

Original paper

The crystal structure of uranyl-oxide mineral schoepite, $[(\text{UO}_2)_4\text{O}(\text{OH})_6](\text{H}_2\text{O})_6$, revisited

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New single-crystal X-ray diffraction experiments have revealed that the crystal structure of schoepite, one of the more common U-oxide minerals, is centrosymmetric, rather than acentric as reported in the past. Schoepite is orthorhombic, space group $Pbca$, $a = 16.7810(5)$, $b = 14.7044(4)$, $c = 14.2985(5)$ Å, with $V = 3528.22(19)$ Å³ and $Z = 8$. Its structure was solved by charge-flipping algorithm and refined to an agreement index (R) of 4.7 % for 4662 unique reflections collected using microfocus X-ray source. Schoepite structure, in line with its previous determination, is based upon U–O–OH sheets of the fourmarierite topology and an interlayer filled only by molecular H₂O. The complexity calculations show that the difference in complexity values between schoepite, $[(\text{UO}_2)_4\text{O}(\text{OH})_6](\text{H}_2\text{O})_6$, and metaschoepite, $[(\text{UO}_2)_4\text{O}(\text{OH})_6](\text{H}_2\text{O})_5$, are much smaller (about 100 bits/cell) than considered previously (about 1000 bits/cell). Such small difference is in line with the easy transformation of schoepite to metaschoepite under ambient conditions and a joint occurrence of both minerals.

Keywords: schoepite, uranyl-oxide mineral, crystal structure, centrosymmetric

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1. Introduction

Uranyl-oxide hydroxy-hydrate minerals (further labeled as UOH) are important products of supergene weathering of primary U⁴⁺ minerals, most commonly uraninite (nominally UO_{2+x}), and are common constituents of the oxidized parts of uranium deposits (Plášil 2014). These minerals form early during weathering, commonly replacing uraninite *in-situ* (Finch and Ewing 1992; Finch and Murakami 1999; Krivovichev and Plášil 2013; Plášil 2014, 2018). Natural weathering of uraninite, also referred to as oxidation–hydration weathering, is also of interest because of its analogy to the alteration of UO_{2+x} in spent nuclear fuel (Janeczek et al. 1996). Schoepite is one of the most widely occurring UOHs in Nature (Plášil 2018). Due to reasons mentioned above, the crystallography and crystal chemistry of this mineral group has attracted much attention, and the number of minerals known to belong to this group has grown substantially in recent years (Plášil 2018 and references therein).

Schoepite was first described by Walker (1923) from the Shinkolobwe (originally Kasolo) mine, the Haut-Katanga province, Democratic Republic of Congo. The name honors Professor Alfred Schoep (1881–1966), the famous Belgian mineralogist who widely contributed to the knowledge of uranium minerals from Congo. The first reliable X-ray studies were undertaken by Christ and Clark (1960), and the structure was eventually determined by Finch et al. (1996),

who reported that schoepite is orthorhombic, $P2_1ca$, with $a = 14.337(3)$, $b = 16.813(5)$, $c = 14.731(4)$ Å, $V = 3551(2)$ Å³, $Z = 4$; the chemical formula was given as $[(\text{UO}_2)_8\text{O}_2(\text{OH})_{12}](\text{H}_2\text{O})_{12}$, with $Z = 4$. Recently, we have undertaken new studies on the structures of schoepite-related minerals (Plášil et al. 2017; Olds et al. 2018), which revealed several issues, among them the fact that all related studied structures are centrosymmetric. Thus, it prompted our re-examination of the schoepite structure.

2. Experimental

2.1. Sample

The schoepite crystal used in this study was recovered from a specimen stored in the collections of the Royal Museum for Central Africa in Tervuren (Belgium): n° RGM2708. This specimen originates from the Shinkolobwe mine, the Haut-Katanga Province, Democratic Republic of Congo. The specimen is composed of a massive mixture of uranyl-oxide minerals. On the surface and fissures, there are yellow tabular to prismatic crystals of schoepite (described originally as paraschoepite) (Fig. 1), reddish-orange needle-like curite and bipyramidal soddyite. It should be noted that we found no evidence for paraschoepite on the specimen (cf. Christ and Clark 1960).

