

# HOW SUBSURFACE BACTERIA BREATHE AFFECTS URANIUM MOBILITY AND DISPERSAL

**U**ranium contamination in aquatic and terrestrial environments has resulted from power generation, nuclear weapons production, and the weathering of uranium (U)-bearing minerals. Under oxic conditions, uranium is stable as uranyl  $U^{VI}$ , which is the more soluble and mobile form in groundwater. However, when bacteria are active in subsurface environments they can reduce  $U^{VI}$  to the less-soluble  $U^{IV}$  form; stimulating indigenous microbes to reduce  $U^{VI}$  in subsurface plumes has been investigated as a remediation strategy for over 15 years. Researchers have thought that the reduced  $U^{IV}$  always formed uraninite ( $UO_2$ ), the most stable and insoluble uranium mineral. However, recent discoveries suggest that bio-reduced  $U^{IV}$  in natural sediments may remain as single atoms for extended periods, either complexed to bacterial or mineral surfaces or incorporated in less-stable  $U^{IV}$  minerals. Researchers carrying out experiments at the MR-CAT 10-ID-B beamline at the APS have gained a new understanding of how uranium reduction occurs so that it may be used to control the spread of uranium contamination, and how a form of reduced uranium could be used as an indicator of how bacteria breathe, providing insight into bacterial physiology. >>>

X-ray spectroscopy  $\longleftrightarrow$   $U^{IV}$  speciation  $\longleftrightarrow$  U plume remediation

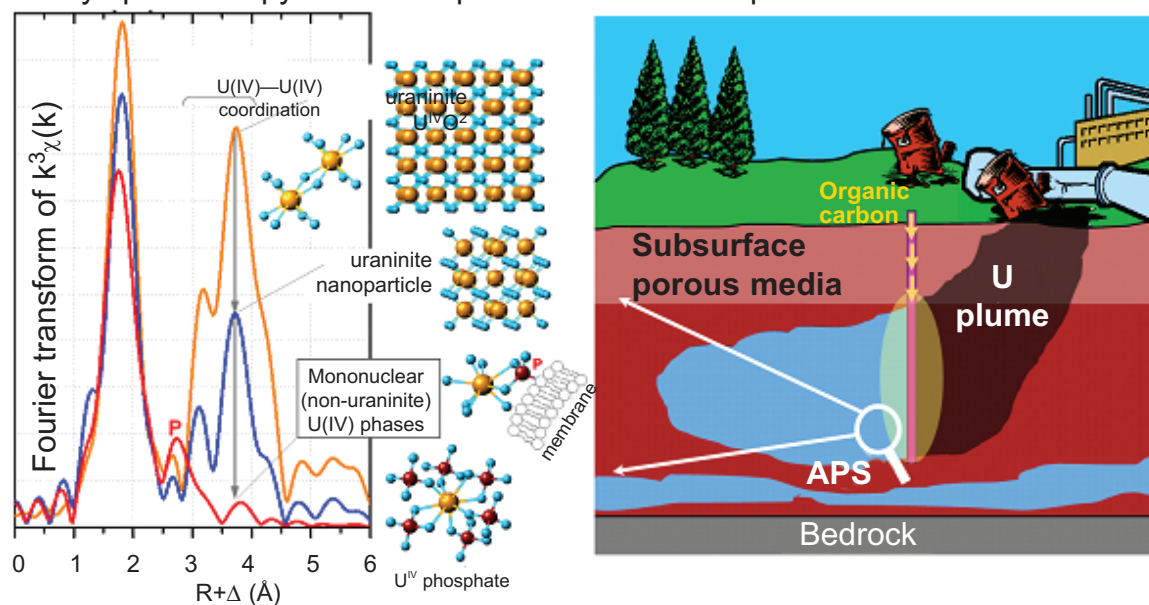


Fig. 1. Left: Fourier transform of U  $L_{III}$ -edge EXAFS data collected from  $U^{VI}$  bioreduction samples at the MR-CAT beamline 10-ID. Analysis of these data provides insight on the molecular speciation of reduced  $U^{IV}$  (middle). This information is essential to predicting uranium plume propagation and devising effective remediation strategies.

