Environmental Spectroscopy and Biogeochemistry Facility

The Environmental Spectroscopy and Biogeochemistry (ES&B) Facility supports experimental and modeling studies of chemical phenomena and mechanisms on mineral and microbe surfaces and on complex heterogeneous environmental materials from soils, sediments, and groundwater zones. ES&B Facility staff members, along with other Pacific Northwest National Laboratory staff, form a multidisciplinary research team with expertise in chemistry, mineral physics, geochemistry, soil chemistry, microbiology, and hydrology and advanced computational methods.

Capabilities

Capabilities are available for materials characterization, aqueous- and solid-phase speciation and reaction/kinetic measurements, analytical environmental chemistry, molecular and thermodynamic geochemical process modeling, and intermediate-scale, reactive-transport studies. Research includes studies on:

- surface chemistry of Fe, Mn, and Al oxides; carbonates; and layer silicates
- redox reactions of organic and metal contaminants with Fe- and Mn-containing mineral solids
- biogeochemistry of Fe(III) and Mn(IV) oxide reduction by bacteria and associated bio-mineralization processes
- mineral surface structure and dynamics by modeling and microscopy
- sorbate surface structure and dynamics on mineral surfaces by spectroscopy
- reactivity and thermodynamics of contaminants at high ionic strengths
- intermediate scale subsurface flow and transport
- molecular, thermodynamic and kinetic modeling.

The ES&B Facility consists of seven laboratories that are proximally located to facilitate multi-technique studies. For example, environmental chambers are available with spectroscopic access to allow

Instrumentation & Capabilities

- Analytical chemistry instrumentation
- Scanning probe microscopy
- Spectrophotometers
- Laser fluorescence microscopy
- Laser spectroscopy and kinetic systems
- Scanning and transmission electronic microscopies
- Mössbauer spectroscopy
- Electron paramagnetic resonance spectroscopy
- Controlled atmosphere chambers
- Computational geochemical molecular modeling software and hardware
- Hydro- and biogeochemical modeling and software
- Subsurface flow and transport experimental laboratory
- Thermodynamics measurements of aqueous and adsorption reactions

controlled-atmosphere experiments. These laboratories are located near other instruments that are integral to environmental molecular science, including high-resolution scanning and transmission electron microscopies and a variety of ultrahigh vacuum microprobe techniques for surface analyses. The seven ES&B Facility laboratories are described below.

Optical Spectroscopy Laboratory. Laser-based-fluorescence, breakdown, nonlinear, and Raman spectroscopies and microscopies (Figure 1) are available to use in investigations of aqueous and interfacial reactions. Kinetic studies ranging from stopped-flow to ultra-fast optical pump-probe methods can be performed. Cryogenic capabilities and time-resolved detection methods from pico-second to millisecond for enhanced spectroscopic studies of solution and heterogeneous materials are available. State-of-science Fourier transform infrared (FTIR) spectrometers enable the study of various mineral-chemistry topics as well as sorbate binding mechanisms at mineral, biotic, and organic interfaces. The modular design of the spectrometers in this laboratory enables rapid changing of detector and beam-splitter combinations so researchers can readily change from the visible to the near-, mid-, or far-infrared wavelength ranges. A vacuum bench equipped with a helium-cooled bolometer and step-scanning capabilities is optimized for far-infrared measurements as well as time-resolved spectroscopy. A nitrogen-purged system equipped with a microscope and temperature-controlled mapping stage (-200 to 600°C) allows spatially resolved infrared measurements at the 60-µm level. A variety of cells are available for analyzing gas, liquid, solid, and slurry samples using a variety of techniques. Raman vibrational analyses can be obtained using the FT-Raman module and Raman confocal microscope.

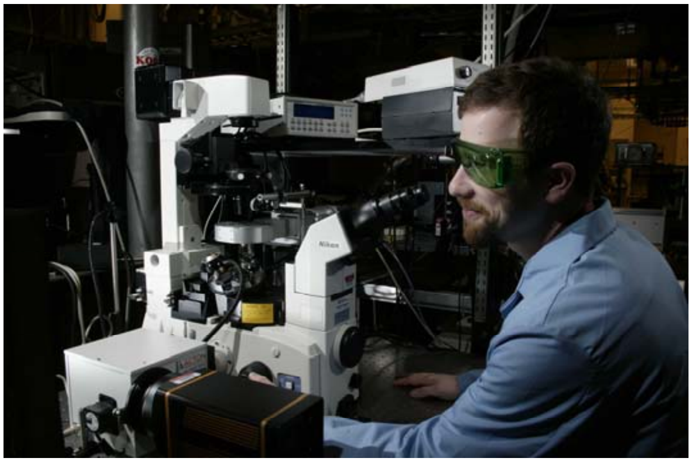

Figure 1. The ES&B Facility offers users an array of instruments, including fluorescence microscopies.

Mössbauer Spectroscopy Laboratory. Four Mössbauer spectrometers with cryogenic capabilities allow studies of Fe structure and redox chemistry in oxides, clays, sediments and biogeochemical systems. Software incorporating Voigt-line fitting and quadrupole-splitting distributions enable state-of-science spectral deconvolution and fitting.

Electron Paramagnetic Resonance (EPR) Spectroscopy Laboratory. A continuous-wave, multi-frequency (S, X, and Q bands) EPR spectrometer equipped with helium-cooled cryostats and a stop-flow/freeze-quench system allows studies of free-radical reactions and electronic environments of paramagnetic species in solids, suspensions, and at surfaces.

