PNNL-SA-60523

Conceptual model of mass transfer at 300 A

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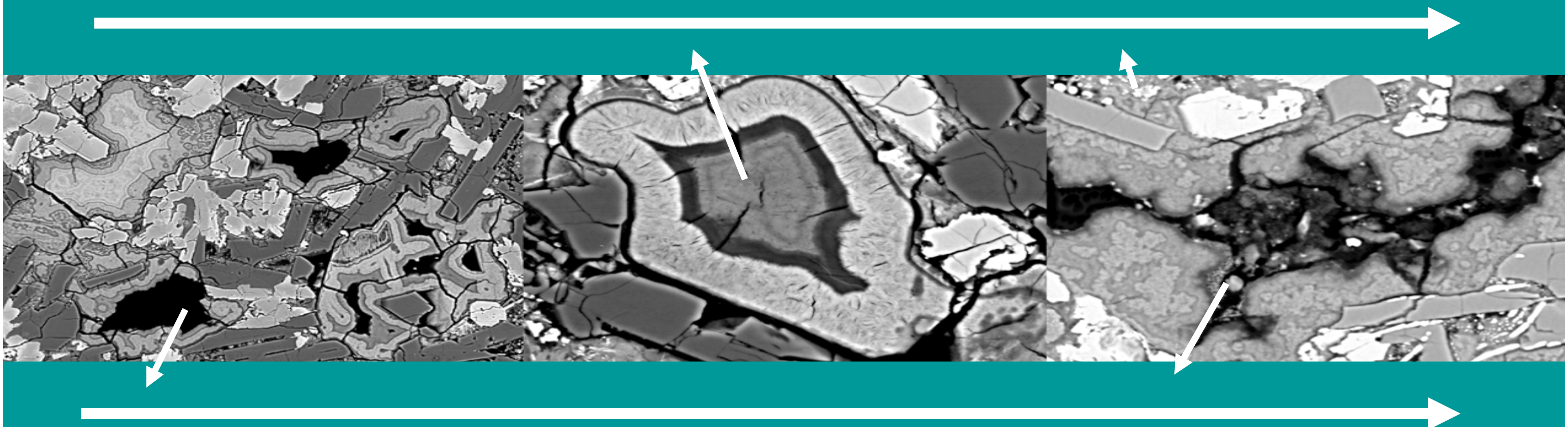
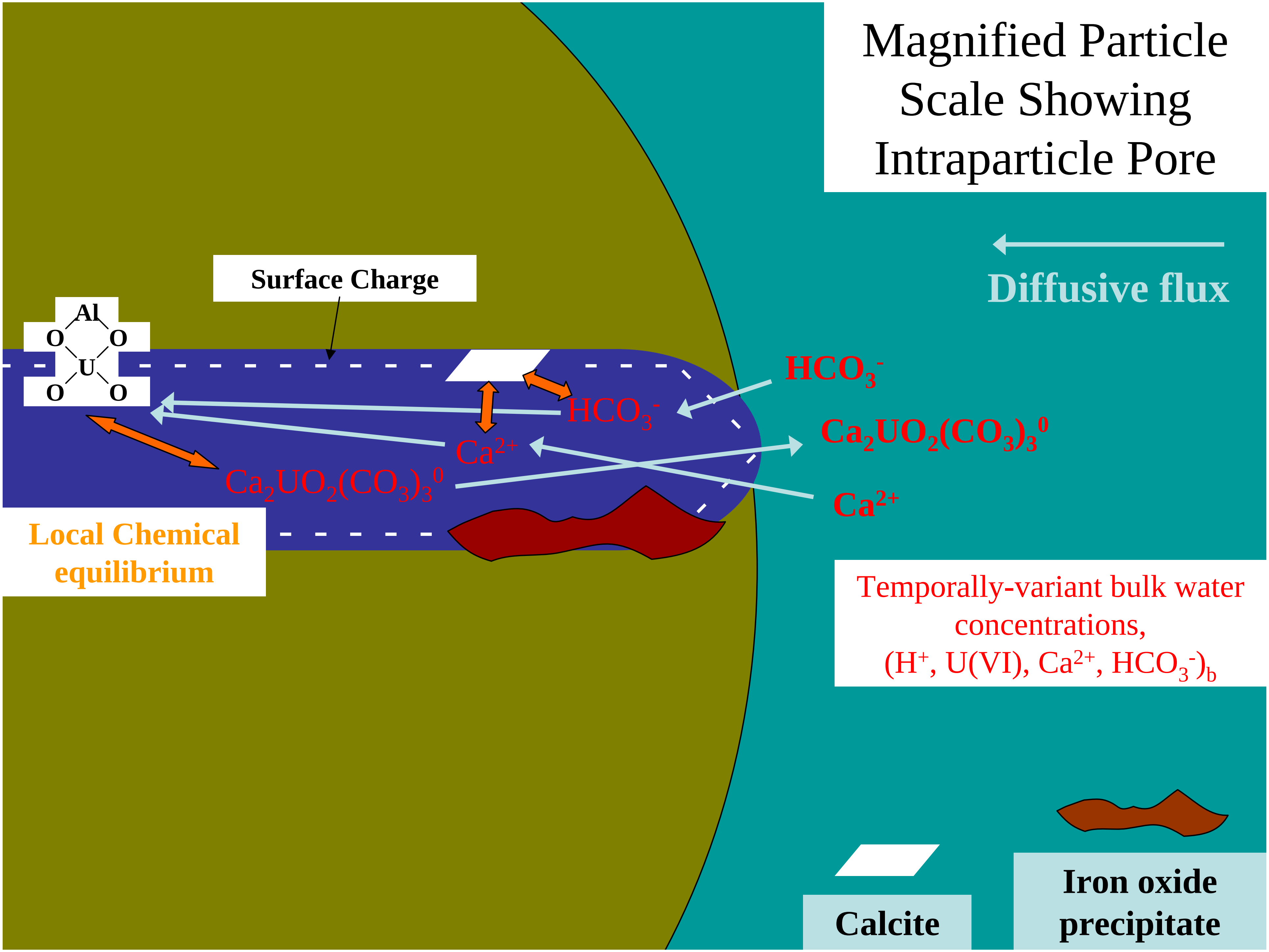
