

URANIUM GEOCHEMISTRY

William R. Wiley

EMSL NEWS

Environmental Molecular Sciences Laboratory

Spectra-tacular Uranium

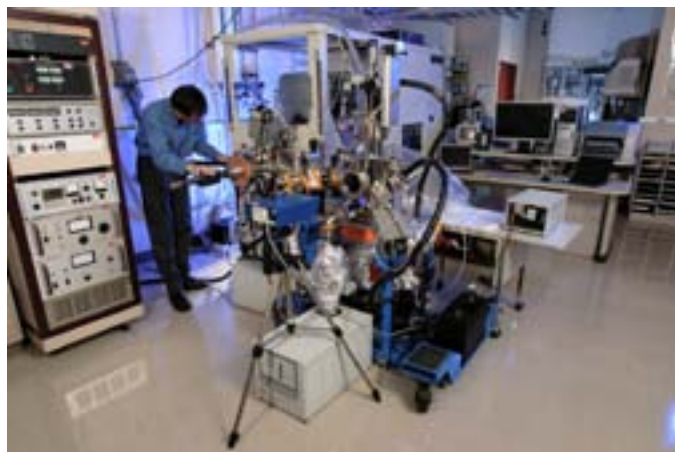
Theory and experiment join forces to find elusive U^{5+} in spectra

Users of the Environmental Molecular Sciences Laboratory are applying a mix of the user facility's scientific capabilities to study the geochemical properties of a lesser known form of uranium, U^{5+} . The study, supported by the U.S. Department of Energy's Office of Basic Energy Sciences, constitutes a powerful and close user collaboration between theorist Paul Bagus, University of North Texas, and experimentalist Eugene Ilton, Pacific Northwest National Laboratory.

Uranium—a contaminant of concern in groundwater—has been predominantly observed by researchers focusing on environmental remediation in two oxidation states: the soluble, mobile, oxidized U^{6+} and the insoluble, less mobile, reduced U^{4+} . But evidence also points to existence of a third form of uranium, U^{5+} .

"The evidence for U^{5+} indicates this form is rare, but this could be for at least three reasons: it *truly* is rare, it has not been looked for properly, or it has been missed because of a sampling issue, say if it readily oxidizes to U^{6+} when exposed to air in the laboratory," said Ilton.

The team found that U^{4+} , U^{5+} , and U^{6+} can be distinguished by examining the very fine features of spectra generated by X-ray photoelectron spectroscopy (XPS). These fine features depend on the oxidation state and bonding environment of the uranium sample. However, the more dependent a feature is on the bonding environment, the more difficult it is to distinguish U^{5+} in the spectra. To help differentiate U^{5+} from the other compounds, the team began incorporating theory by comparing theoretical predictions to experimental data, making analysis of spectra more certain and scientifically convincing.



XPS (shown above) used in combination with computation is helping EMSL users distinguish oxidation states in uranium—including the lesser known U^{5+} .

Bagus and Ilton are now making major advances over earlier work to interpret XPS spectra of uranium compounds, especially in terms of relating the spectra to the chemistry and oxidation states of uranium. Prior theoretical work involved semi-empirical studies, where parameters are adjusted until the best match with experiment is found. However, Bagus, Ilton, and Ria Broer, their collaborator in The Netherlands, showed how misleading such parameter adjustments can be in a 2004 *Chemical Physics Letters* publication. Now Bagus and Ilton are using only *ab initio* methods, meaning that when theory does not agree with experiment they look for missing chemistry in their theoretical models or for unexpected properties of their materials.

Much of the team's theoretical work has focused on atomic models of uranium, but recently their research has extended to models of solid uranium oxides. This advance

Providing the Computational and Experimental Tools in the Fight against Uranium

One of the most challenging and pressing issues confronting the Department of Energy and the nation is the safe, cost-effective management of environmental pollutants and the remediation of hazardous waste sites. DOE is responsible for managing millions of cubic meters of contaminated soils and more than one trillion gallons of contaminated groundwater.



Allison Campbell
EMSL Director

One area of research at EMSL focuses on addressing challenges in geochemistry/biogeochemistry and subsurface science. One of the major challenges being addressed in this research area is uranium—a toxic and radioactive metal. Many sites across the DOE complex where nuclear materials were processed contain high levels of uranium. Uranium compounds can migrate from soils and sediments to groundwater, posing a hazard to human health and the environment.