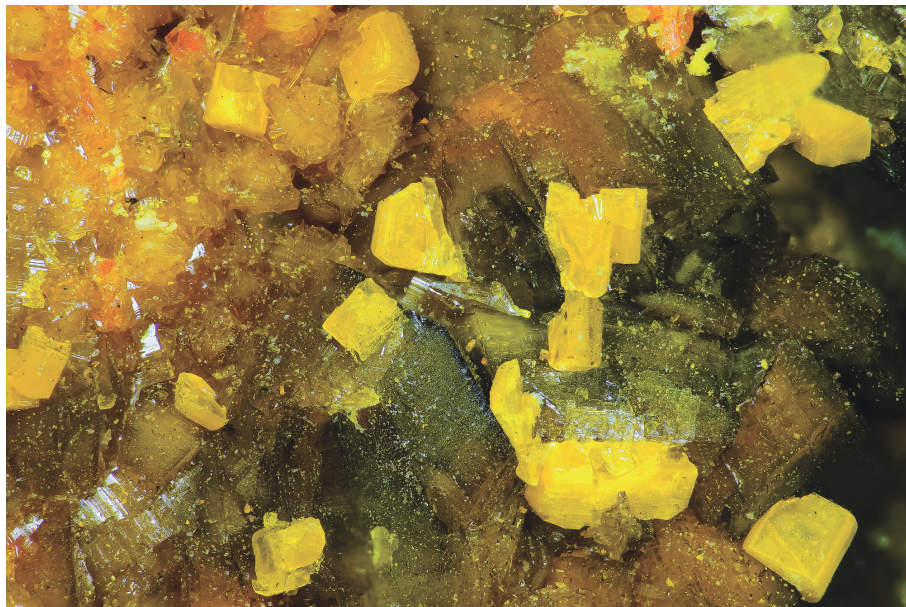


Fig. 1 Yellow tabular to blocky schoepite crystals grown on greenish soddyite. A specimen of the Royal Museum for Central Africa in Tervuren (Belgium) n° RGM2708. Width of photograph is 3.8 mm (photo by E. Van Der Meersche).

2.2. Single-crystal X-ray crystallography

Diffraction data were collected by a Rigaku SuperNova diffractometer, using MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$) from a micro-focus X-ray tube collimated and monochromatized by mirror optics and detected by an Atlas S2 CCD detector. The data reduction was done using CrysAlis software (Rigaku 2017). Basic crystallographic data are given in Tab. 1.

At the first step, the structure of schoepite was aimed to be refined based on the model in $P2_1ca$ given by Finch et al. (1996), using the full-matrix least-squares algorithm of the Jana2006 program (Petříček et al. 2014) based on F^2 . Despite considerable efforts, these attempts failed (due to a singular matrix in the refinement), or led to unstable refinements. Namely, strong correlations (correlation parameter > 0.9) of refined parameters (especially of fractional coordinates of U atoms as well as for displacement parameters) occurred, along with a high value of the Flack parameter ~ 0.5 , when refined in $P2_1ca$. Correlations mentioned above and the value of Flack parameter suggested that the structure is centrosymmetric. The quick check of original structure by Finch et al. (1996) using ADDSYMM routine in Platon (Le Page 1987; Spek 2003) revealed that their structure is centrosymmetric of the $Pbca$ space group (see Supplementary file S1). An independent structure solution was obtained by the SHELXT (Sheldrick 2015) and refined using the

Jana2006 program. The reflection conditions were consistent with the space-group $Pbca$, which was further fully confirmed by the successful refinement. The structure solution provided complete structure sheets, and missing interlayer atoms were located from the difference-Fourier maps. Anisotropic displacement parameters were used for all atoms in the structure. Unconstrained and unrestrained refinement converged smoothly to $R_{\text{obs}} \sim 2.7\%$ (Tab. 2). Final atom coordinates and displacement parameters are listed in Tabs 3 and 4, selected interatomic distances are in Tab. 5, and the bond-valence analysis in Tab. 6 (using the bond-valence parameters given by Gagné and Hawthorne 2015). The CIF file, also containing a block with the reflections, is deposited at the Journal's webpage www.jgeosci.org.

2.3. Structural complexity calculations

In order to compare schoepite and related phases from the viewpoint of structural complexity, the Shannon information content per atom (I_G) and per unit cell ($I_{G,\text{total}}$) were calculated. This approach was developed by Krivovichev (2012, 2013, 2014); the complexity of a crystal structure can be quantitatively characterized by the amount of Shannon information, which is measured in bits (binary digits) per atom (bits/atom) and per unit cell (bits/cell), respectively. The concept of Shannon information, also known as Shannon entropy, used herein originates from information theory (Shannon and Weaver 1949). The amount of Shannon information reflects the diversity and relative proportion of different objects, e.g., the number and relative pro-

Tab. 1 Unit-cell parameters of schoepite crystals studied

Sample	<i>a</i>	<i>b</i>	<i>c</i>	Reflections for unit cell	Reflections, [$I > 3\sigma(I)$]	R_{obs}
n° RGM2708	16.7810(5)	14.7044(4)	14.2985(5)	13376	3354	0.0264
#2	16.7974(4)	15.1785(4)	14.1323(3)	8849	3519	0.0343

#2 from the collection of JP

portion of different sites in an elementary unit cell of a crystal structure.

