Iron and Sulfur Biogeochemistry in Redox Dynamic Environments Scientific Focus Area

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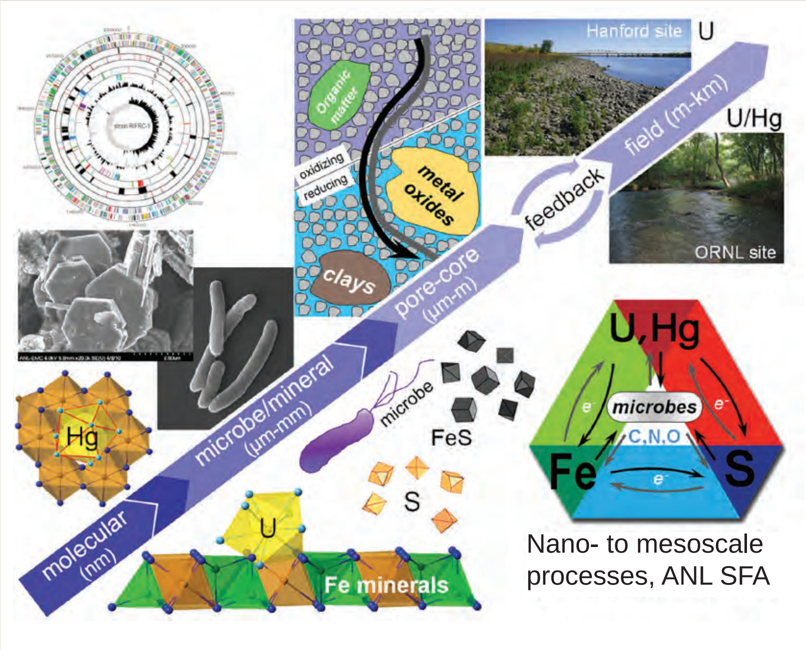
Elucidating the interplay among microbial metabolic activities, solution chemistry, and mineralogy contributing to element and contaminant transformation

The movement of water and constituents dissolved therein, along with biogeochemically catalyzed transformations of those constituents, determine the mobility of contaminants (uranium and mercury), emissions of atmospheric greenhouse gases (e.g., carbon dioxide, methane, and nitrous oxide), nutrient (e.g., carbon and nitrogen) mobility, and water quality. Iron (Fe) is a highly abundant element in the lithosphere, and its biogeochemistry in many aquatic and terrestrial environments is driven largely by microbial activity. Similarly, sulfur (S) is commonly found in groundwater; its transformations, often driven by microbially catalyzed redox reactions, can also greatly affect the cycling of elements. Redox-dynamic environments—where Fe or S biogeochemical cycling can be a major driver of other elemental cycles—include terrestrial-aquatic interfaces and subsurface environments (e.g., marshes, wetlands, floodplains, soil aggregates, plant root-soil interfaces, and locations where groundwater and surface waters mix). Although much is known about the respective biogeochemical cycles of Fe and S, the interplay between these two cycles is less understood.



Multiscale Biogeochemistry. *The Argonne SBR SFA is developing an understanding of coupled biotic-abiotic molecular- (sub nanometer) to core- (~meter) scale Fe and S transformations within redox-dynamic environments. The effects of Fe and S biogeochemistry on nutrient and contaminant transformation also are being explored to better understand and model transport. These investigations are advancing understanding of how smaller-scale processes can lead to emergent properties at the field scale.*

A Scientific Focus Area (SFA) project led by Argonne National Laboratory is investigating this interplay between the Fe and S cycles and their roles in controlling contaminant mobility, carbon and nutrient cycling, and greenhouse gas emissions. The project's long-term vision is to integrate SFA findings into multiscale modeling approaches to understand and predict relevant environmental processes. The project is supported by the Department of Energy's (DOE) Office of Biological and Environmental Research (BER) as part of BER's Subsurface Biogeochemical Research (SBR) program. The goal is to advance fundamental understanding of coupled biogeochemical processes in complex subsurface environments to enable system-level environmental prediction and decision support.

Key Knowledge Gaps

The Argonne National Laboratory SBR SFA seeks to identify and understand coupled biotic-abiotic molecular- to core-scale transformations of Fe and S within redox-dynamic environments, as well as understand the effects of Fe and S biogeochemistry on the transformation and mobility of various elements and contaminants. SFA research addresses four critical knowledge gaps related to accomplishing this goal:

- Molecular processes affecting Fe, S, and contaminant speciation in dynamic redox environments.
- Role of biogenic and abiotic redox-active products and intermediates in Fe, S, and contaminant transformations.
- Mechanistic factors controlling the mass transfer of Fe, S, and contaminants in heterogeneous media.
- Relationship of microbial community dynamics and function and coupled biotic-abiotic controls and their effects on element cycling and contaminant transformations.