Imaging Microscopy Laboratory. Optical and scanning-probe microscopies are available for particle imaging from millimeter to nanometer scales. An inverted optical microscope is available for time-resolved fluorescence imaging in a broad temperature range. Expertise is also available in the characterization of processes of microbial reduction and biogenic mineral formation by high-resolution transmission electron microscopy, involving lattice imaging, selected area diffraction, and energy dispersive spectrometer analysis. A state-of-science scanning-probe microscopy facility has been developed for imaging water-wet samples and microbe-water and mineral-microbe interfaces, and for characterizing a wide variety of environmental materials. A bio-atomic force microscope (AFM) scanning probe is available for protein imaging and force measurements. This new instrument will help researchers meet the special requirements of life sciences microscopy (e.g., studies of delicate biological samples under physiological conditions) and provide detailed observations of molecular structures with unprecedented resolution and without the need for rigorous sample preparation and labeling. The system can be used for studying cellular membrane structures, drug-receptor and virus-cell binding, as well as single-molecule recognition of molecular complexes (e.g., antibody-antigen, ligand-receptor, DNA-protein, DNA-DNA, and protein-protein interactions).

Environmental Analytical Chemistry Laboratory. A wide variety of instrumentation is available for quantification of inorganic and organic contaminants and their reaction, transformation, or degradation products. State-of-science separation instruments, including gas and high-performance liquid chromatographs coupled with mass spectrometry, are available to users engaged in diverse research activities. An inductively coupled plasma mass spectrometer with laser ablation for solids analysis and a collision cell for improved detection of oxide-interfering elements (e.g., Fe) is available for broad-spectrum, high-sensitivity inorganic analyses.

Computational Geochemistry. Multiple workstations linked to the computational infrastructure of the EMSL are available for molecular-level simulations and modeling to support research in the ES&B Facility. Experts are available to perform first-principles molecular dynamics calculations of molecular liquids and solid state systems as well as electronic structure calculations either as stand-alone activity or in support of experimental or spectroscopic measurements. Thermodynamic and kinetic geochemical codes also are available to users, as are multidimensional geochemical reaction/transport codes for numerical experiments or simulations of the intermediate-scale flow and transport experiments described below.

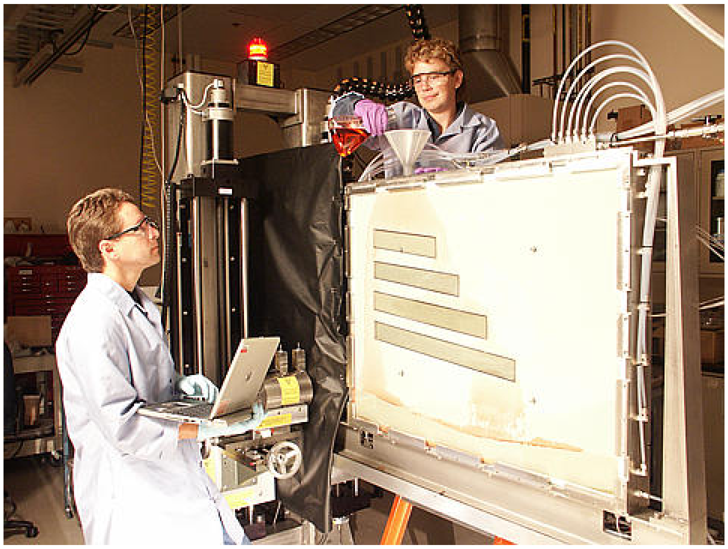

Figure 2. EMSL's Subsurface Flow and Transport Laboratory.

Subsurface Flow and Transport Experimental Laboratory (SFTEL). This laboratory (Figure 2) is uniquely equipped for intermediate-scale (i.e., meter-scale) experimentation in single-fluid and multifluid (air-water, air-nonaqueous-phase liquid [NAPL]-water, NAPL-water) porous media systems. These distinctive experimental systems allow testing of basic theories of flow and transport; studies of coupled processes involved with microbial, reactive chemical, or colloid transport; and experimental simulation of subsurface remediation scenarios. Close linkages exist between this center and the modeling facility, as both pre- and post-experiment modeling efforts are key to experimental design and interpretation. The main focus of the SFTEL is on intermediate-scale experimentation. The laboratory offers several meter-scale flow cells and columns for research in saturated and unsaturated porous media. Some of the flow cells and columns can be used in conjunction with a dual-energy gamma radiation system. The SFTEL also offers a fully automated saturation-pressure apparatus, as well as an automated system to measure fundamental hydraulic properties of soil.

Instrument Upgrades

In Fiscal Year 2006, the ES&B Facility made several upgrades and procurements. These capabilities are grouped by resource.

- **Spectroscopies.** The ES&B Facility demonstrated a laser-induced breakdown spectroscopy capability that will provide spatially resolved elemental analysis of geochemical samples at the micron scale. An infrared diode array detector became operational this past year and has been used to measure infrared fluorescence from technetium species and carbon nanotubes. A fluorescence spectrometer and an electronics upgrade for the confocal Raman spectrometer were procured to increase the efficiency of data collection. Continued investments have been made in an applied-field Mossbauer spectrometer, which is targeted for demonstration in Fiscal Year 2007.