The quantity of information contained in the crystal structure is given by:

$$I_G = -\sum_{i=1}^k p_i \log_2 p_i \text{ (bits/atom)} \quad (1)$$

$$\text{and } I_{G,\text{total}} = -vI_G = -v\sum_{i=1}^k p_i \log_2 p_i \text{ (bits/cell)} \quad (2)$$

where k is the number of different crystallographic orbits (independent crystallographic Wyckoff sites) in the structure and p_i is the random-choice probability for an atom from the i^{th} crystallographic orbit, that is:

$$p_i = \frac{m_i}{v} \quad (3)$$

where m_i is a multiplicity of a crystallographic orbit (*i.e.*, the number of atoms at a specific Wyckoff site in the reduced unit cell), and v is the total number of atoms in the reduced unit cell. The information-based structural-complexity values were calculated using the TOPOS software package (Blatov et al. 2014).

3. Results – the structure of schoepite

The structure of schoepite (space group *Pbca*; Tab. 3) contains four unique U sites and twenty-one O sites (of which six correspond to OH groups, and six to H₂O groups) (Figs 2 and 3a). Each of the U sites is coordinated by seven ligands (O or OH⁻) in two classes of distances: ~1.8 Å (characteristic for the UO₂²⁺ ion; Evans 1963; Burns et al. 1997; Lussier et al. 2016) and ~2.2 to ~2.6 Å (Tab. 5). Uranyl coordination polyhedra polymerize into the sheets of the so-called fourmarierite topology, which is composed of pentagons and triangles (Miller et al. 1996; Burns 2005; Lussier et al. 2016). Each pentagon of the corresponding anion topology is occupied by a uranyl ion, whereas all triangles remain vacant. The triangles share vertices, forming bowtie-like pairs that are in two orientations. These sheets are stacked perpendicular to **b**. The interlayer

hosts six independent O sites, all corresponding to H₂O groups (Tab. 6, Fig. 3a), yielding 48 H₂O per unit cell. The structural formula of the schoepite crystal we studied is, therefore, [(UO₂)₄O(OH)₆](H₂O)₆, $Z = 8$.

4. Discussion

4.1. The symmetry of schoepite structure

Schoepite structure reported for the first time by Finch et al. (1996) was given as non-centrosymmetric, of the space group *P2₁ca* (with the current unit cell settings). They argued for the absence of the inversion center due to the presence of a positional disorder of O atoms around U sites. After they lowered the symmetry from *Pbca* to *P2₁ca* (other possibilities were indicated as unsuccessful), the realistic crystal-chemical solution had been achieved. Finch et al. (1996) also documented that only three weak reflections violated *b* glide in the *Pbca*, and they mentioned some significant correlations occurring namely between atomic displacement parameters for U atoms.

Tab. 2 Crystallographic data and refinement details for schoepite

Crystal data	
Structure formula	[(UO ₂) ₄ O(OH) ₆](H ₂ O) ₆
Crystal system	orthorhombic
Space group	<i>Pbca</i>
Unit-cell parameters: <i>a</i> , <i>b</i> , <i>c</i> [Å]	16.7810(5), 14.7044(4), 14.2985(5)
Unit-cell volume [Å ³]	3528.22(19)
<i>Z</i>	8
Calculated density [g/cm ³]	4.918 (for above mentioned formula)
Crystal size [mm]	0.072 × 0.049 × 0.027
<i>F</i> ₀₀₀	4288
Data collection	
Diffractometer	Rigaku SuperNova with Atlas S2 detector
Temperature [K]	297
Radiation, wavelength [Å]	MoK _α , 0.71073 (50 kV, 30 mA)
θ range for data collection [°]	3.34–29.63
Limiting Miller indices	<i>h</i> = –23→21, <i>k</i> = –18→19, <i>l</i> = –15 → 18
Axis, frame width (°), time per frame (s)	ω, 1, 300
Total reflections collected	47279
Unique reflections	4662
Unique observed reflections, criterion	3354, [<i>I</i> > 3σ(<i>I</i>)]
Absorption coefficient [mm ⁻¹], type	36.71; multi-scan
<i>T</i> _{min} / <i>T</i> _{max}	0.285/1
<i>R</i> _{int}	0.0498
Structure refinement by Jana2006	
Number of refined parameters, restraints, constraints	226, 0, 0
<i>R</i> , <i>wR</i> (obs)	0.0264, 0.0579
<i>R</i> , <i>wR</i> (all)	0.0466, 0.0658
GOF obs/all	1.38, 1.31
Weighting scheme, weights	σ, <i>w</i> = 1/(σ ² (<i>I</i>)+0.0004 ²)
Largest diffraction peak and hole (e ⁻ /Å ³)	2.19, –2.36

