Microscopic Mass Transfer of U and Tc in Subsurface Sediments

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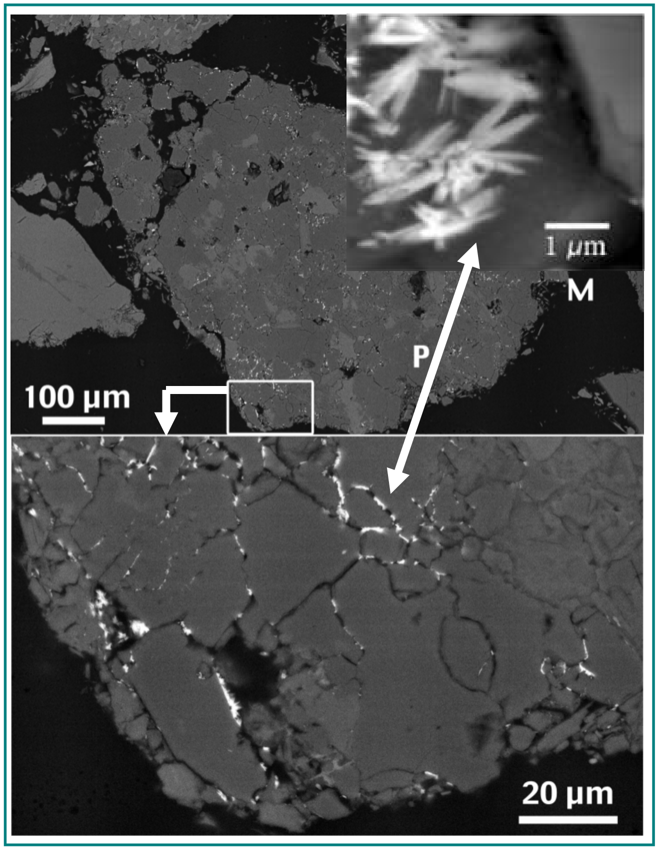
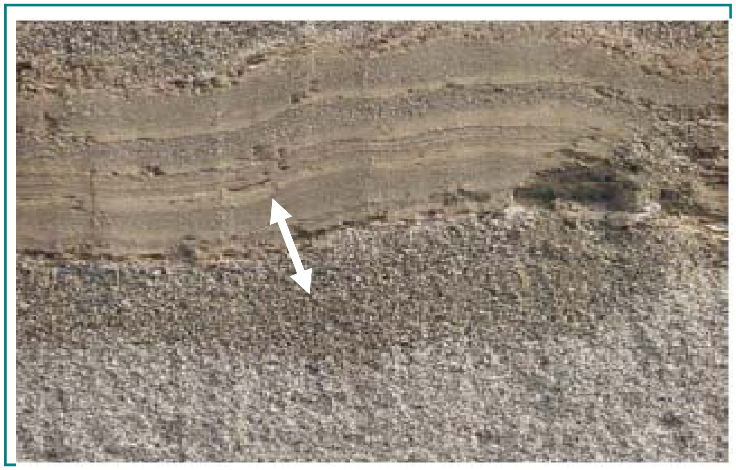
Microscopic Mass Transfer In Subsurface

Grain/Subgrain Mass Transfer



Mass Transfer in Low Permeability Zones



- Diffusive mass transfer controls reactant supplies and removal of products for biogeochemical reactions in intragrain, intra-coating, and intra-aggregate domains.
- Diffusion and/or slow advective mass transfer controls the rate of contaminant storage and release back to aquifer in low permeability zones.

Objectives

- Characterize microscopic mass transfer processes in sediments (rates, mechanisms, and models).
- Investigate the effects of mass transfer on (bio)geochemical reactions (rates and coupling).
- Scale coupled microscopic mass transfer and (bio) geochemical reactions to large systems.

Approaches

- Various experimental and numerical approaches will be used and/or developed to investigate the microscopic mass transfer and its effects on geochemical reactions and large scale mass transport.

