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Argonne Subsurface Science Program

Synchrotron-based Characterization of Coupled Biotic-Abiotic Processes Relevant to Subsurface Contaminant Fate and Transport

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UChicago Argonne LLC

Office of Science
U.S. DEPARTMENT OF ENERGY

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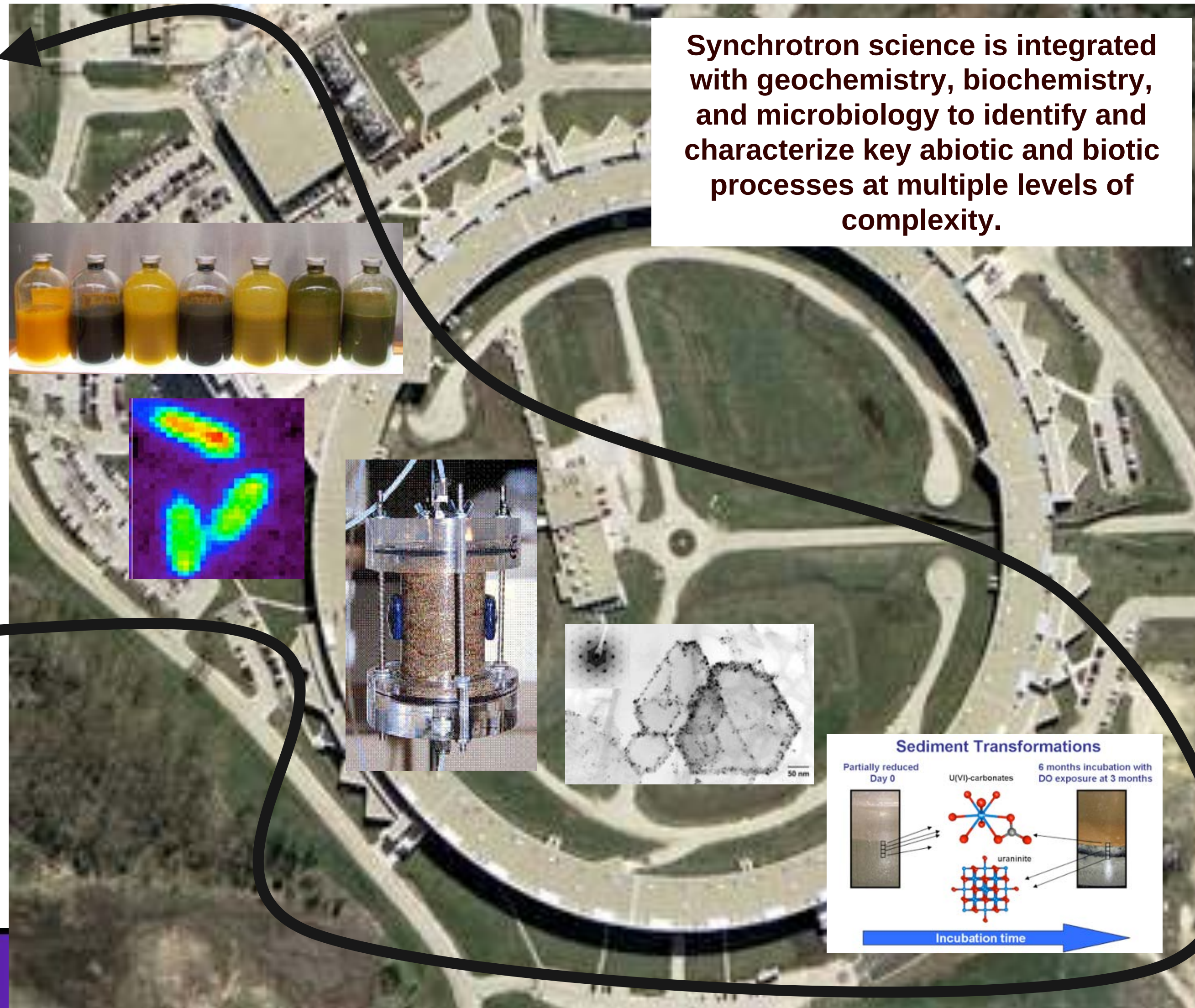
ANL Subsurface Science SFA Relevance to ERSP Mission:
An Integrated Approach to Understanding Subsurface Contaminant Fate and Transport

Samples from the IFC sites are characterized in parallel with laboratory monocultures to ensure the relevance of scientific observations.

Synchrotron capabilities are developed and optimized in response to science drivers.



