

Ewingite: Earth's most complex mineral

Travis A. Olds¹, Jakub Plášil², Anthony R. Kampf³, Antonio Simonetti¹, Luke R. Sadergaski¹, Yu-Sheng Chen⁴, and Peter C. Burns^{1,5*}

¹Department of Civil and Environmental Engineering and Earth Sciences, University of Notre Dame, Notre Dame, Indiana 46556, USA

²Institute of Physics, Academy of Sciences of the Czech Republic, 18221 Prague 8, Czech Republic

³Mineral Sciences Department, Natural History Museum of Los Angeles County, Los Angeles, California 90007, USA

⁴Center for Advanced Radiation Sources, University of Chicago, Chicago, Illinois 60632, USA

⁵Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556, USA

ABSTRACT

The newly discovered mineral ewingite is the most structurally complex mineral known. Ewingite is found in the abandoned Plavno mine in the Jáchymov ore district, western Bohemia (Czech Republic), and was studied by synchrotron X-ray diffraction. The structure of ewingite contains nanometer-scale anionic uranyl carbonate cages that contain 24 uranyl polyhedra, as well as Ca and Mg cations and H₂O groups located in interstitial regions inside and between the cages. The discovery of ewingite suggests that nanoscale uranyl carbonate cages could be aqueous species in some systems, and these may affect the geochemical behavior of uranium.

INTRODUCTION

Earth by mass consists almost entirely of structurally simple minerals, with an explosion of diversity and complexity in the volumetrically insignificant crust, and especially in near-surface environments (Hazen, 2010). Mineral species diversity and the complexity of individual mineral species have increased through geologic time as geochemical processes fractionated elements and the atmosphere became oxidizing (Hazen, 2010). Anthropogenically modified systems including mines and their related tailings have produced many new mineral species. Our exploration of an abandoned uranium mine in the Czech Republic has yielded ewingite, which is now Earth's most structurally complex known mineral. Ewingite, named in honor of Rodney C. Ewing (Stanford University, California, USA), formed on a damp wall of the old Plavno mine of the Jáchymov ore district, western Bohemia, in the same region where uranium ore was mined for the studies of Marie and Pierre Curie that resulted in the discovery of polonium and radium more than 100 yr ago. Here we describe ewingite, the structural reasons for its complexity, and its potential significance for modeling of geochemical systems containing uranium.

Most uranium in Earth's crust occurs as the U(IV)-oxide mineral uraninite, UO_{2+x}, and this is also the case in the Plavno mine. In the presence of water and oxidizing conditions, U(IV) is susceptible to hydrolysis (Sylva and Davidson, 1979) and oxidation to U(VI), and readily dissolves as the uranyl ion, (UO₂)²⁺, in groundwater

(Finch and Ewing, 1992; Janeczek and Ewing, 1992; Plášil, 2014). Crystallization from uranyl-bearing solutions often results in fascinating assemblages of brightly colored uranyl minerals, including ewingite (Fig. 1). Uranyl minerals are important for understanding the geochemical history of uranium deposits, and have broader societal importance because they form due to the alteration of spent nuclear fuel in laboratory studies intended to simulate conditions in a geologic repository for nuclear waste (Wronkiewicz et al., 1992, 1996), on radioactive so-called lava (a nuclear reactor meltdown product) produced by the Chernobyl nuclear accident (Burakov et al., 1996), on uranium mine tailings including in Europe, Canada, Australia, and the United States, and in subsurfaces contaminated due to inadequate containment of wastes created during production of nuclear weapons (Buck et al., 1996, 1995). Uranyl minerals affect transport of uranium in the environment, and record the history of natural and anthropogenic processes involving uranium.

METHODS

Chemical Analyses

High-resolution-inductively coupled plasma-mass spectrometry (HR-ICP-MS) was used to determine the empirical formula for ewingite. We hand-picked ~40 small crystals, weighing ~250 µg, with the aid of a microscope and placed them in two separate microcentrifuge tubes. The crystals were digested in 1 mL of high-purity, double-distilled 2% HNO₃ acid and subsequently diluted 200-fold. Solution-mode ICP-MS analyses were done using the AttoM HR-ICP-MS (by

Nu Instruments, <http://nu-ins.com>) in medium mass resolution ($\Delta m/m \sim 3300$). An external calibration method was used to determine the concentrations of U, Mg, Mn, and Ca by measuring ion signals for the isotopes ²³⁸U, ²³⁵U, ²⁴Mg, ²⁵Mg, ⁵⁵Mn, and ⁴⁴Ca.

