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

Role of Microenvironments and Transition Zones in Subsurface Reactive Contaminant Transport

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Pacific Northwest National Laboratory, Richland, WA

SFA Project Meeting
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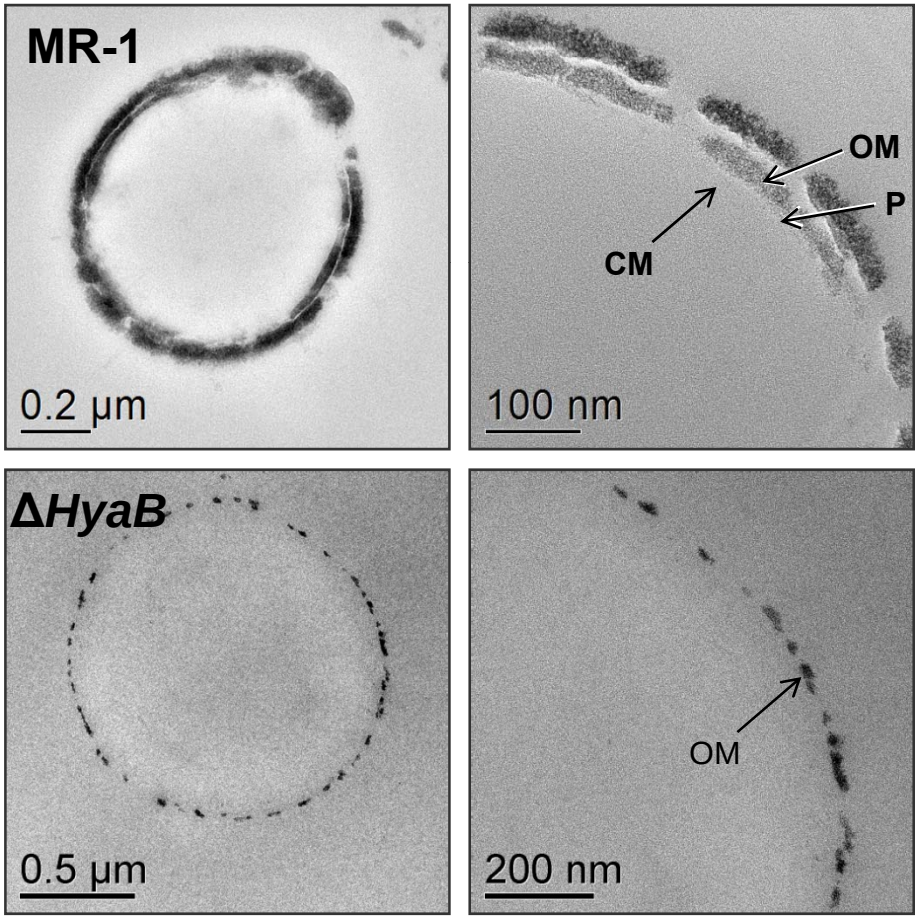
Microenvironments – Disproportionate Influence on Chemistry

Biogenic TcO_2

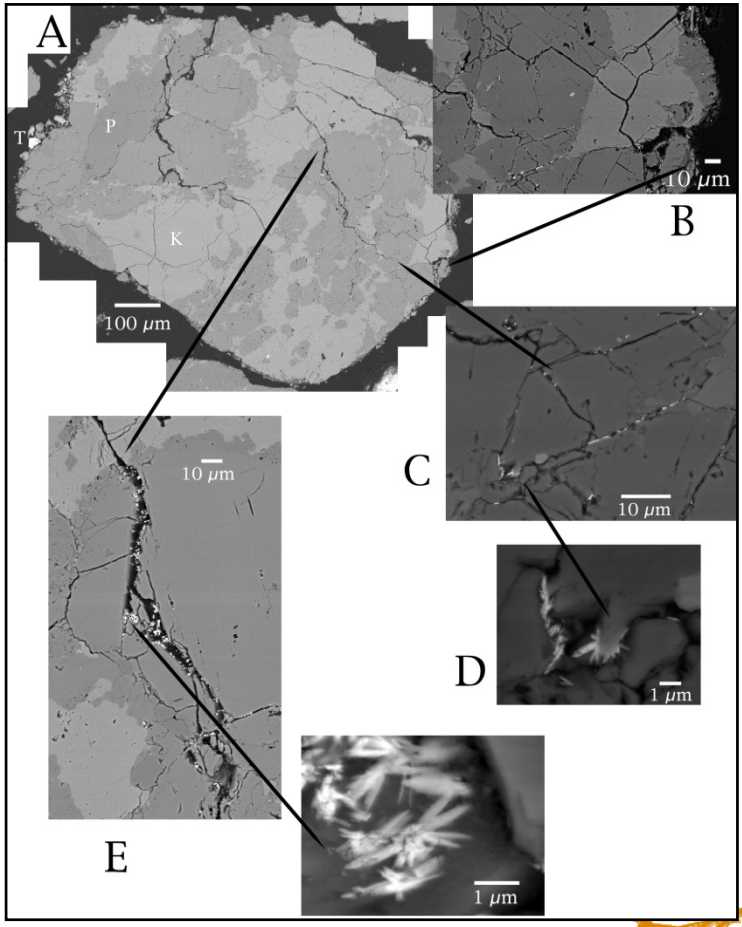
$Tc(VII)O_4^- + 4H^+ + 3e^- = Tc(IV)O_2 \bullet nH_2O + (2-n)H_2O$