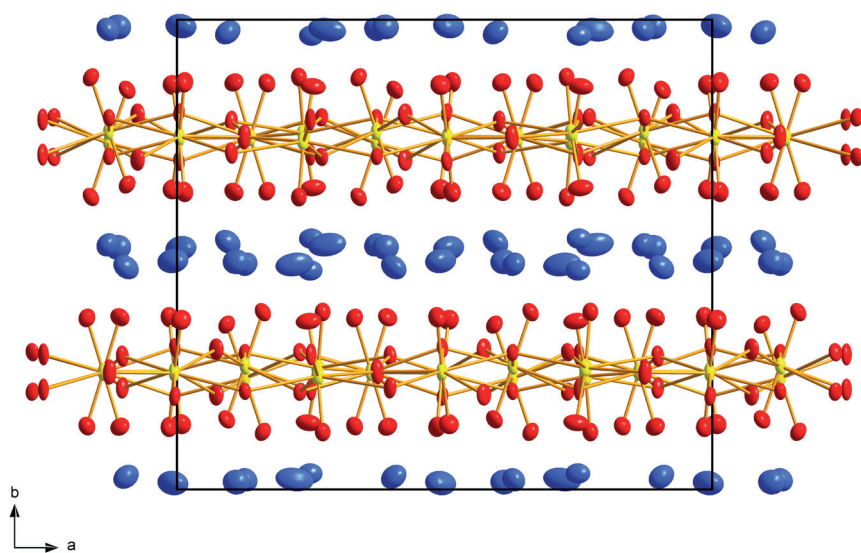
Tab. 3 Atom coordinates and displacement parameters for the crystal structure of schoepite

Atom	x/a	y/b	z/c	U_{eq}
U1	0.627411(14)	0.262876(17)	0.757923(16)	0.01123(8)
U2	0.362942(14)	0.250132(17)	0.270301(17)	0.01140(8)
U3	0.263355(15)	0.258859(16)	0.510397(16)	0.01196(8)
U4	0.495078(14)	0.247823(17)	0.490738(18)	0.01138(8)
O1	0.3982(2)	0.2161(3)	0.1113(3)	0.0161(14)
O2	0.6268(2)	0.2088(3)	0.4339(3)	0.0133(13)
O3	0.5736(2)	0.2986(3)	0.6156(3)	0.0178(15)
O4	0.6606(3)	0.3774(3)	0.7582(3)	0.0177(15)
O5	0.3935(3)	0.3665(3)	0.2609(3)	0.0222(17)
O6	0.3742(2)	0.2493(3)	0.4249(3)	0.0187(16)
O7	0.3319(3)	0.1348(3)	0.2745(3)	0.0184(15)
O8	0.2722(2)	0.3778(3)	0.5281(3)	0.0192(15)
O9	0.4861(3)	0.1333(3)	0.5308(3)	0.0245(17)
O10	0.2300(2)	0.2921(3)	0.3520(3)	0.0136(14)
O11	0.5930(3)	0.1491(3)	0.7580(3)	0.0207(16)
O12	0.5079(3)	0.3610(3)	0.4486(3)	0.0216(16)
O13	0.2457(3)	0.1419(3)	0.4896(3)	0.0265(17)
O14	0.4961(2)	0.3017(3)	0.8133(3)	0.0143(14)
O15	0.6289(3)	0.0207(4)	0.4602(4)	0.040(2)
O16	0.2507(2)	0.2126(3)	0.6695(3)	0.0152(14)
O17	0.2488(3)	0.0338(3)	0.6635(3)	0.0288(17)
O18	0.4925(3)	0.4864(4)	0.8029(5)	0.062(3)
O19	0.6105(3)	0.4846(4)	0.5855(4)	0.039(2)
O20	0.4050(3)	0.0269(4)	0.1092(4)	0.040(2)
O21	0.2195(4)	0.4789(4)	0.3689(4)	0.051(2)

Our check of the structure model of Finch et al. (1996) in Platon using ADDSYM procedure (Le Page 1987; Spek 2003) confirmed that the structure is centrosymmetric, of the space group $Pbca$. Refinements against the current dataset using a non-centrosymmetric space group yielded a large number of correlations (in fact positional and displacement parameters of all U atoms in the structure) with the correlation factor >0.9 . The refined Flack parameter, 0.50(2), also suggested the problematic ap-

proach to the refinement using non-centrosymmetric model. The new dataset contains seven reflections (before averaging) contradicting the b glide in the $Pbca$. However, in the current refinement, no indication of positional disorder was observed for the refinement in the centrosymmetric space group $Pbca$ and, moreover, it was possible to refine all atoms with anisotropic displacement parameters. The comparison of the interlayer configurations of both models, *i.e.*, centrosymmetric one (Fig. 3c) and the model provided by Finch et al. (1996) (Fig. 3d), is made in Fig. 3e. The comparison (*i.e.*, overlay of both interlayers) documents that the interlayers of the two distinct crystals (described in different space groups) are identical. Based on all these facts, the structure model proposed in the centrosymmetric space group $Pbca$ was considered to be correct.

An additional crystal of a different sample from the Shinkolobwe mine has been studied to confirm the more general validity of the currently obtained results. It has been found to be of the centrosymmetric space group $Pbca$ as well, and the structure was refined down to R_1 ranging between 2 and 3 %. It is also possible that the crystals used by Finch et al. (1996) were more altered than those used by the present study and therefore consequent difficulties hardened structure solution and refinement.