Research Team

Chongxuan Liu, mass transfer experiment and modeling

Sebastian Kerisit, molecular simulation of ion diffusion

Toby Ewing, ISU, percolation and particle tracking

Scott Fendorf, Stanford U, microscopic experiments of coupled mass transfer and biogeochemical reactions.

Collaboration with other SFA projects

Jim Fredrickson, pore scale biogeochemical reactions

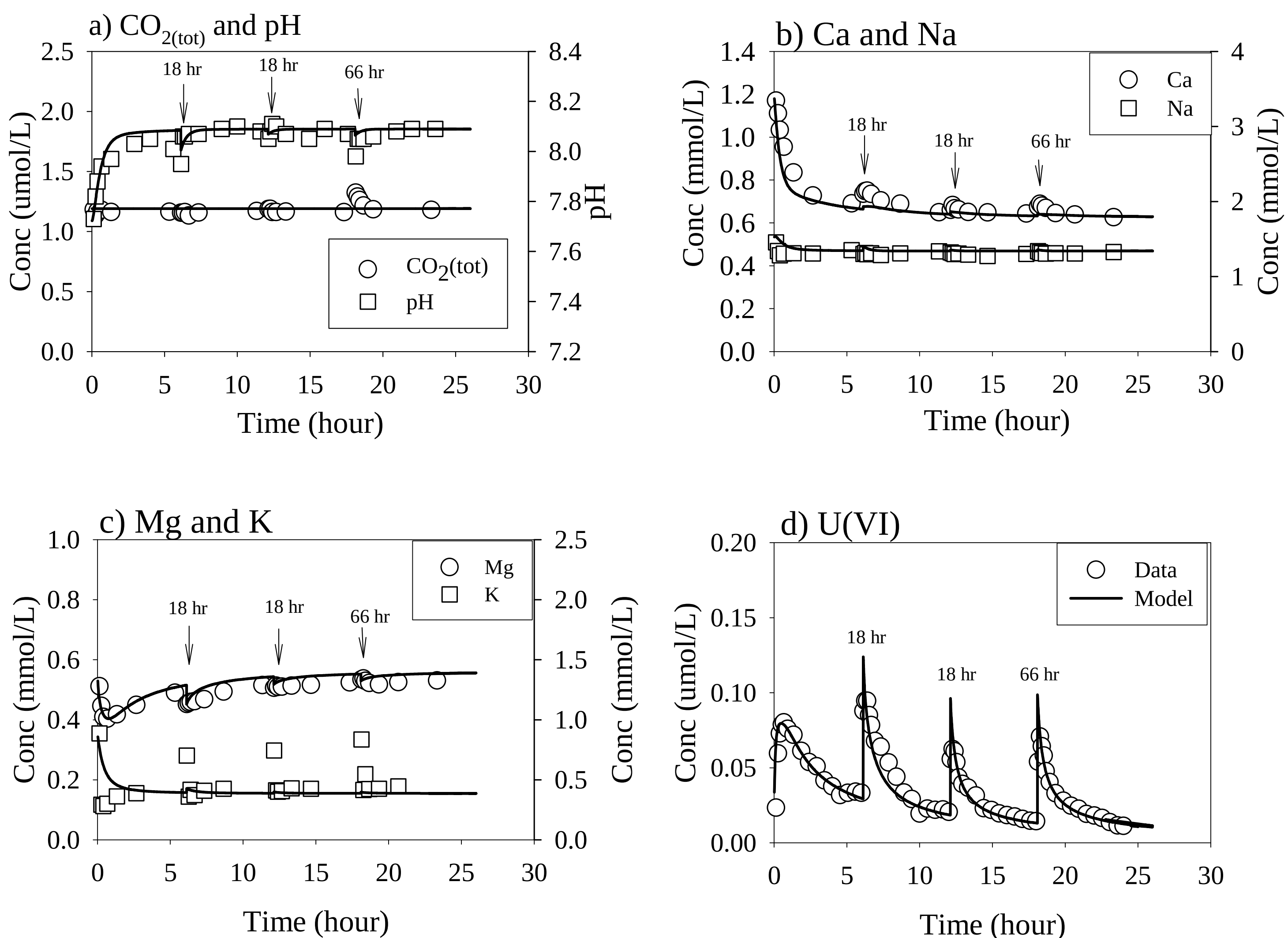
John Zachara, reactive transport experiments