(Marshall et al. 2008, *Environ. Microbiol.*)

Intragrain U(VI) Precipitates

$UO_2^{2+} + Na^+ + H_4SiO_4 + 1.5H_2O = Na[UO_2(SiO_3OH)](H_2O)_{1.5} + 3H^+$



(McKinley et al. 2006, *GCA*)

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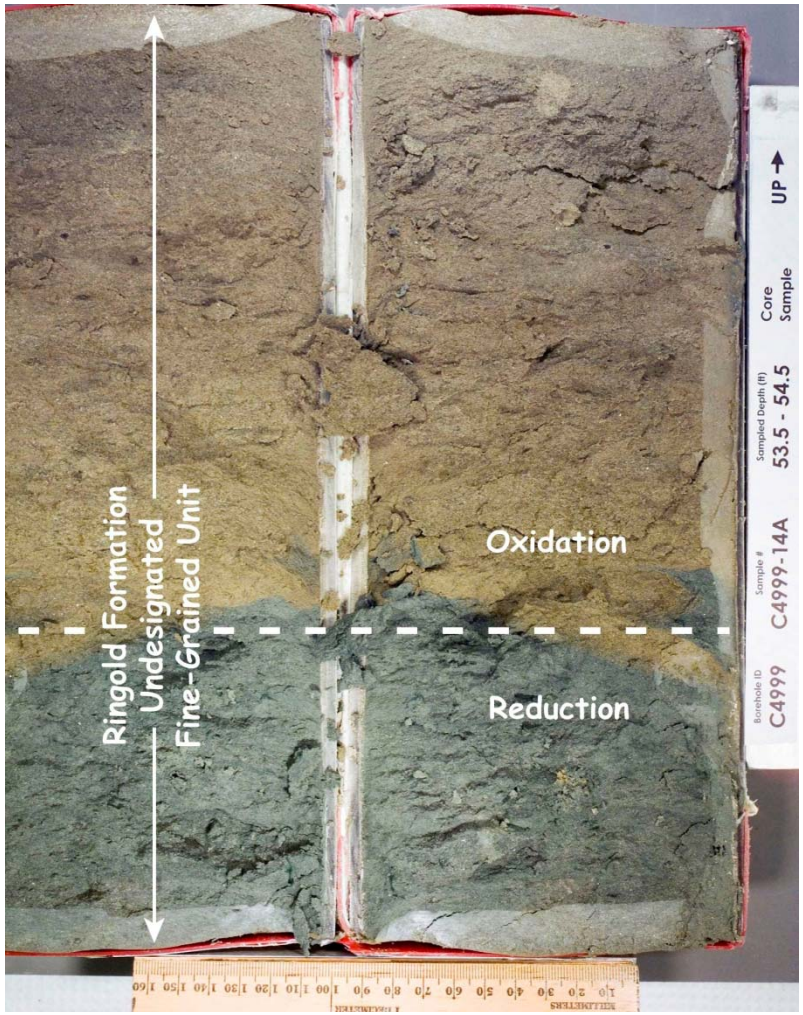
Transition Zones – Exhibit Chem-Phys-Bio Changes Over Short Distances

Ringold Formation - Redox Boundary



Columbia River - Hyporheic Zone

(Moser et al. 2003, *ES&T*)

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Different Scales ~ Different Issues

SFA ——— **IFC**

Molecular

- Bonding environment and local structure
- Fundamental mechanisms
- Energetics and structural controls
- Solvation effects

