PNNL SFA: Role of Microenvironments and Transition Zones in Subsurface Reactive Contaminant Transport

Pore-Scale Biogeochemical Processes Controlling Contaminant Fate & Transport

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Office of Science
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Environmental Remediation Sciences

William R. Wiley EMSL
Environmental Molecular Sciences Laboratory

Pacific Northwest
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PNNL-SA-64964

Research Team & Expertise

Jim Fredrickson (PNNL) - *geomicrobiology, contaminant biogeochemistry*

Ji-Hoon Lee (PNNL/Post-doc) - *geomicrobiology*

Matt Marshall (PNNL) - *microbiology, molecular biology*

Alice Dohnalkova (EMSL) - *microscopy*

Dave Kennedy & Andy Plymale (PNNL) - *radionuclide & metal biotransformations*

Eric Roden (UW-Madison) - *microscale redox cycling*

Ken Kemner/Steve Heald (ANL-APS) - *X-ray spectroscopy and microscopy*

Science Issues & SFA Hypotheses

Science Problems

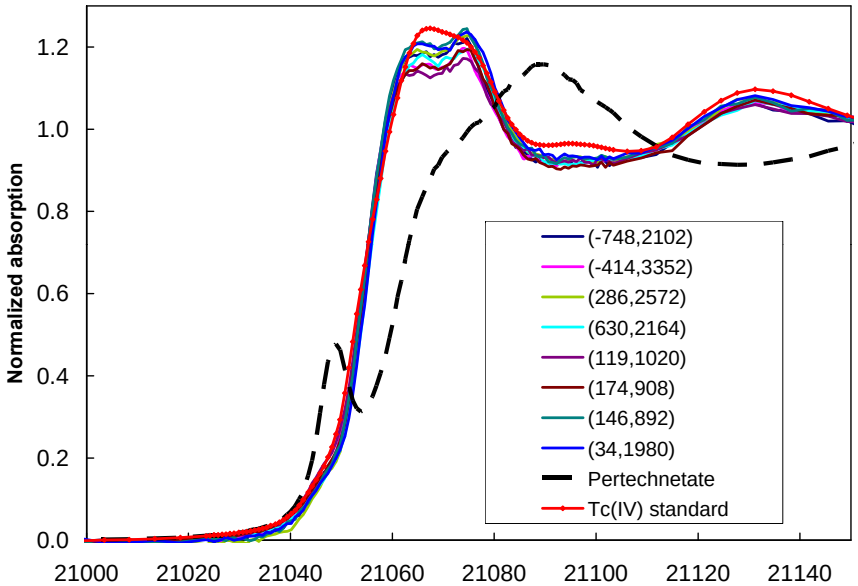
- Reaction mechanisms & rates controlling microscale distributions of Tc, U, O_2, & mineral Fe redox transformations in subsurface sediments
- Interactions (e.g., redox, complexation, sorption) between cells/ biomolecules, minerals, and contaminants
- Biogeochemical processes contributing to microscale chemical & redox gradients
- Diffusion/advection constraints on biogeochemical reactions in porous, mineralogically & microbiologically heterogeneous sediments

SFA Hypotheses

- Reductive valence transformations will occur in microenvironments where: O_2 is consumed by microbes and reactive Fe-containing minerals are accessible.
- Heterogeneities in mineral and biological structures will promote microsites of disproportionate molecular reactivity that dominate the (bio)geochemical behavior.