  A confocal Raman microscope for the analysis of radiological samples was added to the facility. The research-grade Dilor XY 800 Raman spectrometer is a high-resolution, modular triple spectrometer that can be operated in high-resolution or high-throughput modes, with both bulk sample and confocal microscopic capability for spatially revolved analysis. In its current location at PNNL's 331 Building, significant quantities of radioactive materials and diverse radionuclides can be investigated. Research of this type has included the investigation of the effects of radiation damage in ^{238}P-substituted silicates as potential radioactive waste storage materials, characterization of novel uranium mineral phases, characterization of contaminated soils from the Hanford Site, and identification of technetium-carboxylate solution species.

- **Quantitative analysis capability.** A single-crystal x-ray diffraction capability, a joint venture with PNNL's Fundamental Science Directorate, became operational. The single crystal diffractometer is a Bruker Proteum rotating annode instrument that supplies brilliant copper radiation. Detection is by a large-format charged-coupled device. This combination of source and detector makes it ideal for determining the structure of very large biological molecules as part of PNNL's Structural Biology research program. Recently, the software was upgraded so that "small molecule" research such as inorganic compounds can be accommodated. For the "small molecule" application, in addition to *de novo* structural determinations, this instrument can provide extremely high-resolution measurements of defect structures and lattice strain as a function of composition that would not be possible on a diffractometer with molybdenum radiation. It also is equipped with a liquid nitrogen cooling stage for temperature-dependent measurements.

  Procurements were also made to upgrade and increase the efficiency of the atmospheric control of four anaerobic chambers. A new ion chromatography system was purchased to replace three older systems that required larger sample volumes and generated higher volumes of waste

- **Geochemical modeling.** The Spokane cluster, a replacement for the dated Seattle cluster, became operational. The system possesses a 32-node (64-processor) cluster, and each node consists of dual 3.0 GHz Intel EM64T Xeon processors, 4-Gb memory, and 73-Gb of disk storage. The system provides EMSL users with increased computational capacity and number of nodes, allowing more jobs to run simultaneously. This machine fills a critical computational need for the ES&B Facility because, historically, many of the projects involve small molecules where large-scale computing resources, such as MPP2, are not required. The scientific systems under study emphasize environmental remediation, including electron transfer involving metal oxides and metal complexes; reactions involving halogenated organic molecules; and reactions at mineral surfaces.

- **Subsurface flow and transport.** Low-flow pumps were procured for the SFTEL. These pumps will allow a better match between flow rates observed in the field and those attained at the laboratory scale.

Future Directions

The ES&B Facility will continue to solicit productive users who publish high-impact science in top-10 journals. The facility will encourage its scientific consultants to travel to either national meetings or to present seminars at universities not currently represented at EMSL. The facility will also coordinate efforts with EMSL User Administration to develop an electronic portfolio of facility research and capabilities to distribute to potential users. The facility will proactively notify users of upcoming national meetings and coordinate attendance so they can present EMSL research.

The ES&B Facility is targeting procurement of the following instruments for Fiscal Year 2007:

- **Applied-field Mossbauer.** Mossbauer spectroscopy is used to characterize both the oxidation state of iron and distribution of iron between different site symmetries in a material due to the electronic spins of the iron d-electrons. The effect of an applied magnetic field on iron in a sample depends on its intrinsic magnetic character (e.g., diamagnetic, paramagnetic, ferromagnetic). Because of this effect, it is possible to resolve peaks that otherwise overlie each other at zero-field. By adjusting the temperature of the sample and magnitude of the applied field, it is possible to completely characterize the iron chemistry of the sample. For example, using an applied field it is possible to distinguish between Fe(II) and Fe(III) in octahedral sites in magnetite. As a result, it is possible to characterize non-stoichiometric magnetite, as the result of incomplete reduction processes, and is difficult to characterize by other techniques. EMSL users have already inquired whether this capability is available.

- **Second harmonic generations (SHG).** With recent improvements in laser technology, stable powerful lasers necessary for SHG and sum frequency generation (SFG) are available and much easier to maintain and use. As a result, interest in SHG and SFG has resurfaced. SHG/SFG provides unparalleled sensitivity to *in-situ* surface speciation as a result of the symmetry relationships required for non-linear optical response.

- **Microfluidics capability**. A capability in microfluidics would serve to bridge the gap between the laboratory-scale flow capabilities currently available in the SFTEL and the spectroscopic and modeling efforts on the molecular scale at interfaces that dominate research in EMSL. Flow experiments in intricately patterned wafers were conducted using fluorescent imaging to monitor mixing of various chemical and biochemical reactants. These experiments involved use of two-dimensional flow cells less than 1 cm long and allowed researchers to investigate how mixing occurs with ion-milled pillars of different diameter, shape, and packing density. These experiments could be extended so that the silicon surface itself is functionalized.

Solution State Structure Determination of Silicate Oligomers by ^{29}Si NMR Spectroscopy and Molecular Modeling

H Cho[a], AR Felmy[b], R Craciun[c], JPKeenum[c], N Shah[c], and DA Dixon[c]

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Silica solution species are an important complexant for many toxic contaminants in the environment, including radionuclides. Establishing a fundamental understanding of all silica solution species allows better prediction of the fate and transport of contaminants in the environment.