Microscopic

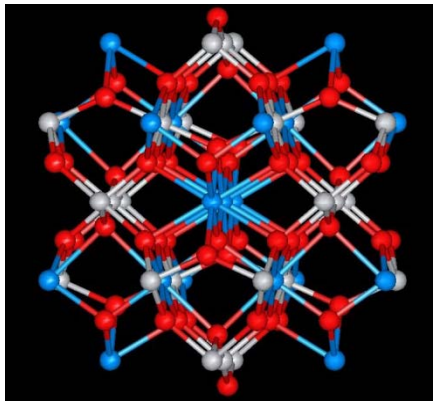
- Mineral residence phase identity & composition
- Reaction networks and kinetics
- Morphologic and surface issues
- Fundamental process coupling

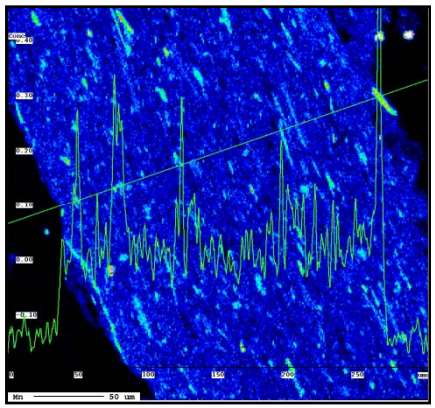
Macroscopic

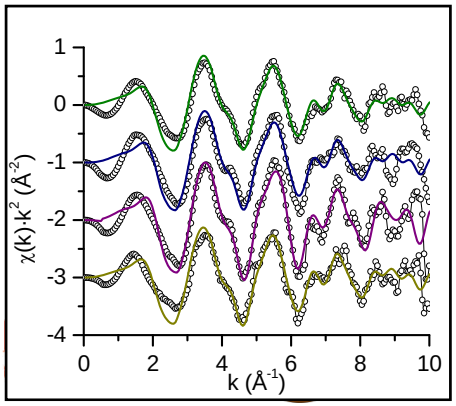
- Rate processes
  - Chemical
  - Microbiologic
  - Mass transfer
- Advection effects
- 1-D scaling issues
- Pore scale process coupling

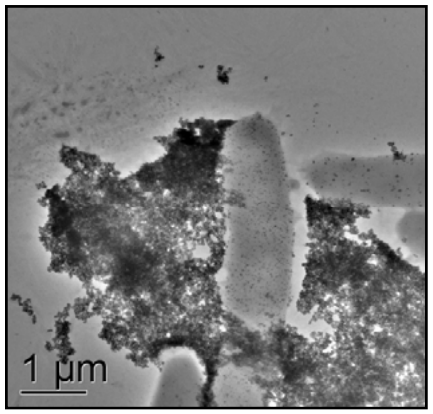
Field

- Physical heterogeneity
  - Water velocities/directions
  - Reactants
- Multi-scale mass transfer
- Mixing & averaging
- Distributed properties
- Seasonal issues (temperature, precipitation)









SFA/IFRC Relationship

- IFRC Theme: Multiscale mass transfer controls on reactive transport
  - Field research with site-specific emphasis
  - Provides context for significance of microenvironments and transition zones, representative materials & organisms
  - Field-scale reactive transport modeling

- SFA Theme: Role of microenvironments and transition zones in reactive transport
  - Laboratory and limited field research with fundamental emphasis
  - Microenvironments and transition zones give rise to mass transfer effects important to field-scale transport
  - Pore-scale reactive transport modeling with upscaling to define field-scale models and parameters

