

THE EVOLUTION OF URANYL INTO AN ORGANIC-RICH CALCITE

The Earth's crust contains some 4% by weight of the mineral calcite, making it one of the most common materials in the crust. While the mechanism was not understood, it has been shown that calcite (CaCO_3) can incorporate hexavalent uranium (U(VI)) into its chemical composition. This leads to two important effects: first, uranium bound in a calcite could be used for geological dating; second, calcite that incorporates excess uranium—perhaps from a contaminated site—will keep that uranium out of groundwater over the long term. By studying an ancient 298-million-year-old organic-rich calcite (calcrete), researchers from Argonne and SUNY Stony Brook have, for the first time, shown the mineral's chemical composition around a stable uranyl—the most common form of U(VI) —contained therein. The researchers believe that the uranyl environment may evolve over long time scales, becoming more calcite-like and even more stable. This is good news for those interested in remediation and dating techniques alike.

The researchers studied a calcrete sample that was precisely dated at 298 ± 1 millennia. The sample shows no evidence of loss of uranium over its lifetime and is believed to have been formed near a water table with some exposure to a reducing environment. Using the MR-CAT sector 10-ID beamline at the APS, the team examined the calcrete with x-ray fluorescence (XRF), microprobe x-ray absorption near-edge spectra (μXANES), and microprobe x-ray absorption fine structure (μEXAFS) data processing.

Previous laboratory studies failed to show how uranium is incorporated into calcite, suggesting that the UO_2^{2+} didn't substitute for the Ca^{2+} in the calcite's crystal structure. It was hypothesized that perhaps the linear UO_2^{2+} moiety could not substitute for the spherically shaped Ca^{2+} and in changing its symmetry from the hexagonal bipyramidal structure of aqueous uranyl triscarbonate to the square bipyramidal structure of the solid calcite, the UO_2^{2+} simply became randomly oriented in the Ca^{2+} site within the calcite.

With the use of the brilliant x-ray beams from the APS, however, the researchers in this study were able to spot the low concentration of uranium and show a different reality. The researchers found that UO_2^{2+} is indeed incorporated at the Ca^{2+} site within the calcite structure, within a well-ordered square bipyramidal geometry. Inside the crystal, one calcium and two carbonate groups are replaced with one uranium and two oxygen of the uranyl structure. The calcite showed three coordination shells of calcium atoms surrounding this uranyl at a distance of approximately 6.5 Å. The presence of the Ca signals at such a large distance attests to the well incorporated uranyl within the calcite structure.

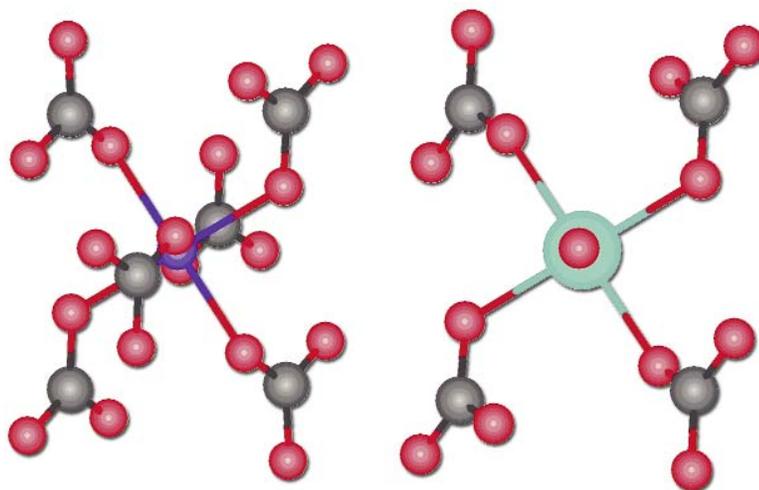


Fig. 1. Schematic of two calcites. The left diagram shows calcium (small dark blue) at the center, and the right diagram has uranyl (large light blue) at the center. Surrounding the centers are oxygen (small red) and carbon (small grey) atoms.

The mechanism of uranium incorporation is still unknown. Biological processes, organic matter, or other impurities may be necessary to incorporate the uranyl into calcite, and understanding this process is certainly not trivial. While this study shows that uranium can be incorporated into calcite under natural conditions, knowing the details of uranium uptake and its stability under different atomic environments is crucial for remediation purposes. This calcite does, however, show a path towards reliable long-term sequestration of uranium. In addition, the stability of the uranium confirms its usefulness as a geological dating technique. — *Karen Fox*

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“Evolution of Uranyl” continued from page 107

See: Shelly D. Kelly^{1*}, E. Troy Rasbury², Soma Chattopadhyay¹, A. Jeremy Kropf¹, and Kenneth M. Kemner¹, “Evidence of a Stable Uranyl Site in Ancient Organic-Rich Calcite,” *Environ. Sci. Tech.* **40**, 2262 (2006).

