

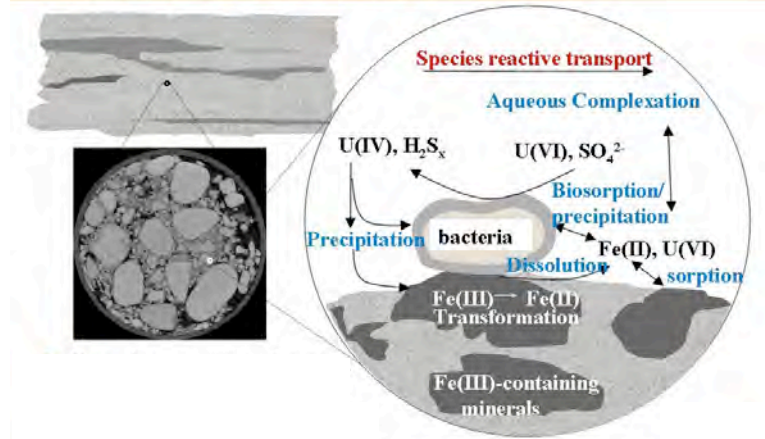
Summary of Presentations and Discussions at Breakout Session of Biogeochemical Scaling Transitions

5th Annual SBR Program PI Meeting, March 29, 2010, Washington, D.C.

Subsurface biogeochemical processes that govern the transport/fate of contaminants and carbon operate at a broad range of scales, from molecular to field, with numerous intermediate levels. Transitions of processes across scale boundaries (*e.g.*, molecular to pore scale, or pore to Darcy scale) correspond to transitions in complexity of media and process characteristics that challenge our ability to model subsurface characteristics and dynamics. For example, rules (*e.g.*, rate laws) that apply to a process at one scale may not necessarily apply to other scales. Detailed knowledge of processes at individual scales therefore can inform our efforts to predict solute behavior in the subsurface using reactive transport models that account for processes occurring a variety of scales and/or averaging volumes. This breakout session focused on issues that impact scaling of subsystem biogeochemical processes and rate laws to larger spatial scales. Four speakers presented talks on the impact of nanopores on solute sorption and transport (Huifang Xu, University of Wisconsin), measurement and variation of reaction rates at the pore- and Darcy scales (Chongxuan Liu, PNNL), surface complexation models to estimate K_d values for application in aquifer-scale reactive transport models (Jim Davis, USGS), and accounting for subsurface heterogeneity in biogeochemical models at the field scale (Li Li, Penn State University). Important observations that were noted during the presentations include the following:

- Nanopore surfaces may comprise a significant fraction of reactive surface area in sediments. This observation has not been widely discussed in the literature, and it helps to focus attention on processes associated with porosity exhibiting very small dimensions.
- The surface chemical properties of nanopores in oxides may differ significantly from bulk oxide powder surfaces with respect to sorptive capacity, redox behavior of sorbed solutes, and proton affinities for (hydr-)oxo surface sites.
- Uranium desorption rates depend strongly on scale due to the large surface area to volume ratio in pores, which leads to relatively faster reaction (desorption) rates in relatively smaller pores. Because the sizes of individual grid blocks (Darcy scale) for macroscopic reactive transport models at the column or field scales are larger than the spatial dimension of pores, rates extracted in the laboratory that correspond to pore-scale processes generally do not accurately predict reactive transport rates at the column and field scales.
- Rates of pore-scale processes can be scaled to account for this behavior if measurements can be performed that directly probe rates at the pore and Darcy scales. However, this will generally not be possible experimentally and consequently will require the establishment of mathematical scaling laws to scale rates extracted from the laboratory (pore-scale) to Darcy scale.
- Distribution coefficient (K_d) values for most metal-ion contaminants including U(VI) exhibit strong dependence on pH, and groundwater solute concentrations (*e.g.*, P_{CO_2}). Constant K_d approaches neglect this behavior and yield poor model predictions.

- Surface complexation models (SCMs) can be used to account for the dependence of K_d on solution conditions and substrate properties. However, their use in field-scale reactive transport models is challenged by the great degree of molecular-scale details that are required by widely used SCMs such as the CD-music models.
- Biogeochemical models that capture key field scale behavior (by matching field aqueous geochemistry data) can be used to predict microbial biomass growth, microbial-driven mineral precipitation, and field scale system dynamics using relatively simple modeling approaches.



Variability in sediment clast size gives rise abundant pores with a distribution of sizes and to a variety of flow domains. Biogeochemical reactions that control solute transport and redox state occur within these pores.

Subsequent discussions focused on overarching issues and research needs related to model scaling and development. Two points that emerged as common concerns from the session were: (a) there is a need to better characterize and account for nanometer to micron-scale physical/chemical sediment heterogeneities when developing models, particularly grain coatings and nano-scale porosity that may exist within individual mineral crystals or is created by aggregation, cementation, or sintering of colloid-sized grains, and (b) there is a need for methods that can quantitatively assess sediment properties (*e.g.*, sediment surface area, amount of a sorbed species) at the aquifer scale (meters to kilometers). Davis noted that mineral grain surfaces are generally coated with complex assemblages of mineral colloids, the specifics of which are neither known nor directly reconciled in transport models. The impact of nanopores on mineral reactivity similarly is not taken into account in geochemical models. The development of geophysical characterization methods that can provide information about sediment properties from sensors arrays was specifically highlighted as a critical need for improving current and future reactive transport models.