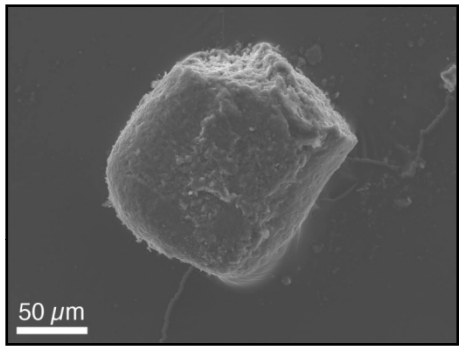
Motivation: Oxidation-Resistant Tc(IV) Associated with Fe-Containing Mica

µXANES, APS



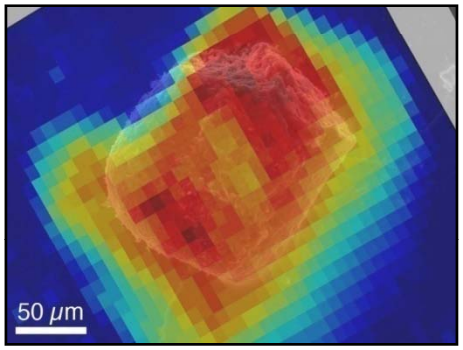
Fredrickson et al. *GCA* (in press)

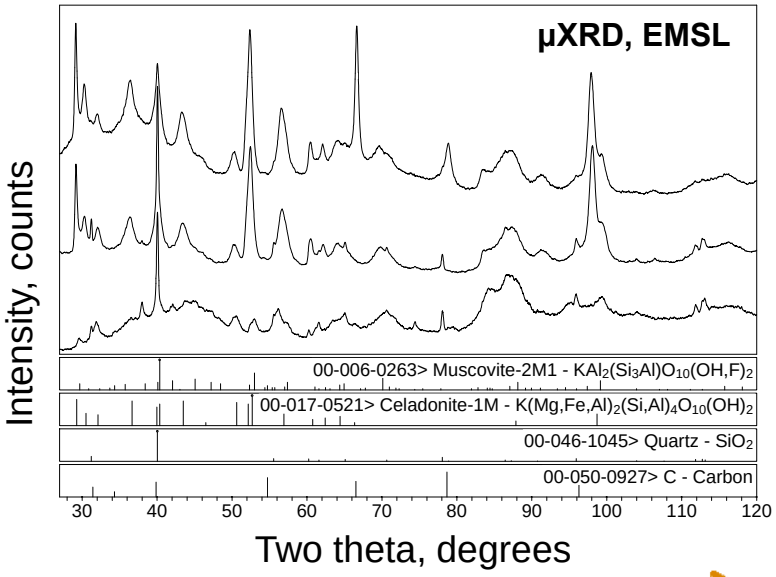
ORNL FRC Sediment



X-ray microprobe

Tc concentration





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FY09 Scope

- Biogeochemical redox transformations in Hanford sediments (w/ Konopka)
  - 300A sediment microcosms with and w/o nutrients
  - Redox transformations involving O_2, nitrate, sediment Fe, sulfate, Tc, U
  - Microscale distributions & speciation (SEM/TEM & XAS)
  - Deployment of redox reactive phases in 300A IFRC wells
- Isolation, characterization of 300A metal-biotransforming organisms (w/ Beliaev, Konopka, Marshall)
  - Mechanistic microbe metal/mineral interactions
  - Microscale distributions & speciation
- 300A DM Hanford & Ringold sediment Fe(II) geochemistry (w/Zachara)
  - Biogeochemistry
  - Reactivity w/ O_2, Tc
- Collaborative/supporting experiments as needed

Collaborators – Proposed Scope

- Eric Roden – U. of Wisconsin
  - Enrichment and isolation of phyllosilicate oxidizing and reducing organisms from Hanford sediments
  - Relative significance of different Fe redox-based pathways *in situ* – 300 A subsurface
- Ken Kemner/Steve Heald – Argonne National Lab.
  - Application of Advanced Photon Source beamlines for:
    - Spatial distribution of elements in microenvironments
    - Oxidation state and bonding environments of metals & radionuclides in representative microenvironments environments

Approach

Microscale distributions & chemistries
EMSL & APS

Characterizations

Hanford sediments
- 300 A
- Other

Sediment microcosms
- Biogeo processes
- Microscale distributions

Microbial isolates
- DMRB
- MOB
- Others (SRB?)