SFA and IFRC efforts are fully complementary across multiple scales

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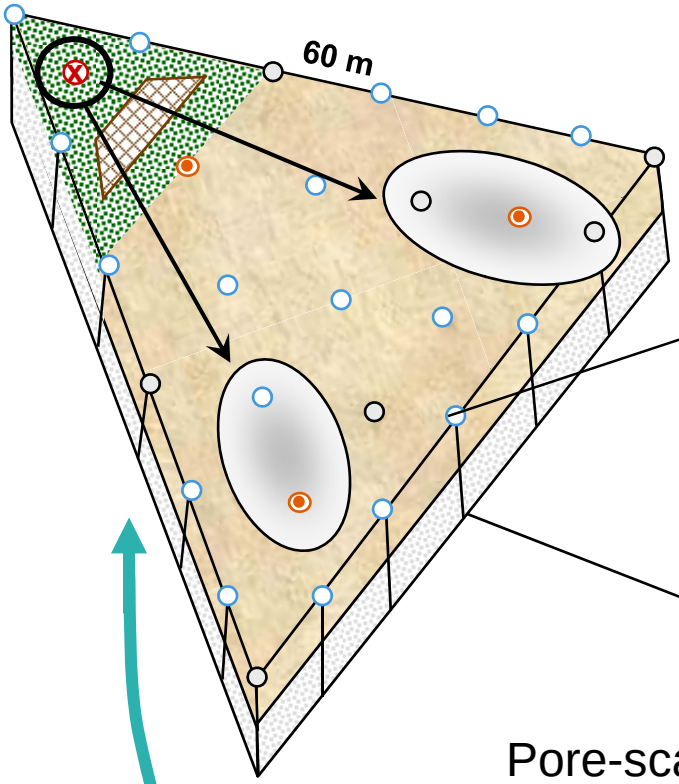
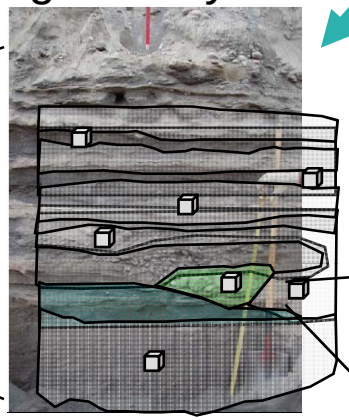
Hanford IFC Field Research

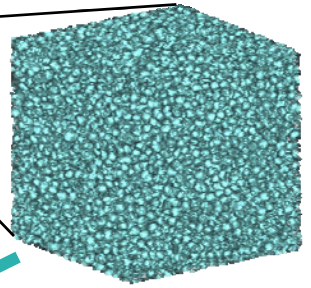
(Geophysical, geological, and geostatistical characterization – SFA and IFRC)



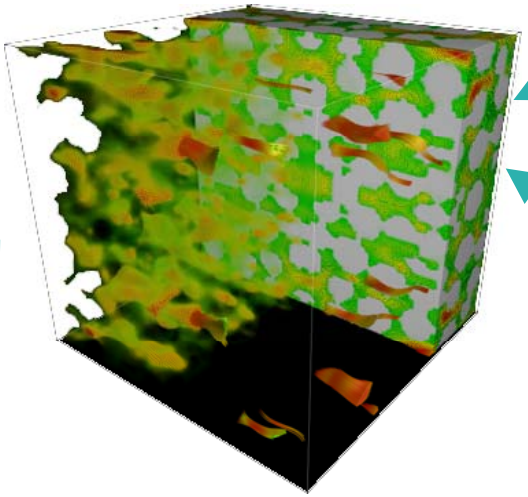
Facies-scale geometry



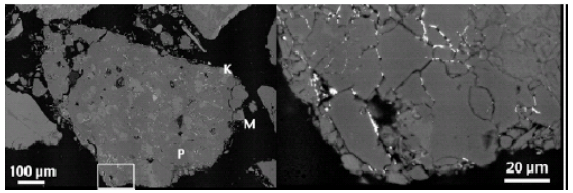
Pore-scale characterization



Pore-scale simulations



SFA Molecular and Pore-Scale Process Research



Upscaled models and parameters

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Guiding Hypotheses

- Microbial community structure & function determined by local microscale conditions and mass transfer properties of sediments.
- Microenvironments & transition zones will be dominant regions of contaminant reaction.
- Diffusion-controlled mass transfer will establish & maintain microenvironments.
- Dominant processes within such domains will vary with scale (microns to meters).

Microbiologic & Geochemical Characterization of Deep Borehole Sediments

July 2008 -- ~17 samples across geological formations and transition zones joint w/ IFRC

Cultivation-independent analyses

Biomass
- Direct microscopic counts
- Phospholipid phosphate
- % Respiring cells

Phylogenetic / functional diversity and relative abundance
- Census of Bacterial/Archaeal 16S rRNA gene sequences (JGI CSP Sanger sequencing + pyrosequencing)
- Real time PCR for specific phylogenetic and functional groups

Assessment of potential for U or Tc reduction
- Amend samples with electron donor
- Depend upon natural abundance of Fe(III) or exogenously added ferrihydrite as terminal electron acceptor (TEA)

Cultivation-dependent analyses
- Enrichment cultures with various TEA's
- High-efficiency cultivation strategies
- Analysis of metabolic versatility in cultivars

Provide Hanford-relevant microbes for molecular- to pore-scale research

Multivariate statistical Analysis of microbial census + geochemical / mineralogical data to generate hypotheses for field-scale studies

