

Structural complexity of uranophane and uranophane- β : implications for their formation and occurrence

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Abstract: Information-based parameters of structural complexity for two polymorphs of $\text{Ca}[(\text{UO}_2)_2(\text{SiO}_3\text{OH})_2] \cdot 5\text{H}_2\text{O}$, uranophane and uranophane- β , were calculated in order to assess the impact of the structural complexity on their stability and formation. Calculations proved that uranophane- β is far more complex ($I_{G,\text{total}} = 691.90$ bits/cell) than uranophane ($I_{G,\text{total}} = 345.95$ bits/cell), which indirectly suggests that uranophane may form as a metastable phase during crystallization process. This suggestion is further supported by the lower density of uranophane (3.834 g/cm^3) compared to that of uranophane- β (3.983 g/cm^3). The hypothesis of a metastable character of uranophane is in agreement with Goldsmith's simplicity principle and the Ostwald–Volmer rule and is well supported by the frequency of occurrences of both dimorphic minerals in Nature.

Key-words: uranophane; uranophane- β ; uranyl silicates; structural complexity; crystallization path; metastability; crystal structure.

1. Introduction

Uranyl silicates are the common constituents of the oxidized portions of U deposits and results from the oxidation-hydration weathering of uraninite in environments rich in Si^{4+} (Finch & Murakami, 1999; Krivovichev & Plášil, 2013; Plášil, 2014). Uranyl silicate minerals commonly replace *in situ* primary U minerals in vein fillings, and they form under more reducing conditions than, for example, uranyl phosphates or arsenates. This has been documented by paragenetic observations (Ondruš *et al.*, 2003; Plášil *et al.*, 2006) as well as geochemical studies (Göb *et al.*, 2013). Currently, about 20 uranyl silicate minerals are known (Krivovichev & Plášil, 2013), among which the polymorph minerals uranophane and uranophane- β are the most frequent, being reported from more than 900 localities (source: Mindat.org).

Recently, Krivovichev (2012, 2013) has developed an approach to quantitative evaluation of structural complexity of minerals. This approach is based on Shannon information theory and it allows determination of structural complexity in terms of information stored in the structure (see Section 2). More recently, Krivovichev (2016) demonstrated using statistical arguments that structural information per atom provides a negative contribution to configurational entropy of crystals and, therefore, is a physically important parameter. One of the interesting implications of a quantitative measure of structural complexity is that it provides the possibility to evaluate Goldsmith's (1953) simplicity principle in numerical terms. This principle

states that, under kinetically favoured crystallization regime (such as crystallization from supersaturated solutions or supercooled melts), the crystalline phase that first forms in the system is not the most stable one; it has a simpler structure than that of the stable phase.

Herein, uranophane and uranophane- β , polymorphs of $\text{Ca}[(\text{UO}_2)_2(\text{SiO}_3\text{OH})_2] \cdot 5\text{H}_2\text{O}$, are considered from the perspective of information theory. In order to have relevant structure data for calculation of their structural complexity, a new crystal-structure refinement was undertaken for uranophane- β , since the positions of H atoms were lacking.

2. Methods

2.1. Single-crystal X-ray diffraction

The crystals of uranophane- β were obtained from the samples originating from the Zálesí U deposit (the Rychlebské hory Mts., Silesia, Czech Republic).

An Oxford Diffraction Gemini diffractometer with Atlas CCD detector and $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) from a conventional X-ray tube was used. The structure was solved from diffraction data employing SHELXT program (Sheldrick, 2015) and refined by the Jana2006 program (Petříček *et al.*, 2014). The crystallographic details and refinement parameters are given in Table 1. The original crystallographic information file (cif) is provided as Supplementary Material linked to this article and freely available from the GSW website of the journal: <http://eurjmin.geoscienceworld.org/>. The crystal data for uranophane were taken from the paper by Ginderow (1988).

Table 1. Summary of data-collection conditions and refinement parameters for uranophane- β .