Evidence for nine new solution-state silicate oligomers was discovered at EMSL using ^{29}Si nuclear magnetic resonance (NMR) homonuclear correlation experiments of ^{29}Si-enriched samples. In addition to enhancing signal sensitivity, the isotopic enrichment increases the probability of the ^{29}Si-^{29}Si two-bond scalar couplings that are necessary for the observation of internuclear correlations in two-dimensional experiments. The proposed assignments are validated by comparisons of experimental and simulated cross-peaks obtained with high-digital resolution. The internuclear connectivity indicated by the NMR data suggests that several of these oligomers can have multiple stereoisomers, including conformers and/or diastereomers. The stabilities of these oligomers and their possible stereoisomers have been investigated by electronic structure calculations.

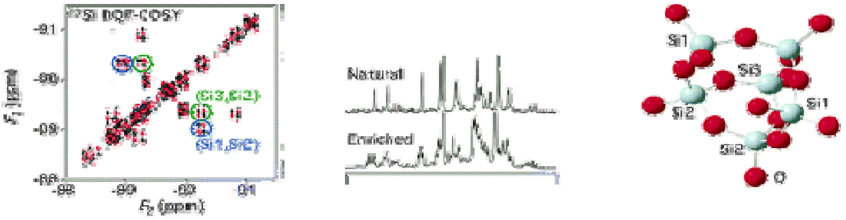

Figure 1. (Left) Two-dimensional ^{29}Si DQF-COSY spectrum of bicyclic hexamer, (center) comparison of one-dimensional ^{29}Si spectra natural and enriched abundance spectra, (right) energy-minimized trans bicyclic hexamer structure.

Experimentally, the significant advancement made in this study was the use of a double-quantum filter (DQF) in collection of the two-dimensional ^{29}Si COSY (COrrelation SpectroscopY) measurements of isotopically enriched silicate solutions. This was essential to suppress the intense dispersive diagonal peaks of singlet lines, which obscure several cross-peaks and autocorrelation multiplets near the diagonal in the nonfiltered experiment (Figure 1).

Computationally, analysis of the correlation experiments is that the newly detected oligomers contain only a small number of chemically inequivalent silicon sites, in most cases three or less. In addition, from the integrated one-dimensional peak intensities, it can be inferred that the new oligomers are comparable in concentration to the small oligomers discovered in the past. These observations imply that the new oligomers should have relatively simple, small, symmetric structures. From a survey of traditional ball-and-stick drawings of oligomer structures, it might appear that there are too few plausible candidate structures with NSi e 6 to support this conclusion, but such drawings fail to adequately represent the multiplicity of isomeric forms a silicate network can assume, especially when the potential chirality of Q3 and Q3t sites is considered. Computational models confirm that several oligomers have several stereoisomers that are stable energy minima, and thus are satisfactory structures. The chirality of certain silicon sites greatly expands the spectrum of geometries that a silicate network can have, both in solution-state species and in solid lattices. These diastereomers will have different NMR parameters, chemical properties, and structures, which suggest greater attention will be needed in future experimental and theoretical studies in the specification of silicate structures with the potential for configurational and conformational isomerism. This research is discussed in further detail in Cho et al. 2006.

Citation

Cho H, AR Felmy, R Craciun, JP Keenum, N Shah, and DA Dixon. 2006. "Solution State Structure Determination of Silicate Oligomers by ^{29}Si NMR Spectroscopy and Molecular Modeling." *Journal of the American Chemical Society* 128(7):2324-2335.

The Effect of Calcium on Aqueous Uranium(VI) Speciation and Adsorption to Ferrihydrite and Quartz

***PM Fox,*[a] *JA Davis,*[a] *and JM Zachara*[b]**

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(b) Pacific Northwest National Laboratory, Richland, Washington

This study demonstrated that the presence of calcium at environmentally relevant concentrations significantly reduces the amount of uranium adsorbed on ferrihydrate and quartz and increases the concentration of soluble and mobile uranium(VI) species.

Recent studies of uranium(VI) geochemistry have focused on the potentially important role of the aqueous species, $CaUO_2(CO_3)_3^{2-}$ and $Ca_2UO_2(CO_3)_3^0$(aq), on inhibition of microbial reduction and uranium(VI) aqueous speciation in contaminated groundwater. However, to our knowledge, there have been no direct studies of the effects of these species on uranium(VI) adsorption by mineral phases. The sorption of uranium(VI) on quartz and ferrihydrite was investigated in $NaNO_3$ solutions equilibrated with either ambient air (430 ppm CO_2) or 2% CO_2 in the presence of 0, 1.8, or 8.9 mM Ca^{2+}. Under conditions in which the $Ca_2UO_2(CO_3)_3^0$(aq) species predominates uranium(VI) aqueous speciation, the presence of calcium in solution lowered uranium(VI) adsorption on quartz from 77% in the absence of calcium to 42% and 10% at calcium concentrations of 1.8 and 8.9 mM, respectively. Uranium(VI) adsorption to ferrihydrite decreased from 83% in the absence of calcium to 57% in the presence of 1.8 mM calcium. Surface complexation model predictions that included the formation constant for aqueous $Ca_2UO_2(CO_3)_3^0(aq)$ accurately simulated the effect of Ca^{2+} on uranium(VI) sorption onto quartz and ferrihydrite within the thermodynamic uncertainty of the stability constant value. This study confirms that Ca^{2+} can have a significant impact on the aqueous speciation of uranium(VI), and consequently, on the sorption and mobility of uranium(VI) in aquifers.