Hypotheses

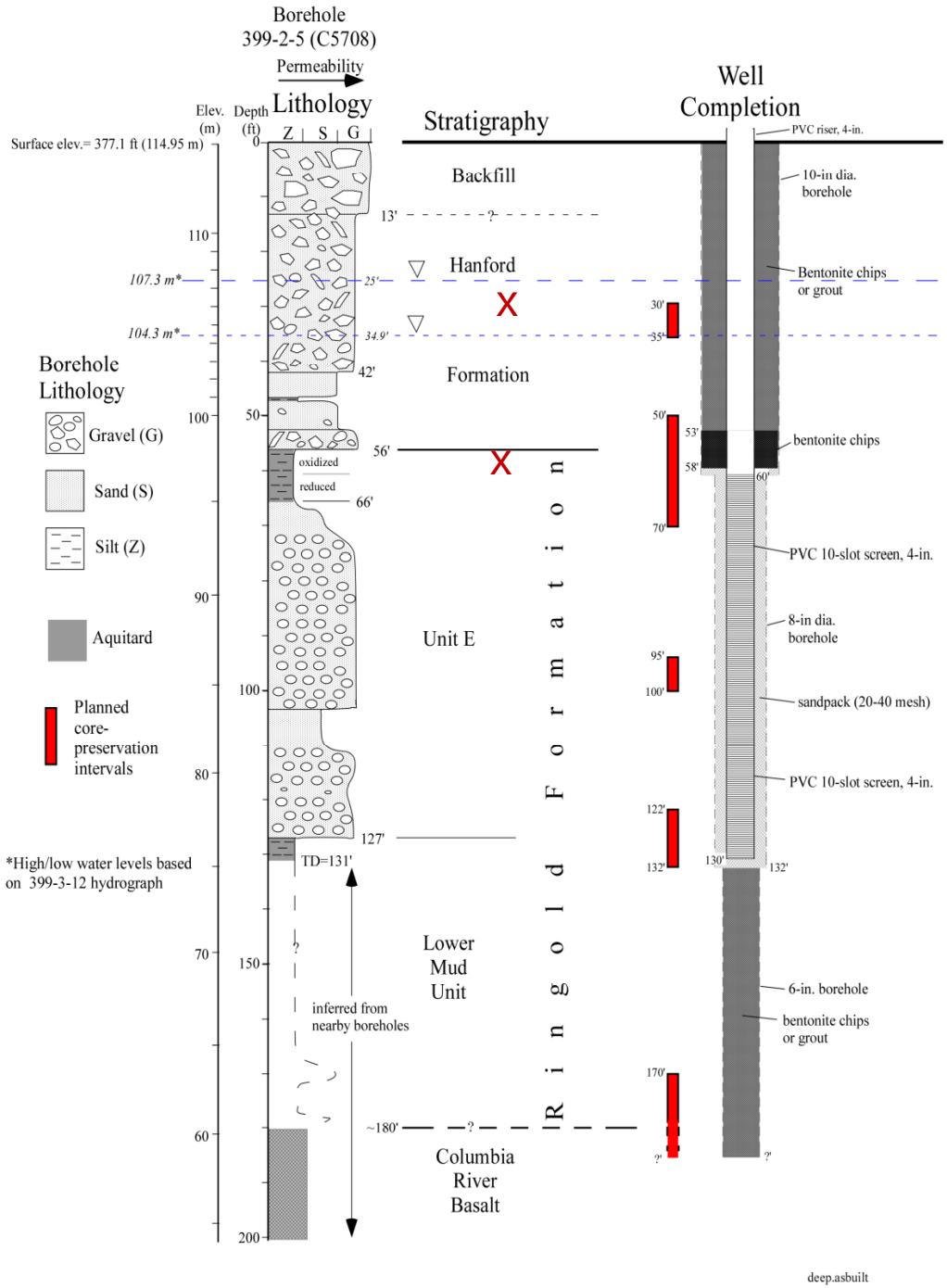
Fundamental lab experiments in defined systems

Significance of processes in situ?