Synchrotron science is integrated with geochemistry, biochemistry, and microbiology to identify and characterize key abiotic and biotic processes at multiple levels of complexity.

Interdisciplinary Collaborative Science Projects FY2009-2013

Science Projects

Metabolic and Geochemical/Mineralogical Controls on the Speciation of Biogenic Fe^{II}
O'Loughlin; Kemner, Giometti, Cook, *Scherer, Boyanov, McCormick, Sanford, Fredrickson*

U^{VI} and Hg^{II} Reduction by Biogenic Fe^{II} phases
O'Loughlin; Kemner, Kelly, Cook, *Scherer, Boyanov*

Monitoring Contaminant (U) Transformations within Intact Microcosms and Columns
Kelly; Kemner, O'Loughlin, Giometti, *Marsh, Criddle, Wu*

Nano(spectroscopy): Investigations of Transformations at the Mineral-Microbe Interface
Kemner; O'Loughlin, Cook, Lai, *Boyanov, Sanford*

Technology Project

Synchrotron-Based Molecular Environmental Science
Kemner; Kelly, O'Loughlin, *Boyanov, IIT, Bargar (SSRL), Nico (ALS)*

Collaborating Institutions

ANL ERSP-Related Activities

Argonne National Laboratory

Subsurface Science SFA

University-led ERSP Projects

Argonne National Laboratory subcontrator

ORNL IFC and SFA ERSP Projects

PNNL SFA Projects

Argonne National Laboratory

ERSP Investigator User Support

Advanced Photon Source (APS) at Argonne National Laboratory

Global Hypothesis

- Microbial metabolic activity- together with changes in solution chemistry, mineralogy, and solid-phase surface reactivity, and the presence of electron donors, acceptors, and shuttles- affects the distribution of (bio)mineral phases, as well as the rate, extent, and mechanisms of contaminant transformation.

Objectives

- Identify factors controlling formation of biogenic Fe(II) species
- Define relative reactivity of reduced Fe and S species with U(VI) and Hg(II)
- Identify Hg and U species that persist *in situ* in the presence of reduced Fe and S species
- Define speciation of Hg and U at the microbe-mineral interface
- Optimize Molecular Environmental Science capabilities at the APS

Project 1: Metabolic and Geochemical/Mineralogical Controls on the Speciation of Biogenic Fe(II)

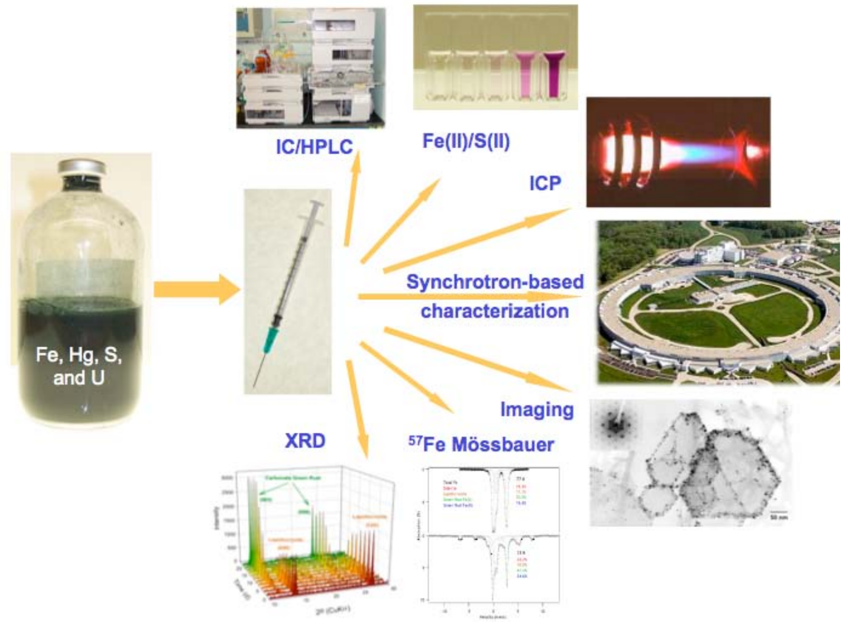
Project 2: U(VI) and Hg(II) Reduction by Biogenic Fe(II) Phases

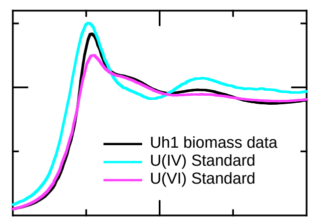
Lead: O'Loughlin[1]
Collaborators: Kemner[1], Kelly[1], Giometti[1], Cook[1], Scherer[2], Boyanov[3], McCormick[4], Sanford[5], Fredrickson[6]
[1]ANL, [2]U. of Iowa, [3]U. of Sofia, [4]Hamilton College, [5]U. of Illinois, [6]PNNL