Discussions also focused on the question, “could these studies benefit from approaches used in models developed to predict complex behavior (*i.e.*, behavior that generally cannot be predicted by additive modeling of subsystem processes) in complicated systems?” So-called complexity models are often considered to be “top-down” approaches because they use statistically validated parameters that may not correspond to subsystem processes in a 1:1 fashion, but rather are selected for their ability to capture key dynamics. Complexity approaches contrast to reductionist approaches, the latter being commonly used for geochemical reactive transport modeling, in which (increasingly greater numbers of) subsystem process mechanistic details (*e.g.*, adsorption, dissolution, precipitation, microbial growth and consumption/production of solute reactants/products) are quantitatively represented in the model. Such approaches have often improved model flexibility and agreement with field solute data, and they make it possible to identify subsystem processes having the greatest impact on macroscale observables. However, reductionist approaches ultimately may not be practical due to the amount of parameters that

must be estimated, their intensive requirement for (scarce) computational resources, and the associated prediction uncertainties. It also has been suggested that, for some highly complicated systems (e.g., a contaminated aquifer such as that at the Hanford 300 area, which exhibits extensive sediment heterogeneity and seasonally varying water table levels and hydrologic flow directions), reductionist approaches fundamentally may be unable to accurately predict future states due to the emergence of complex behavior in the system at the aquifer scale. Complexity modeling approaches have been proposed as alternative paradigms for such systems.

One example of a geochemical model that adopts aspects of a top-down complexity approach is the work of the USGS-Menlo Park group led by Jim Davis to model uranium reactive transport in a contaminated shallow sand-and-gravel aquifer at Naturita, Co, which was discussed during the break-out session. This work used a simplified surface complexation model to parameterize K_d in terms of two surface complexation reactions (corresponding to uranyl carbonate and uranyl hydroxo surface complexes) that can occur at three surface binding sites, evaluated as average sediment properties. Myriad molecular-scale details were not explicitly represented in this model, notably including mineral-specific surface complexation reactions, mineral surface site densities, and surface electric double layer terms. This example provided a point of departure for discussions regarding the perceived applicability of complexity approaches to biogeochemical modeling. Most participants in the session were skeptical that pure complexity based models could lead to improved model prediction in the systems discussed. As noted above, several participants voiced a need for increasing amounts of nm to Darcy-scale detail (better knowledge of pore characteristics, sediment surface properties). However, it should also be noted (again) that successful biogeochemical models are rarely purely reductionist. For (another) example, the biogeochemical model presented by Li successfully matches the field scale aqueous geochemistry data and predicts biomass growth in the Old Rifle site aquifer following acetate injection without input of 3-D tomographic pore structure or detailed characterization of microbial phylogeny and its evolution with time. Instead, Li et al. used a conceptual probability correlation between physical and geochemical properties and a few key statistical parameters to represent the spatial heterogeneities of the system. The biogeochemical model also incorporated a bulk surface complexation model without taking into account all the detailed pore-scale sorption and desorption processes. These considerations suggest that biogeochemical model will continue to proceed via hybrid approaches that incorporate both reductionist and complexity approach characteristics.

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Stanford Synchrotron Radiation Lightsource

Agenda from the 2010 PI Meeting

Breakout Session B: Biogeochemical Scale Transitions

Moderators: John Bargar (SLAC) and Roland Hirsch (DOE-BER)

Description of Session: Subsurface biogeochemical processes that govern the transport /fate of contaminants and CO₂ operate across a range of scales, from molecular to field, with numerous intermediate levels. Transitions of processes across scale boundaries (e.g., molecular to pore) correspond to transitions in complexity of media and process characteristics and challenge our ability to model subsurface characteristics and dynamics.

Knowledge of how such processes occurring at different levels of a hierarchical system link with each other and control higher-level behavior (and visa versa) is essential to predicting solute behavior in complex subsurface systems. Of particular interest for this breakout session is the ability to understand and quantify the influence of molecular-scale processes on solute behavior at larger length scales or in more complex systems.

This breakout session will highlight scaling of molecular-scale biogeochemical processes to larger spatial scales and across different types/levels of complexity. Talks on this subject area will be followed by discussions to identify overarching issues, field research infrastructure needs, and approaches to understanding the roles and functions of molecular-scale processes at the field scale. The breakout session will produce a 2-page report that summarizes overarching scientific questions, logistics issues, and highlights example questions that penetrate deeply into this subject area.

Speakers:

- 2:00-2:30pm **Dr. Huifang Xu**, University of Wisconsin
Title: Role of nanopores in regulating U(VI) speciation and mobility
- 2:30-3:00pm **Dr. Chongxuan Liu**, PNNL
Title: The role of pore-scale reactive mass transfer in the scale-dependency of geochemical and biogeochemical reaction rates: a uranyl desorption case
- 3:00-3:30pm **Dr. James A. Davis**, USGS
Title: Upscaling Sorption Processes in Porous Media
- 3:30-4:00pm **Coffee Break**
- 4:00-4:30pm **Dr. Li Li**, Penn State University
Title: Effects of Physical and Geochemical Heterogeneities on Biogeochemical Processes and Implications for Uranium Bioremediation
- 4:30-5:00pm **Group Discussion**