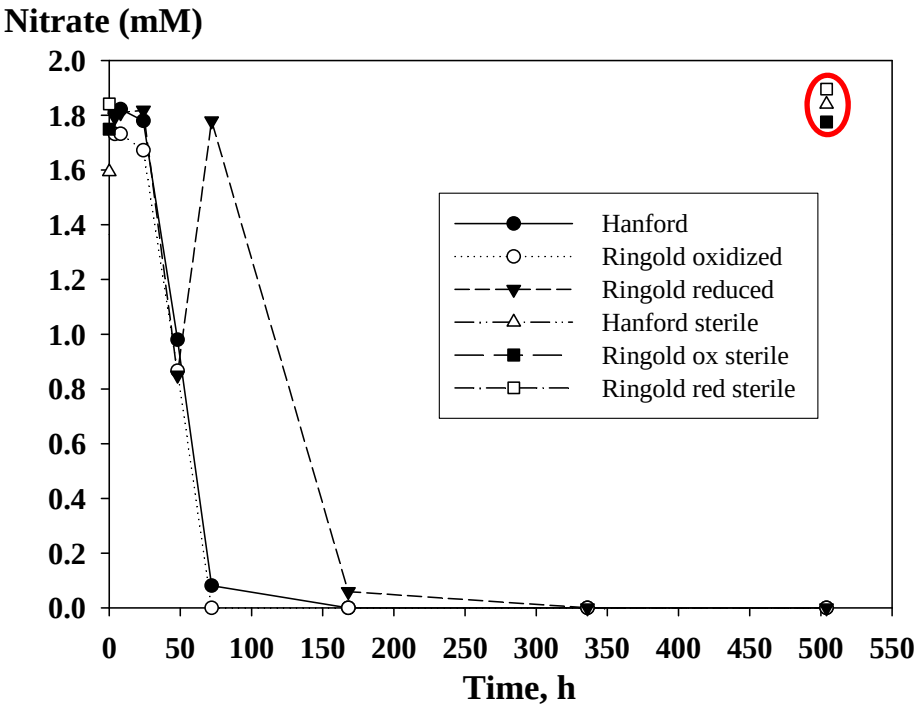
Field microscale, facies, & interface characteristics - 300 A subsurface