Researchers are applying experimental and computational tools available at EMSL to study uranium chemistry and environmental transport as well as to find ways to sequester uranium. This issue of EMSL News introduces you to a small sampling of uranium geochemistry/biogeochemistry research and capabilities enabled by EMSL, highlighting the scientific advances of users who hail from the University of North Texas, University of Michigan, and Pacific Northwest National Laboratory. These highlighted projects are examples of successful radionuclide research enabled by EMSL. In the coming years, EMSL plans to continue to expand on that success by providing our users with a radiological annex that will push the frontiers of work with radionuclides.

If you are thinking about becoming an EMSL user, I welcome you to investigate the capabilities and expertise we offer—just go to <http://www.emsl.pnl.gov>.

Allison A. Campbell
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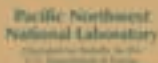
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TRLIFS: Studying Uranium on the Move

A tool available to users at the Environmental Molecular Sciences Laboratory is helping solve one of the nation's most challenging problems: safe, cost-effective management of environmental pollutants and the remediation of hazardous waste sites. EMSL's time-resolved laser-induced fluorescence spectroscopy (TRLIFS) capability can detect and characterize radionuclides and heavy metal ions, including uranium, near their solubility limits, even differentiating species of ions. For these reasons, it is a key tool for understanding the behavior of environmental contaminants at a fundamental level, predicting their behavior with models based on solid experimental measurements, determining their long-term risk, and devising remediation strategies.

TRLIFS and Uranium

Zheming Wang, an EMSL user from Pacific Northwest National Laboratory, helped bring EMSL's TRLIFS system online, and he has applied TRLIFS to study the toxic heavy metal and environmental contaminant, uranium. Uranium mobility in the environment is dependent on the chemical form it assumes in soil, sediment, or water. Uranium commonly exists in the environment as uranyl species, in which uranium is in the soluble, and therefore mobile, oxidation state, U^{6+} . Different uranyl species, for example, uranyl carbonates and uranyl silicates, have different environmental transport characteristics. TRLIFS detects uranium compounds at very low concentrations and yields specific information about the chemical form of uranium in samples, even differentiating among the varied uranyl species.

Wang and his collaborators, including fellow EMSL user from Stanford University, Jeff Catalano, applied TRLIFS to measure uranium in soils and sediments contaminated with tank waste from the Hanford Site in southeastern Washington. These studies provided unparalleled data for use in uranium transport models, enabling more accurate predictions of uranium mobility.

TRLIFS has also been applied to bioremediation studies. Because TRLIFS spectral features are specific to each uranyl

species, whether the species is one of many different mineral phases or aqueous complexes, by measuring the fluorescence of uranium before, during, and after microbial reduction, any change in mineral transformation or uranium complexation can be followed. In addition, Wang's studies have shown that microbial reduction of uranium may be transient over the long term because the byproducts of microbial respiration create an environment favorable for uranium oxidation.

Instrument Detail

TRLIFS is ideally suited for studying ions and molecules that, upon optical excitation, display luminescence (i.e., fluorescence or phosphorescence) lifetimes on the order of nanoseconds or longer. It is commonly used to evaluate the speciation, oxidation state, equilibrium distribution, structure, and bonding of lanthanides, actinides, and transition metal ions. TRLIFS samples may be prepared as solutions, solids, solid suspensions, or as sorbates at solid and sediment surfaces. Applications of TRLIFS include the characterization of environmental contaminants, nanoparticles, aromatics and their derivatives, optical materials commonly used in the telecommunication industry, specialty glasses, as well as illumination devices and optical sensors.

TRLIFS Quick Specs

Nanosecond laser excitation sources

Spectra-Physics Quanta-Ray PRO Nd:YAG laser-pumped MOPO-730 laser

- equipped with a FDO-900 scanning frequency doubler
- allows continuous scanning from 440 nm to 690 nm, 735 nm to 1800 nm, and with the FDO-900 frequency doubler from 220 nm to 440 nm.

Light Age, Inc. Model 101 PAL Alexandrite laser

- tunable from 700 to 800 nm with maximum power up to 16 W
- maximum second harmonics power up to 4.0 W
- maximum third harmonics power up to 0.18 W.

