to which the following limiting conditions can be applied: $0 \leq f_{\{\square_4\}}, f_{\{Pb\square_3\}} \leq 1$, and $0 \leq f_{\{Pb_2\square_2\}} \leq 0.64$, as $f_{\{Pb_2\square_2\}} \geq 2[Pb(1)_{SREF-SOF} = 0.64]$ would exceed the total site scattering. Repeating this process for the range of $Pb(1)_{SREF-SOF}$ values observed through modulation (Fig. 11a) results in a series of vectors parallel to that given in Equation 2. Figure 13 shows the total range (blue shading) of possible compositions in the $f_{\{\square_4\}}-f_{\{Pb\square_3\}}-f_{\{Pb_2\square_2\}}$ ternary. Here,

for any observed value of $Pb(1)_{SREF-SOF}$, the distribution of clusters $\{Pb_x\square_{4-x}\}$ is constrained to the corresponding vertical line. The mean composition, given by Equation 2 for $Pb(1)_{SREF-SOF} = 0.32$, is shown by the dashed red line in Figure 13.

Although the occurrence of $\{\square_4\}$ clusters is arithmetically possible, these may initially be considered as unlikely, owing to the large void space that would result in the structure. As shown in Figure 13, for regions of the structure in which $Pb(1)_{SREF-SOF} > 0.25$, the absence of a cluster of composition $\{\square_4\}$ is a necessity. However, for regions of the structure where $Pb(1)_{SREF-SOF} < 0.25$, clusters of composition $\{\square_4\}$ must occur.

RELATIONSHIP TO OTHER SPECIES

Shinkolobweite is most closely related to other U-OH minerals that crystallize with the β - U_3O_8 topology, including spriggite (Brugger *et al.* 2004) and rameauite (Plášil *et al.* 2016, 2021), as well as the mixed-valence U minerals ianthinite, wyartite, dehydrated wyartite, and nollmotzite. Shinkolobweite is the fifth mineral recognized to contain essential U^{5+} after wyartite, dehydrated wyartite, richetite, and nollmotzite,

and it is now the third uranyl mineral known to exhibit modulated ordering, after swamboite-Nd (Plášil *et al.* 2018b) and baumoite (Elliott *et al.* 2019). Shinkolobweite is structurally most closely related to the synthetic mixed-valence $U^{5+/6+}$ phase prepared by Belai *et al.* (2008), $[U^{5+}(H_2O)_2(UO_2)_2O_4(OH)](H_2O)_4$. The synthetic phase possesses a similar-sized cell ($7.176 \times 11.400 \times 15.310$) with a similar space-group symmetry (*Immm*) relative to shinkolobweite. The synthetic phase also contains sheets based on the β - U_3O_8 topology, although its interlayer is devoid of cations and its sheets are electroneutral. Belai *et al.* (2008) note that the synthetic phase is only stable for a few months under ambient conditions, as it slowly oxidizes over time. This may suggest that structural modulation, specifically the arrangement and occupancy of interlayer Pb^{2+} , is essential for the long-term stability of U^{5+} in shinkolobweite.

The PXRD pattern of shinkolobweite closely resembles that of protasite (Pagoaga *et al.* 1987), masuyite (Burns & Hanchar 1999), and richetite (Plášil 2017). These three minerals contain uranyl oxide hydrate sheets based on the α - U_3O_8 topology, which feature edge-sharing uranyl pentagonal bipyramids (Fig. 7). Though distinct from the β - U_3O_8 type sheet found in shinkolobweite, the inclusion or omission of a single $U-O_{eq}$ bond differentiates the two topologies, and thus they differ in the subtle details of the positioning of a single oxygen atom. The bond length corresponding to this transition measures >3.4 Å in the average crystal structure of shinkolobweite [$U(2)-O(7)$] and does not represent a chemical bond; however, through modulation, it periodically approaches ~ 2.85 Å (Figs. 6, 7). In the crystal structure of synthetic α - U_3O_8 , the corresponding bond length measures 2.71 Å (Loopstra 1964). Therefore, it may be interpreted that the modulation at the $U(2)$ site represents the transition between multiple local configurational states for different valences of U: (1) octahedral U^{5+} with two long (>2.0 Å) apically bonded O/OH; (2) octahedral U^{6+} with short (~ 1.79 Å) apical oxide O^{2-} atoms; and (3) intermediate pentagonal bipyramidal or octahedral configuration with variably protonated, apical O atoms and mixed U^{5+} and U^{6+} valence that periodically produces an α - U_3O_8 type topology (Fig. 7). Although it is currently unclear what structure fully oxidized shinkolobweite might adopt, it hypothetically may rearrange into an α - U_3O_8 -type topology and chemically would closely resemble fourmarierite, $Pb(UO_2)_4O_3(OH)_4 \cdot 4H_2O$, albeit requiring additional rearrangements to adopt its structure. This is noteworthy because the U mixed-valence mineral, ianthinite, is reported to transform to schoepite or metaschoepite on oxidation, the latter two minerals having crystal structures that are also built upon the fourmarierite-anion topology (Schoep & Stradiot 1947).