In the absence of oxygen, bacteria oxidize carbon to gain energy, using oxidized metals, including uranium, as electron acceptors. With their different cell envelopes, cellular respiration occurs differently in gram-positive and gram-negative bacteria. Each type uses a different mechanism to transfer electrons out of the envelope to external electron receptors. Gram-negative bacteria have outer membrane reductases, allowing direct electron transfer to dissolved or solid electron receptors. In contrast, gram-positive bacteria do not have exposed electron transport proteins on their outer surface, suggesting that electron transfer may occur through soluble intermediates called electron shuttles. Both types of bacteria are found in natural environments and at contaminated field sites.

The researchers from Argonne, the Georgia Institute of Technology, the University of Notre Dame, the University of Tennessee, and Oak Ridge National Laboratory studied the reduction of carbonate-complexed  $U^{VI}$  by active gram-positive and gram-negative bacteria, and compared the results to reduction by a soluble reductant in the same medium. Using the 10-ID-B beamline at the APS for uranium  $L_{III}$ -edge x-ray absorption spectroscopy analyses (via x-ray absorption near-edge spectroscopy, XANES, and extended x-ray absorption fine structure, EXAFS), the authors determined the precise atomic coordination of  $U^{IV}$  produced biotically and abiotically in phosphate-free and phosphate-amended media.

The XANES measurements demonstrated that both types of bacteria reduce dissolved uranium  $U^{VI}$  to  $U^{IV}$ . When phosphate was not present, the researchers observed different  $U^{IV}$  reduction products for the two bacteria types from analysis of the  $U^{IV}$  EXAFS measurements. Gram-negative bacteria create uraninite; in contrast, gram-positive bacteria create a mononuclear, complexed form of  $U^{IV}$ , which may be less stable, and more easily dissolved and dispersed. These findings indicate that gram-positive and gram-negative strains use distinct mechanisms to reduce  $U^{VI}$ . Conversely, by determining the coordination environment of reduced  $U^{IV}$  atoms, the chemical conditions of their formation and the mechanism of electron transfer to  $U^{VI}$  can be inferred. With the addition of phosphate, EXAFS shows  $U^{VI}$  reduction to nonuraninite, phosphate-complexed  $U^{IV}$  species independent of microbial activity (Fig. 1). This result highlights a previously unappreciated control of phosphate on reduced  $U^{IV}$  speciation.

Besides aiding in the understanding of how uranium reduction occurs so that it may be used to control the spread of uranium contamination, the form of reduced uranium could be used as an indicator of how bacteria breathe, providing insight into bacterial physiology. Using the APS, uranium speciation could be employed as a “tag” to uncover electron transfer pathways in highly coupled biotic-abiotic redox systems such as the subsurface.

— Dana Desonie

**See:** Maxim I. Boyanov<sup>1\*</sup>, Kelly E. Fletcher<sup>2</sup>, Man Jae Kwon<sup>1</sup>, Xue Rui<sup>3</sup>, Edward J. O’Loughlin<sup>1</sup>, Frank E. Löffler<sup>4,5</sup>, and Kenneth M. Kemner<sup>1</sup>, “Solution and Microbial Controls on the Formation of Reduced U(IV) Species,” *Environ. Sci. Technol.* **45**, 8336 (2011). DOI:10.1021/es2014049

**Author affiliations:** <sup>1</sup>Argonne National Laboratory, <sup>2</sup>Georgia Institute of Technology, <sup>3</sup>University of Notre Dame, <sup>4</sup>University of Tennessee, <sup>5</sup>Oak Ridge National Laboratory

**Correspondence:** \*mboyanov@anl.gov.

Research under the Subsurface Science Focus Area program at Argonne National Laboratory was supported by the Subsurface Biogeochemical Research Program, U.S. Department of Energy (DOE) Office of Science under contract DE-AC02-06CH11357. Additional DOE funding was provided by the U.S. DOE Environmental Remediation Sciences Program (grant numbers ER63718 and ER64782). K.E.F. acknowledges support through a National Science Foundation graduate research fellowship. M.J.K. was supported by an Argonne Director’s Fellowship and the KIST-Gangneung Institute (Grant 2Z03402). MR-CAT operations are supported by the DOE and the MR-CAT member institutions. Use of the Advanced Photon Source at Argonne National Laboratory was supported by the DOE Office of Science under Contract No. DE-AC02-06CH11357.

10-ID-B • Materials science, environmental science, chemistry • X-ray absorption fine structure, time-resolved x-ray absorption fine structure, micro x-ray absorption fine structure, microfluorescence (hard x-ray) • 4.3-27 keV, 4.3-32 keV, 15-90 keV • On-site • Accepting general users •