Tim Scheibe, reactive transport modeling

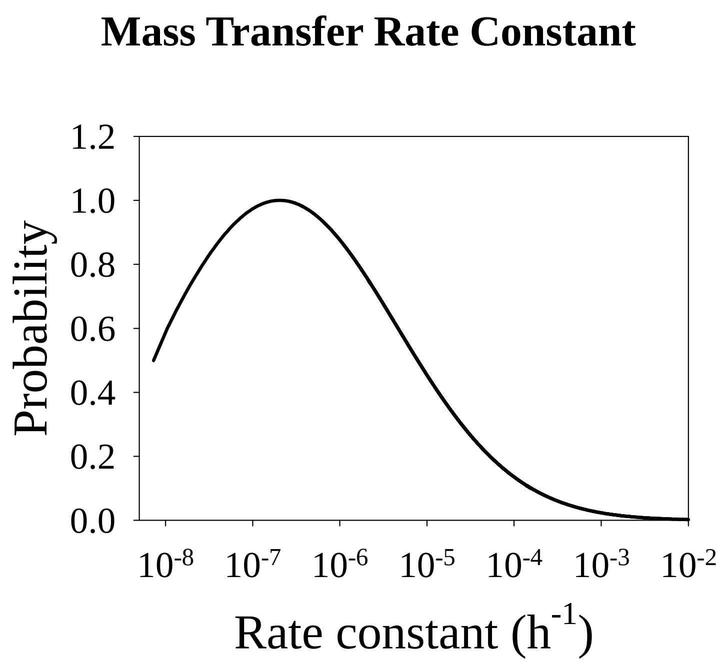
Research Plan for FY09 and FY10
(U(VI) mass transfer in < 2mm 300A sediment)

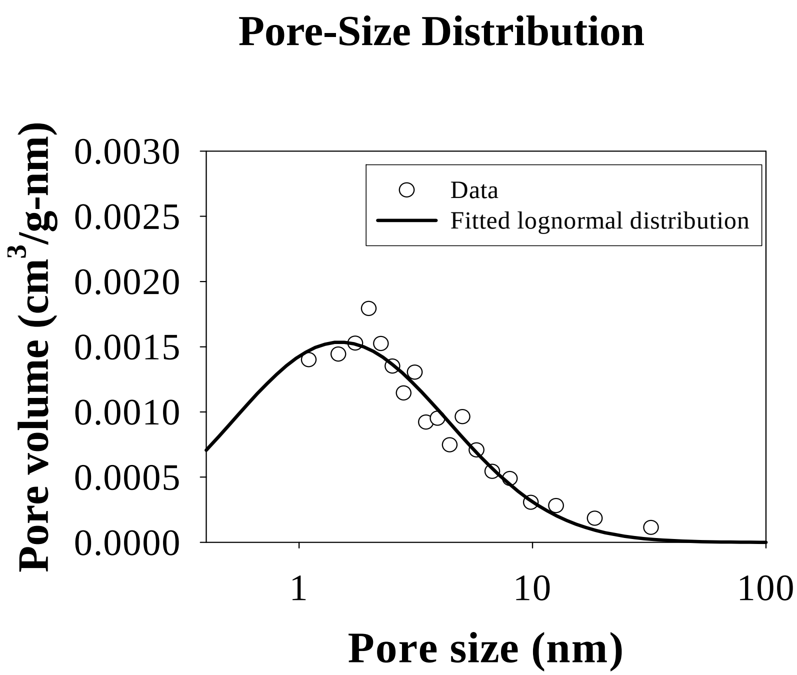
- U(VI) mass transfer and mechanisms: a) laboratory batch and flow-cell experiments for apparent mass transfer rates; b) pore-network and molecular insights; and c) relevant numerical models.
- Coupled processes: a) laboratory experiments for apparent rates of coupled mass transfer and (bio)geochemical reactions (Fredrickson); b) microscopic measurements of mass fluxes and reaction rates (Fendorf); and c) coupled numerical models.
- Model upscaling: a) evaluate scaling concepts (Zachara and Scheibe); and b) identify important parameters and processes in field-scale reactive transport (IFRC collaborators).