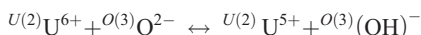
IDEAL FORMULA DERIVATION

An idealized formula, $Pb_{1.333}[U^{5+}O(OH)][(UO_2)_5O_7(OH)_3](H_2O)_5$, can be invoked by assuming stoichiometric structural unit occupancy with 50:50 occupancy of U^{5+} : U^{6+} at the $U(2)$ site and using the average bond valence of sheet O atoms to set the O/OH ratio; however, it is highly deficient in positive charge (net charge = -2.33). The correct ideal formula is significantly more complex. It is inferred that the large variability in bond lengths and bond valences of the apical O atoms of the $U(2)$ site [$O(3)$ and $O(9)$] reflects a mixture of $U^{6+}-O_{yl}$ and $U^{5+}-O/OH$ bonds (Fig. 9b). It is also possible that a higher-than-measured U^{5+} content, or, as is commonly observed in other UOH minerals, partial protonation of other bridging O^{2-} atoms within the sheet may alternatively account for the charge deficiency. The $U(2)$ site exhibits variable bond-valence sums at different regions of superspace: the minimum, maximum, and average bond valences are 5.40, 5.59, and 5.51 *vu*, respectively, which were calculated using the $U^{5+}-O$ parameters given by Gagné & Hawthorne (2015) (Table 6).

The equatorially bonded oxygen atoms $O(5)$ and $O(6)$ surrounding the $U(2)$ site may also be protonated. While the $O(6)$ atom exhibits consistent oxide character (O^{2-}) throughout superspace, the $O(5)$ site exhibits larger valence fluctuations, between 2.04 *vu* and 1.51 *vu*, averaging 1.73 *vu*, and signifying partial protonation of this site ($\sim 1:4$ OH:O). The wide bond-valence ranges brought on by structural modulation thus requires numerous assumptions about how charge may be balanced within a wide field of compositional space. This problem can be approached from a simplified perspective to explore specific charge balance requirements at the $U(2)$ site by holding the protonation state of sheet atoms $O(5)$ and $O(6)$ constant. This provides several advantages, including derivation of a formula that is stoichiometric and charge balanced for all possible compositions at the $U(2)$ site.

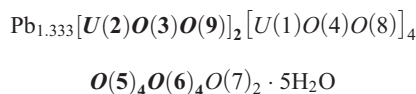
To summarize, derivation of an ideal, charge-balanced formula for shinkolobweite is complicated by: (1) the occurrence of uranium cations of mixed-valence; (2) the change in coordination about the $U(2)$ position as a function of structure modulation; (3) the ability of anion positions within the U_3O_8 sheet layers to accommodate mixed occupancies of O^{2-} , $(OH)^-$, and (H_2O) ; (4) the highly variable nature of observed bond lengths within the structure, complicating the use of bond-valence arguments to confirm site occupancies; and (5) the fractionally-occupied $O(2)'$ position in the interlayer, whose occupancy (and thus charge contribution) remains enigmatic.

