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

Reactive Transport of U and Tc in Heterogeneous Sediment Systems

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http://www.pnl.gov/biology/sfa/

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Reactive Transport of U and Tc in Heterogeneous Sediment Systems

Objective

- Determine how heterogeneities in pore scale environments (mm-cm) and properties zonation (cm-m) influence the biogeochemical transport of U and Tc in field-relevant sediment systems.

Scope

- Integration experiments leading to field; coupled reaction and transport processes; biotic and abiotic oxygen consumption, Tc redox reactions, and Fe(II) minerals; U(VI) surface complexation and precipitation/dissolution in varied physicochemical domains. Heterogeneity effects, pragmatic scaling concepts, and reactive transport modeling.

Research Team and Expertise

John Zachara (*PNNL*) - Geochemistry, biogeochemistry, and mineralogy

Mart Oostrom (*PNNL-EMSL*) - Hydrology and reactive transport science

Jim McKinley (*EMSL*) - Electron microscopy and microprobe

Steve Heald (*ANL-APS*) - Tc x-ray spectroscopy, microscopy, and diffraction

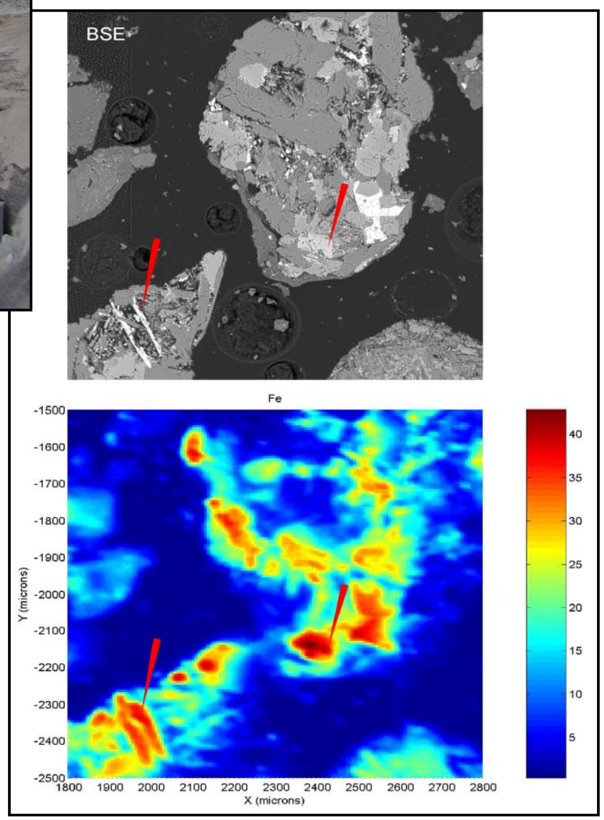
Jim Davis (*USGS*) - Uranium geochemistry and microscopic reactive transport

Phil Jardine (*ORNL*) - Mesoscale reactive transport experiments

Chongxuan Liu and Mark Rockhold (*PNNL*) – Reactive transport modeling through SFA and IFRC collaboration

Hanford Science Motivation

- Reactive transport vectors run both normal and parallel to complex sediment stratigraphy
- Contaminants experience different reaction networks and flow velocities in different layers.
- In-layer reactivity is complex because of pore-scale variations.
- Predicting system level breakthrough requires understanding of integrated behavior.



- Hanford sediments contain complex Fe mineralogy that is not well understood.
- Over 50% is Fe(II) with high potential for reactivity with oxidants [O_2, Tc(VII)].
- Hanford (~15 K bp) and Ringold (~120 K bp) formations display different weathering extents and lithic fragment distributions.
- Large repository of Fe(II/III) minerals in lithic fragment interiors with variable fractures and porosities.

Research Structure and Logic

- Address various heterogeneities leading to field, with IFRC as emphasis
- Strong linkage with other projects is required
- Emphasis on macroscopic and mesoscopic experiments linking reaction and transport (batch, flow-cell, column, tank/block)
- Focus on select/key contaminant reaction scenarios (U, Tc)

Field	**Intact Sediments** • **Uncontrolled heterogeneities**	**Model Structures** • **Controlled heterogeneities**	**Field Textured Materials** • **Pore scale heterogeneity**	**Particle Size Fractions** • **Particle heterogeneity**
▪ 300 A IFRC ▪ 200 A	▪ Influence of depositional features ▪ In-situ organism distributions ▪ Complex advection flow paths ▪ Impacts of in-situ associations of all type ▪ Comprehensive data sets for understanding and model application	▪ Function of complex physical, chemical, and microorganism structures or distribution ▪ Multi-scale mass transfer between advective regions ▪ Mass transfer controlled kinetic effects ▪ Kinetic transport models	▪ Basic parameter upscaling ▪ Geochemical additivity effect ▪ Biogeochemical processes ▪ Hydraulic effects of gravel ▪ Macroscopic transport model	▪ Size/mineralogy effects on reactivity and mass transfer ▪ Behavior of <2 mm fraction and controlling variables ▪ Microscopic to macroscopic reaction model