5. Implications for weathering of UO_{2+x}

Schoepite is an important mineral since it commonly precipitates early during the weathering of uraninite and oxidation–hydration alteration of spent nuclear fuel (Finch and Ewing 1992; Wronkiewicz et al. 1992, 1996; Janeczek et al. 1996; Krivovichev and Plášil 2013; Plášil

Fig. 2 Crystal structure of schoepite viewed down c . Uranium atoms are yellow, O atoms red, O atoms of the H_2O groups blue. All atoms are drawn as thermal ellipsoids (75% probability level). Unit-cell edges are outlined by solid black line.

2014, 2018). Also, schoepite is a commonly occurring UOH mineral, reported from nearly 80 localities (Plášil 2018). Schoepite, $[(\text{UO}_2)_4\text{O}(\text{OH})_6](\text{H}_2\text{O})_6$ and metaschoepite, $[(\text{UO}_2)_4\text{O}(\text{OH})_6](\text{H}_2\text{O})_5$ (Weller et al. 2000) are closely related minerals. A transformation of schoepite to metaschoepite, connected with a loss of the H_2O molecule from interlayer (*i.e.*, partial dehydration), was observed in air under the room temperature (Christ and Clark 1960; O'Hare et al. 1988; Finch et al. 1998; Sowder et al. 1999; Kubatko et al. 2006). From the thermodynamic point of view the process is clearer now, however the exact mechanism remains unknown.

Krivovichev (2012, 2013) developed a quantitative approach to the evaluation of structural complexity of minerals, based on Shannon information theory. More recently, Krivovichev (2016) demonstrated with statistical arguments that structural information per atom provides a negative contribution to the configurational entropy of crystals and, therefore, is a physically important thermodynamic parameter. The complexity values for schoepite and metaschoepite are given in Tab. 7. The ease of dehydration from schoepite to metaschoepite might also reflect the small difference in their complexity values. While the difference for the proposed two centrosymmetric structures is small (~ 130 bits/cell), it would be much higher if schoepite was considered as non-centrosymmetric (~ 860 bits/cell).

5.1. Schoepite formation

Schoepite is a common constituent of massive accumulations of uranyl-oxide minerals, formerly called “*gummites*”, occurring worldwide (Finch and Ewing 1992; Plášil 2014, 2018). Finch et al. (1998), as well as Sowder et al. (1999), studied the phase relations among schoepite and related minerals and their formation in detail. They claimed that schoepite precipitation takes place at 25 °C while metaschoepite precipitates at 50 °C in water; schoepite has been reported to undergo a transition to metaschoepite in the air at room temperature (Christ and Clark 1960; O'Hare et al. 1988; Finch et al. 1998; Sowder et al. 1999; Kubatko et al. 2006).

Tab. 4 Anisotropic displacement parameters for the crystal structure of schoepite

Atom	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
U1	0.00754(12)	0.01830(14)	0.00783(13)	-0.00079(10)	-0.00003(8)	0.00022(9)
U2	0.00808(12)	0.01904(14)	0.00708(14)	-0.00080(9)	-0.00092(8)	0.00023(9)
U3	0.00987(13)	0.01919(14)	0.00682(13)	0.00100(9)	0.00143(8)	0.00012(10)
U4	0.00709(13)	0.01892(15)	0.00811(14)	0.00021(9)	-0.00008(8)	0.00103(10)
O1	0.010(2)	0.027(3)	0.011(2)	0.0012(19)	0.0027(17)	0.0031(19)
O2	0.009(2)	0.018(3)	0.013(2)	-0.0006(18)	-0.0004(17)	-0.0017(19)
O3	0.013(2)	0.028(3)	0.012(2)	-0.0003(19)	-0.0062(17)	-0.002(2)
O4	0.016(2)	0.020(3)	0.017(3)	-0.004(2)	-0.0003(18)	0.001(2)
O5	0.022(3)	0.020(3)	0.025(3)	-0.003(2)	-0.006(2)	-0.003(2)
O6	0.011(2)	0.037(3)	0.009(2)	0.002(2)	-0.0007(17)	-0.0001(19)
O7	0.017(2)	0.021(3)	0.017(3)	-0.002(2)	0.0007(19)	0.001(2)
O8	0.015(2)	0.021(3)	0.021(3)	0.0002(19)	-0.0020(19)	-0.001(2)
O9	0.019(3)	0.025(3)	0.029(3)	0.001(2)	0.005(2)	0.007(2)
O10	0.011(2)	0.020(3)	0.010(2)	-0.0013(18)	-0.0031(16)	-0.0037(19)
O11	0.017(2)	0.020(3)	0.025(3)	-0.004(2)	0.004(2)	0.003(2)
O12	0.024(3)	0.024(3)	0.017(3)	0.001(2)	0.001(2)	0.003(2)
O13	0.039(3)	0.017(3)	0.023(3)	-0.003(2)	0.003(2)	0.002(2)
O14	0.008(2)	0.022(3)	0.013(2)	-0.0019(17)	-0.0006(17)	-0.002(2)
O15	0.032(3)	0.033(3)	0.055(4)	-0.004(3)	0.005(3)	0.002(3)
O16	0.007(2)	0.029(3)	0.010(2)	0.0002(18)	-0.0024(17)	0.003(2)
O17	0.037(3)	0.025(3)	0.024(3)	0.000(2)	-0.004(2)	0.000(2)
O18	0.058(4)	0.036(4)	0.091(6)	0.004(3)	-0.022(4)	0.004(4)
O19	0.043(3)	0.037(4)	0.038(4)	0.001(3)	-0.004(3)	0.001(3)
O20	0.039(3)	0.035(4)	0.047(4)	0.008(3)	0.008(3)	0.000(3)
O21	0.086(4)	0.034(4)	0.031(4)	0.008(3)	-0.014(3)	0.002(3)