A Review of Multidimensional, Multifluid Intermediate-Scale Experiments: Nonaqueous Phase Liquid Dissolution and Enhanced Remediation

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Intermediate-scale flow cell experiments are used to simulate field-scale processes in the laboratory under controlled conditions.

An invited review of multidimensional, multifluid, intermediate-scale experiments involving nonaqueous phase liquids (NAPLs) was recently published in *Vadose Zone Journal* (Oostrom et al. 2006). These experiments were conducted at an intermediate scale between column studies and field trials (Figure 1). The primary advantage of intermediate-scale flow cell experiments is that field-scale processes can be simulated under controlled conditions. The experiments are frequently conducted to provide datasets to test and verify numerical and analytical flow and transport models. The controlled setting and laboratory instrumentation reduces the uncertainty in parameter estimation, allowing comparisons between simulation and experimental results to focus on flow and transport processes. A total of about 125 original contributions were identified and reviewed.

Research needs in NAPL dissolution include:

- Long-term dissolution studies of multicomponent NAPL in heterogeneous porous media

- Increased understanding of NAPL dissolution upscaling from the pore scale to the field scale
- New theoretical models for NAPL dissolution in mixed-wet porous media.

Research needs in NAPL remediation include:

- Development of multi-flood techniques that combine alcohol and surfactant flushing
- New dense-brine injection techniques
- Development of neutral buoyancy techniques for application in heterogeneous porous media
- Application of heat-based remediation techniques.

Figure 1. EMSL researchers test theories of flow and transport. The study coupled processes involved with microbial, reactive chemical, NAPLs, colloid transport, or test subsurface remediation scenarios using the Subsurface Flow and Transport Laboratory.

Citation

Oostrom M, JH Dane, and TW Wietsma. 2006. "A Review of Multidimensional, Multifluid Intermediate-Scale Experiments: Nonaqueous Phase Liquid Dissolution and Enhanced Remediation." *Vadose Zone Journal* 5:570-598.

Reductive Biotransformation of Iron in Shale-Limestone Saprolite Containing Fe(III) Oxides And Fe(II)/Fe(III) Phyllosilicates

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(c) Miami University, Oxford, Ohio

Iron reduction by dissimilatory metal-reducing bacteria is an important process in anoxic soils, sediments, and subsurface materials, particularly for bioremediation applications. However, the bioavailability of mineral Fe(III) to metal-reducing bacteria appears limited by numerous incompletely understood factors, such as crystal chemistry, solid-phase thermodynamics and surface area effects, and electron transfer efficiency at the mineral-microbe interface.

In this study, we used Mössbauer spectroscopy to determine 1) the distribution of Fe(III) and Fe(II) between mineral sites and between mineral phases prior to and following microbial reduction and 2) the fate of biogenic Fe(II). Mössbauer measurements on the bioreduced sediments indicated that both goethite and phyllosilicate Fe(III) were partially reduced. Biogenic Fe(II) resulting from phyllosilicate Fe(III) reduction remained in a layer-silicate environment that displayed enhanced solubility in weak acid (Figure 1). The mineralogic nature of the goethite biotransformation product could not be identified but was determined not to be siderite, green rust, magnetite, $Fe(OH)_2$, or Fe(II) adsorbed on phyllosilicate or bacterial surfaces. Several lines of evidence suggested that biogenic Fe(II) existed as surface-associated phase on the residual goethite, and/or as a Fe(II)-Al co-precipitate. The results of this work were published in the journal *Geochimica et Cosmochimica Acta* (Kukkapadu et al. 2006).

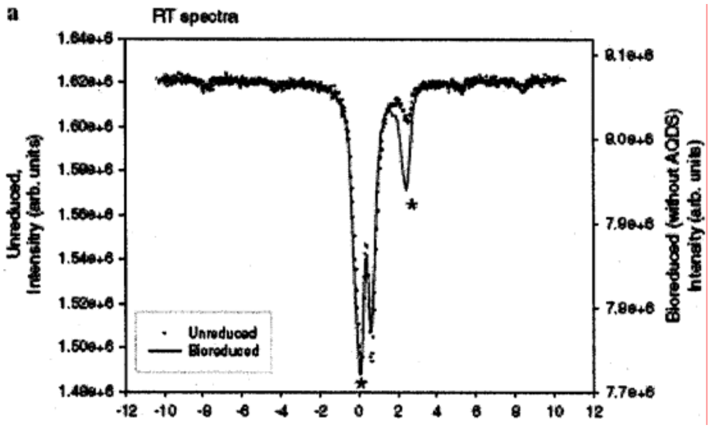

Figure 1. Mössbauer spectra of unreduced and bioreduced sediment.

Citation

Kukkadapu RK, JM Zachara, JK Fredrickson, JP McKinley, DW Kennedy, SC Smith, and HL Dong. 2006. "Reductive Biotransformation of Fe in Shale-Limestone Saprolite Containing Fe(III) Oxides and Fe(II)/Fe(III) Phyllosilicates." *Geochimica et Cosmochimica Acta* 70(14):3662-3676.