Deconstructive Experimentation →

Reactive Transport in Heterogeneous Sediments

Two Primary Lines of FY09 Research

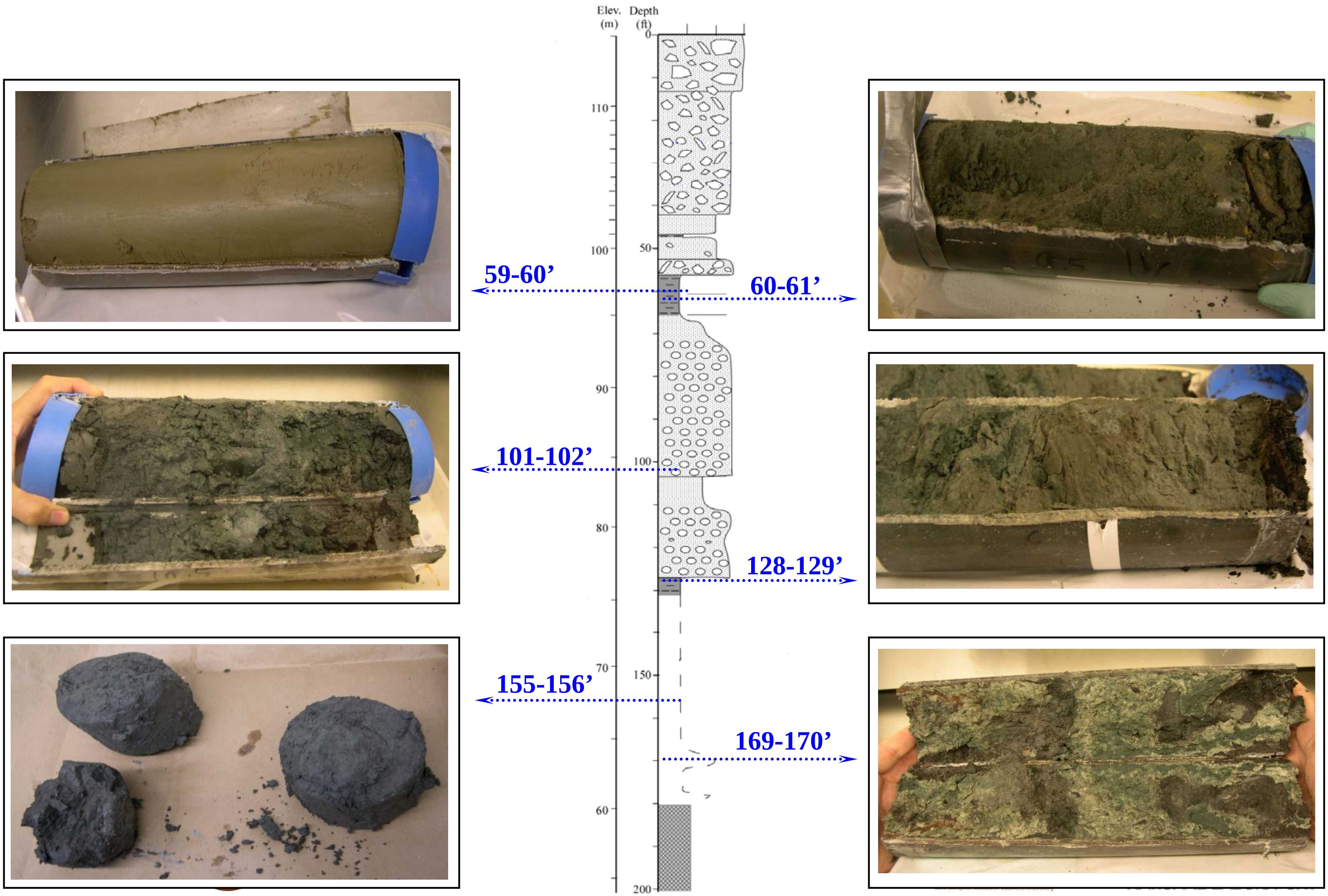
- Tc(VII) reaction kinetics (FY09, 40%)
  - 300 A Ringold/IFRC redox transition zone
  - Correlation of Tc(VII) and O_2 reduction rates (batch and flow cell)
  - XAS (ID, BM), SEM/TEM, and TMS for spatial distribution, location, molecular speciation, and Fe mineralogy

  (Collaborations: Fredrickson, ISFA; Rosso, ISFA)

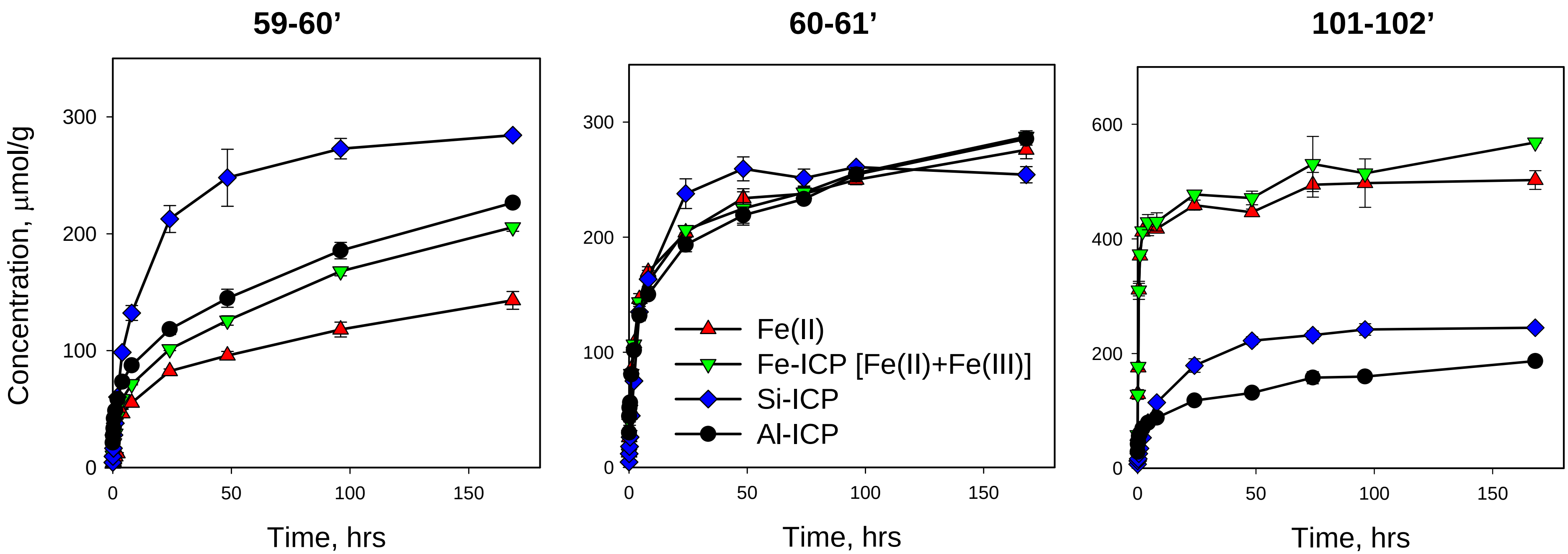
- Intact column experiments with 300 A IFRC site sediments in EMSL-SFTF (FY09, 45%)
  - 3 intact Hanford Formation cores, near WT and center of SZ
  - U(VI) desorption, tracer behavior, U(VI) adsorption/desorption
  - Core deconstruction with subsequent characterization and "mechanistic" study of < 2 mm fraction
  - Multi-scale reactive transport modeling

  (Collaborations: Liu, Scheibe/Rockhold, Ward, Jardine, and Davis)

IFRC Transition Zone Samples (C6209)