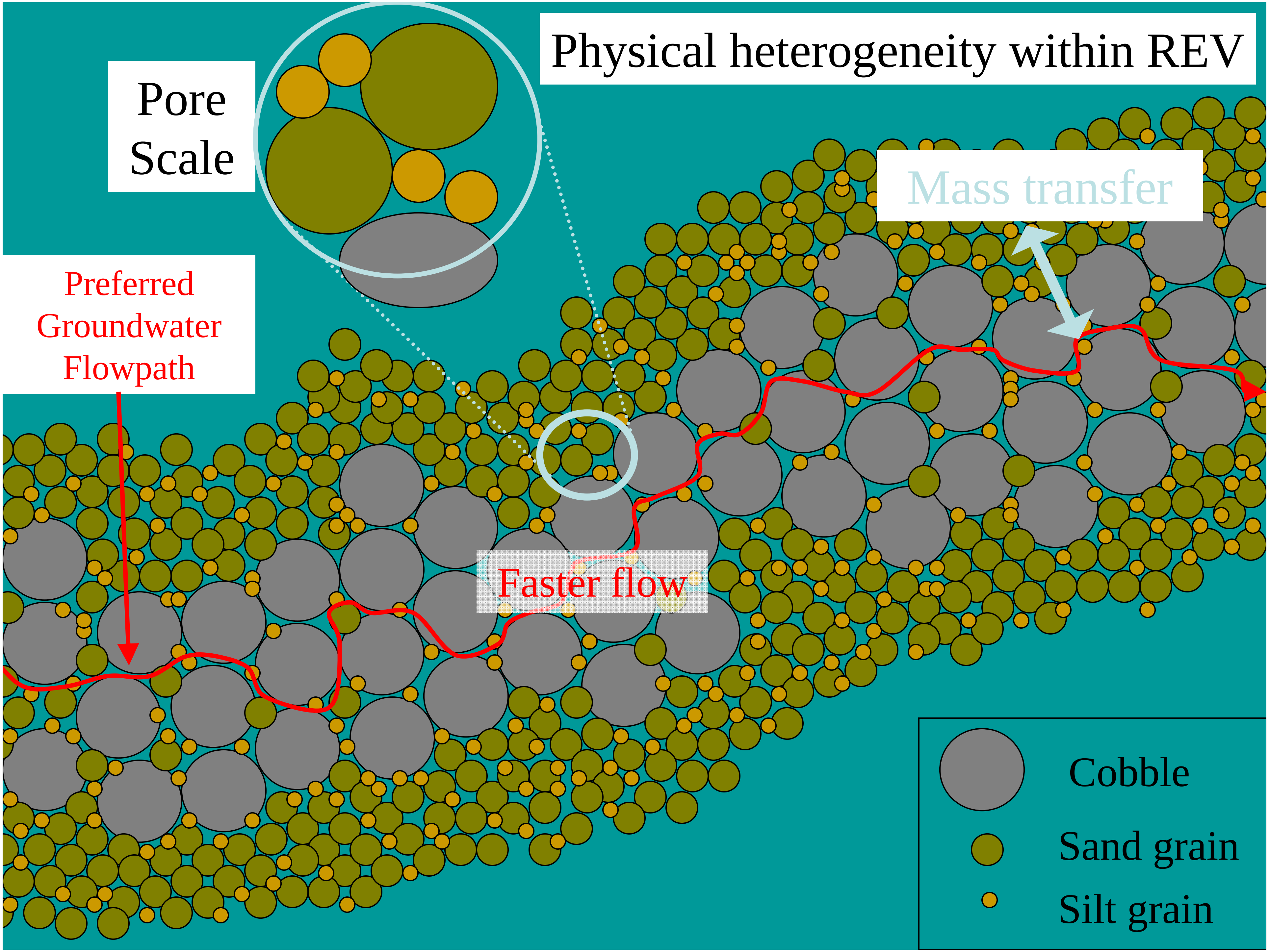
Characterizing mass transfer