Formula	Ca[(UO ₂) ₂ (SiO ₃ OH) ₂](H ₂ O) ₅
Unit-cell parameters	$a = 6.6262(1) \text{ \AA}$ $b = 15.4553(3) \text{ \AA}$ $c = 13.9506(2) \text{ \AA}$ $\beta = 91.439(1)^\circ$ $1428.23(4) \text{ \AA}^3$
$V [\text{\AA}^3]$	4
Z	$P2_1/c$
Space group	3.983
$D_{\text{calc.}} [\text{g cm}^{-3}]$	306
Temperature [K]	MoK α , 0.71073 $\text{\AA}$
Wavelength	$0.22 \times 0.12 \times 0.12$
Crystal dimensions [mm]	$2.92\text{--}29.39^\circ$
Limiting θ angles	$\bar{8} \leq h < 8, \bar{20} \leq k \leq 21, \bar{19} \leq l \leq 19$
Limiting Miller indices	49124
No. of reflections	3784
No. of unique reflections	3457 [$I > 3\sigma(I)$]
No. of observed reflections	23.27, sphere (Jana2006)
Absorption correction (mm^{-1}), method	0.037/0.087
$T_{\text{min}}/T_{\text{max}}$	0.96, 0.052
Completeness to θ_{max} , R_{int}	1520
F_{000}	
Refinement by Jana2006 on F^2	
Param. refined, constraints, restraints	236, 12, 18
R , wR (obs)	0.0249, 0.0675
R , wR (all)	0.0279, 0.0682
GOF (obs, all)	2.32, 2.23
Weighting scheme	$1/(\sigma^2(I) + 0.0004I^2)$
Extinction; coefficient	Becker & Coppens (1974), 870(50)
$\Delta\rho_{\text{min}}$, $\Delta\rho_{\text{max}}$ ($\text{e \AA}^{-3}$)	$-1.11, 1.77$

2.2. Complexity calculations

In order to compare Ca[(UO₂)₂(SiO₃OH)₂] $\cdot$ 5H₂O polymorphs 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, 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. The amount of Shannon information reflects the diversity and relative proportion of different objects, *e.g.*, the number and relative proportion of different sites in an elementary unit cell of a crystal structure. The quantity of information contained in a crystal structure is given by:

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

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

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 the 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 parameters for the Ca[(UO₂)₂(SiO₃OH)₂] $\cdot$ 5H₂O polymorphs were calculated using the software package TOPOS (Blatov *et al.*, 2014) and are given in Table 2.

3. Structural differences

The crystal structures of uranophane and uranophane- β were first determined by Ginderow (1988) and Viswanathan & Harneit (1986), respectively. Since that time their structures have been revisited (Cesbron *et al.*, 1993; Barinova *et al.*, 2001, 2003), however, structure refinements, except for the first determination by Ginderow (1988), did not include positions of H atoms. Both polymorphs have sheet structures based upon the same sheet-anion topology, *i.e.* the uranophane topology (Burns, 2005; Lussier *et al.*, 2016) (Fig. 1a). The topology consists of chains of edge-sharing pentagons that are separated by chains of edge-sharing triangles and squares.

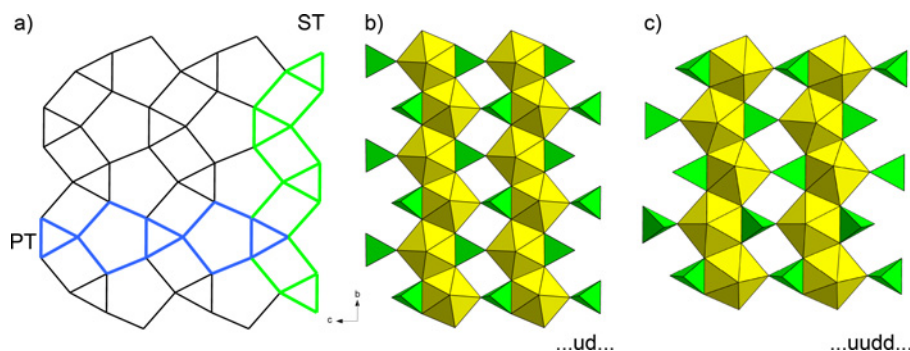


Fig. 1. Structural sheet of uranophane topology. (a) Its graphical anion-sheet topology representation with indicated pentagons-triangles (PT, blue) and squares-triangles (ST, green) chains. (b) Uranophane sheet projected onto (1 0 0). (c) Uranophane- β sheet projected onto (0 1 0). UO_7 bipyramids are in yellow; SiO_4 tetrahedra are in green. The corresponding ST sequences are indicated.

Table 2. Complexity parameters for uranophane and uranophane- β .