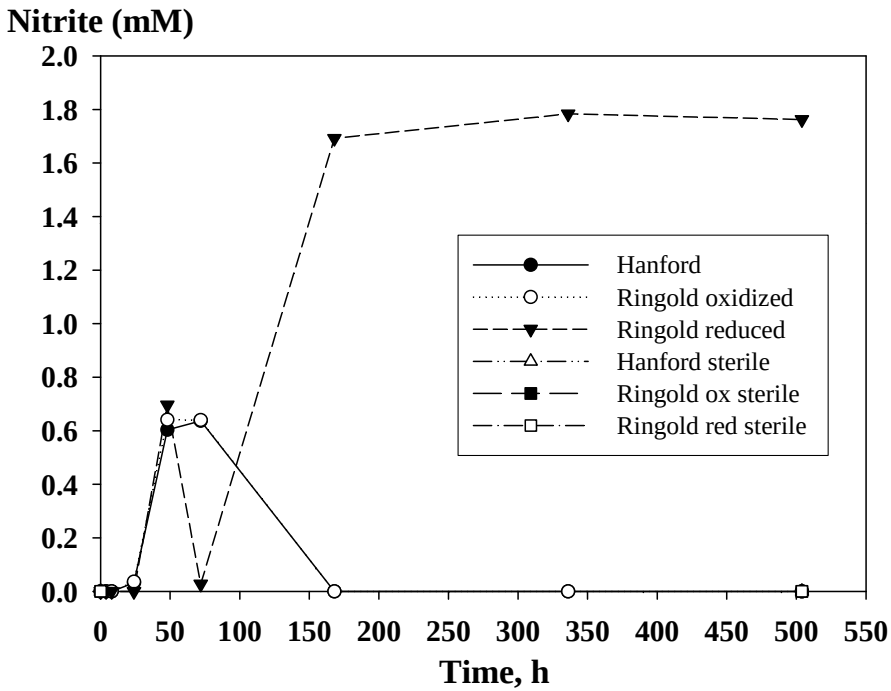
Sediment Microcosm Scoping Experiment

- Composite Hanford 30-31 ft., <4.75 mm
- Upper Ringold oxidized 58-59 ft., unsieved
- Upper Ringold reduced 61-62 ft., unsieved
- Artificial defined groundwater (w/o nitrate, w/0.63 mM sulfate)
- Amended w/ acetate, lactate, glucose
- Nitrate, ferrihydrite, no acceptor
- N_2 headspace