Weak Acid Extraction of Fe, Al, Si



I. 59-60’ [Fe(II)]<[Fe-ICP]<[Al-ICP]<[Si-ICP]

II. 60-61’, 128-129’, 155-156’ [Fe(II)]=[Fe-ICP]=[Al-ICP]=[Si-ICP]

III. 101-102’, 169-170’ [Fe(II)]=[Fe-ICP]>[Si-ICP]>[Al-ICP]

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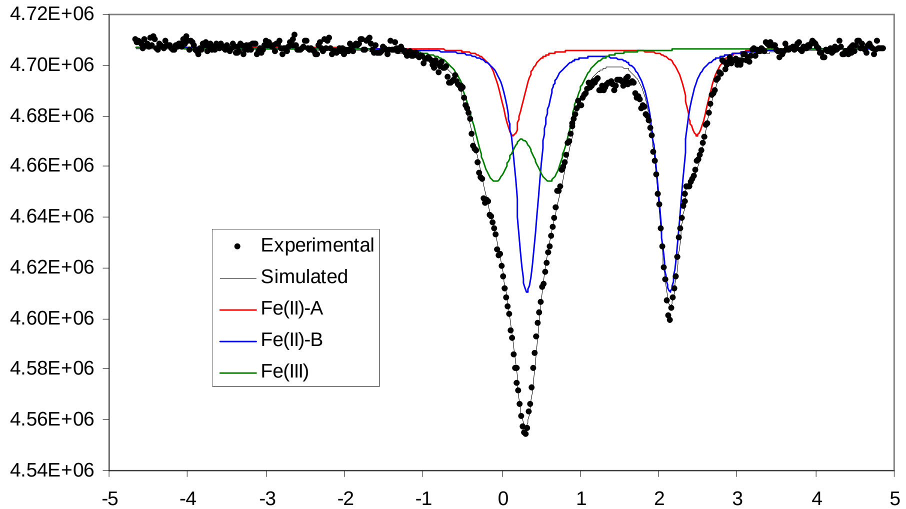
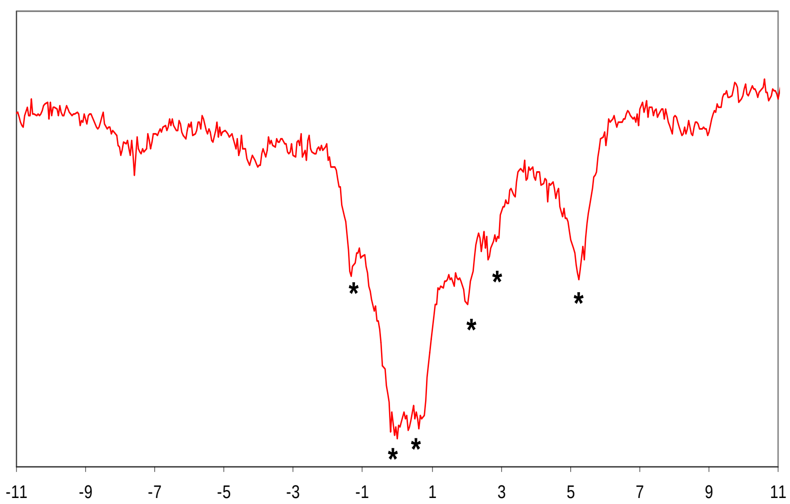
Variable Temperature Mössbauer Spectroscopy for Fe Mineral Forms (101-102')