Mineral	Space group	a, b, c (Å), β (°)	V (Å ³)	v	I_G (bits/atom)	$I_{G,\text{total}}$ (bits/cell)
Uranophane	$P2_1$	15.909, 7.002, 6.665, 97.27	736	68	5.09	345.95
Uranophane- β	$P2_1/c$	6.6262(1), 15.4553(3), 13.9506(2), 91.439(1)	1428	136	5.09	691.90

There are 27 chemically distinct compounds that contain sheets based upon uranophane anion topology, among them ten minerals. In both uranophane and uranophane- β , the triangles of the topology are occupied by Si^{4+} . In minerals with the uranophane sheet–anion topology several orientational isomers, differing in orientation of the free vertices of the TO_4 groups pointing up (u) or down (d) relative to the plane of the sheets, have been observed (Kubatko & Burns, 2006). Both uranophane and uranophane- β have PT (pentagon-triangles) chains with vertices of tetrahedra pointing all up or all down (Fig. 1b and c), while for an ST (square-triangles) chain there is a ...ududud... sequence for uranophane (Fig. 1b) and ...uudduudd... sequence for uranophane- β (Fig. 1c). A considerable and consequent difference between the structures of the two dimorphs lies in the coordination environment of Ca^{2+} in the interlayer. In the case of uranophane, the Ca site is coordinated by a total of seven ligands (Fig. 2a): four H_2O groups, two apical O_{Ur} atoms (from adjacent sheets) and one atom of the SiO_4 tetrahedron, at an average $\langle \text{Ca}-\Phi \rangle$ distance of 2.41 Å. In uranophane- β , the Ca site is coordinated by a total of eight ligands, four of them are H_2O groups, three of them are O_{Ur} atoms (two within the same sheet and one from adjacent) and one atom of the SiO_4 tetrahedron (Fig. 2b). The average $\langle \text{Ca}-\Phi \rangle$ distance is 2.48 Å.

4. Implications for formation, stability and occurrence

The structural complexity parameters for uranophane and uranophane- β (Table 2) indicate that, from the perspective of Shannon's information theory, the amount of information contained in uranophane- β is twice that of uranophane. According to the current interpretation

(Krivovichev, 2013, 2015, 2017) of Goldsmith's simplicity principle (Goldsmith, 1953), such a difference may indicate that uranophane is a metastable phase, crystallizing under conditions in which it is kinetically, as opposed to thermodynamically, favoured. This is supported by comparing the values of physical density, which is equal to 3.834 g/cm³ for uranophane and 3.983 g/cm³ for uranophane- β . According to the Ostwald-Volmer rule (Holleman *et al.*, 2001), for metastable crystallization, the less dense metastable phase forms first, due to the fact that, under supersaturated conditions, its nuclei reach their critical sizes faster than those of the stable phase (Fischer & Jansen, 2002; Bach *et al.*, 2013). In general, the transformation and transition from the metastable phase into a stable phase may occur along different routes: direct transformation (*i.e.* solid-state phase transition), solvent-mediated transformation, including dissolution of the metastable phase and precipitation of the stable phase, and epitaxy-mediated transformation (when a stable phase crystallizes on the surface of metastable one) (Niekawa & Kitamura, 2013).

This implies that uranophane may be more common in occurrence than uranophane- β . Also, for the crystallization of a metastable phase under kinetically favoured conditions, the metastable phase can be less crystalline than the stable phase, “quickly” crystallizing as nano or microcrystalline phase from oversaturated solutions. In the Mindat.org database, 926 entries are given as localities for uranophane, while “only” 97 localities are listed for uranophane- β . The total numbers may differ, of course; however, the difference between frequency of occurrence of uranophane and uranophane- β is significant. This supports the notion that uranophane is far more common than uranophane- β . Differences are also obvious when looking at the habit and appearance of uranophane and uranophane- β (check, *e.g.*, the photographic database

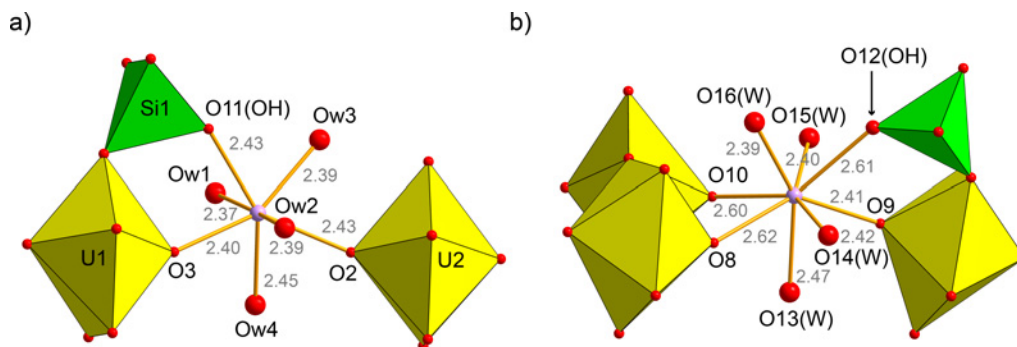


Fig. 2. Coordination environment around Ca²⁺ interstitial cation. (a) In uranophane; (b) in uranophane-β. Bond-lengths are indicated in grey (in Å).