User Projects

Lab Studies of Phytoremediation and Apatite Sequestration

JL Phillips, JE Szecsody, CA Burns, Pacific Northwest National Laboratory, Richland, Washington

TW Wietsma, Environmental Molecular Sciences Laboratory, Richland, Washington

Formation of Iron(II) Secondary Minerals After Iron(III) Bioreduction in Humid Tropical Forest Soils

T Peretyazhko, G Sposito, University of California, Berkeley, Berkeley, California

Mossbauer Analysis for Goethite Reacted with Fe(II) and Membrane Fraction of *Shewanella oneidensis*

J Jang, Pennsylvania State University, University Park, Pennsylvania

Geochemical Testing and Model Development - Residual Tank Waste

KJ Cantrell, WJ Deutsch, Pacific Northwest National Laboratory, Richland, Washington

Novel Nanoporous Getters to Immobilize ^{99}Tc at the Yucca Mountain

HM Cho, OS Qafoku, S Mattigod, KM Rosso, Pacific Northwest National Laboratory, Richland, Washington

Environmental Sensing, Metabolic Response, Regulatory Network

JK Fredrickson, DW Kennedy, Pacific Northwest National Laboratory, Richland, Washington

Proteomics of Bioenergetics

JC Scholten, DW Kennedy, Pacific Northwest National Laboratory, Richland, Washington

Demonstration of the Capability of Mobility-Controlled-Flooding Technology to Overcome Heterogeneity Induced Bypassing in Subsurface Remediation

L Zhong, KJ Cantrell, Pacific Northwest National Laboratory, Richland, Washington

TW Wietsma. Environmental Molecular Sciences Laboratory, Richland, Washington

Low-Cost, Energy-Efficient Nitrogen Fertilizer 48291

JE Amonette, CC Bashore, Pacific Northwest National Laboratory, Richland, Washington

Mechanisms and Dynamics of Abiotic and Biotic Interactions at Environmental Interfaces

GE Brown, Stanford University, Stanford, California

KM Rosso, S Yanina, S Kerisit, Pacific Northwest National Laboratory, Richland, Washington

CS Lo, University of Alaska Fairbanks, Gaithersburg, Maryland

Lignin Content in Natural Fibers Utilizing Fluorescence Microscopy

JD Holbery, Pacific Northwest National Laboratory, Richland, Washington

Theoretical Treatment of the Kinetics of Uranium Reduction by Magnetite Surfaces

MC Wander, MA Schoonen, RJ Reeder, State University of New York at Stony Brook, Stony Brook, New York

JD Kubicki, Pennsylvania State University, University Park, Pennsylvania

The Reduction of Uranyl and Chromate to Insoluble Species by Green Rust and Other Ferrous Hydroxides Surfaces

MC Wander, MA Schoonen, RJ Reeder, State University of New York at Stony Brook, Stony Brook, New York

Scintillator Research

M Bliss, Z Wang, JE Amonette, SD Miller, Pacific Northwest National Laboratory, Richland, Washington

Thrust 3,4: Molecular Forces in Bacterial Adhesion at the Oxide-Water Interface

MF Hochella, S Bose, NS Wigginton, Virginia Polytechnic Institute, Blacksburg, Virginia

TC Droubay, Pacific Northwest National Laboratory, Richland, Washington

Establish a Penn State Center for Environmental Kinetics - as part of the Environmental Molecular Science Institute (EMSI) Program (NSF/DOE-OBER)

T Peretyazhko, University of California, Berkeley, Berkeley, California

JM Zachara, Z Wang, Pacific Northwest National Laboratory, Richland, Washington

A Dohnalkova, PL Gassman, Environmental Molecular Sciences Laboratory, Richland, Washington

WD Burgos, ML Minyard, SL Brantley, DR Hummer, DE Ross, MC Davis, H Tan, Jn Senko, Pennsylvania State University, University Park, Pennsylvania

FTIR Characterization of Fe Films Formed on Ephemeral Pool

GH Grathoff, HR Easterly, Portland State University, Portland, Oregon

Characterization of Synthesized Mixed Valent Naturally Occurring Fe-Films

GH Grathoff, Portland State University, Portland, Oregon

Thrust 4: Whole Cell and Cytochrome Biological Force Microscopy

BH Lower, Pacific Northwest National Laboratory, Richland, Washington

Cr(VI) Removal from Aqueous Solution Using a Commercial Activated Carbon Coated with Quaternized Poly(4-vinylpyridine)

C Liu, Pacific Northwest National Laboratory, Richland, Washington

B Deng, University of Missouri, Columbia, Columbia, Missouri

Probing the Structural Network of Buried Water Molecules in the Hydrophobic Core of Staphylococcal Nuclease

RL Reynald, EE Lattman, Johns Hopkins University, Baltimore, Maryland

Thrust Area 4: How Redox Proteins on the Exterior of the Outer Membrane of *Shewanella* Accomplish Interfacial Electron Transfer to the Fe(III) Oxide Surface

CM Eggleston, University of Wyoming, Laramie, Wyoming

AM Spormann, JN Ha, Stanford University, Stanford, California

TC Droubay, Pacific Northwest National Laboratory, Richland, Washington

Thrust Area 1: The Surface Structure of *Shewanella* and the Localization of Outer Membrane-associated Proteins Hypothesized to be Involved in Electron Transfer from Metal-reducing Bacteria to Metal Oxide Surfaces

