

Support for Synchrotron Access by Environmental Scientists Project #1023760

Research Objectives

To support ERSP-funded scientists in all aspects of synchrotron-based research at the Advanced Photon Source (APS). This support comes in one or more of the following forms: (1) writing proposals to the APS General User (GU) Program, (2) providing time at MRCAT/EnviroCAT beamlines via the membership of the Molecular Environmental Science (MES) Group in MRCAT/EnviroCAT, (3) assistance in experimental design and sample preparation, (4) support at the beamline during the synchrotron experiment, (5) analysis and interpretation of the synchrotron data, and (6) integration of synchrotron experimental results into manuscripts.

Research Progress and Implications

In March of FY2005, Dr. Bruce Ravel was hired into the MES Group specifically to accomplish the majority of the work on this project. A significant amount of the funding provided in FY2006 was used to cover some of the salary of Dr. Ravel. The remainder of the FY2006 funds was used to cover some of the salaries of other members of the MES Group in their efforts to provide support to ERSP-funded scientists. In addition to supporting ERSP-funded scientists, Dr. Ravel serves as a staff member at the MRCAT/EnviroCAT beamline at the APS. In that role, he is involved in development and operations of the existing insertion device beamline and is one of the leads in the development of a bending magnet beamline which will be optimized for x-ray absorption spectroscopy (XAS) measurements directly relevant to ERSP objectives. This new beam line will increase the amount of time available for synchrotron-based research that can be made available to ERSP-funded scientists via either the APS GU program or the membership of the MES group in MRCAT/EnviroCAT.

Dr. Ravel's specific accomplishments towards facilities development at MRCAT/EnviroCAT include: (1) design and implementation of a new signal and control system at the MRCAT/EnviroCAT insertion device beamline, (2) reimplementation of the motor control infrastructure at 10ID to meet APS safety requirements, (3) lead an effort to specify and evaluate bids for major instrumentation – white beam slits – for the MRCAT/EnviroCAT bending magnet beamline, and (4) sourcing and procurement of all experimental, signal, and control components for the bending magnet beamline.

Dr. Ravel continues development of a leading package of XAS data analysis software which is in wide use throughout the world and popular within the synchrotron environmental science community. This gives ERSP scientists direct access to cutting edge data analysis while assuring that the software development is sensitive to the particular needs of environmental research.

Specific research efforts in support of and in collaboration with ERSP-supported scientists follow. Note that in these descriptions, 1 shift equals 8 hours of time at the beamline indicated, and the MES Group members in italics received support from project #1023760 for their work on the projects listed here.

- **Name of PI of project:** Michael Daly
- **Institution:** Uniformed Services University of the Health Sciences
- **MESG Personnel involved:** *Bruce Ravel, Ken Kemner*
- **BER funding ID:** DE-FG02-04ER63918 (under NABIR)
- **Techniques / beamlines / shifts used:** fluorescence microprobe / 2ID-D / 6
- **Outcome/brief comments:**
Synchrotron studies using the fluorescence microprobe to measure elemental distribution at 150 nanometer resolution were undertaken as a continuation of an effort to understand the role of manganese and iron in the unusual radiation resistance of *Deinococcus radiodurans* and other bacteria. This work follows successful XAS and microprobe measurements in 2005. A manuscript to *Public Library of Science: Biology* has been submitted.

- **Name of PI of project:** Andrew Madden, Anthony Palumbo
- **Institution:** ORNL
- **MESG Personnel involved:** *Bruce Ravel*
- **BER funding ID:** 1024834: An Integrated Assessment of Geochemical and Community Structure Determinants of Metal Reduction Rates in Subsurface Environments
- **Techniques / beamlines / shifts used:** XAS / 20BM / 12
- **Outcome/brief comments:**
XAS measurements were performed on uranium contaminated sediments from the Oak Ridge Y-12 plant. The sediments will also be used in microcosm experiments to determine the nature and extent of uranium immobilization through bioreduction. Dr. Ravel provided assistance in all aspects of the experiment at 20BM from writing the GU proposal to performing and interpreting the experiment.

- **Name of PI of project:** A. Palumbo
- **Institution:** ORNL
- **MESG Personnel involved:** *Shelly Kelly, Bruce Ravel, Ken Kemner, Max Boyanov*
- **BER funding ID:** 1024834: An Integrated Assessment of Geochemical and Community Structure Determinants of Metal Reduction Rates in Subsurface Environments
- **Techniques / beamlines / shifts used:** XAS / 10ID / 1
- **Outcome/brief comments:**
Characterization of reduction products in FRC sediments using different electron donors. This preliminary work lead to the GU experiment described immediately above.