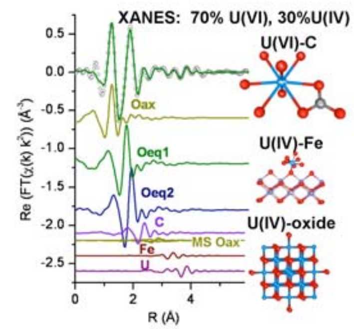
- Develop a fundamental understanding of key factors controlling formation of specific biogenic Fe(II) species
  - microbial metabolism (*Anaeromyxobacter* spp., *Geobacter* spp., cell density, and e^- donor utilization)
  - solution chemistry (pH, [CO_3], [PO_4], [SO_4], e^- shuttles, NOM, etc.)
  - Fe(III) mineralogy
- Systematic evaluation of reactivity of biogenic Fe(II) phases, with U(VI) and Hg(II) as model redox-active contaminants with an emphasis on understanding kinetics and mechanisms of the relevant reactions

Characterizations

- Advanced Photon Source (XANES and EXAFS): Atomic scale chemical speciation (Fe, S, U, Hg)
- IC/HPLC: e^- donor consumption
- BET: mineral surface area
- Metagenomics:T-RFLP
- Proteomics: metabolism
- Electron microscopy: nanoscale structure
- ICP, KPA: elemental analysis solution and solid phases
- XRD: atomic and nanoscale structure
- Fe(II), SO_4: e^- acceptor consumption
- ^{57}Fe Mössbauer: Fe mineralogy







Synergies:

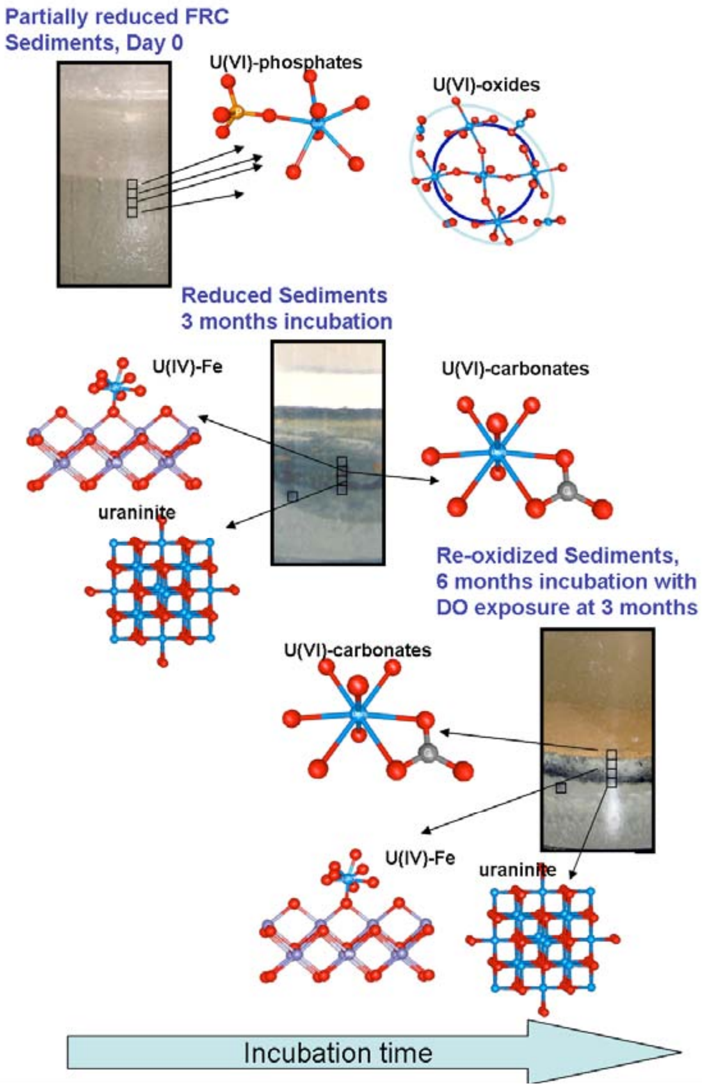
Experimental conditions identified for projects 3 and 4.