TJ Beveridge, JR Dutcher, University of Guelph, Guelph, Ontario, Canada

TC Droubay, Pacific Northwest National Laboratory, Richland, Washington

Thrust Area 3:Mutagenesis and Functional Characterization of *Shewanella oneidensis* Genes Involved in Fe(III) and Mn(IV) Oxide Reduction (LDRD #3)

TJ Beveridge, University of Guelph, Guelph, Ontario, Canada

AS Beliaev, MF Romine, JK Fredrickson, Pacific Northwest National Laboratory, Richland, Washington

T Dichristina, Georgia Institute of Technology, Georgia Tech Research Corporation, Atlanta, Georgia

TW Wietsma, Environmental Molecular Sciences Laboratory, Richland, Washington

Simulating Mineral Interfaces

WH Casey, University of California, Davis, Davis, California

EJ Bylaska, Pacific Northwest National Laboratory, Richland, Washington

JH Weare, SA Bogatko, University of California, San Diego, La Jolla, California

The Interaction Between Uranium(VI) and Magnetite Surfaces: A Combined STM and Electron Transfer Calculation Approach

FN Skomurski, RC Ewing, U Becker, University of Michigan, Ann Arbor, Michigan

Strait Science - Biosensor Task 1.1 of the Coastal and Environmental Effects Program

DW Ewert, M Pinza, JR Adamec, Pacific Northwest National Laboratory, Sequim, Washington

FTIR and SEM Characterization of Desert Varnished Rocks

CA Hibbitts, Johns Hopkins University, Laurel, Maryland

Evaluate Injection of Zero Valent Iron (PNNL Scope# 488994: Oostrom, Fluor Daniel Hanford)

M Oostrom, Pacific Northwest National Laboratory, Richland, Washington

Laser Fluorescence Analysis of Natural Isotopic Abundance Uranium Oxide Samples

JE Amonette, Pacific Northwest National Laboratory, Richland, Washington

Time-Revolved Laser Spectroscopy of Europium Adsorbed on Gibbsite and Silica

GV Korshin, University of Washington, Seattle, Washington

Foldable Polymers

JJ Han, AD Li, Washington State University, Pullman, Washington

Determination of DNAPL Mass Flux Reduction as a Function of Source Zone Mass Removal

EL Difilippo, ML Brusseau, University of Arizona, Tucson, Arizona

Characterization of Novel Arsenic-Iron Precipitates Formed during Biological Iron Reduction

BD Kocar, S Fendorf, Stanford University, Stanford, California

T Borch, Colorado State University, Fort Collins, Colorado

A Dohnalkova, RK Kukkadapu, Environmental Molecular Sciences Laboratory, Richland, Washington

Determining the Effects of Gamma Irradiation on the Oxidation State of Iron using Mossbauer Spectroscopy

TL Bank, PM Jardine, Oak Ridge National Laboratory, Oak Ridge, Tennessee

Investigation of Metals Corrosion in SOFCs Using Raman Spectroscopy

G Xia, Pacific Northwest National Laboratory, Richland, Washington

PL Gassman, Environmental Molecular Sciences Laboratory, Richland, Washington

Mossbauer Effect of Organically Grown Plants

CI Wynter, Nassau Community College, Garden City, New York

Effect of NAPL Dissolution on NAPL-Water Interfacial Area

M Oostrom, MA Covert, Pacific Northwest National Laboratory, Richland, Washington

TW Wietsma, Environmental Molecular Sciences Laboratory, Richland, Washington

M Schroth, Swiss Federal Institute of Technology, Zurich, Switzerland

Couple Proton-electon Dynamics in Iron-containing Phyllosilicates: Annite, $KFe_3AlSi_2O_{10}(OH)^{2}$ - Mössbauer Determination of Fe^{2+}/Fe^{3+} Ratio

NJ Hess, ES Ilton, Pacific Northwest National Laboratory, Richland, Washington

RK Kukkadapu, Environmental Molecular Sciences Laboratory, Richland, Washington

Transformations in Iron Mineralogy Induced by Microbial Processes in Natural Sediments

RG Ford, Environmental Protection Agency, Ada, Oklahoma

Characterization of Synthetic Mixed Valence U Compounds

NJ Hess, ES Ilton, Z Wang, Pacific Northwest National Laboratory, Richland, Washington

CL Cahill, George Washington University, Washington DC, Wash DC

Determination of Hydrolysis Rate for CCl_4 under Ambient Groundwater Conditions

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Zero Emission Research & Technology (ZERT) CO_2 Sequestration Leakage Evaluation Task: Parameterization of Leakage from Geologically Sequestered CO_2

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Microscopic Visualization of Membrane Pores and Bacterial Foulants

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Evaluation of Pore Scale Porous Media Effects on Reactive Transport in Groundwater

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Development of Microscopically-Based Models for Prediction of the Impact of Surface Grain Coating on Mineral Dissolution and Leaching Rates

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Multiscale Design of Advanced Materials based on Hybrid *ab-initio* and Quasicontinuum Methods

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Substrate-specific Binding of *Staphylococcus* Adhesins to Solid Surfaces

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Quorum Sensing in a Dissimilatory Metal Reducing Bacterium

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Raman Capability for EMSL Users

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Development of an Integrated Atomic Force/Fluorescence Microscope at EMSL

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Specificity of *Shewanella oneidensis* Outer Membrane Cytochromes OmcA and OmcB Towards Iron- and Manganese-oxide Surfaces