Pore-scale diffusion

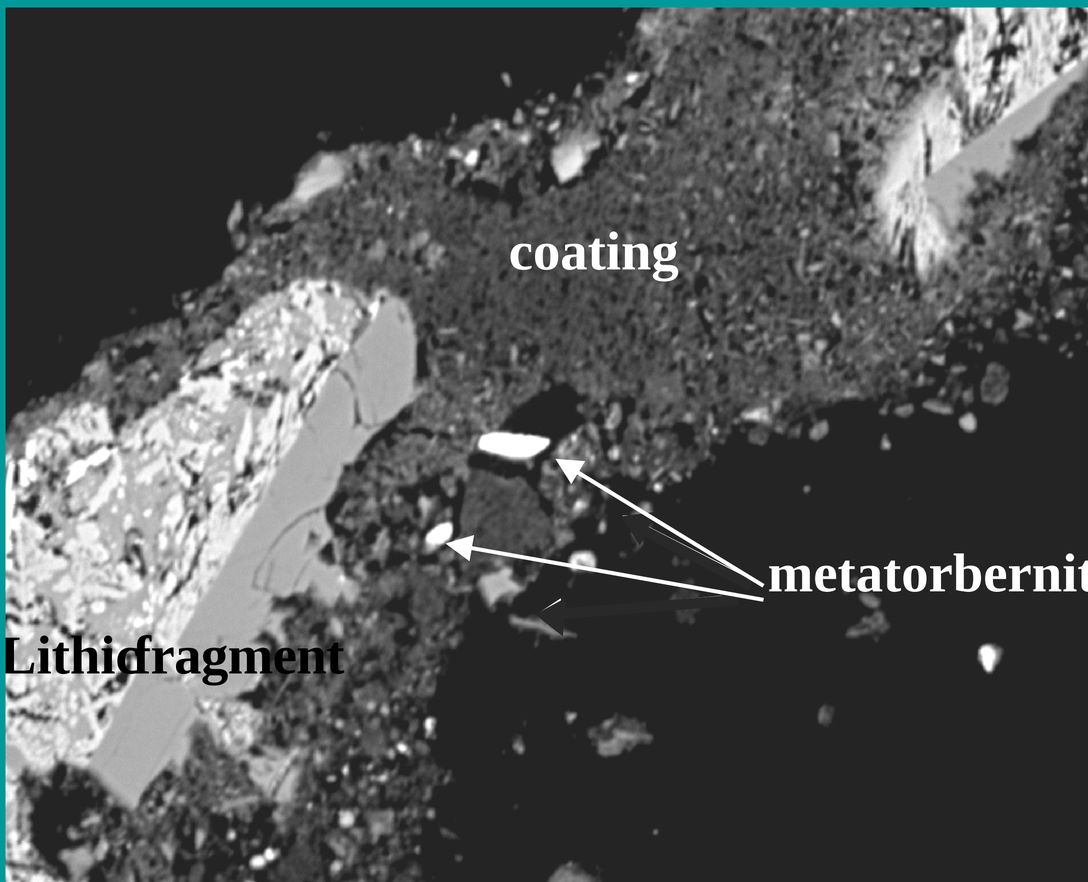
- Migration through pore network in response to $\partial \mu^e_i / \partial x$
- Formation of surface complexes
- Formation of aqueous complexes (f(a_{Ca}, a_{CO3}, a_{UO2}, etc.))

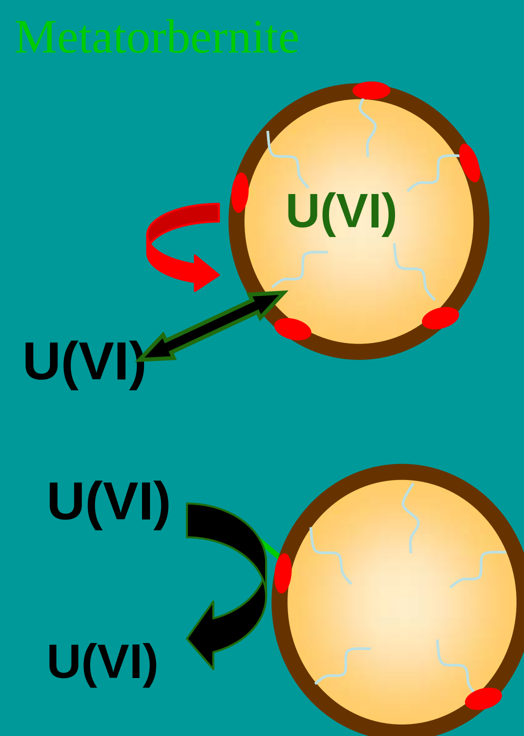

Magnified Particle Scale Showing Intraparticle Pore
Diffusive flux
Surface Charge
Al
O
O
U
O
O
HCO$_3^-$
Ca^{2+}
Ca$_2$UO$_2$(CO$_3$)$_3^0$
HCO$_3^-$
Ca$_2$UO$_2$(CO$_3$)$_3^0$
Ca^{2+}
Local Chemical equilibrium
Temporally-variant bulk water concentrations, (H$^+$, U(VI), Ca^{2+}, HCO$_3^-$)$_b$
Calcite
Iron oxide precipitate



Physical heterogeneity within REV
Pore Scale
Mass transfer
Preferred Groundwater Flowpath
Faster flow
Cobble
Sand grain
Silt grain