Room temperature (RT) *Preliminary fit*

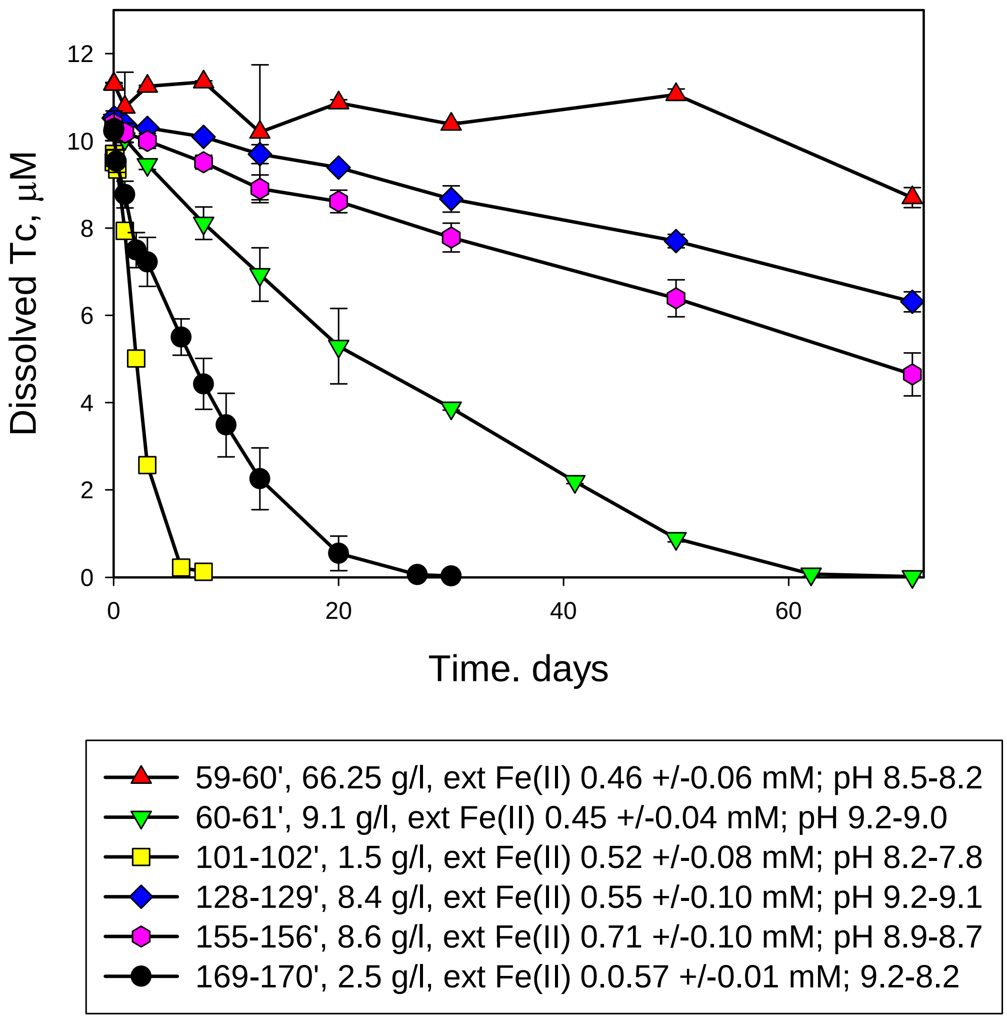


4.2 K

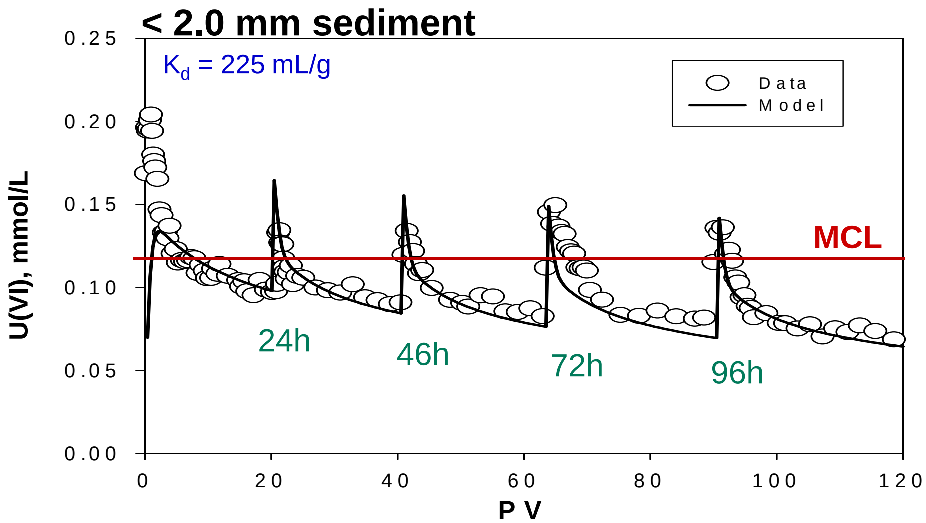


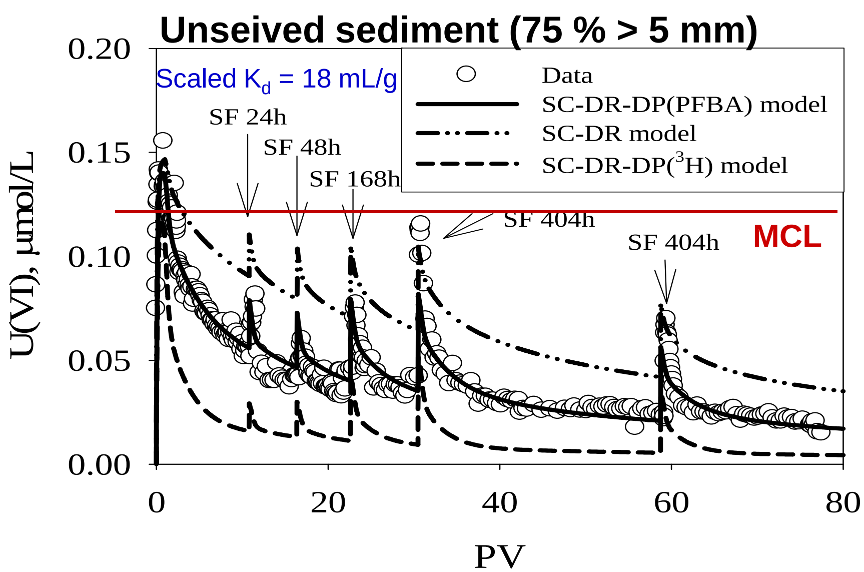
RT	Fe(III) and two Fe(II) species	
77 K and **45 K** virtually identical	no Fe(III) ordering **no Fe(III) oxides**	no Fe(II) ordering **no siderite ($FeCO_3$)**
12 K	no Fe(III) ordering	ordering of one of Fe(II) species **Fe(II) separate phase (?)**
4.2 K	Fe(III) ordering	Fe(II) ordering

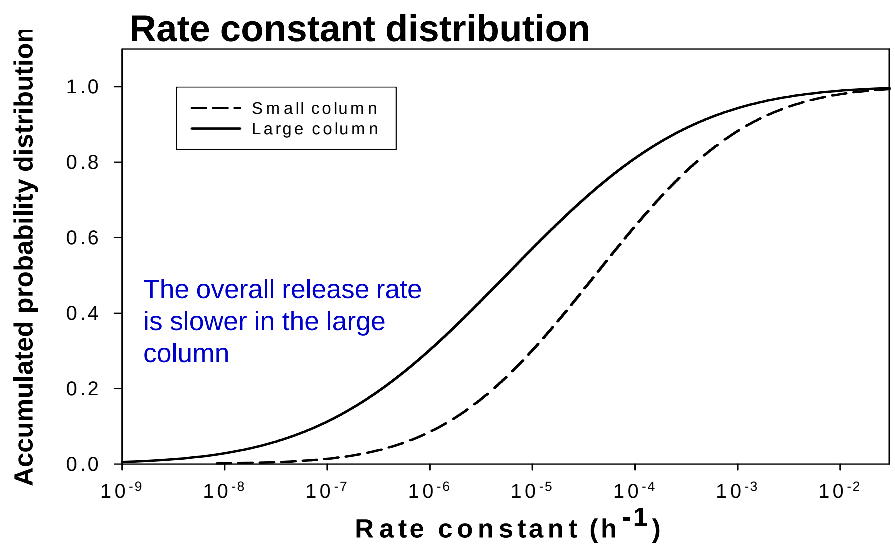
Tc(VII) Reduction: Constant Fe(II) [all C6209 samples]



Mass Transfer: Importance, Modeling, and Scaling







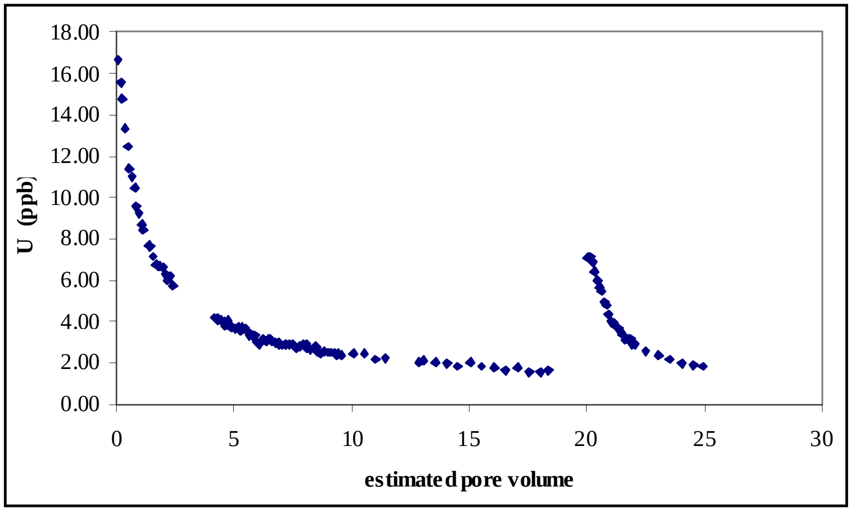
Liu et al. (2008)