Luminescence Analysis

Acton SP-300 triple grating double monochromator spectrograph

- equipped with a Princeton Instruments PIMAX intensified time-gated CCD camera
- equipped with a thermoelectrically cooled Hamamatsu time-gated photomultiplier tube.

Emission Spectra Recording

Thermoelectrically cooled Princeton Instruments PIMAX time-gated intensified CCD camera

- triggered by the delayed output of the laser pulse
- controlled by the Win Spec™ data acquisition software.

Cryogenic Options

Two Cryo Industries cryostats (RC152 and RC102) and one Cryo Industries microscope cryostat

- fitted with four sealed quartz optical windows, readily replacing the existing sample holder
- equipped with internal heating elements and a Lakeshore 330 auto-tuning temperature controller
- connected to an Edwards mechanical pump and an Edwards 501E turbo molecular pump, allowing spectroscopic measurements from ambient pressure to 10^{-7} torr and from room temperature to 4.2 K.

RELATED PUBLICATIONS

Wan J, TK Tokunaga, E Brodie, Z Wang, Z Zheng, D Herman, TC Hazen, MK Firestone, and SR Sutton. 2005. "Reoxidation of Bioreduced Uranium under Reducing Conditions." *Environmental Science and Technology* 39(16):6162-6169.

Wang Z, AR Felmy, Y Xia, and EC Buck. 2006. "Observation of Aqueous Cm(III)/Eu(III) and UO_2^{2+} Nanoparticulates at concentrations Approaching Solubility Limit by Laser-Induced Fluorescence Spectroscopy." *Journal of Alloys and Compounds* 418(1-2):166-170.

Wang Z, JM Zachara, PL Gassman, C Liu, O Qafoku, W Yantasee, and JG Catalano. 2005. "Fluorescence Spectroscopy of U(VI)-Silicates and U(VI)-Contaminated Hanford Sediment." *Geochimica et Cosmochimica Acta* 69(6):1391-1403.

Wang Z, JM Zachara, JP McKinly, and SC Smith. 2005. "Cryogenic Laser Induced U(VI) Fluorescence Studies of a U(VI) Substituted Natural Calcite: Implications to U(VI) Speciation in Contaminated Hanford Sediments." *Environmental Science and Technology* 39(8):2651-2659.

Wang Z, JM Zachara, W Yantasee, PL Gassman, C Liu, and AG Joly. 2004. "Cryogenic Laser Induced Fluorescence Characterization of U(VI) in Hanford Vadose Zone Pore Waters." *Environmental Science and Technology* 38(21):5591-5597.

Mighty Magnetite

Mineral the Focus of Uranium-Reduction Study

EMSL computational and experimental resources helping University of Michigan researchers with environmental remediation efforts

A potential strategy for remediation of environments contaminated with uranium is being brought one step closer to reality by Environmental Molecular Sciences Laboratory user Frances Skomurski and her fellow researchers from the University of Michigan as well as scientists from Pacific Northwest National Laboratory.

Uranium, a toxic and mildly radioactive heavy metal, exists most commonly in the natural environment as uranyl species, which contains the soluble U^{6+} , as opposed to relatively insoluble U^{4+} . At sites where uranium was mined or at plants where nuclear materials were processed, the soils, sediments, and water are often contaminated with U^{6+} at levels far higher than the amount found in the natural environment. Because of its high solubility, U^{6+} is extremely mobile, presenting a hazard to human health and the environment.

One potential remediation strategy for environments contaminated with uranium is to use compounds containing an Fe^{2+} ion to reduce U^{6+} to insoluble U^{4+} . The ferrous iron in these compounds donates electrons to U^{6+} , transforming it into a more easily sequestered form, such as solid UO_2 .

Skomurski, who since joined PNNL in late 2007, and her team are combining experimental and computational approaches to understand the mechanism underlying uranium reduction, using a model system comprising the uranyl ion (UO_2^{2+}) and the ferrous-iron-bearing mineral, magnetite (Fe_3O_4). In addition to the environmental remediation benefits, magnetite reduction of uranium may be advantageous for the safe storage of spent nuclear fuel from commercial reactors. Magnetite and other iron oxides are expected to form as the steel-containing storage vessels corrode over the long term, potentially barring release of uranium to the environment.