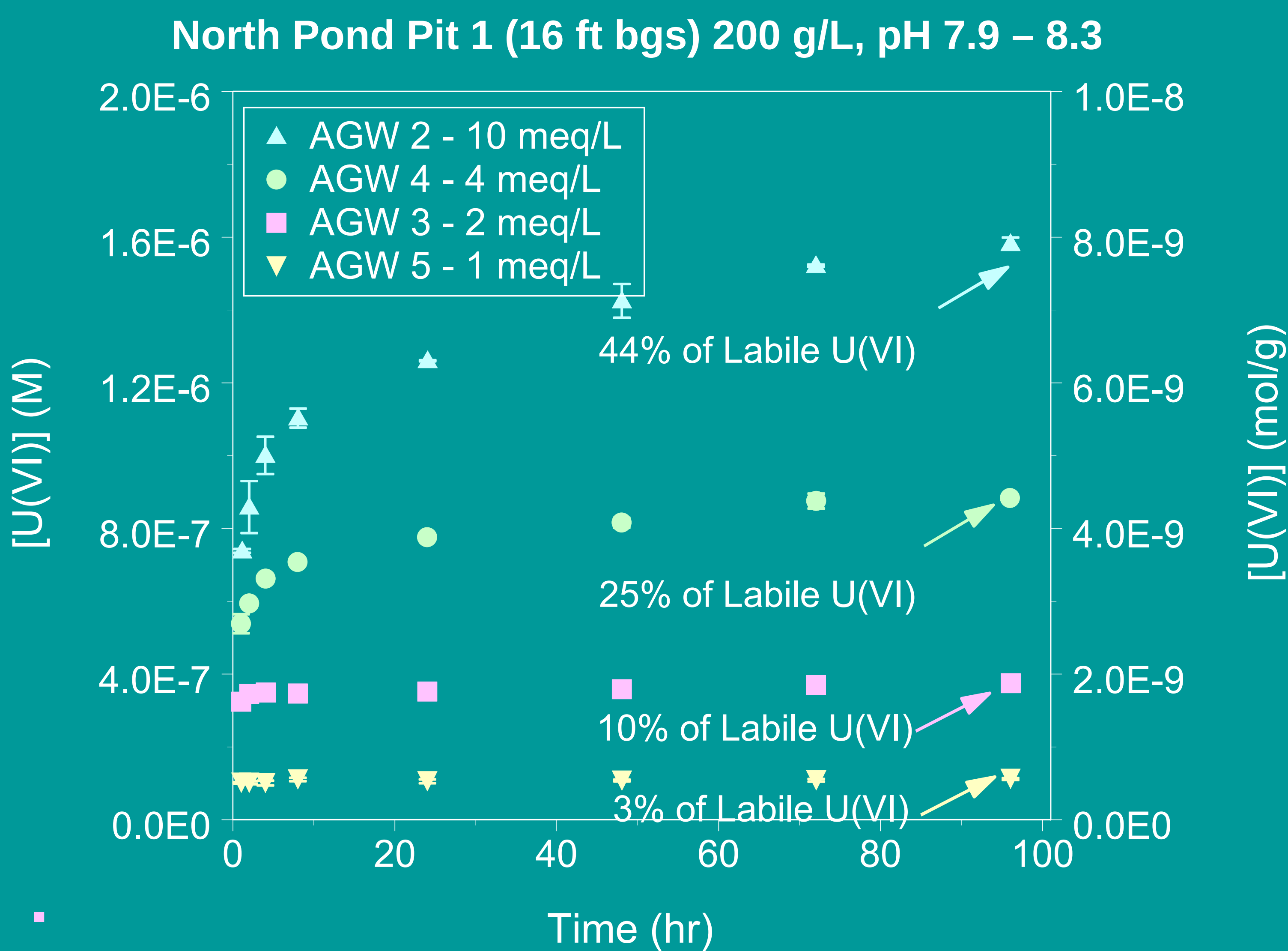
Upper vadose zone