The situation may be simplified by initially applying the following substitution mechanism to accommodate the incorporation of U^{5+} into the structure:

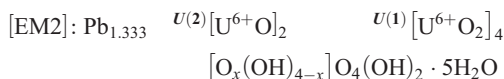
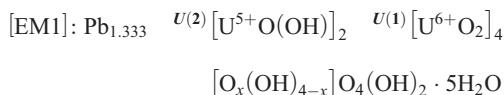


Further, from bond-valence sums, the $O(7)$ and $O(9)$ positions may be considered fully occupied by $(OH)^{-}$ and O^{2-} , respectively, for the purposes of formula derivation.

From the initial crystal-structure formula (key sites being given in bold),

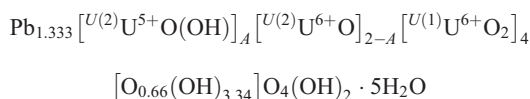


two theoretical endmembers (EM) may be defined:



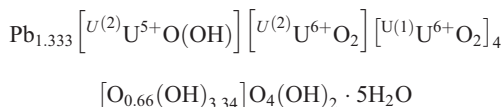
For both endmembers, charge-balancing necessitates that $x = 0.66$.

Combining [EM1] and [EM2] results in the general formula

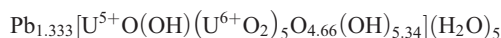


where A indicates the proportion of U^{5+} in the structure.

In the crystal described here, where $A \approx 1$ (Table 2), the formula becomes



which reduces to



which we propose here to be accepted as the ideal shinkolobweite formula.

Several issues still remain with these assumptions. The average bond valence of the sheet oxygen atoms $O(5)$, $O(6)$, and $O(7)$ suggests a composition with significantly less overall OH content, *i.e.*, $\sim O_7OH_3$. This suggests that a complex transition of protonation states occurs for $O(3)$, $O(9)$, and $O(5)$ for different proportions of U^{5+} and indicates that regions of the structure populated by U^{6+} must contain significant (OH) substitution. Our inability to fully resolve these discrepancies lies beyond the resolution of the modulated data; however, given the significant uncertainties in the protonation state of the apical O atoms at the $U(2)$ site, the ideal formula is best represented as $Pb_{1.333}[U^{5+}O(OH)(U^{6+}O_2)_5O_{4.67}(OH)_{5.33}](H_2O)_5$.

CONCLUSIONS

Commensurate modulation in the structure of shinkolobweite manifests itself primarily in the long-range ordering of U^{5+} and U^{6+} at the $U(2)$ site and the local, surrounding O atoms, as well as the occupancy and positions of interlayer Pb atoms. The new mineral is observationally stable to oxidation in air after many years under typical storage conditions, in contrast to other mixed-valence uranyl minerals and the closely related synthetic phase $[U^{5+}(H_2O)_2(UO_2)_2O_4(OH)](H_2O)_4$. Still, more material should be examined and thermodynamic experiments must be conducted to make a definitive statement on the stability of shinkolobweite.

The β - U_3O_8 sheet topology found in shinkolobweite is crystal-chemically versatile and, excepting richetite, which crystallizes with the closely related α - U_3O_8 topology, is the crystal-structure type adopted by all known mixed-valence uranyl minerals. Its ability to stabilize U^{5+} on time scales relevant to geologic disposal of used nuclear fuel, *i.e.*, potentially $> 100,000$ years, may have significant implications for the disposal of nuclear waste. The reducing conditions favored in proposed repositories for nuclear waste could promote the formation and stabilization of U^{5+} phases with the β - U_3O_8 topology, affecting the mobility of radionuclides and the development of long-term geochemical transport models.