Measurements of U(VI) Mass Transfer Rates (flow-cell experiments of U(VI) desorption)



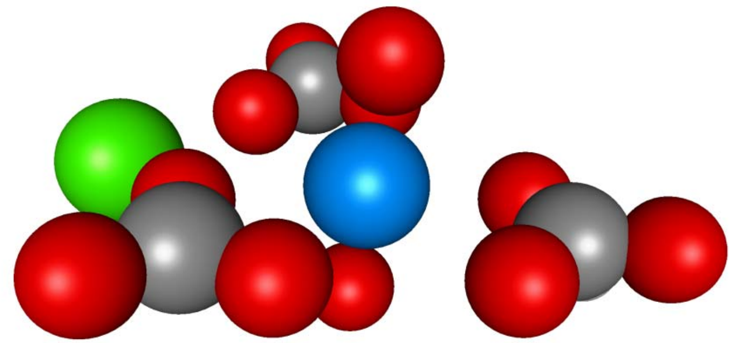
Mass Transfer Rates and Pore Size Distribution

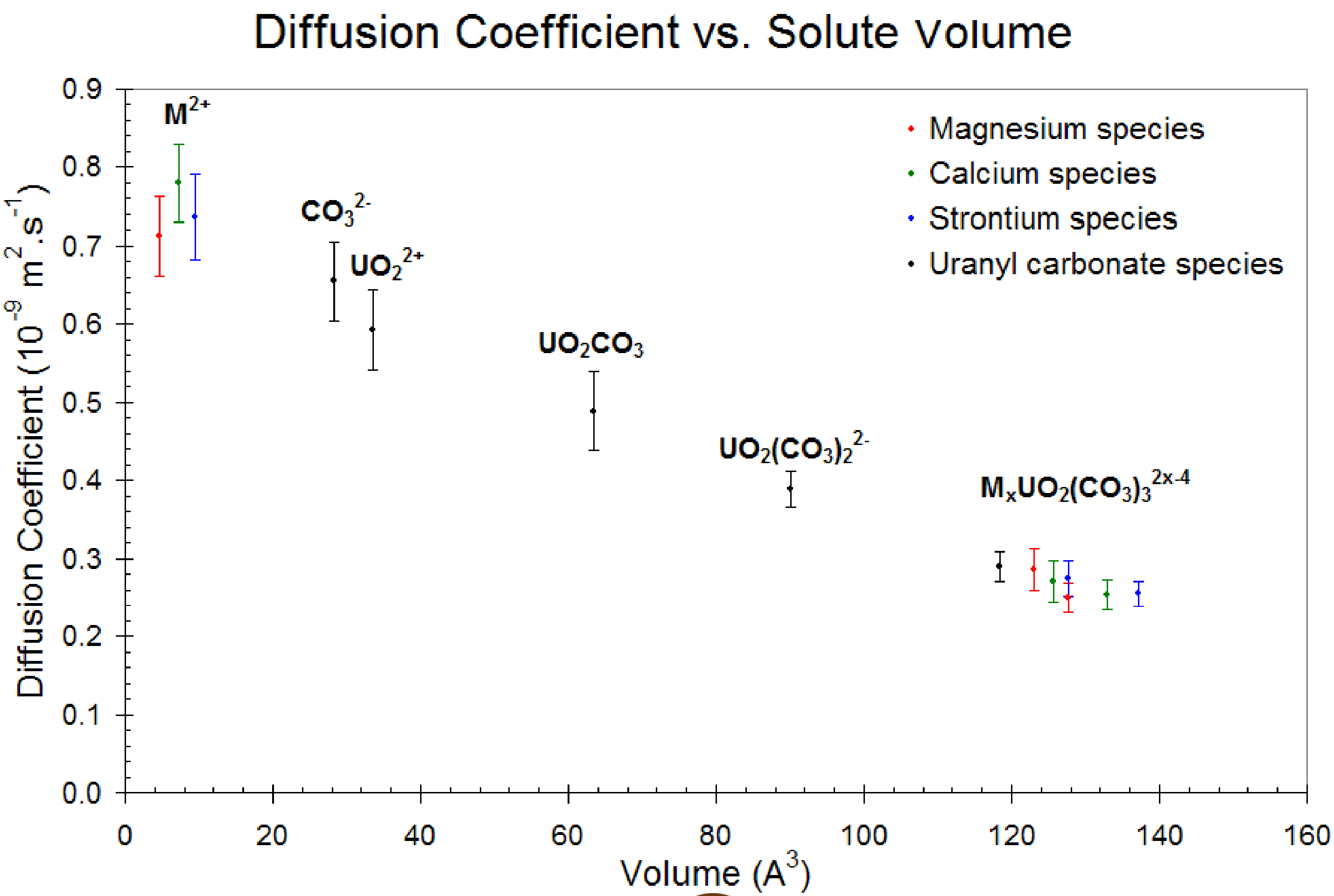




- The rate constants of U(VI) desorption and pore-size distribution in the sediment followed lognormal distribution

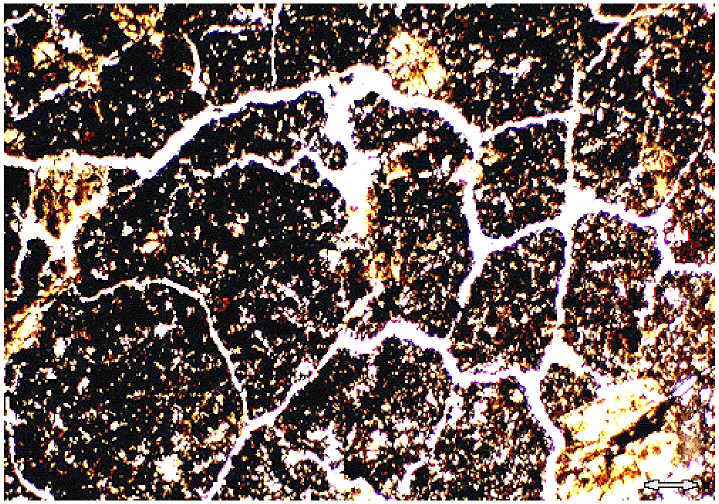
Diffusion Coefficients of Important U(VI) Species

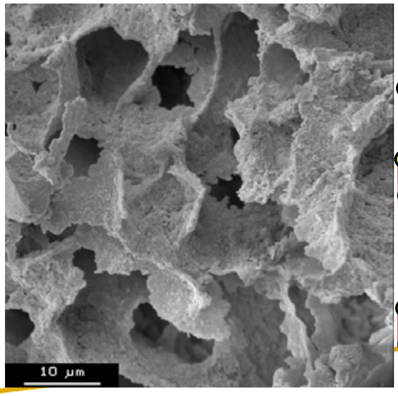


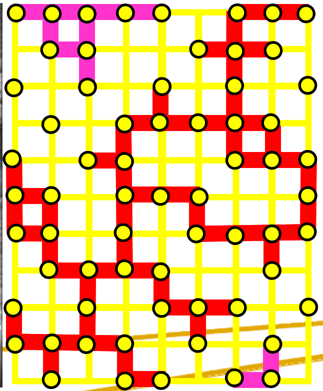


Pore-Network Model for the Observed Rates

- Integrate pore size distribution and molecular ion diffusion into a pore network model,
- Characterize the probability of the pore connectivity in the pore-network model,
- Develop effective medium approximation (EMA) approach for scaling pore network model to describe mass transfer rates.