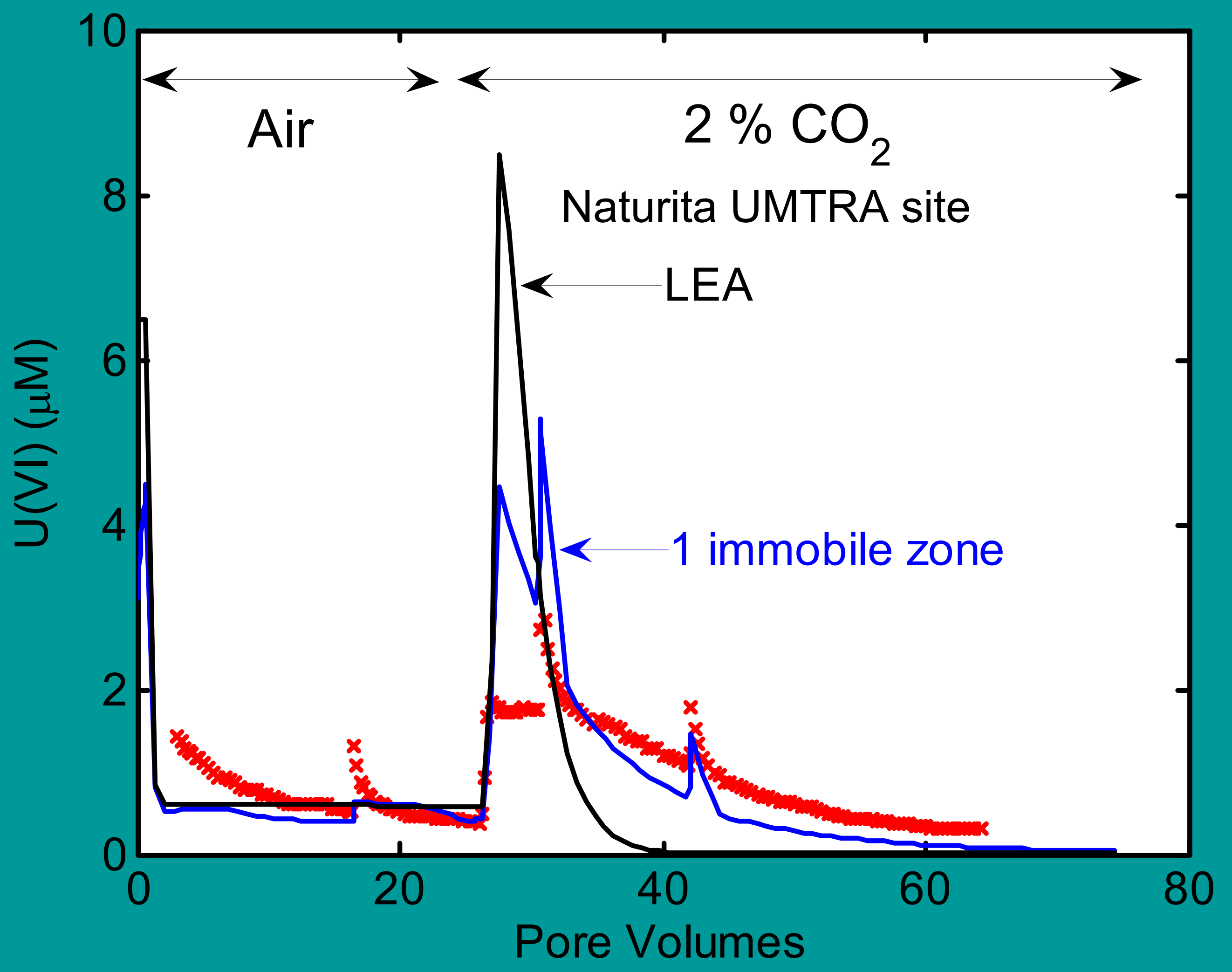


Mass transfer of U(VI) in minerals to adsorbed U(VI)