- **Name of PI of project:** N. Qafoku
- **Institution:** PNNL
- **MESG Personnel involved:** *Shelly Kelly, Bruce Ravel*
- **BER funding ID:** FWP number: 47582
- **Techniques / beamlines / shifts used:** XRF and microXAS / 20ID / 9
- **Outcome/brief comments:**
This project is related to understanding the spatial distribution of uranyl chemical species in Hanford sediments. X-ray fluorescence maps at 5 micron resolution were made on core sections. Several spots of high uranium concentration were then selected for XAS measurements. The speciation of U in these sediments is critical for understanding and predicting the biogeochemical processes that will affect the fate and transport of U in the

subsurface at Hanford. Dr. Ravel provided advice on writing the GU proposal for this experiment and on navigating the GU system, resulting in a very successful experiment by Drs. Kelly and Ravel at 20ID using samples provided by Dr. Qafoku.

- **Name of PI of project:** N. Qafoku
- **Institution:** PNNL
- **MESG Personnel involved:** *Shelly Kelly, Bruce Ravel, Ken Kemner, Max Boyanov*
- **BER funding ID:** FWP number: 47582
- **Techniques / beamlines / shifts used:** XAS / 10ID / 7
- **Outcome/brief comments:**

This project is related to understanding the uranyl chemical speciation in Hanford sediments. These bulk XAS experiments make use of the extreme intensity of the APS undulator source to characterize the structural environment of uranium at very low concentrations. The success of these bulk XAS measurements motivated the GU experiment described immediately above.

- **Name of PI of project:** D. Watson
- **Institution:** ORNL
- **MESG Personnel involved:** *Shelly Kelly, Bruce Ravel, Ken Kemner, Max Boyanov*
- **BER funding ID:** 1014578: NABIR Field Site Activities
- **Techniques / beamlines / shifts used:** XRF and microXAS / 10ID / 10
- **Outcome/brief comments:**

A series of XRF images at 400 micron resolution were obtained and correlated to optical and UV images on an epoxy-stabilized, polished gravel sample taken from the FRC Area 2. At spots of high uranium concentration, XAS spectra were measured to provide a chemical speciation map correlated to the optical and UV images.

- **Name of PI of project:** S. C. Brooks
- **Institution:** ORNL
- **MESG Personnel involved:** *Shelly Kelly, Bruce Ravel, Ken Kemner*
- **BER funding ID:** NABIR: *Aqueous Complexation Reactions Governing the Rate and Extent of Biogeochemical U(VI) Reduction*
- **Techniques / beamlines / shifts used:** XAS / 10ID / 7
- **Outcome/brief comments:**

Determine the uranyl complexation and speciation in carbonate rich water in the presence of calcium and/or the chelator, EDTA.

- **Name of PI of project:** C. Criddle
- **Institution:** ORNL
- **MESG Personnel involved:** *Shelly Kelly, Ken Kemner, Max Boyanov, Bruce Ravel*
- **BER funding ID:** 1022978: Field-Scale Evaluation of Biostimulation for Remediation of Uranium-Contaminated Groundwater at a Proposed NABIR Field Research Center in Oak Ridge, TN
- **Techniques / beamlines / shifts used:** XAS / 10ID / 5
- **Outcome/brief comments:**

Samples surged from FRC Area 2 injection/extraction system were characterized with

uranium XAS to understand reduction and reoxidation processes in the treated subsurface water system.

- **Name of PI of project:** W. Burgos, E. Roden
- **Institution:** Pennsylvania State University, University of Wisconsin
- **MESG Personnel involved:** Shelly Kelly, Ken Kemner, *Max Boyanov, Bruce Ravel*
- **BER funding ID:** NABIR: *Fe Reduction and Radionuclide Immobilization: Influence of Natural Organic Matter & Reaction-Based Modeling*
- **Techniques / beamlines / shifts used:** XAS / 10ID / 2
- **Outcome/brief comments:**

Uranium XAS measurements verified the transport of a U(IV) species through a 0.2 micron filter after bioreduction of U(VI) in the presence of soil humic acids. These results indicate that U(IV) may not always form insoluble non-transportable U(IV)-oxide precipitates. (W. Burgos et al, accepted in *Environ. Sci. & Technol.*)

- **Name of PI of project:** J.K. Fredrickson, J.M. Zachara, M. Marshall
- **Institution:** PNNL
- **MESG Personnel involved:** *Max Boyanov, Bruce Ravel, Ken Kemner, Shelly Kelly*
- **BER funding ID:** NABIR FWP: 42302, BER Grand Challenge
- **Techniques / beamlines / shifts used:** XAS / 10ID / 9
- **Outcome/brief comments:**

XAS characterization of uranium reduction by *Shewanella oneidensis* MR-1 and other strains in the presence of different electron donors.

