William R. Wiley EMSL Environmental Molecular Sciences Laboratory

Applying EMSL Capabilities to Biogeochemistry and Environmental Research

Office of Science U.S. DEPARTMENT OF ENERGY

Pacific Northwest National Laboratory
Operated by Battelle for the U.S. Department of Energy

The Environmental Molecular Sciences laboratory (EMSL) is a national scientific user facility operated by the Pacific Northwest National Laboratory (PNNL) for the U.S. Department of Energy's Office of Biological and Environmental Research.

Located in Richland, Washington, EMSL offers researchers a comprehensive array of cutting-edge capabilities unmatched anywhere else in the world and access to the expertise of over 300 resident users – all at one location.

EMSL's resources are available on a peer-reviewed proposal basis and are offered at no cost if research results are shared in the open literature.

Researchers are encouraged to submit a proposal centered around one of EMSL's four Science Themes, which represent growing areas of research:

- Geochemistry/Biogeochemistry and Subsurface Science
- Atmospheric Aerosol Chemistry
- Biological Interactions and Dynamics
- Science of Interfacial Phenomena.

To learn more about EMSL, visit www.emsl.pnl.gov.

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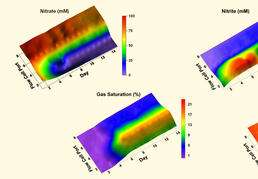
Subsurface Flow and Transport

Examining the impacts of microbial growth (Intermediate Scale Flow Cell)



- Research was performed in Support of the U.S. Department of Energy's Field Research Center.
- Microbial activity was monitored by measuring nitrate, nitrite, and ethanol concentrations. Gas saturations were measured using a gamma imaging system.
- Results show the response of the geochemical system to microbial denitrification and the impact on permeability from microbial groth and gas generation.

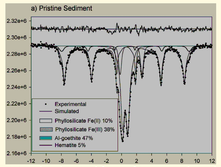
J. Istok, Oregon State University

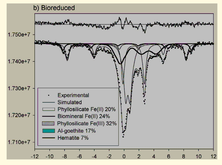
Determining Chemical Forms in Sediments and Solutions

Iron determination (Mössbauer Spectroscopy)

Mössbauer spectra of unreduced and bioreduced FRC sediments

Upon bioreduction, phyllosilicate Fe(III) and Al-goethite content decreased with concurrent increase in phyllosilicate Fe(II) and precipitation of a biogenic Fe(II) mineral (Kukkadapu et al., GCA, 70, (2006), 3662-3676).





- Determining the chemical form of iron in soils and sediments during bioreduction is a key factor in determining the chemical form of radionuclides as well as in microbial growth.
- Mössbauer spectroscopy is a highly sensitive probe of both the chemical form of iron and the relative mass in each chemical form.

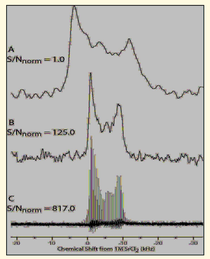
EMSL currently has three functional Mössbauer units that can operate from room temperature to 4K.

Coming Soon: Applied-field Mössbauer maghemite/magnetite, pyrite/iron oxides

Tc and Sr determination (Nuclear Magnetic Resonance)

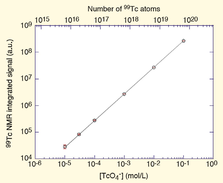
Highly sensitive NMR capabilities

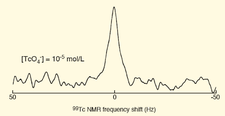
Sr (EMSL 900 MHz)



Strontium carbonate ^{87}Sr NMR spectra: (A) static echo at 11.74 T (800-MHz), (B) static echo at 21.14 T scaled by 1/37, and (C) QCPMG at 21.14 T (900-MHz) scaled by 1/275.

99Tc (EMSL Radiological NMR)

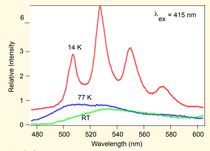




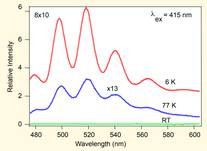
G. Bowers, et al., Penn State University

Uranium determination (Laser Fluorescence Spectroscopy)

Hanford sediment S01014-53A
[U] = 142 µg/g



Uranyl carbonate solution at pH 11
[U] = 2x10-5M, [Na_2CO_3] = 0.008 M



EMSL Capabilities

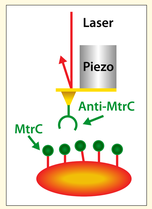
- Dramatic spectral intensity/resolution enhancement at LHeT
- Applicable to solid, liquid, solid suspension, paste
- High sensitivity
- **Creation of U(VI) fluorescence spectral library**

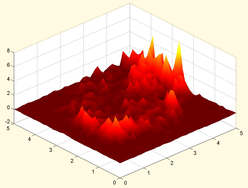
Z. Wang, PNNL

Characterizing Biological Systems

Determining proteins in the outer microbial membrane (Atomic Force Microscopy)

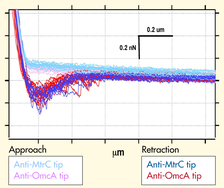
Surface-exposed cytochrome MtrC/OmcA on *Shewanella oneidensis* indicates possible involvement with electron transfer during iron reduction



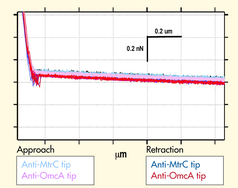


Force-volume mapping of a *Shewanella* cell using an Anti-MtrC functionalized AFM tip.