Impact of variable chemistry on diffusive mass transfer: batch experiments



Impact of variable chemistry on diffusive mass transfer: column experiments



Characterization of porosity

- Bulk characterization (N_2 adsorption, Hg-porisimetry)
- Stop flow elution (tritium, other tracers with high values of C_0/ql)
- Microscopic characterization (e.g., EM)

- Current grain-scale mass transfer models
- Parameters in the models
- Upscaling of grain-scale model to large or field scale systems

Current modeling approaches of grain-scale mass transfer:

Multi-rate approach (WRR, in press)

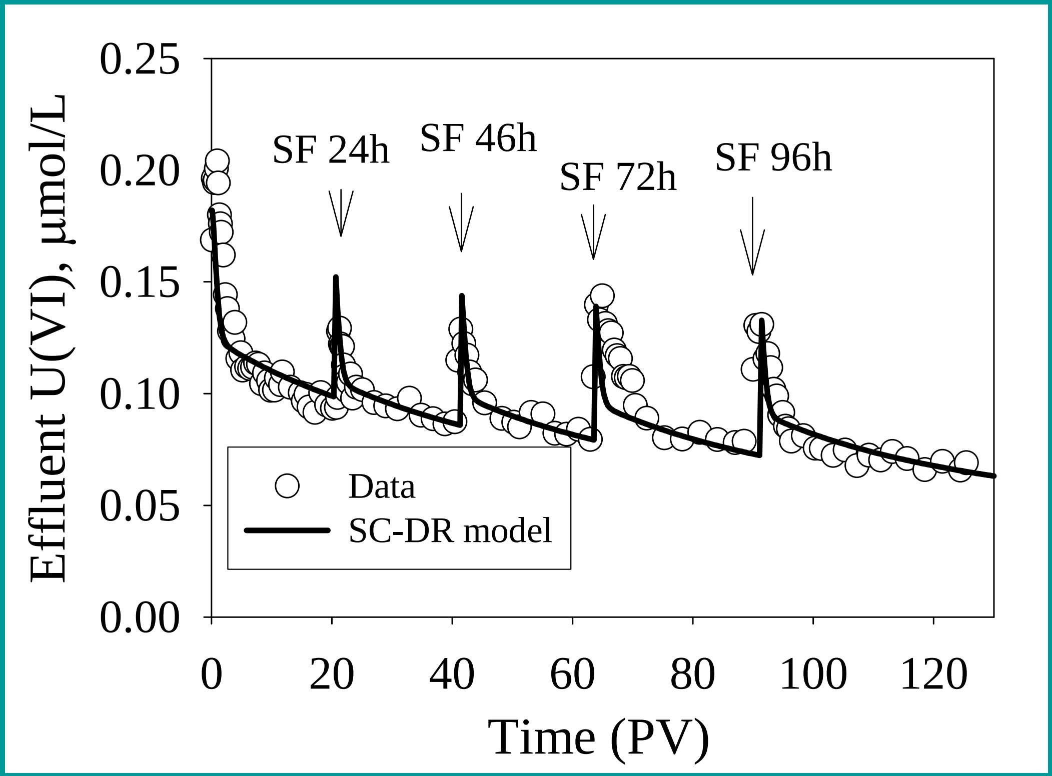
$$\frac{\partial q_i^k}{\partial t} = \alpha_k (S_i^k - q_i^k) \qquad i = 1, 2, \ldots, N;\ k = 1, 2, \ldots M$$

q: sorbed concentration, S: sorption at equilibrium, α: mass transfer rate coefficient, N: number of species, M: number of rate sites.

- Link with surface complexation (SC) and aqueous speciation
- Requirement of mass-transfer rate coefficients
- Empirical nature: rate coefficients dependent on geochemical conditions?
- Difficulty to link with dissolution/precipitation reactions in mass transfer-limited domains?