Single Crystal X-Ray Diffraction

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

RESULTS AND DISCUSSION

Ewingite forms aggregates of golden-yellow crystals as large as 0.2 mm in diameter on altered uraninite, and is associated with other uranyl carbonate minerals, including liebigite and metazellerite (Fig. 1). Uranyl minerals, including ewingite, are typically various shades of yellow, green, and orange because they incorporate the (UO₂)²⁺ uranyl ion, which is a strong coloring agent owing to its electronic transitions. Single-crystal synchrotron X-ray diffraction at the Advanced Photon Source (Argonne National Laboratory, Illinois, USA) allowed solution of the structure; this, in combination with HR-ICP-MS (see the GSA Data Repository¹), established that ewingite is a uranyl carbonate with the composition Mg₈Ca₈(UO₂)₂₄(CO₃)₃₀O₄(OH)₁₂(H₂O)₁₃₈.

The structure analysis revealed that ewingite is tetragonal, space group *I4₁/acd*, with unit cell dimensions *a* = 35.142(2) Å, *b* = 35.142(2) Å, *c* = 47.974(3) Å, and *V* = 59245(8) Å³. The

¹GSA Data Repository item 2017341, complete details of all analytical procedures used during the characterization of ewingite, is available online at <http://www.geosociety.org/datarepository/2017/> or on request from editing@geosociety.org.

*E-mail: pburns@nd.edu

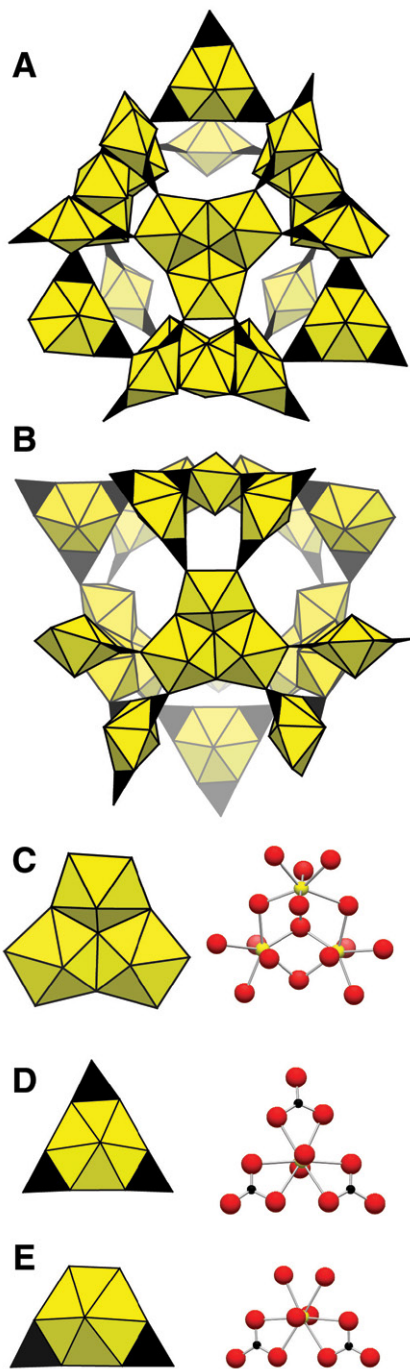


Figure 1. A, B: Polyhedral representations of the uranyl carbonate cage in ewingite in two orientations. **C:** Polyhedral and ball-and-stick representations of the fundamental building unit FBU-1. **D:** FBU-2. **E:** FBU-3. Uranyl pentagonal and hexagonal bipyramids are yellow, carbonate triangles are black. Uranium, carbon, and oxygen atoms are shown as yellow, black, and red balls, respectively.

unit cell volume of ewingite is much larger than those of most minerals, and is a consequence of the presence of a 2.3-nm-diameter cage consisting of uranyl and carbonate polyhedra (Figs. 2A and 2B).

The uranyl carbonate cage in ewingite contains three fundamental building units (FBUs)



Figure 2. Golden-yellow crystals of ewingite on top of massive uraninite, with transparent gypsum, and green crystals of an unnamed Ca-Cu uranyl carbonate. From the Plavno mine (Vladimir shaft), second level (Jáchymov ore district, western Bohemia, Czech Republic). Horizontal field of view is 2.5 mm (photo by Pavel Skacha).

known from other uranyl compounds (Figs. 2A and 2B). In all of these, $(\text{UO}_2)^{2+}$ uranyl ions are approximately linear and have U-O bond lengths of $\sim 1.8 \text{ \AA}$. FBU-1 consists of three uranyl ions, each of which is coordinated by five oxygen atoms arranged about the equatorial regions of pentagonal bipyramids (Fig. 2C). A single oxygen atom in the equatorial planes of the bipyramids is bonded to all three uranyl ions, and the bipyramids each share two of their equatorial edges with two other bipyramids. In FBU-2, a uranyl ion is coordinated by three bidentate carbonate groups, resulting in a hexagonal bipyramid with carbonate groups in the equatorial region of the uranyl ion (Fig. 2D). In FBU-3, a uranyl ion is coordinated by two bidentate carbonate groups and two H_2O groups in the equatorial region of a hexagonal bipyramid (Fig. 2E). One carbon site in the cage is 50% occupied, and the average makeup of the cage requires four FBU-1 and six each of FBU-2 and FBU-3. In Figures 2A and 2B, the partially occupied carbon site is included, and the cage corresponds to four each of FBU-1 and FBU-3, and eight of FBU-3. Linkages between the FBUs within the cage are through carbonate groups.