As has been demonstrated above, schoepite is slightly more complex than metaschoepite. As documented by Krivovichev (2012, 2013, 2014), structural complexity is a negative contribution to the configurational entropy of a crystal. At 50 °C the entropy term will be slightly more important (comparison of compositions of schoepite, $[(\text{UO}_2)_4\text{O}(\text{OH})_6](\text{H}_2\text{O})_6$ and metaschoepite, $[(\text{UO}_2)_4\text{O}(\text{OH})_6](\text{H}_2\text{O})_5$ gives one H_2O molecule difference, when $Z = 8$) than at 25 °C. Therefore, at 50 °C, metaschoepite may precipitate first as metastable since it is the less complex phase (with the lower crystallization barrier against entropy). Interestingly, schoepite is a less-dense phase, with 4.918 g cm⁻³, compared to metaschoepite, with 4.989 g cm⁻³, although this difference is relatively low. According to the Ostwald-Volmer rule (Holleman et al. 2001; Krivovichev 2017), the less-dense phase is commonly the metastable one. That might be a reason why it precipitates first before metaschoepite; despite the higher complexity (which is in contrast with the Goldsmith's principle).

Let us consider pair torbernite–metatorbernite, which is somewhat similar to schoepite–metaschoepite. Torbernite, $\text{Cu}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_{12}$, *P4/nnc* (Locock and Burns 2003) is a higher hydrate of metatorbernite, $\text{Cu}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_8$, *P4/n* (Locock and Burns 2003); their structural complexities are given also in Tab. 7. Interestingly, the difference in complexities for the pair torber-