Shewanella wild

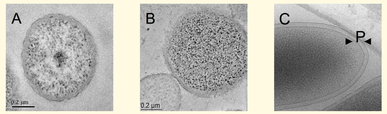


Shewanella MtrC/OmcA genes deleted



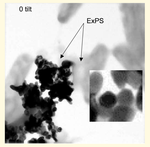
EMSL Biogeochemistry Grand Challenge

Visualizing the closest-to-native-state cellular morphology of hydrated bacteria (Cryo-Transmission Electron Microscopy)

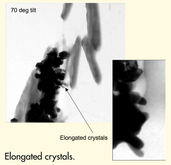


Shewanella prepared by A – chemical fixation, B – high-pressure freezing and plastic embedding, C – frozen cell in vitrified ice as observed in cryostage. Notice the pronounced periplasm (P).

Enabling high-resolution 3D reconstruction of bacterial-mineral associations.
0.5 mM hematite (10 mM lactate) 4h: 0.09 mM HCl-ext Fe(II)



Typical hematite structure as we know it.

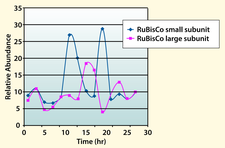


Elongated crystals.

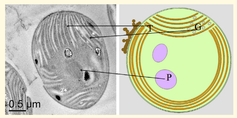
EMSL Biogeochemistry Grand Challenge

Protein Identification (Mass Spectrometry)

- *Cyanothece* cyanobacteria performs photosynthesis during the day and nitrogen fixation at night.
- EMSL's High-Performance Mass Spectrometry Facility was used to measure global protein abundances across a 24-hour time course to observe potential protein circadian rhythms.
- More than 2,500 proteins hav e been identified, representing 46% of the proteome.
- Structures of the key proteins being determined.



Amounts of the subunits of the photosynthetic protein, RuBisCo, peak approximately every 12 hours



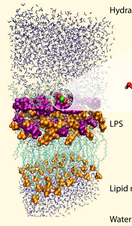
Model of a cyanobacterial cell with its cellular comparmemts that undergo dynamic changes during teh light and dark cycle:

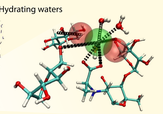
T=thylakoid membranes, P=poly-phosphate body, G=glycogen granules, C=cyanophycin granules, PB=phycobilisomes, ExPS=extracellular polymeric substances, R=ribosomes

EMSL Membranae Biology Grand Challenge

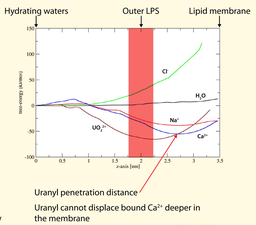
Unraveling molecular mechanisms and providing ideas for macroscopic experimentation (Molecular Simulation)

Molecular Dynamics model of uranyl binding in the outer membrane of *Pseudomonas aeruginosa*





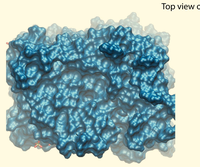
Uranyl in membrane - coordinated to one carboxylate, two hydroxyls, and four waters



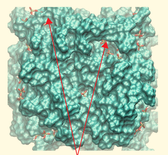
Uranyl cannot displace bound Ca^{2+} deeper in the membrane

Current work: Change in binding mechanism with pH

Top view of membrane



Slightly basic pH – membrane crosslinked membrane difficult for uranyl to penetrate



Slightly acid pH – groups protonated creating channels and exposed phosphate groups for uranyl binding

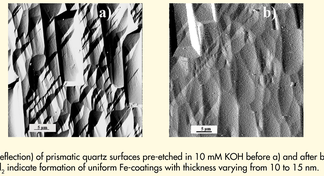
R. Lins, PNNL

Mineral Surface Chemistry

Combining techniques for unique insight (Atomic Force Microscopy)

The impact of solution composition on iron coatings of quartz surfaces

Surface morphology: Fe coating in low NaCl (air dried)



AFM images (deflection) of prismatic quartz surfaces pre-etched in 10 mM KOH before a) and after b) treatment with 1 mM $FeCl_3$ indicate formation of uniform Fe-coatings with thickness varying from 10 to 15 nm.

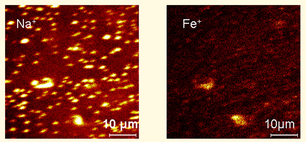
Surface morphology: Fe coating in 0.1 M NaCl (air dried)

Before coating (deflection image) | After coating (height image) | After coating and rinsing (deflection image)

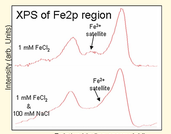
Prismatic quartz surfaces equilibrated for 24 h with 100 mM NaCl and 1 mM $FeCl_3$. The AFM images taken before equilibration a), after equilibration - not rinsed b), and after equilibration - DI rinsed c) demonstrate the absence of the uniform Fe coating. These images suggest the presence of NaCl solids inside the etch pits b) as well as the presence of Fe precipitates (yellow arrows) inside etch pits c) as residuals after NaCl was dissolved.

Determining surface chemical composition (Secondary Ion Mass Spectrometry and X-Ray Photoelectron Spectroscopy)

SIMS – Sensitive map of surface composition



XPS – Surface Fe oxidation state



- **Solution composition impacts the extent, composition, and location of Fe coatings.**
- The impact of these different coatings on mineral dissolution is under investigation.

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