There are six calcium cations and two magnesium cations inside the uranyl carbonate cage, where they are coordinated by O atoms of the cage, as well as H_2O groups. The uranyl carbonate cages are linked to other cages in the crystal structure by bonds to calcium and magnesium cations, as well as H bonds associated with H_2O groups in the interstitial regions. The interstitial components typically exhibit partial occupancy and disorder.

Mineral structure complexity, or that of any inorganic compound, is quantifiable as the information content of the unit cell, with a higher information content indicating higher complexity (Krivovichev, 2013). Krivovichev (2013) established that the complexity of a crystal structure has implications for modeling assemblages of complex minerals, and how they evolve. Krivovichev's approach quantifies the information content, I_G , of a crystal structure in terms of bits of information per atom:

$$I_G = - \sum_{i=0}^k p_i \log_2 p_i \left(\frac{\text{bits}}{\text{atom}} \right). \quad (1)$$

Here k is the number of crystallographic orbits, where symmetrically equivalent atoms belong to the same orbit, and $p_i = m_i/v$, where m_i is the multiplicity of the crystallographic orbit and v is the number of atoms in the reduced cell. The total information content of the unit cell, I_{Gtotal} , is I_G multiplied by the number of atoms in the reduced cell. The average information content of 3949 minerals is 228(6) bits per unit cell (Krivovichev, 2013). Minerals with more than 1000 bits of information per unit cell are designated very complex, and this designation applies to $\sim 2.5\%$ of known minerals (Krivovichev, 2013).

The TOPOS program (Blatov et al., 2000) was used to calculate that the information content (Krivovichev, 2013) of the structure of ewingite, as determined by the single-crystal X-ray diffraction analysis, is 12,684.86 bits per unit cell. The X-ray data did not provide locations of some of the disordered H_2O groups or any of the H atoms in the structure, although they also contribute to its information content. The total information content is $\sim 23,000$ bits/unit cell when all unit cell constituents are accounted for, more than three times higher than paulingite, a rare zeolite that was formerly the most complex mineral, with 6766.99 bits of information per unit cell (Krivovichev, 2013). The most complex inorganic structure currently is that of the synthetic compound $\text{Al}_{55.4}\text{Cu}_{5.4}\text{Ta}_{39.1}$, with an information content of 48,538.63 bits per unit cell (Krivovichev, 2014). The large family of synthetic compounds that contain uranyl peroxide cages are the most complex inorganic uranium-based materials known (Qiu and Burns, 2013); among the 2000 most complex inorganic structures, these are the seventh-most abundant group (Krivovichev, 2014).

The high information content of the structure of ewingite reflects the presence of the nanometer-scale uranyl carbonate cage (Figs. 2A and 2B). There are eight symmetrically equivalent

cages in the unit cell. The large unit cell contains 121 symmetrically unique atoms, all but 4 of which are on general sites in space group $I4_1/acd$ with a general site multiplicity of 32. Structurally, 5087.59 bits per unit cell is attributable to the nanometer-scale uranyl carbonate cages alone; the remainder of the information content is due to the interstitial species (Ca, Mg, H₂O) within and between the cages.

The structures of 11 uranyl carbonate minerals are known, and their corresponding information contents per unit cell are listed in Table 1. The structure with the lowest information content is that of rutherfordine, with 15.65 bits per unit cell. Bayleyite, línekite, and braunerite have information contents exceeding 1000 bits per unit cell, with braunerite being the second-most complex uranyl carbonate at 2305.36 bits per unit cell.

Uranyl carbonate aqueous species can be important constituents of groundwater under neutral to alkaline conditions (Gorman-Lewis et al., 2008), and efforts have focused on fully defining their speciation in solution (Guillaumont et al., 2003). The uranyl carbonate systems are complicated because multiple species coexist in equilibrium with one another (Clark et al., 1995), some of which constitute only a minor proportion of the total uranium in solution. Despite extensive studies of aqueous uranyl carbonate systems (Clark et al., 1995), including those with Ca uranyl carbonate species (Bernhard et al., 2001; Dong and Brooks, 2006), nanoscale uranyl carbonate cages have not been reported, nor have they been predicted to occur in minerals (Hazen et al., 2009). The uranyl carbonate cage in ewingite may have assembled in aqueous solution prior to crystallization, or it may have formed during the crystallization process. Uranyl peroxide cages with a similar size and the same number of uranyl polyhedra self-assemble in solution prior to crystallization in laboratory experiments (Nyman and Burns, 2012). If the ewingite cage forms in solution it may be necessary to account for such nanoscale cages in geochemical modeling of some uranium-bearing systems.