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Basis of Microbial Membrane Attachment to Mineral Surfaces and Ionic Contaminants Uptake

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Mössbauer Analysis of Microbial Redox Transformations of Naturally Occurring Fe(III)-bearing Phyllosilicates

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Determination of Hydraulic Conductivity and Soil Moisture Retention Relations with the EMSL Hydraulic Properties Apparatus

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IR and RAMAN Analysis of Water Diffusion in the Surface of Glasses for Nuclear Waste Immobilization

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Determination of Fluorescence Lifetime of Natural Organic Matter

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Enhancing C Sequestration in Terrestrial Ecosystems: Linking C and N Cycling in Soils (Part of Center for Research on Carbon Sequestration in the Terrestrial

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Mineralogical Analysis of Substrates and End-products of Microbial Fe Redox Transformations

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A Theoretical and Experimental Investigation of Multiplet Splitting for CR and U Spectra Generated by X-ray Photoelectron Spectroscopy

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Microbial Reduction of Iron in Sedimentary Clays: Implications for Subsurface Microbial Ecology and Bioremediation

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Nanoscale Investigation of Microbial Role in Promoting the Smectite to Illite Transformation

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Characterization of Biologically Reduced U Particles

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Formulating the CD-MUSIC Surface Complexation Model from First Principles Calculations for Phosphate Adsorption on Goethite

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Analyses of Electron Density Distributions in Earth Materials with Implications for Reactivity

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Surface Structure Effects on Direct Reduction of Iron Oxides by *Shewanella oneidensis*

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Structure and Reactivity of the Basal and Edge Surfaces of Gibbsite

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Critical Point Properties of Electron Density Distributions in High-pressure Mineral Phases

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Investigation into the Polarized Raman Spectra of Benzene, Benzene-d6 and Hexafluorobenzene

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The Aqueous Thermodynamics and Complexation Reactions of Anionic Silica and Uranium Species to High Concentration

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Multi-Resolution Structure and Reactivity of Kinetically Roughened Oxide Surfaces: Nanometric Scaling Behavior and Molecular-Scale Controls

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The Development of Thermodynamic Models for Actinide Species in Mixed Solvent Systems: Application to Binding in Microbial Membranes

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Model Porous Solids and Sediments

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Enhancing Carbon Sequestration and Reclamation of Degraded Lands and Sequester C in Soils

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Carbon Tetrachloride Degradation Reaction Mechanisms

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A Bioengineering Approach to the Production of Metal and Metal Oxide Nanoparticles

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Chemical Speciation of Americium, Curium, and Selected Tetravalent Actinides in High Level Waste

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Interactions Between Fe(III) - Reducing Bacteria and Fe Oxides: Microbial and Geochemical Dissolution Controls

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Coupling of Fe and Tc Speciation in Subsurface Sediments: Implications to Long-Term Tc Immobilization

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Mineralogic Residence and Desorption Rates of Sorbed ^{90}Sr in Contaminated Subsurface Sediments: Implications to Future Behavior and In-Ground Stability

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Characterization of U(VI) Sorption-Desorption Processes and Model Upscaling

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Influence of Mass Transfer on Bioavailablility and Kinetic Rate of U(VI) Biotransformation

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Reactions and Transport of Toxic Metals in Rock Forming Silicates at ^{25}C

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Actinide Interactions with Environmental Bacteria

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Characterization of U(VI) Speciation in Samples from Laboratory Batch and Column Experiments

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Liquid Infrared Spectroscopy and Spill Phenomenology

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Movement and Dissolution of a Viscous, Multicomponent Light Nonaqueous-Phase Liquid in a Fluctuating Water Table System

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Quantification and Chemical Analysis of Iron Oxidation in Microbially-Reduced Sediments

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Model Development on Using Clay Membranes for Arsenic Removal from Drinking Water

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Biogeochemical Heterogeneity in the Subsurface

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Intermediate Flow Cells

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Computational Investigation of Acid Base, Surface Complexation, and Oxidation/Reduction Reaction Mechanisms on Iron Oxide and Iron Silicate Surfaces

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Enhance Plutonium Mobility during Long-Term Transport through an Unsaturated Subsurface Environment: Iron and Manganese Oxide Characterization

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Uranium Immobilization by Sulfate-Reducing Biofilms

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Fate of Nitrogen Gas Produced by Denitrification during U and Tc Bioreduction

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Interfacial Reduction-Oxidation Mechanisms

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How Aluminum Substitution in Goethite Affects Iron Release

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Characterization of Coupled Hydrologic-Biogeochemical Processes Using Geophysical Data

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Separation of Corn Fiber and Conversion to Fuels and Chemicals - Pilot Operation

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Influence of Calcium on Aqueous U(VI) Speciation and U(VI) Sorption to the Hanford Sediments

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Photophysics of Organophosphorous Compounds

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Influence of Flow on Abiotic and Biotic Reactivity of CL--20 (hexaanitrohexaazaiso-wurtzitane)

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Conductivity of Bacterial Nanowires

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Transmission Electron Microscopy Analysis of a Novel Organo-Cr(III) Degrading Bacterium

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Mossbauer Spectroscopic Investigations of Fe Doped SnO_2 Powders

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Synthesis and Characterization of Limited Solubility U(VI) Bearing Compounds in Concrete

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