Nitrate Reduction in Hanford & Ringold 300A Subsurface Sediments





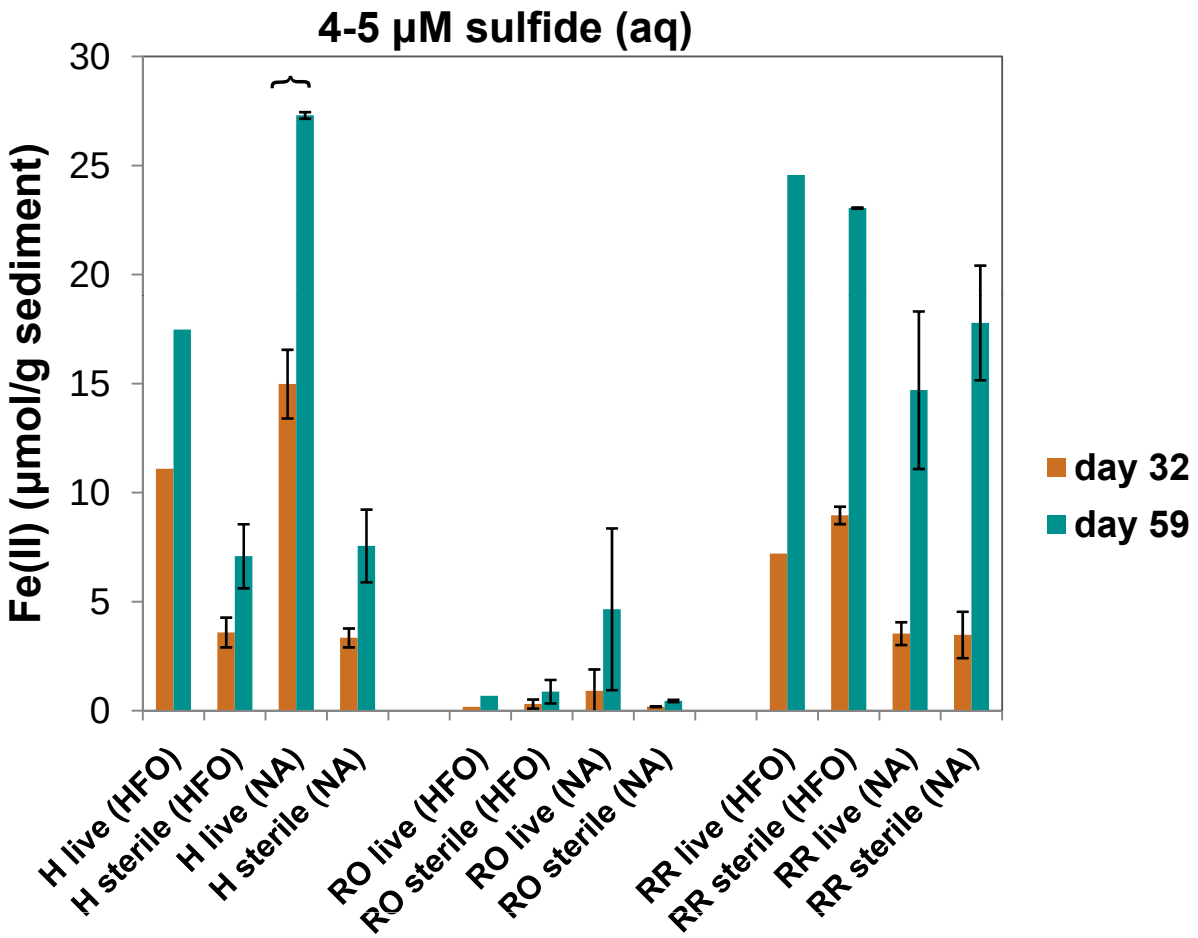
Extractable Fe

Fe(II), µmol/g (ferrozine)				
	OHamine -HCl	DCB	0.5 N HCl 1h	0.5 N HCl 24h
Hanford	41.8	49.1	9.7	61.6
Ringold ox	28.5	53.9	3.2	14.0
Ringold red	47.4	30.7	34.7	124.8

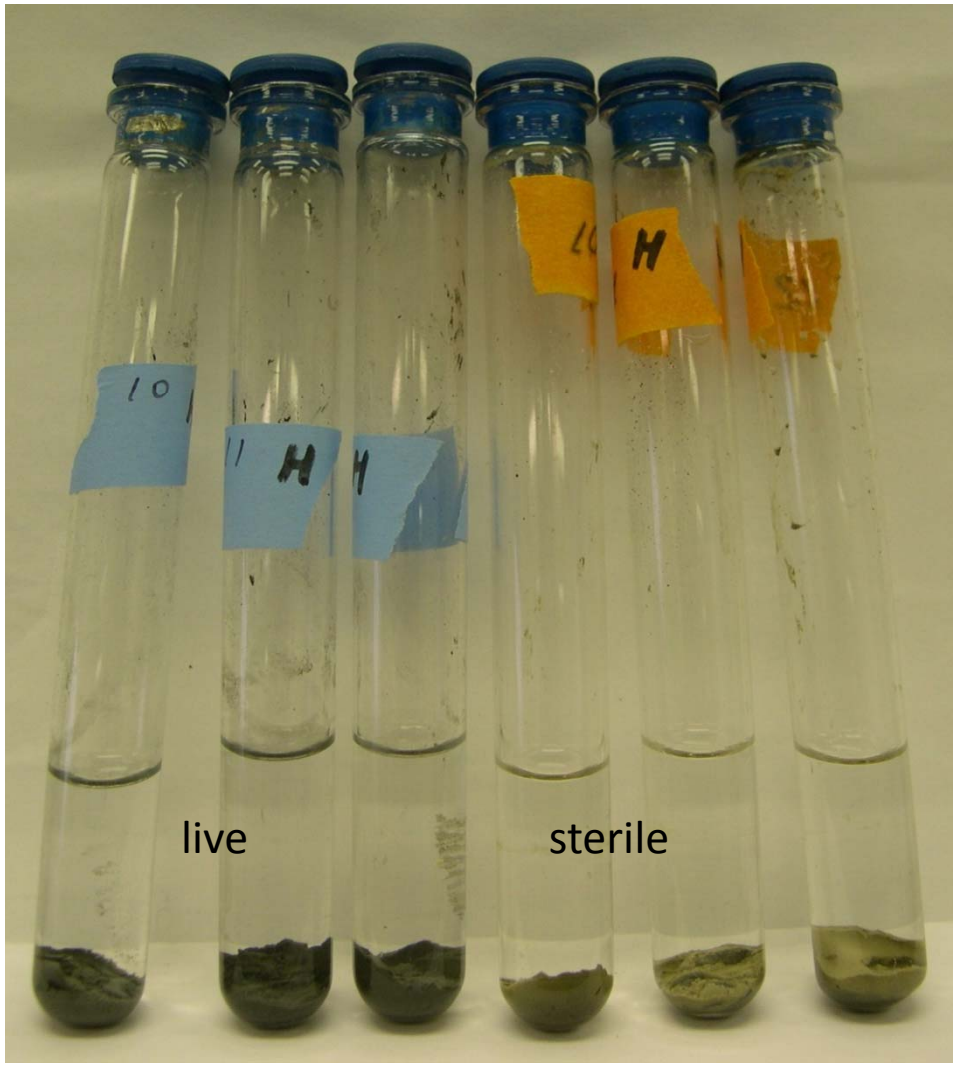
0.5 N HCl, µmol/g (ICP)						
	Fe, 1h	Fe, 24h	Al, 1h	Al, 24h	Mn, 1h	Mn, 24h
Hanford	31.5	149.9	25.9	79.1	1.2	2.5
Ringold ox	31.9	114.1	60.1	151.9	2.0	3.5
Ringold red	44.7	154.4	55.0	159.7	0.5	1.3