ORNL SFA (ANL SFA emphasis on role of Fe(II) reduction on Hg transformations)

PNNL SFA (ANL SFA emphasis on synchrotron-based investigations of U)

Project 3: Monitoring Contaminant Transformations Within Intact Microcosms and Columns

Lead: Kelly[1]
Collaborators: Kemner[1], O'Loughlin[1], Giometti[1], Marsh[2], Criddle[3], Wu[3]
[1]ANL, [2]Michigan State U., [3]Stanford



- Development/Application of Synchrotron-based approaches to investigate spatially heterogeneous (~0.1-10 mm) abiotic and biotic transformations of sediments (Fe and S) and contaminants (U) within intact microcosms/columns
  - Subsurface material and microbial communities from ORNL IFC
  - [CO_3], [SO_4]

Synergies:

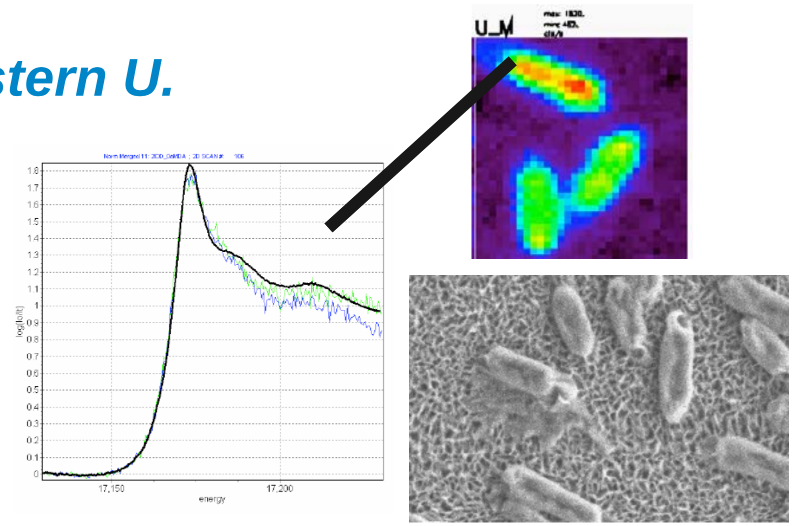
Insight into role of spatial heterogeneities (10s of microns to cm) on transformations investigated in projects 1 and 2, ORNL IFC (coordinated investigations), ORNL SFA (U), PNNL SFA (U)

Project 4: Nano(spectro)scopy: Investigations of Mineral-Microbe Interfaces

Lead: Kemner[1]

Collaborators: O'Loughlin[1], Cook[1], Lai[1], Boyanov[2], Sanford[3], Harris[4]

[1]ANL, [2]U. of Sofia, [3]U. of Illinois, [4]Northeastern U.



- Characterize biotic/abiotic interactions among contaminants (U and Hg), bacteria, EPS, and mineral surfaces at or near the mineral-microbe interface that effect contaminant transformations and fate and transport, via the development and use of micron- and nano-sized x-ray beams
  - microbial metabolism (*Shewanella* spp., *Geobacter* spp., *Anaeromyxobacter* spp.)
  - solution chemistry (pH, [CO_3], [PO_4], e^- shuttles)
  - Fe(III) mineralogy (iron (hydr)oxide thin films)

Synergies:

Insight into transformation mechanisms investigated in projects 1 and 2 at the mineral-microbe interface, ORNL SFA (U and Hg), PNNL SFA (U)

Project 5: Synchrotron-based Molecular Environmental Science

Lead: Kemner[1]
Collaborators: Kelly[1], O'Loughlin[1], Boyanov[2], Segre[3], Bargar[4], Nico[5]
[1]ANL, [2]U. of Sofia, [3]Illinois Institute of Technology, [4]SSRL, [5]LBNL