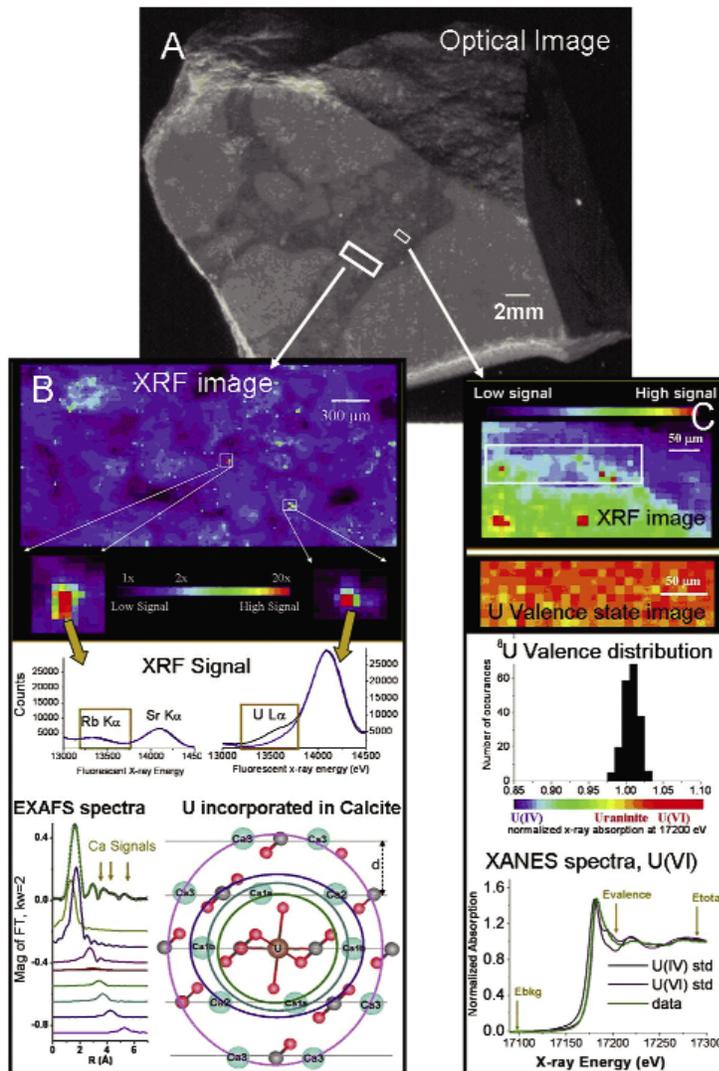
DOI: 10.1021/es051970v

Author affiliations: ¹Argonne National Laboratory, ²SUNY Stony Brook

Correspondence: *skelly@anl.gov.

This work is supported by the Environmental Remediation Science Program, Office of Biological and Environmental Research, Office of Science, U.S. Department of Energy (DOE), under contract W-31-109-Eng-38. The MR-CAT operations are supported by DOE and the MR-CAT member institutions. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38.

Fig. 2 (A): The centimeter-sized calcrite with dark traces representing the remains of dark organic-rich matter around lighter circular regions left from the cross sections of roots. Fig. 2 (B). Shown at the top, the μ -XRF signal, for a spatial distribution of uranium concentration, was determined in the dark organic-rich region outlined with a large square. Within this region, a relatively enriched location was selected for μ -EXAFS measurement. The measured spectrum was determined to be consistent with full incorporation of uranium into the calcite structure, as shown by the μ -EXAFS spectra, model, model components, and molecular diagram at the bottom of the figure. Fig. 3 (C). In another region, outlined by the smaller rectangle in Figure 1a, the μ -XANES structure was imaged (shown at the top). These measurements indicate that the coordination environment of uranium in this region is similar to that where the μ -EXAFS signal was collected, as shown by the Gaussian distribution (shown in the middle) of the absorption signal at the valence state energy above the absorption edge. An example of the full XANES spectra is shown at the bottom of the figure.



“Charged Ions” continued from page 106

fully and partially hydrated Sr^{2+} provides an unprecedented description of ion adsorption at mineral-water interfaces.

The distribution of the Sr^{2+} in two different interfacial sites involves a balance between the energy needed to remove water molecules from the ion's hydration shell and the energy released by compensating the surface charge. The authors theorize that the total structure represents a dynamic equilibrium between partially and fully hydrated species of Sr^{2+} . Therefore the adsorption strengths for the inner and outer spheres must be comparable, contrary to the common assumption that the outer-sphere type is inherently weaker. Ion-hydration energies alone are not, however, able to explain the results given the electrostatic energy difference between the two adsorbed divalent cation species, since the reduction in energy is not large enough. Thus, the difference in hydration energies for Rb^+ and Sr^{2+} can explain their different distributions, but the interfacial hydration structure must also play a role in stabilizing the distri-

butions. Direct determination of such structures, therefore, must be incorporated into theoretical descriptions. — *Karen Fox*

See: Changyong Park^{1*}, Paul A. Fenter¹, Kathryn L. Nagy², and Neil C. Sturchio², “Hydration and Distribution of Ions at the Mica-Water Interface,” *Phys. Rev. Lett.* **97**, 016101 (7 July 2006). DOI: 10.1103/PhysRevLett.97.016101

Author affiliations: ¹Argonne National Laboratory, ²University of Illinois at Chicago

Correspondence: *cypark@anl.gov

This work was supported by the Geosciences Research Program of the Office of Basic Energy Sciences, U.S. Department of Energy, through Contract No. W-31-109-ENG-38 to Argonne National Laboratory and DOE Grants No. FG02-03ER15381 and No. FG02-02ER15364 to the University of Illinois at Chicago. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38.