Table 3. Thermodynamic data for uranophane and related uranyl silicates.

Mineral	Formula	$\Delta G_{f, el}$ (kJ/mol), reference	$\Delta G_{f, el}$, predicted (kJ/mol), reference
Uranophane	$1/2 \{ \text{Ca}[(\text{UO}_2)_2(\text{SiO}_3(\text{OH})_2)(\text{H}_2\text{O})_5] \}$	-3099.3 ± 5.6 , Shvareva <i>et al.</i> (2011)	-3123 ± 16 , Clark <i>et al.</i> (1998)
Boltwoodite	$\text{K}[(\text{UO}_2)(\text{SiO}_3(\text{OH}))(\text{H}_2\text{O})]$	-2758.6 ± 3.5 , Shvareva <i>et al.</i> (2011)	-2763 ± 8 , Clark <i>et al.</i> (1998)
Na-boltwoodite	$\text{Na}[(\text{UO}_2)(\text{SiO}_3(\text{OH}))(\text{H}_2\text{O})]$	-2752 ± 2.6 , Shvareva <i>et al.</i> (2011)	-2984 ± 13 , Clark <i>et al.</i> (1998)
Soddyite	$1/2 \{ (\text{UO}_2)_2(\text{SiO}_4)(\text{H}_2\text{O})_2 \}$	-1826.1 ± 2.1 , Shvareva <i>et al.</i> (2011)	-1818 ± 7 , Clark <i>et al.</i> (1998)

within Mindat.org). Uranophane commonly forms long, hair-like or fine needle-like crystals, seldom thick and euhedral. It also forms massive vug-fillings. On contrary, uranophane-β usually forms thick, individual, prismatic crystals in cavities. This also supports the hypothesis that uranophane is a product of kinetically favoured metastable crystallization.

Available thermodynamic data for uranophane (Table 3; Clark *et al.*, 1998; Chen *et al.*, 1999; Shvareva *et al.*, 2011) indicate that uranophane is a stable phase under standard conditions and will preferably form from aqueous solutions at higher pH and Ca²⁺ activity than becquerelite (Shvareva *et al.*, 2011). Comparing boltwoodite, Na-boltwoodite and uranophane, the last is the most stable phase, based on thermodynamic data. Metal-free uranyl-oxide minerals as schoepite, $[(\text{UO}_2)_8\text{O}_2(\text{OH})_{12}](\text{H}_2\text{O})_{12}$ (Finch *et al.*, 1996), or metaschoepite, $[(\text{UO}_2)_4\text{O}(\text{OH})_6](\text{H}_2\text{O})_5$ (Weller *et al.*, 2000) are easily replaced by uranophane when exposed to solutions with high concentrations of Ca and Si (Shvareva *et al.*, 2011); Wronkiewicz *et al.* (1992) observed for long-term alteration experiments with spent nuclear fuel that the formation of uranophane is preceded by that of becquerelite. During laboratory experiments (literature data) and field observations of recently formed (~tens of years) uranyl silicates, as products of recent oxidation-hydration weathering of uraninite in old mines in Jáchymov, Czech Republic, usually only uranophane is reported. However, Wronkiewicz *et al.* (1996) documented by transmission electron microscopy the presence of a sparse zone of uranophane-β in aggregates of uranophane; this is probably a case of dissolution of the metastable uranophane and precipitation of uranophane-β as epitaxy-mediated transformation. From the thermody-

namic data it is obvious that uranophane-β should be even more stable than uranophane (*cf.* values from Clark *et al.*, 1998; Chen *et al.*, 1999; Shvareva *et al.*, 2011) and should preferably form. However, crystallization kinetics appear to favour the formation of uranophane as this phase occurs more frequently in Nature as well as in syntheses (*e.g.*, Cesbron *et al.*, 1993). The cited synthetic experiments yielded uranophane only. The formation of uranophane-β is thus probably restricted to conditions when kinetics effects are less dominant, or it replaces uranophane in later alteration stages through the above-mentioned mechanisms.

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