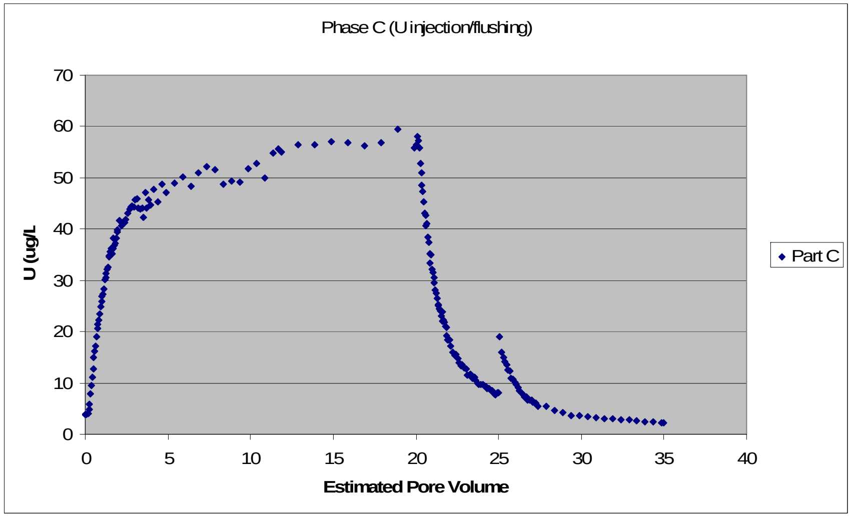
Determination of Ex-Situ/In-Situ Reaction Parameters

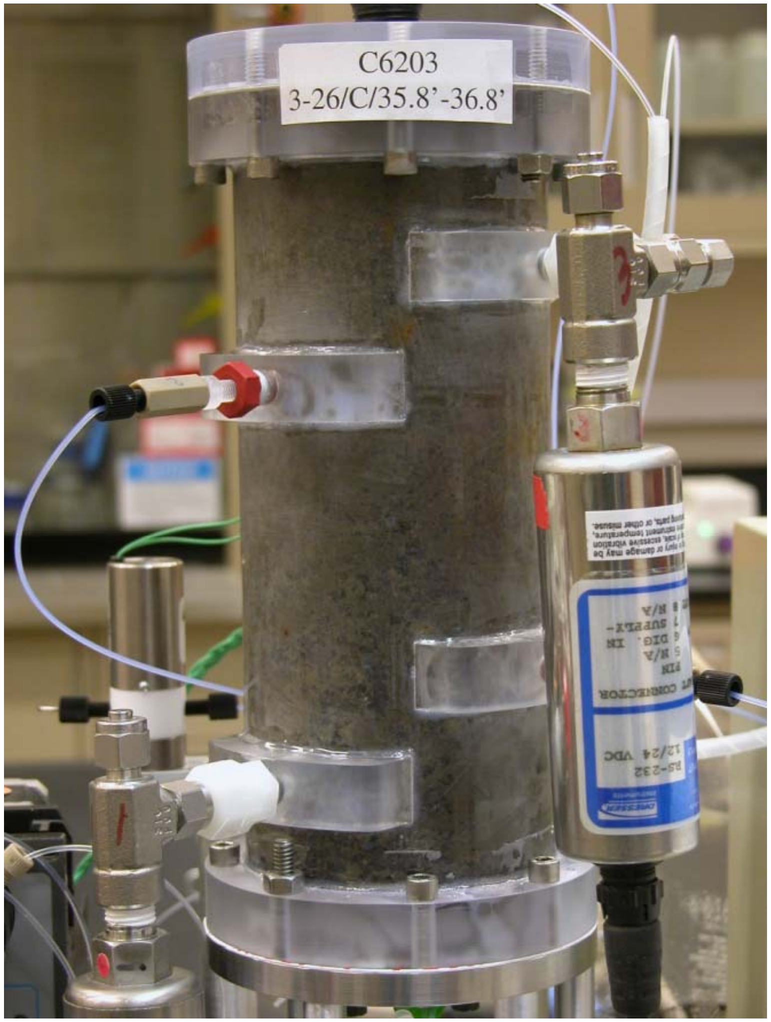
Intact Column Studies

- RT experiments at 10'/d, 3 cores from different aquifer depths
  - A-desorption, B-tracer, C-adsorption/desorption SGW-1, D-hydrologic properties
  - Contaminant versus spiked U(VI)
  - Unique structured behavior
- Deconstruction
  - PSD, SA (< 2 mm), < 2 µm mineralogy
  - Low [U(VI)] isotherm (< 2 mm) with two SGW
  - Mass transfer parameters by flow cell (< 2 mm)
  - AAO Fe(III) (< 2 mm)
  - CLIFS spectroscopy
- Upscaled modeling
  - SC-DR-DP (PFBA)
  - Other

U(VI) Desorption and Adsorption/Desorption from Intact IFRC Core 3-26/35.8-36.8'