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REFERENCES

- ARNOLD, P.L., LOVE, J.B., & PATEL, D. (2009) Pentavalent uranyl complexes. *Coordination Chemistry Reviews* **253**, 1973–1978.
- BARTLETT, J.R. & COONEY, R.P. (1989) On the determination of uranium-oxygen bond lengths in dioxouranium (VI) compounds by Raman spectroscopy. *Journal of Molecular Structure* **193**, 295–300.
- BELAI, N., FRISCH, M., ILTON, E.S., RAVEL, B., & CAHILL, C.L. (2008) Pentavalent uranium oxide via reduction of $[\text{UO}_2]^{2+}$ Under Hydrothermal Reaction Conditions. *Inorganic Chemistry* **47**, 10135–10140.
- BRUGGER, J., KRIVOVICHEV, S.V., BERLEPSCH, P., MEISSER, N., ANSERMET, S., & ARMBRUSTER, T. (2004) Spriggite, $\text{Pb}_3[(\text{UO}_2)_6\text{O}_8(\text{OH})_2](\text{H}_2\text{O})_3$, a new mineral with $\beta\text{-U}_3\text{O}_8$ -type sheets: Description and crystal structure. *American Mineralogist* **89**, 339–347.
- BURNS, P.C. (1998a) The structure of richetite, a rare lead uranyl oxide hydrate. *The Canadian Mineralogist* **36**, 187–199.
- BURNS, P.C. (1998b) The structure of compreignacite, $\text{K}_2(\text{UO}_2)_3\text{O}_2(\text{OH})_3 \cdot 2(\text{H}_2\text{O})$. *The Canadian Mineralogist* **36**, 1061–1067.
- BURNS, P.C. & FINCH, R.J. (1999) Wyartite; crystallographic evidence for the first pentavalent-uranium mineral. *American Mineralogist* **84**, 1456–1460.
- BURNS, P.C. & HANCHAR, J.M. (1999) The structure of masuyite, $\text{Pb}[(\text{UO}_2)_3\text{O}_3(\text{OH})_2](\text{H}_2\text{O})_3$, and its relationship to protasite. *The Canadian Mineralogist* **37**, 1483–1491.
- BURNS, P.C., EWING, R.C., & HAWTHORNE, F.C. (1997a) The crystal chemistry of hexavalent uranium; polyhedron geometries, bond-valence parameters, and polymerization of polyhedra. *The Canadian Mineralogist* **35**, 1551–1570.
- BURNS, P.C., FINCH, R.J., HAWTHORNE, F.C., MILLER, M.L., & EWING, R.C. (1997b) The crystal structure of ianthinite, $[\text{U}_2^{4+}(\text{UO}_2)_4\text{O}_6(\text{OH})_4(\text{H}_2\text{O})_4](\text{H}_2\text{O})_5$: A possible phase for Pu^{4+} incorporation during the oxidation of spent nuclear fuel. *Journal of Nuclear Materials* **249**, 199–206.
- ČEJKA, J. (1999) Infrared spectroscopy and thermal analysis of the uranyl minerals. In *Uranium: Mineralogy, Geochemistry and the Environment* (P.C. Burns & R.C. Ewing eds.). *Reviews in Mineralogical Society of America* **38** (521–622).
- DECREE, S., DELOULE, É., DE PUTTER, T., DEWAELE, S., MEES, F., BAELE, J.-M., & MARIGNA, C.C. (2014) Dating of U-rich heterogenite: New insights into U deposit genesis and U cycling in the Katanga Copperbelt. *Precambrian Research* **241**, 17–28.