Sediment Microcosm Fe(II) - Scoping

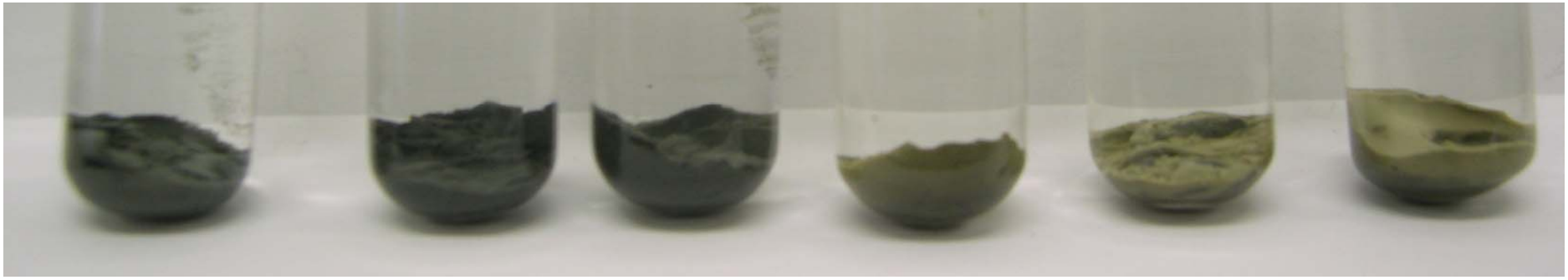
1 hour 0.5 N HCl extraction



Hanford Sediment (44d)



No FH or nitrate (0.62 mM sulfate)



FY09: In Progress & Planned

- Follow-on sediment microcosm experiments to sort out Fe(III) & sulfate reduction, characterize mineral phases, end products etc.
- U & Tc biogeochemical transformations (sediment microcosms)
- Initiate incubations in Hanford 300A IFRC wells to probe in situ biogeochemical processes - transition zones & microscale environments (w/ Konopka microbial ecology)

Hanford 300A IFRC Wells – In Situ Biogeochemistry/Microbial Ecology

- In situ passive 4'' multi-level samplers (McKinley) base of Hanford formation
- Cells packed w/ reactive & non-reactive materials to probe Fe redox reactions & microbial ecology
  - Accusand, Bio-Sep beads, ferrihydrite- & nanomagnetite-coated accusand, CR flood basalt coupons
- Incubation for extended periods to assess colonization, diversity, biogeochemical reactions, products, reactivity
- Other concepts:
  - Microporous beads, other artificial microenvironments to control diffusions, organism access
  - Slow-release microbial substrates, isotopic labeling

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