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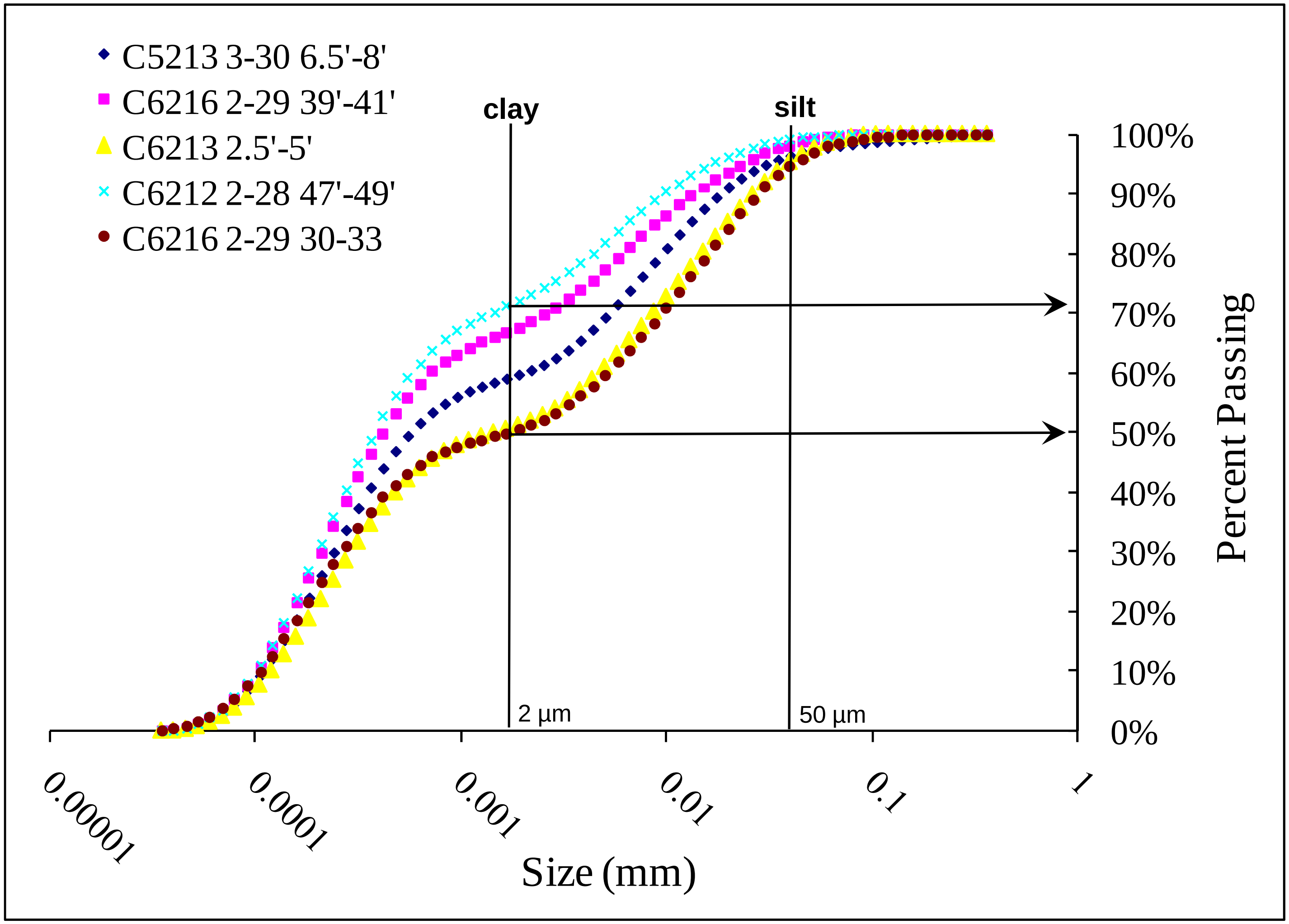
Particle Size of Coatings on Gravel (32 mm)

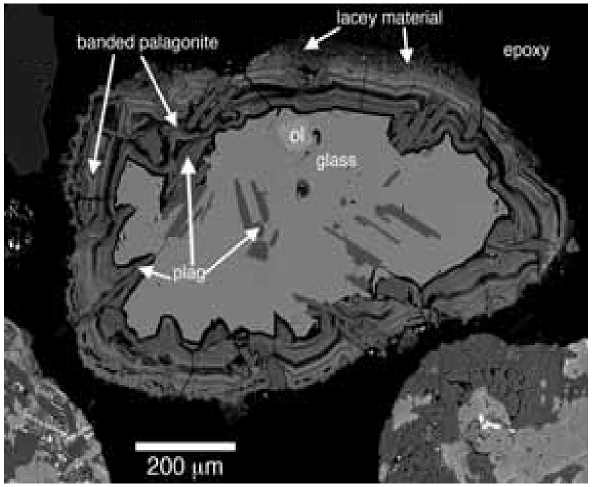


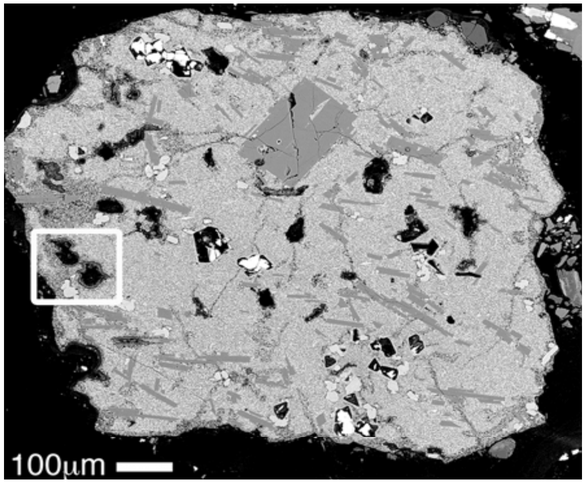
ESFA Collaborations

Davis – Particle heterogeneity

<u>Objective</u>: Quantify impact of intergranular porosity (IGP) on rates of U(VI) adsorption/ desorption

- IGP of different sediment fractions and responsible phases w CL ISFA
- XRM studies of tracer in-diffusion w KK ESFA
- Species specific diffusion rates, cross diffusion, and effects in diffusion w CL ISFA
- Microscopic reactive transport modeling w CL ISFA and MR IFRC
- Focus on Hf (300 A), RF (300 A), RF (200 A)
- Paper from FY08 in progress





ESFA Collaborations

Jardine – Macroscopic heterogeneities and unsaturated conditions (mm to dm scale)

Objectives: Determine how dual porosity develops with gravel content and provide experimental basis for upscaling < 2 mm reaction parameters

- Reactive transport experimentation under unsaturated and saturated conditions
- Initial target is the role of gravel on U adsorption/desorption at the 300 A IFRC
  - Quantify reactivity of different < 2 mm fractions with varying volume fractions of gravel
  - Vary flow rate, water composition, and U(VI) concentration
  - Investigate transition between equilibrium and kinetically dominated reactions and causes
- Requires modeling support; other issues

FY09 Science Deliverables

- Relationship of oxygen consumption and Tc(VII) reduction rates to Fe(II) mineralogy of Hanford sediments.
- Spectroscopically based surface complex reaction model for U(VI) in 300 A saturated zone sediments.
- U(VI) reactive transport behavior in naturally structured 300 A sediments, role of kinetic and thermodynamic processes.
- Modeling approach to scale < 2 mm U(VI) reaction parameters (rate constants, site concentrations, diffusivities) to whole sediment (with others).