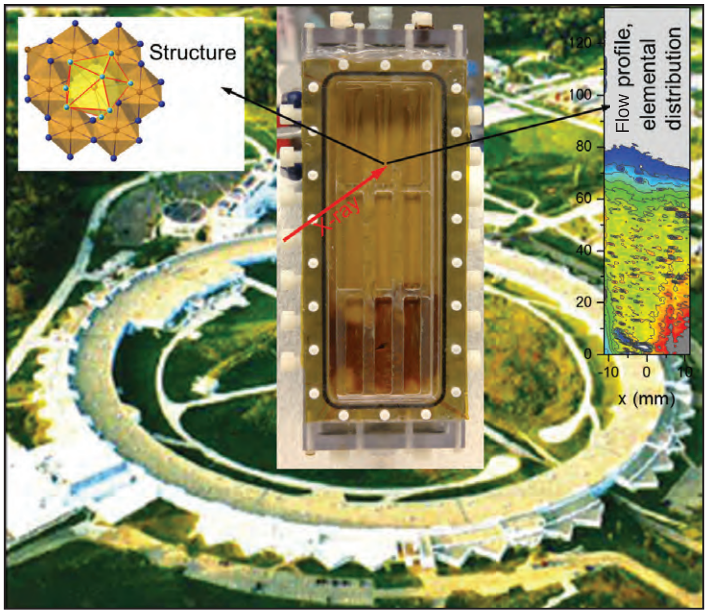
Integrating Synchrotron-Based Biogeochemistry with DNA Sequencing and Bioinformatics

The Argonne SBR SFA integrates two unique strengths—(1) the Advanced Photon Source (APS) for synchrotron-based interrogation of systems, and (2) next-generation DNA sequencing and bioinformatics approaches for microbial community and metabolic pathway analysis—with biogeochemistry and microbial ecology. SFA findings are providing mechanistic insights into cryptic biogeochemical reaction mechanisms and pathways that are crucial components of larger reaction networks driven by microbial communities.

DNA Sequencing and Bioinformatics. *The development and use of omics-based approaches to understand microbially driven controls on coupled Fe and S biogeochemical processes in the field are a cornerstone of the Argonne SBR SFA. The structure and function of microbial communities within lab-generated and field samples are determined with next-generation sequencing technologies and bioinformatics.*

Research emphasizes laboratory-based experiments with single-crystalline-phase Fe minerals (oxides and Fe-containing clays), fabricated Fe-rich mineral assemblies designed to mimic mineralogical conditions found in subsurface environments, and geomaterial collected from field environments (e.g., groundwater-surface water mixing zone at the Hanford 300 Area in Richland, Washington, and stream sediments around Oak Ridge National Laboratory (ORNL) in Tennessee). Inocula for promoting bioreducing or bio-oxidizing conditions include (1) monocultures of well-characterized organisms representing dominant genera with recognized roles in Fe and S redox transformations (e.g., *Geobacter* spp., *Shewanella* spp., *Desulfitobacterium* spp., *Desulfovibrio* spp., *Desulfotomaculum* spp., *Thiobacillus* spp., and *Acidithiobacillus* spp.), and (2) natural microbial populations collected from field sites. Model minerals with mixed microbial communities are used to reduce the complexity of the system's mineralogical aspects. Similarly, model microbial monocultures are used to reduce the microbial complexity of biogeochemical systems.

In addition, Argonne SBR SFA experimental work drives optimization of synchrotron-based techniques at APS beamlines with the characteristics required for the project. This optimization increases X-ray beamline availability and productivity while also benefitting the larger international synchrotron-based biogeochemistry research community.



Synchrotron-Based Biogeochemistry. (Overlay) *The spatial heterogeneity of molecular-scale information within sediment cores can be gathered via X-ray measurements made at the Advanced Photon Source. Synchrotron-based approaches are used to develop molecular- to core-scale mechanistic understanding of the role of coupled Fe and S biogeochemical processes on nutrient and contaminant cycling. The development of these synchrotron-based approaches is another cornerstone of the Argonne SBR SFA.*

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