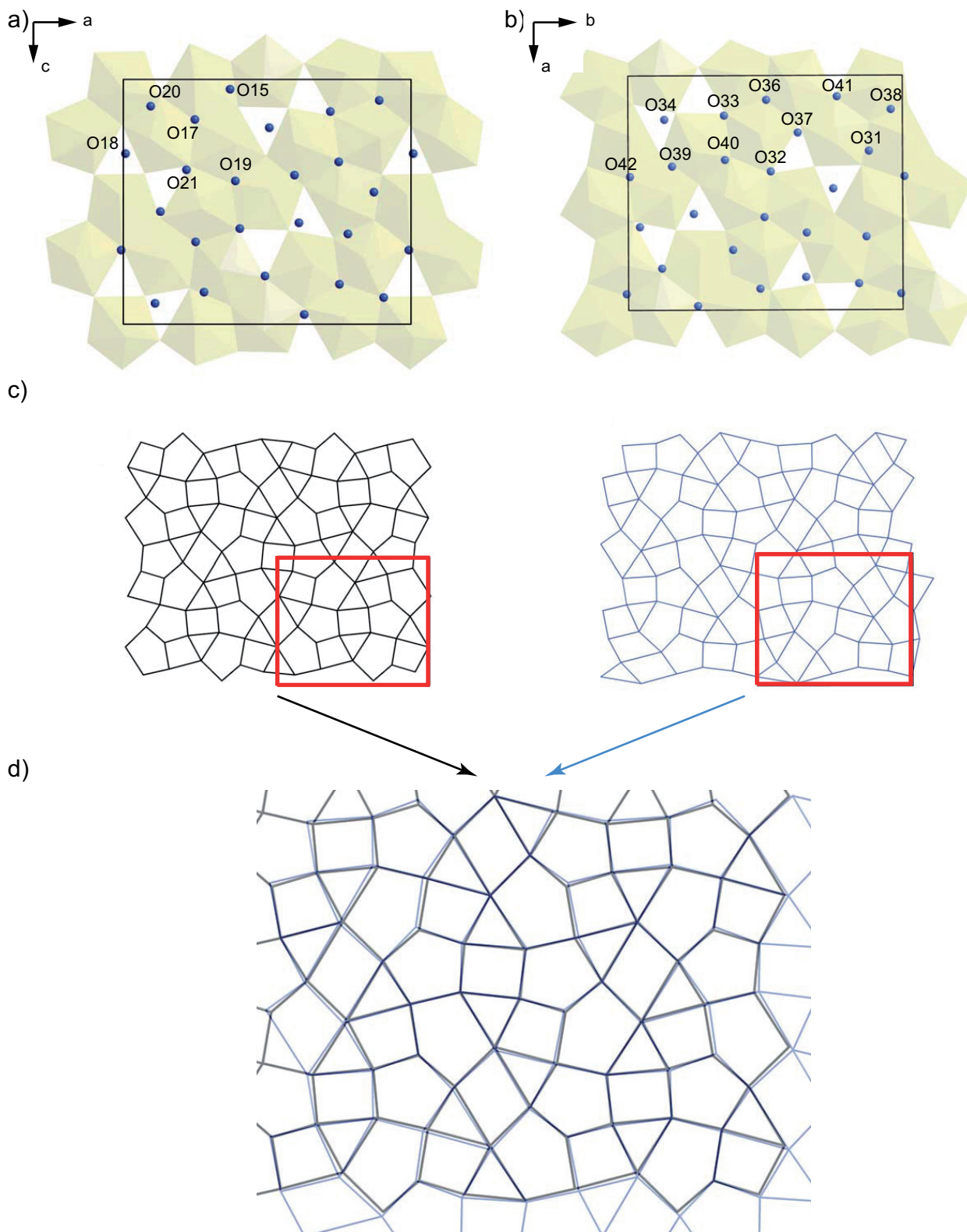


Fig. 3 Interlayer in schoepite. **a** – As determined by current structure study (space group Pbc_a). **b** – Model of Finch et al. (1996). In both figures, underlying pale yellow are UO_7 polyhedra of the structural sheet. Unit-cell edges outlined by solid black lines. **c** – The respective topology of the interlayer in schoepite (Pbc_a ; current study). **d** – The respective topology of an interlayer of schoepite from Finch et al. (1996). Unit-cell edges are outlined by solid red lines. The shift between these two overlays is due to distinct origin. **e** – Comparison of these two graphical representations.

Tab. 5 Selected interatomic distances in the crystal structure of schoepite

U1–O4	1.774(4)	U2–O5	1.791(4)
U1–O11	1.770(4)	U2–O7	1.775(4)
U1–O2 ⁱ	2.550(4)	U2–O1	2.402(4)
U1–O3	2.287(4)	U2–O6	2.219(4)
U1–O10 ⁱⁱ	2.467(4)	U2–O10	2.593(4)
U1–O14	2.410(4)	U2–O14 ^{iv}	2.440(4)
U1–O16 ⁱⁱⁱ	2.430(4)	U2–O16 ^{iv}	2.434(4)
<U1–O _{Ur} >	1.77	<U2–O _{Ur} >	1.78
<U1–O _{eq} >	2.43	<U2–O _{eq} >	2.42
U3–O8	1.773(4)	U4–O9	1.785(4)
U3–O13	1.770(4)	U4–O12	1.783(4)
U3–O1 ⁱ	2.709(4)	U4–O1 ⁱ	2.428(4)
U3–O2 ^v	2.472(4)	U4–O2	2.424(4)
U3–O6	2.230(4)	U4–O3	2.341(4)
U3–O10	2.384(4)	U4–O6	2.236(4)
U3–O16	2.384(4)	U4–O14 ^{iv}	2.640(4)
<U3–O _{Ur} >	1.77	<U4–O _{Ur} >	1.78
<U3–O _{eq} >	2.44	<U4–O _{eq} >	2.41
O1–O3 ^{iv}	2.952(5)	O6–O14 ^{iv}	2.701(5)
O1–O6 ^{iv}	2.743(6)	O7–O14 ^{iv}	2.962(6)
O1–O7	2.848(6)	O7–O21 ^{vii}	2.797(7)
O1–O8 ^{iv}	2.791(5)	O8–O10	2.903(6)
O1–O9 ^{iv}	2.899(6)	O8–O15 ^v	2.835(6)
O1–O16 ^{iv}	2.814(5)	O8–O20 ⁱ	2.877(7)
O1–O20	2.785(7)	O8–O21	2.859(7)
O2–O4 ^{iv}	2.870(6)	O9–O15 ^{viii}	2.978(7)
O2–O8 ⁱⁱ	2.805(5)	O10–O11 ^v	2.917(6)
O2–O9	2.954(6)	O10–O13	2.970(6)
O2–O14 ^{iv}	2.794(5)	O10–O16 ^{iv}	2.633(6)
O2–O15	2.792(7)	O10–O21	2.763(7)
O2–O16 ⁱⁱ	2.801(5)	O11–O14	2.882(6)
O3–O4	2.763(6)	O11–O16 ⁱⁱⁱ	2.992(6)
O3–O10 ⁱⁱ	2.980(5)	O11–O18 ^{ix}	2.922(7)
O3–O12	2.786(6)	O12–O20 ^x	2.961(7)
O3–O19	2.837(7)	O13–O16	2.776(6)
O4–O7 ⁱⁱ	2.918(7)	O13–O17	2.952(6)
O4–O17 ^{vi}	2.976(6)	O14–O18	2.721(7)
O5–O6	2.928(6)	O15–O17 ^{viii}	2.825(7)
O5–O16 ^{iv}	2.967(6)	O15–O21 ⁱⁱ	2.878(8)
O6–O7	2.822(6)	O16–O17	2.631(6)
O6–O8	2.946(6)	O17–O20 ^{xi}	2.839(7)
O6–O9	2.954(6)	O17–O21 ⁱ	2.984(7)
O6–O10	2.709(5)	O19–O20 ^x	2.864(8)
O6–O12	2.801(6)	O19–O21 ^{xiii}	2.975(8)
O6–O13	2.828(6)		