- DELIENS, M. (1974) *Les oxydes hydratés de cobalt du Shaba méridional (République du Zaïre)*. Musée royal de l'Afrique centrale, Tervuren (in French).
- ELLIOTT, P., PLÁŠIL, J., PETŘÍČEK, V., ČEJKA, J., & BINDI, L. (2019) Twinning and incommensurate modulation in baumoite, $\text{Ba}_{0.5}[(\text{UO}_2)_3\text{O}_8\text{Mo}_2(\text{OH})_3](\text{H}_2\text{O})_{\sim 3}$, the first natural Ba uranyl molybdate. *Mineralogical Magazine* **83**, 507–514.
- FINCH, K.J., SUKSI, J., RASILAINEN, K., & EWING, R.C. (1996). Uranium-series ages of secondary uranium minerals with applications to the long-term evolution of spent nuclear fuel. In *Scientific Basis for Nuclear Waste Management XIX* (W.M. Murphy & D.A. Knecht, eds.). *Materials Research Society* **412**, 823–830.
- GAGNÉ, O.C. & HAWTHORNE, F.C. (2015) Comprehensive derivation of bond-valence parameters for ion pairs involving oxygen. *Acta Crystallographica Section B-Structural Science Crystal Engineering and Materials* **71**, 562–578.
- GRAVES, C.R. & KIPLINGER, J.L. (2009) Pentavalent uranium chemistry—Synthetic pursuit of a rare oxidation state. *Chemical Communications* **26**, 3831–3853.
- GUNTER, M., BANDLI, B., BLOSS, F., EVANS, S., SU, S.-C., & WEAVER, R. (2004) Results from a McCrone spindle stage short course, a new version of EXCALIBUR, and how to build a spindle stage. *Microscope* **52**, 23–29.
- HAWTHORNE, F.C. (1992) The role of OH and H_2O in oxide and oxysalt minerals. *Zeitschrift Fur Kristallographie* **201**, 183–206.
- HAWTHORNE, F.C., FINCH, R.J., & EWING, R.C. (2006) The crystal structure of dehydrated wyartite, $\text{Ca}(\text{CO}_3)[\text{U}^{5+}(\text{U}^{6+}\text{O}_2)_2\text{O}_4(\text{OH})](\text{H}_2\text{O})_3$. *The Canadian Mineralogist* **44**, 1379–1385.
- ILTON, E.S., HAIDUC, A., CAHILL, C.L., & FELMY, A.R. (2005) Mica surfaces stabilize pentavalent uranium. *Inorganic Chemistry* **44**, 2986–2988.
- ILTON, E.S., BOILY, J.F., & BAGUS, P.S. (2007) Beam induced reduction of U(VI) during X-ray photoelectron spectroscopy: The utility of the U4f satellite structure for identifying uranium oxidation states in mixed valence uranium oxides. *Surface Science* **601**, 908–916.
- JANECEK, J. & EWING, R.C. (1992) Structural formula of uraninite. *Journal of Nuclear Materials* **190**, 128–132.
- LARSEN, E.S. (1921) The microscopic determination of the nonopaque minerals. *U.S. Geological Survey Bulletin* **679**, 1–294.
- LI, Y. & BURNS, P.C. (2000) Investigations of crystal-chemical variability in lead uranyl oxide hydrates. II. Fourmarierite. *The Canadian Mineralogist* **38**, 737–749.