FY10 Research Scope

- Continued studies on Hanford Fe(II) mineralogy and heterogeneous Fe(II)-promoted reactions
- Mineral-microbe studies on Fe(II) mineralogy, oxygen consumption and bacterial Fe(II) oxidation, Tc(VII) reduction, and U(VI) adsorption
- Influence of gravel on adsorption-desorption or dissolution rates with U(VI) in known speciation states/concentration [Fe(III) oxides, chlorite, and weathered mica; or metatorbernite]
- Reactive transport experiments with model transition zones and interfaces (Hanford-Ringold contact, Ringold redox transition)

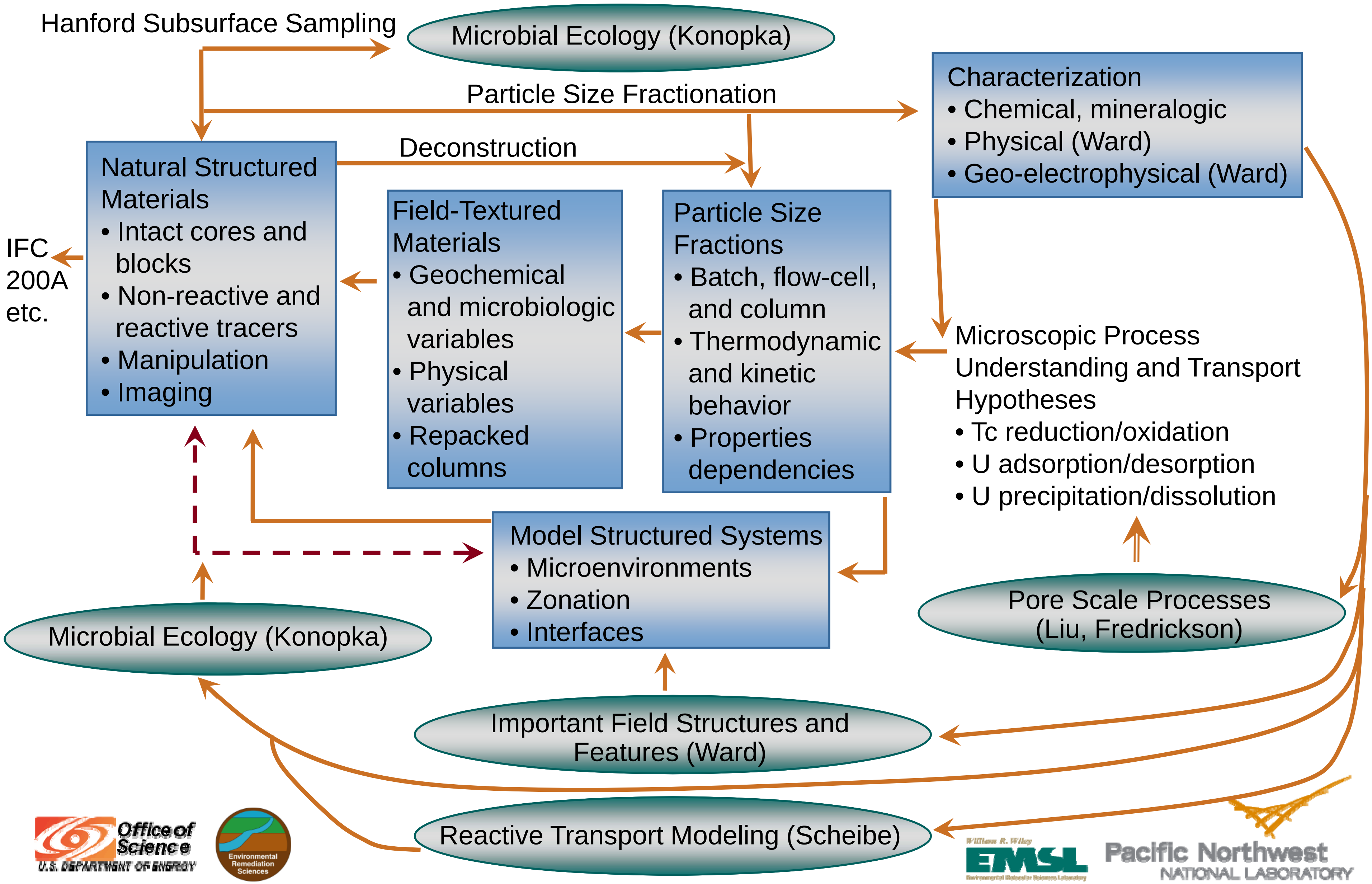
Expected Science Accomplishment and Impact

- Cross scale reactive transport experimentation that identifies critical features, properties, and parameters controlling Tc and U migration behavior from microscopic to mesoscopic scale for important Hanford scenarios.
- Improved understanding of key factors controlling process-coupling at different scales.
- Experimentally based modeling approaches to describe U and Tc migration in naturally complex materials with heterogeneities of different size, type, and orientation.

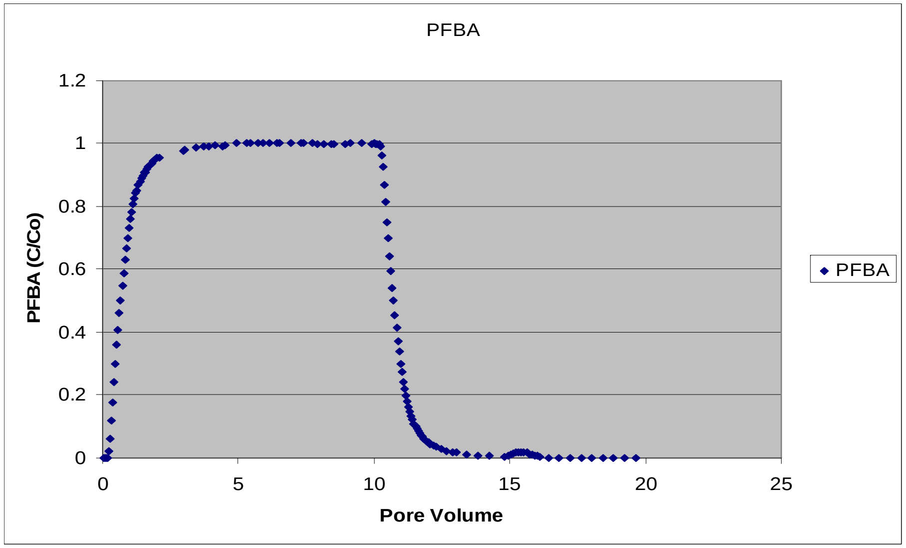
Impact: Risk reduction, insights for remediation, improved transport simulations that properly describe processes, and account for heterogeneities at different scales.