To fully characterize uranium reduction in their model system at the atomic level, Skomurski and her team are employing a suite of EMSL tools, including:

- Atomic force microscopy to observe changes in the topography of magnetite before and after exposure to U^{6+} -bearing solution; for example, to observe sites on the magnetite where U^{6+} was adsorbed
- X-ray photoelectron spectroscopy to observe oxidation states of iron in magnetite before and after exposure

to U^{6+} -bearing solution, and the degree of uranium reduction on the magnetite surface

- Molecular dynamics computational tools to determine energetically favorable conformations of U^{6+} adsorbed on magnetite.

In addition, the team is using the computational chemistry software, Crystal03, developed and maintained by researchers at the University of Torino in Italy, to determine the surface structure of magnetite under environmental conditions as well as the distribution of Fe^{2+} in near-surface environments.



Atomic cluster used to calculate the stability of uranium as a function of its oxidation state. Fe atoms (purple) are in the geometry of Fe in magnetite. The U atom is blue, O atoms are red, and H atoms are white.

For magnetite to be an ideal remediation tool, there should be no significant rate-limiting steps in the transfer of electrons from magnetite to U^{6+} . In the team's model system, the donation of electrons happens via a two-step process: first the electron must be transferred within the magnetite, then it must be transferred from the magnetite to the U^{6+} . To search for a rate-limiting step, Skomurski and her team are using the NWChem computational chemistry software developed at EMSL to determine electron transfer rates at both steps of the process.

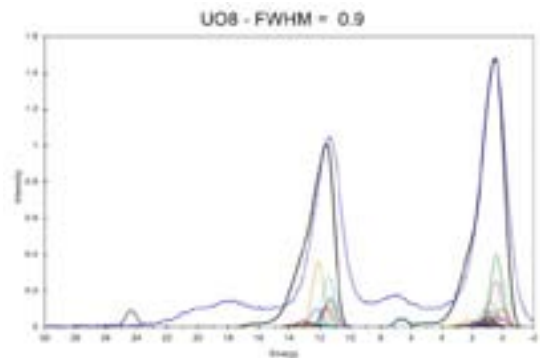
The experimental methods employed by Skomurski and her team have yielded evidence for coupled oxidation-reduction reactions between $Fe^{2+} \rightarrow Fe^{3+}$ in magnetite and $U^{6+} \rightarrow U^{4+}$ on the surface of magnetite. However, not all of the U^{6+} is reduced to U^{4+} . The team's preliminary computational results support the experimental data, suggesting that uranium can be reduced by Fe^{2+} in magnetite, and U^{5+} may be a stable intermediate phase in the uranium-reduction process.

Skomurski's research is funded by the U.S. Department of Energy's Office of Civilian and Radioactive Waste Management Graduate Fellowship Program. The research is also affiliated with the Stanford Environmental Molecular Sciences Institute, which is funded in part by DOE's Office of Biological and Environmental Research. ■

Spectra-tacular Uranium (continued from page 1)

is unique because it constitutes the first *ab initio* relativistic many-body study of the XPS spectra of uranium oxides.

In addition to using computational tools to interpret the fine features of XPS spectra, Bagus and Ilton have begun adapting their method to X-ray absorption near-edge structure—or XANES—spectra, which allows examination of samples *in situ*. The team is now also optimizing its method using laboratory-generated samples. In the future, the team's findings could be adapted to real-world samples, such as those from sites where nuclear materials were processed. ■



Theoretical predictions of (solid lines) and experimental data from (dotted line) high-resolution XPS spectra of UO_2 . The solid black line is the theoretical prediction for the total XPS spectra; color lines represent the individual contributions of different XPS ionized states. These states cannot be resolved experimentally; they can only be obtained with theory.

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The William R. Wiley Environmental Molecular Sciences Laboratory is a Department of Energy national scientific user facility located at Pacific Northwest National Laboratory in Richland, Washington. The EMSL is operated by PNNL for the DOE Office of Biological and Environmental Research.

For additional details about the capabilities and research being performed at EMSL, please visit our web site at <http://www.emsl.pnl.gov> or call us at 509-376-1343.