- LIBOWITZKY, E. (1999) Correlation of O–H stretching frequencies and O–H···O hydrogen bond lengths in minerals. *Monatshefte Fur Chemie* **130**, 1047–1059.
- LOOPSTRA, B. (1964) Neutron diffraction investigation of U_3O_8 . *Acta Crystallographica* **17**, 651–654.
- LUSSIER, A.J., BURNS, P.C., & KING-LOPEZ, R. (2016) A revised and expanded structure hierarchy of natural and synthetic hexavalent uranium compounds. *The Canadian Mineralogist* **54**, 177–283.
- MANDARINO, J.A. (2007) The Gladstone–Dale compatibility of minerals and its use in selecting mineral species for further study. *The Canadian Mineralogist* **45**, 1307–1324.
- OLDS, T.A., PLÁŠIL, J., KAMPE, A.R., ŠKODA, R., BURNS, P.C., ČEJKA, J., BOURGOIN, V., & BOULLIARD, J.-C. (2016) Gauthierite, $KPb[(UO_2)_7O_5(OH)_7] \cdot 8H_2O$, a new uranyl-oxide hydroxy-hydrate mineral from Shinkolobwe with a novel uranyl-anion sheet-topology. *European Journal of Mineralogy* **29**, 129–141.
- PAGOAGA, M.K., APPLEMAN, D.E., & STEWART, J.M. (1987) Crystal structures and crystal chemistry of the uranyl oxide hydrates becquerelite, billietite, and protasite. *American Mineralogist* **72**, 1230–1238.
- PALATINUS, L. & CHAPUIS, G. (2007) SUPERFLIP – A computer program for the solution of crystal structures by charge flipping in arbitrary dimensions. *Journal of Applied Crystallography* **40**, 786–790.
- PETŘÍČEK, V., DUŠEK, M., & PALATINUS, L. (2014) Crystallographic Computing System JANA2006: General features. *Zeitschrift Fur Kristallographie* **229**, 345–352.
- PIRET, P., DELIENS, M., PIETMEUNIER, J., & GERMAIN, G. (1983) Sayrite, $Pb_2(UO_2)_5O_6(OH)_2 \cdot 4H_2O$ a new mineral – Properites and crystal-structure. *Bulletin De Minéralogie* **106**, 299–304.
- PIRET, P. (1984) Structure cristalline de la fourmariérite, $Pb(UO_2)_4O_3(OH)_4(H_2O)_4$. *Bulletin de la Société française de Minéralogie et Cristallographie* **108**, 659–665 (in French).
- PLÁŠIL, J. (2017) Crystal structure of richetite revisited: Crystallographic evidence for the presence of pentavalent uranium. *American Mineralogist* **102**, 1771–1775.
- PLÁŠIL, J., ŠKODA, R., ČEJKA, J., BOURGOIN, V., & BOULLIARD, J.-C. (2016) Crystal structure of the uranyl-oxide mineral rameauite. *European Journal of Mineralogy* **28**, 959–967.
- PLÁŠIL, J., KAMPE, A.R., ŠKODA, R., & ČEJKA, J. (2018a) Nollmotzite, $Mg[U^V(U^{VI}O_2)_2O_4F_3] \cdot 4H_2O$, the first natural uranium oxide containing fluorine. *Acta Crystallographica Section B* **74**, 362–369.
- PLÁŠIL, J., PETŘÍČEK, V., LOCOCK, A.J., ŠKODA, R., & BURNS, P.C. (2018b) The (3 + 3) commensurately modulated structure of the uranyl silicate mineral swamboite-(Nd), $Nd_{0.333}[(UO_2)(SiO_3OH)(H_2O)_{2.41}]$. *Zeitschrift für Kristallographie* **233**, 223–231.
- PLÁŠIL, J., KAMPE, A.R., OLDS, T.A., SEJKORA, J., ŠKODA, R., BURNS, P.C., & ČEJKA, J. (2020) The new K, Pb-bearing uranyl-oxide mineral kroupaite: Crystal-chemical implications for the structures of uranyl-oxide hydroxy-hydrates. *American Mineralogist* **105**, 561–568.
- PLÁŠIL, J., PETŘÍČEK, V., ŠKODA, R., MEISSER, N., & KASATKIN, A.V. (2021) Hidden and apparent twins in uranyl-oxide minerals agrinierite and rameauite: A demonstration of metric and reticular merohedry. *Journal of Applied Crystallography* **54**, 1656–1663.
- POUCHOU, J.L. & PICOIR, F. (1985) “PAP” ($\rho\rho Z$) procedure for improved quantitative microanalysis. In *Microbeam Analysis* (J.T. Armstrong ed.). San Francisco Press, California, USA (104–106).
- RENSHAW, J.C., BUTCHINS, L.J.C., LIVENS, F.R., MAY, I., CHARNOCK, J.M., & LLOYD, J.R. (2005) Bioreduction of uranium: Environmental implications of a pentavalent intermediate. *Environmental Science & Technology* **39**, 5657–5660.
- SCHINDLER, M., HAWTHORNE, F.C., FREUND, M.S., & BURNS, P.C. (2009) XPS spectra of uranyl minerals and synthetic uranyl compounds. I: The U 4f spectrum. *Geochimica et Cosmochimica Acta* **73**, 2471–2487.
- SCHOEP, A. (1923) Sur la chinkolobwite, nouveau minéral uranifère du Katanga. *Bulletin de la Société Belge de Géologie, de Paléontologie et d'hydrologie* **33**, 87–88 (in French).
- SCHOEP, A. (1926) Sur l'indetité entre la chinkolobwite et la sklodowskite. *Annales de la Société Géologique de Belgique* **48**, B303 (in French).
- SCHOEP, A. & STRADIOT, S. (1947) Paraschoepite and epianthinite, two new uranium minerals from Shinkolobwe (Belgian Congo). *American Mineralogist* **32**, 344–350.
- SHIRLEY, D.A. (1972) High-resolution X-ray photoemission spectrum of the valence bands of gold. *Physical Review B* **5**, 4709–4714.
- SUZUKI, Y., KELLY, S.D., KEMNER, K.M., & BANFIELD, J.F. (2002) Nanometre-size products of uranium bioreduction. *Nature* **419**, 134–134.

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