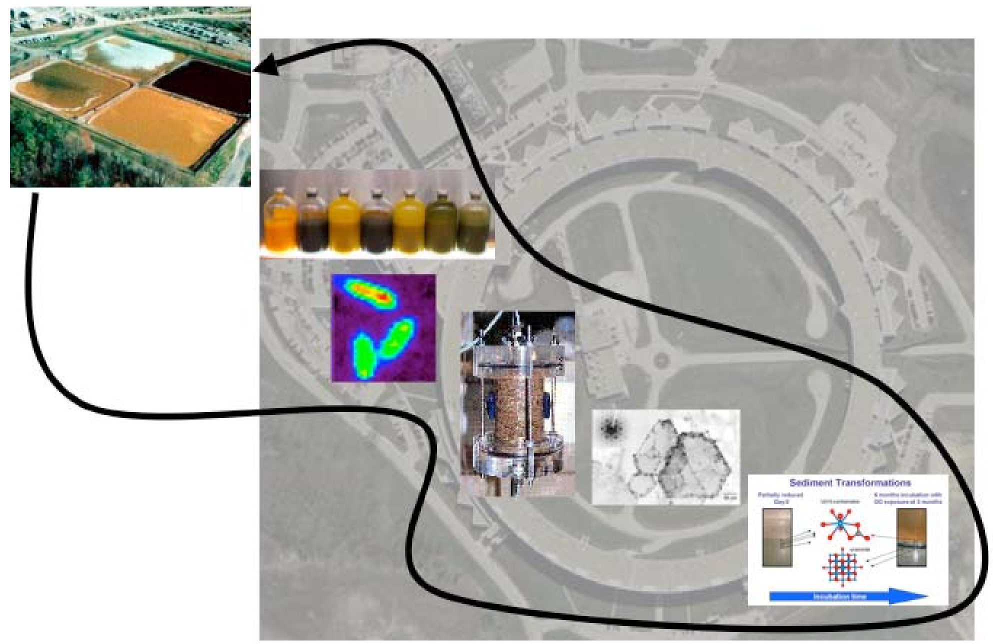
- The APS offers a unique opportunity to apply the nation's most brilliant high-energy x-ray source to fundamental problems in MES and address many ERSP needs, particularly those requiring a molecular level understanding of the key microbiological and geochemical processes that control contaminant transformation and mobility in the subsurface.
- Access to APS beam lines
  - General User
    - *At least 25% of beam time available*
    - *Beam time determined by beam time proposal review committee*
    - *Oversubscription rate of 2-3 X*
  - Member of Collaborative Access Team (CAT)
    - *Intimate association with design, construction, and operation of beam line- (beam line can be tailored to the science)*
    - *Up to 75% of beam time available to members of CAT*

Objectives

- Development of MRCAT/EnviroCAT First Optical Enclosure XAFS beam line
  - Increase available beam time to General Users
  - Increase available beam time to ERSP scientists
  - Beam line design tailored to ERSP research
- Hire a beam line scientist to support MES research at the APS
  - Continue development of beam line for MES research
  - Develop high throughput techniques (increase productivity)
  - Support MES researchers (particularly ERSP scientists) at all APS beamlines and coordinate efforts with SSRL and ALS
- National Integration of Synchrotron-based MES
  - SSRL-Bargar, ALS-Nico
  - Envirosynch, SES-IV
  - Synchrotron technique Workshops

After Five Years:

- We will have a fundamental understanding of coupled biotic and abiotic processes that affect the fate and transport of U and Hg under field-relevant conditions, particularly the role of different:
  - Electron donors
  - Fe minerals
  - Microbial species/communities
  - Anions
  - Electron shuttles
- We will have new technological capabilities that will enable high throughput synchrotron-based analysis of chemical and structural transformations of subsurface mineral and contaminant constituents from the angstrom to meter length scales.



Specific Hypotheses

- H1 Metabolic pathways involved in the utilization of electron donors for dissimilatory Fe(III) reduction influence the distribution of biogenic Fe(II) phases
- H2 For a given species of dissimilatory metal reducing bacteria (DMRB) or a given microbial community, changes in solution chemistry (pH, concentrations of carbonate, sulfate, electron shuttles, phosphate, natural organic matter, etc.) and Fe(III) mineralogy (Fe(III) oxides and oxyhydroxides, structural Fe(III) in clay minerals, etc.) affect the distribution of Fe(II) products
- H3 The rate, extent, and mechanism(s) of U(VI) and Hg(II) transformations by the products of dissimilatory iron reduction (DIR) and dissimilatory sulfur reduction (DSR) are affected by the speciation of the reactive phase (magnetite, siderite, vivianite, green rust, ferrous sulfide, sorbed Fe(II), structural Fe(II) in clays, etc.)

Specific Hypotheses (continued)

- H4 The rate, extent, and mechanism(s) of U(VI) transformations by the products of DIR and DSR are affected by U speciation- which is largely controlled by the solution composition (pH, concentrations of U, complexants, calcium, carbonate, sulfide, sulfate, electron shuttling compounds, etc.)
- H5 Probing the spatial heterogeneities of the chemical speciation of contaminants and mineral constituents in samples uniquely characterizes the microbial and geochemical processes that control the transformation of contaminants
- H6 The rate, extent, and mechanism(s) of biotic transformation of U(VI) and Hg(II) by DIRB and dissimilatory sulfur reducing bacteria (DSRB) are affected by the microbial species and community dynamics