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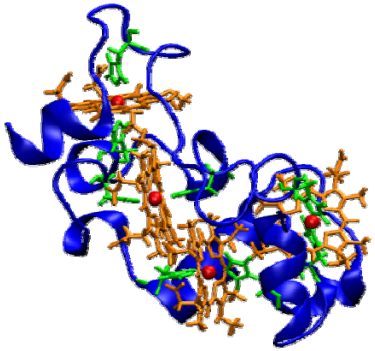
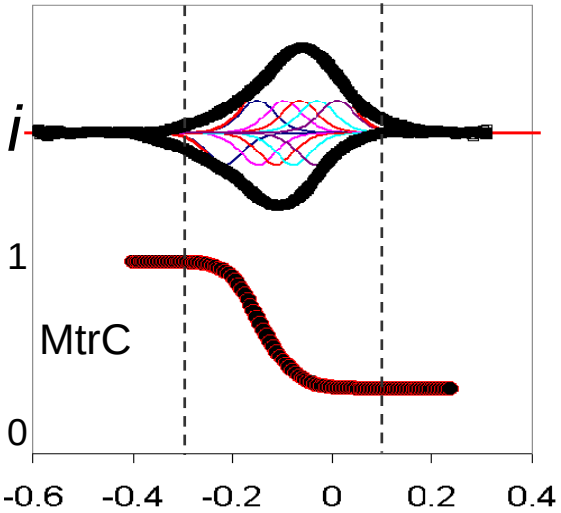
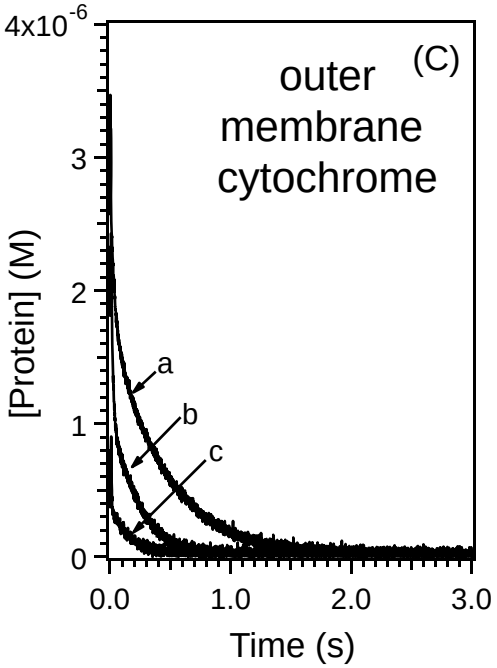
Molecular-Pore Scale Research

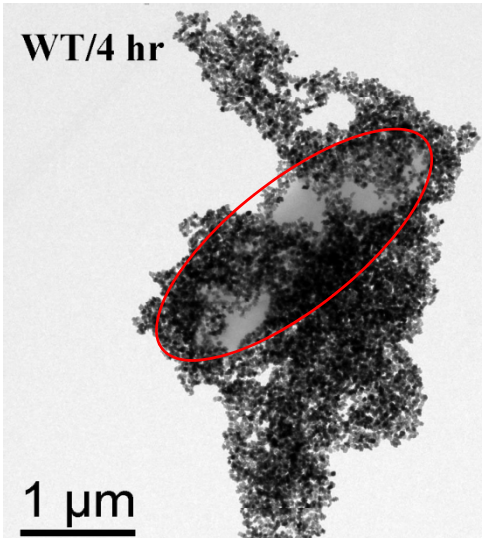
Identify & characterize reactive molecules ⟷ *In vitro* kinetic behavior ⟷ Interfacial properties & *in vivo* reactivity







Homogeneous electron transfer to Fe(III)-NTA



MRB w/ hematite nanoparticles

Biogeochemistry Grand Challenge

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SFA Implementation (FY09-10)

Initial/Transition Science Themes

- Microbial ecology investigations of unconfined aquifer in 300A & biogeochemical studies (U and Tc) w/ sediments & isolates (lab & field)
- Molecular/microscopic studies of 300A isolates & derived biomolecules in model mineral-water systems
- Molecular speciation & biogeochemical reaction studies of Pu in Z crib sediments and model systems
- Competitive interfacial redox reactions of O_2 and Tc(VII) in Hanford Fe^{2+}-containing minerals and subsurface sediments
- Pore-scale reaction networks, macroscopic transport behavior, and coupled kinetic transport models in 300A sediments
- Geophysical imaging & measurements of different types for facies and transition zone delineation in 300A U plume