The ewingite cage resulted from assembly of pre-formed polynuclear species in solution or at the solution-crystal interface during crystal growth. The trimer of uranyl pentagonal bipyramids (FBU-1; Fig. 2C) may be derived from the trimeric hydrolyzed complex $(\text{UO}_2)_3(\text{OH})_5^+$, which is a dominant species in the aqueous uranyl carbonate system over the pH range of 5–6 (Sylva and Davidson, 1979). The uranyl tricarbonate species (FBU-2) is dominant under more alkaline conditions at a pH of ~8 (Bernhard et al., 2001), although elevated concentrations of Ca²⁺ could significantly change the species distribution. As ewingite is intimately associated with liebigite, a calcium uranyl tricarbonate, dissolution of liebigite in a microgeochemical

TABLE 1. A COMPARISON OF STRUCTURAL COMPLEXITY BETWEEN URANYL CARBONATE MINERALS

Mineral	Formula	Unit cell volume	I_{total} (bits/unit cell)
andersonite ⁱ	Na ₂ Ca[(UO ₂)(CO ₃) ₃](H ₂ O) ₆	6544.4	567.38
bayleyite ⁱⁱ	Mg ₂ [(UO ₂)(CO ₃) ₃](H ₂ O) ₁₈	2624.4	1510.28
braunerite ⁱⁱⁱ	K ₂ O[(UO ₂)(CO ₃) ₃](H ₂ O) ₆₋₇	5958	2305.36
čejkaite ^{iv}	Na ₂ [(UO ₂)(CO ₃) ₃]	963.62	161.42
ewingite [*]	Mg ₈ Ca ₈ (UO ₂) ₂₄ (CO ₃) ₃₀ O ₄ (OH) ₁₂ (H ₂ O) ₁₃₈	59245	12684.86
leószilárdite ^v	Na ₂ Mg[(UO ₂)(CO ₃) ₃](H ₂ O) ₆	1189.4	179.33
liebigite ^{vi}	Ca ₂ Mg(UO ₂)(CO ₃) ₃ (H ₂ O) ₁₁	4021.52	567.53
línekite ^{vii}	K ₂ Ca ₃ [(UO ₂)(CO ₃) ₂](H ₂ O) ₈	5622	2140.57
rutherfordine ^{viii}	UO ₂ (CO ₃)	192.9	15.65
schröckingerite ^{ix}	NaCa ₃ (UO ₂)(CO ₃) ₃ (SO ₄)F(H ₂ O) ₁₀	1151.29	578.59
swartzite ^x	CaMg[(UO ₂)(CO ₃) ₃](H ₂ O) ₁₂	1029.94	527.16

Note: I_{G} is information content (see text). References: ⁱCoda et al. (1981); ⁱⁱMayer and Mereiter (1986); ⁱⁱⁱPlášil et al. (2016); ^{iv}Plášil et al. (2013a); ^vthis work; ^{vi}Olds et al. (2016); ^{vii}Mereiter (1982); ^{viii}Plášil et al. (2013b); ^{ix}Finch et al. (1999); ^xMereiter (1986a); ^xMereiter (1986b).

environment may have produced high concentrations of Ca²⁺ ions as well as the uranyl tricarbonate species. In any case, ewingite records evidence of a complex geochemical environment.

The ewingite cage should inspire further synthetic exploration of the aqueous uranyl carbonate system. It establishes that nanoscale cages of uranyl polyhedra exist naturally, and in some cases these may affect the aqueous transport of uranium, which would require modification of existing geochemical models.

ACKNOWLEDGMENTS

This work was funded by the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy, grant DE-FG02-07ER15880. The AttoM high-resolution-inductively coupled plasma-mass spectrometry instrument used for chemical analyses is housed at the Midwest Isotope and Trace Element Research Analytical Center (MITERAC) at Notre Dame University (Indiana, USA). A portion of this study was funded by the John Jago Trelawney Endowment to the Mineral Sciences Department of the Natural History Museum of Los Angeles County (California, USA). Plášil is grateful for the support provided by project LO1603 under the Ministry of Education, Youth and Sports National Sustainability Program I of the Czech Republic.

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Manuscript received 22 June 2017

Revised manuscript received 3 August 2017

Manuscript accepted 4 August 2017

Printed in USA