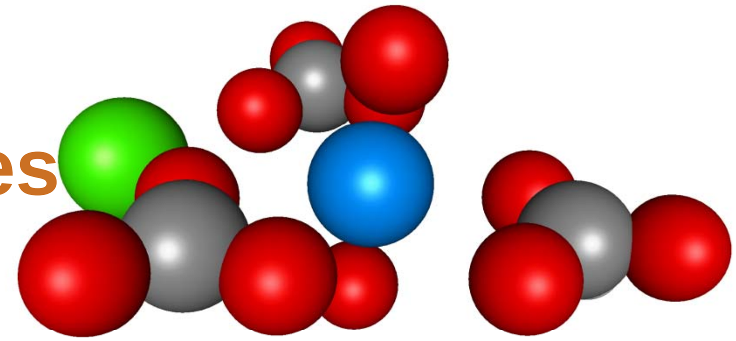
FY09 Deliverables

- Molecular diffusion coefficients of uranyl carbonate species.
- Multi-component, multi-rate models of U mass transfer in subsurface sediments.
- Comparison of diffusion-based and multi-rate models of microscopic reactive transport of U.
- Coupled U mass transfer and biogeochemical reactions in microenvironments ?

FY10 Deliverables

- Molecular diffusion coefficients of uranyl hydroxyl species.
- Effects of charge and species coupling on apparent U(VI) diffusion.
- Pore-network based interpretation of multi-rates of U(VI) desorption ?
- Coupled U mass transfer and biogeochemical reactions in microenvironments ?

Diffusion Coefficients of Important U(VI) Species



Species	$UO_2(CO_3)$	$UO_2(CO_3)_2^{2-}$	$UO_2(CO_3)_3^{4-}$
D (10^{-9} $m^2.s^{-1}$)	0.49(5)	0.39(2)	0.29(2)
Species	Mg^{2+}	$MgUO_2(CO_3)_3^{2-}$	$Mg_2UO_2(CO_3)_3$
D (10^{-9} $m^2.s^{-1}$)	0.71(5)	0.29(3)	0.25(2)
Species	Ca^{2+}	$CaUO_2(CO_3)_3^{2-}$	$Ca_2UO_2(CO_3)_3$
D (10^{-9} $m^2.s^{-1}$)	0.78(7)	0.27(3)	0.25(2)
Species	Sr^{2+}	$SrUO_2(CO_3)_3^{2-}$	$Sr_2UO_2(CO_3)_3$
D (10^{-9} $m^2.s^{-1}$)	0.74(5)	0.27(2)	0.26(2)

Investigation of U(VI) Desorption Kinetics in Hanford 300 A Sediment

Solution Composition

	K	Ca	Na	Mg	CO_2(tot)	pH
			mM			
SGW2	0.387	0.626	1.39	0.559	1.19	8.12
SGW4	0.0026	68.5	0.036	0.36	0.35	7.28
SGW7	0.014	0.032	80.7	0	9.78	9.09

Multi-rate model

$$\frac{\partial C_i}{\partial t} + \frac{(1-\theta)\rho_s}{\theta}\sum_{j=1}^{Ns}\left(a_{ij}\sum_{k=1}^{M_j}\frac{\partial q_j^k}{\partial t}\right) = L(C_i) \qquad i = 1, 2, \ldots, N$$

$$\frac{\partial q_j^k}{\partial t} = \alpha_j^k (Q_j^k - q_j^k) \qquad j = 1, 2, \ldots, Ns;\ k = 1, 2, \ldots, M_j$$