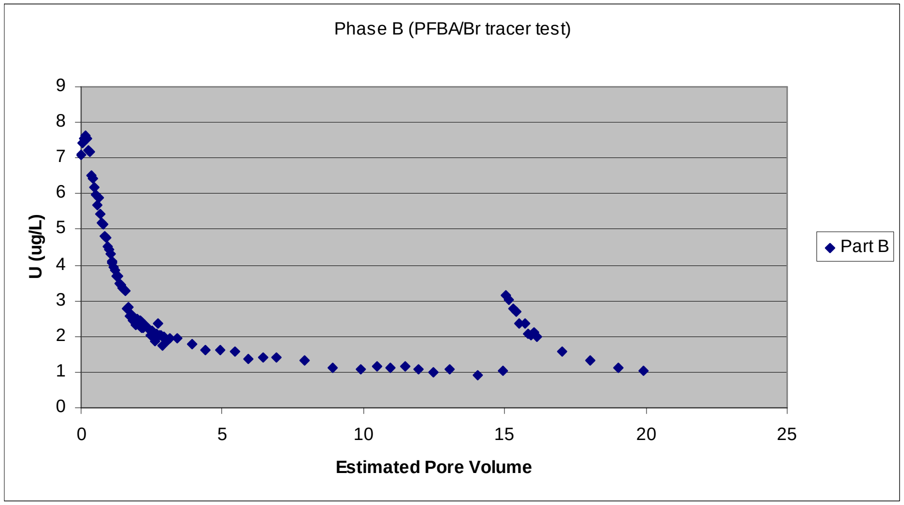
Approach and Collaborators

Key Hanford Science Issues



Tracer Behavior and U(VI) Desorption During Phase B





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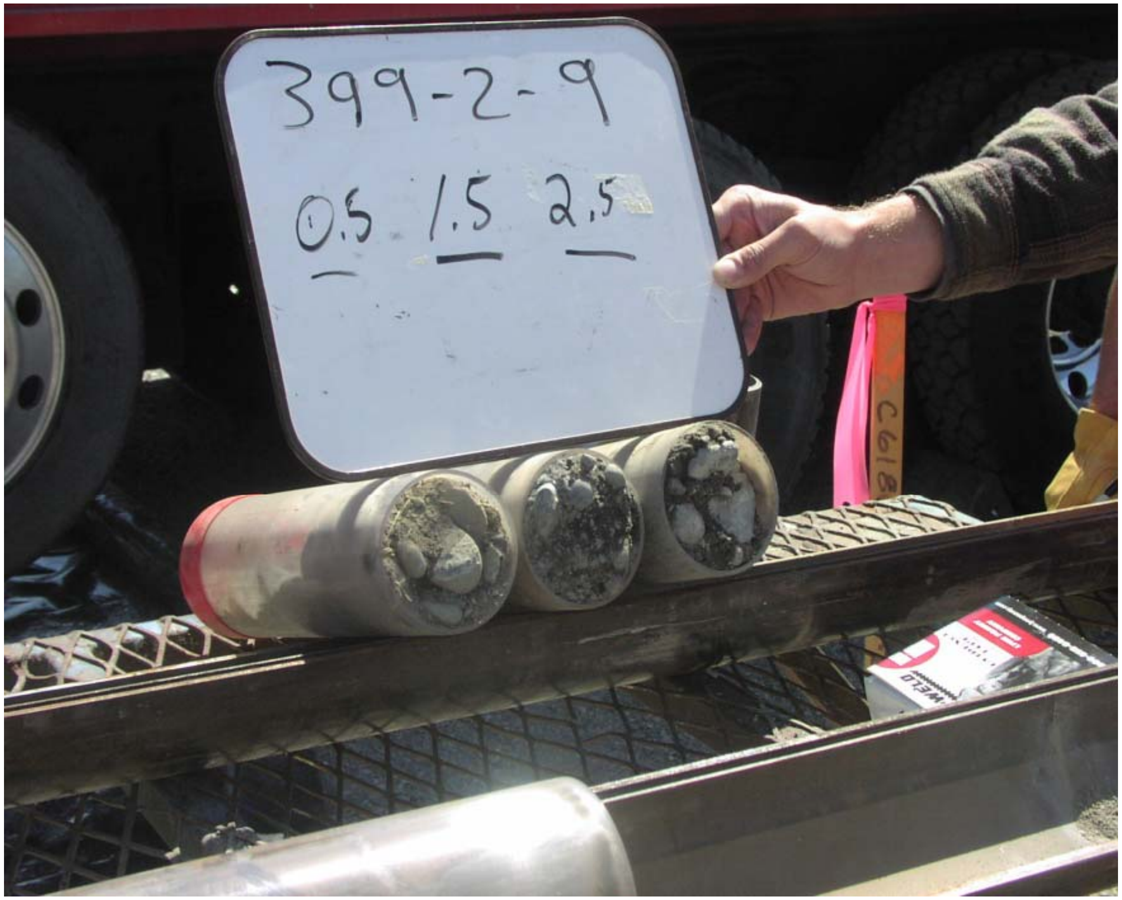
Science Issues and SFA Hypotheses

Science Problems

- Reactivity of different ferrous iron mineral types in varied structural/pore environments. Locations, scales, and effects of O_2 consumption on Tc and U transport.
- Importance of in-situ depositional features, structures, and natural mineral associations on redox, complexation, and precipitation/dissolution processes.
  - Reaction issues - biotic versus abiotic effects and their locations
  - Spatial issues - locations of water flow versus reaction
  - Transport issues - exchange between zones of different velocities
- Scaling process understanding to the field.
  - Critical process-level information, parameters, or abstractions that must be preserved
  - Effects of different heterogeneity types
  - Characterization/imaging of essential in-situ features and properties

SFA Hypotheses

- Reduction reactions will occur where oxygen consumption occurs by ferrous iron mineral reaction or microbiologic activity.
- Contaminant adsorption and precipitation will occur in grain interiors, lithic fragments, and fine-grained sediment bodies. Mass transfer will regulate contaminant exchanges between these zones and advective conduits.
- Understanding effects of in-situ features and geologic heterogeneities critical for lab-field transfer.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