- **Name of PI of project:** G. Redden
- **Institution:** INEEL
- **MESG Personnel involved:** *Shelly Kelly*
- **BER funding ID:** 1020913: Coupling Between Flow and Precipitation in Heterogeneous Subsurface Environments and Effects on Contaminant Fate and Transport
- **Techniques / beamlines / shifts used:** XAS / – / 0
- **Outcome/brief comments:**

Dr. Kelly has helped George Redden prepare an APS general user proposal entitled *Strontium uptake mechanisms due to calcium carbonate precipitation* to compare the affect of calcium carbonate precipitation rates and relative concentration on the local atomic coordination of Sr. Beam time at the APS has not yet been awarded on this project.

- **Name of PI of project:** C. Criddle, W. Wu / D. Phillips, P. Jardine, D. Watson
- **Institution:** Stanford / ORNL
- **MESG Personnel involved:** *Shelly Kelly, Ken Kemner*
- **BER funding ID:** NABIR: *Field-Scale Evaluation of Biological U Reduction and Reoxidation In the Near-Source Zone at the NABIR Field Research Center in Oak Ridge, TN*
- **Techniques / beamlines / shifts used:** XAS / 10ID / 0
- **Outcome/brief comments from user:**

Publication: W. Wu, et al., *In-situ bioreduction of uranium (VI) to submicromolar levels and reoxidation by dissolved oxygen*, submitted to *Environ. Science and Technol.*

- **Name of PI of project:** T. Beveridge and S. Glasauer
- **Institution:** University of Guelph, Ontario
- **MESG Personnel involved:** *Max Boyanov, Ken Kemner*
- **BER funding ID:** NABIR-DE-FG02-99ER62730
- **Techniques / beamlines / shifts used:** microprobe / 2ID-D / 0
- **Techniques used:** microprobe, microXANES
- **Beam lines used:** 2ID-D
- **Total amount of beam time used over the year:** 0 shifts
- **Outcome/brief comments from user:**
 Publication: S. Glasauer, et al., "Mixed valence cytoplasmic iron granules linked to anaerobic respiration," **submitted** to *Applied and Environmental Microbiology*.

- **Name of PI of project:** J.K. Fredrickson and J.M. Zachara
- **Institution:** PNNL
- **MESG Personnel involved:** *Max Boyanov, Ken Kemner*
- **BER funding ID:** NABIR FWP: 42302, BER Grand Challenge
- **Techniques / beamlines / shifts used:** microprobe / 2ID-D / 0
- **Outcome/brief comments from user:**
 Publication: M. J. Marshall, et al, *c-Type Cytochrome-Dependent Formation of U(IV) Nanoparticles by Shewanella oneidensis*, PLoS Biology 4(8), 1324-1333 (2006)

Planned activities

Support of our various collaborations with ERSP-supported scientists will continue in 2007. Time will continue to be provided through our membership in MRCAT/EnviroCAT at the APS. Efforts to guide ERSP scientists through the APS General User Program will also continue with an eye towards expanding the use of the GU Program by ERSP scientists.

\$330K of equipment money was spent in FY2004 for the purchase of an x-ray monochromator to develop XAS capabilities at the MRCAT/EnviroCAT bending magnet beam line. Delivery of the monochromator was long delayed at the source, but final acceptance testing is scheduled for 11 December, 2006. Delivery should follow in January, 2007.

In recent months, other components of the bending magnet beamline have been procured in conjunction with funds from the Environmental Protection Agency, another MRCAT/EnviroCAT member institution. Installation of all components will begin in January, 2007 with installation of the monochromator and other major components scheduled for early Spring, 2007. We anticipate commissioning to be completed by the end of Spring, 2007 and operations to begin in Summer, 2007. At that time we can begin accepting experiments from ERSP collaborators.

Information Access

In FY2006 related to work described in this report: 10 publications in refereed journals, 6 invited talks, 21 contributed talks