Symmetry codes: (i) $x, -y+1/2, z+1/2$; (ii) $x+1/2, -y+1/2, -z+1$; (iii) $x+1/2, y, -z+3/2$; (iv) $x, -y+1/2, z-1/2$; (v) $x-1/2, -y+1/2, -z+1$; (vi) $-x+1, y+1/2, -z+3/2$; (vii) $-x+1/2, y-1/2, z$; (viii) $-x+1, -y, -z+1$; (ix) $-x+1, y-1/2, -z+3/2$; (x) $-x+1, y+1/2, -z+1/2$; (xi) $-x+1/2, -y, z+1/2$; (xii) $-x+1, -y+1, -z+1$; (xiii) $x-1/2, y, -z+3/2$; (xiv) $-x+1, y-1/2, -z+1/2$; (xv) $-x+1/2, -y, z-1/2$; (xvi) $-x+1/2, y+1/2, z$.

nite–metatorbernite is of the same order as for schoepite–metaschoepite (~7–8 %). The reported behavior of torbernite–metatorbernite resembles above-mentioned phase transitions in schoepite–metaschoepite, dehydra-

Tab. 6 Bond-valence analysis of the crystal structure of schoepite

Atom	U1	U2	U3	U4	Sum of BV	Assignment
O1		0.47	0.25	0.45	1.16	OH
O2	0.34		0.41	0.45	1.20	OH
O3	0.60			0.54	1.14	OH
O4	1.78				1.78	O
O5		1.71			1.71	O
O6		0.69	0.68	0.67	2.04	O
O7		1.77			1.77	O
O8			1.78		1.78	O
O9				1.74	1.74	O
O10	0.41	0.64	0.49		1.54	OH
O11	1.79				1.79	O
O12				1.74	1.74	O
O13			1.79		1.79	O
O14	0.46	0.43		0.28	1.18	OH
O15					0.00	H ₂ O
O16	0.44	0.44	0.49		1.37	OH
O17					0.00	H ₂ O
O18					0.00	H ₂ O
O19					0.00	H ₂ O
O20					0.00	H ₂ O
O21					0.00	H ₂ O
	5.83	6.16	5.88	5.87		

tion of torbernite to metatorbernite in the air at the room temperature as well as torbernite formation at lower temperatures than metatorbernite (from the experiment; Locock and Burns 2003 and references therein). We can speculate that it goes about the same phenomenon during their formation as discussed above in case of schoepite and metaschoepite.

6. Conclusions

Single-crystal X-ray diffraction experiments on two schoepite crystals from the Shinkolobwe mine (Africa) showed that the structure of this mineral is centrosymmetric, of the orthorhombic space group *Pbca*. The fact that the structure is centrosymmetric rather than acentric implies that there is a smaller difference in the value of structural complexity of schoepite and its related mineral metaschoepite that forms by schoepite dehydration (loss of the 1 H₂O from interlayer). This can be also used as evidence that the real structure is centrosymmetric, because the difference in complexity values, when schoepite is considered to be acentric, would be rather large. Dehydration of schoepite to metaschoepite on air is thermodynamically driven, and schoepite is formed from aqueous solutions as a metastable phase during kinetically forced precipitation from supersaturated solutions.

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Tab. 7 Complexity values (including H atoms) for selected minerals

Mineral	Chemical formula	Reference	SG*	ν	I_G (bits/atom)	$I_{G, total}$ (bits/cell)
Schoepite	[(UO ₂) ₄ O(OH) ₆](H ₂ O) ₆	This paper	<i>Pbca</i>	344	5.43	1866.64
		Finch et al. (1996)	<i>P2₁ca</i>	392	6.62	2529.97
Metaschoepite	[(UO ₂) ₄ O(OH) ₆](H ₂ O)	Weller et al. (2000)	<i>Pbcn</i>	324	5.35	1734.11
Torbernite	Cu[(UO ₂)(PO ₄) ₂](H ₂ O) ₁₂	Locock and Burns (2003)	<i>P4/nnc</i>	106	3.16	335.16
Metatorbernite	Cu[(UO ₂)(PO ₄) ₂](H ₂ O) ₈	Locock and Burns (2003)	<i>P4/n</i>	82	3.80	311.32

*Space group

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