Example of the multi-rate approach

NPP 1-14 fine-grained materials (< 2mm), SGW



Multi-rate coefficient distribution:

$$p(\alpha) = \frac{1}{\sqrt{2\pi}\alpha\sigma} \exp\left(-\frac{1}{2\sigma^2} (\ln(\alpha) - \mu)^2 \right)$$

Is $p(a)$ dependent on geochemical conditions?

Current modeling approaches of grain-scale mass transfer:

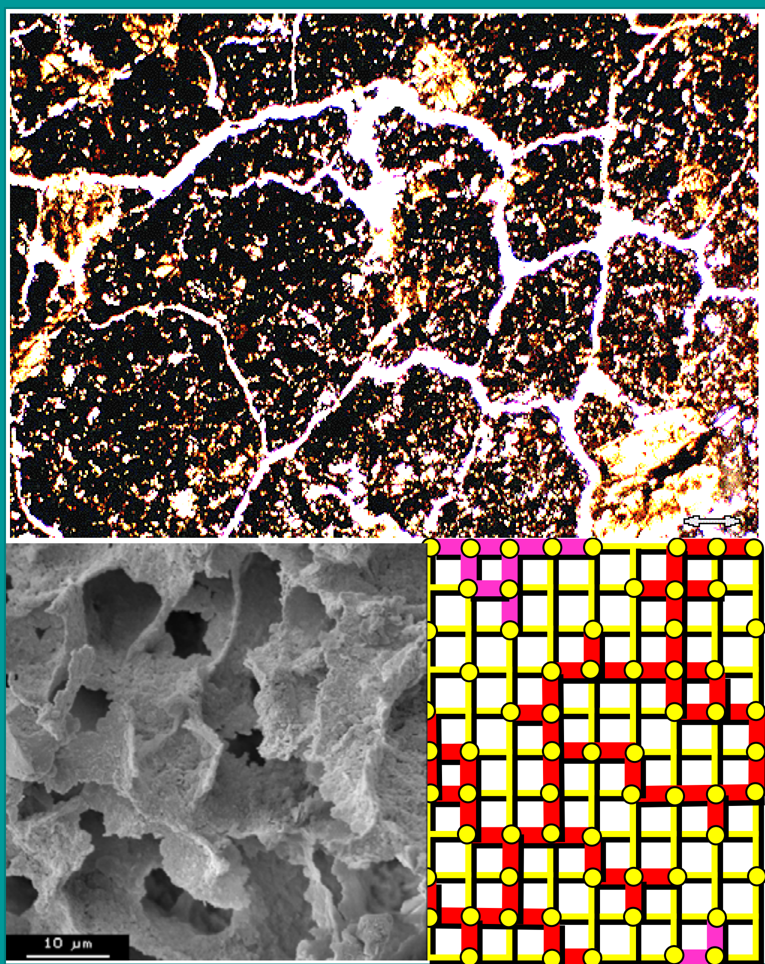
Diffusion-based approach (WRR, 2006)

$$\theta_d \frac{\partial c_i}{\partial t} + (1-\theta_d)\rho_s \frac{\partial s_i}{\partial t} = \sum_{k=1}^{N} \frac{\partial}{\partial x}\left(\theta_d D_{ik} \frac{\partial c_k}{\partial x}\right) + \theta_d r_i \qquad D_{ik} = \tau\left(D_i \delta_{ik} - \frac{Z_i Z_k D_i D_k c_i}{\sum_{k=1}^{N} Z_k^2 c_k D_k}\right)$$

c and *s*: aqueous and sorbed concentration in diffusion-zone, τ: apparent tortuosity; D_i: molecular diffusion coefficient of species *i*, θ_d: diffusion zone porosity.

- Link with surface complexation (SC), aqueous speciation, and dissolution/precipitation reactions
- More mechanistic and predictive?
- Requirements of molecular diffusion coefficients, apparent tortuosity factor, and diffusion zone porosity

Diffusion coefficient and apparent tortuosity



Diffusion coefficient:

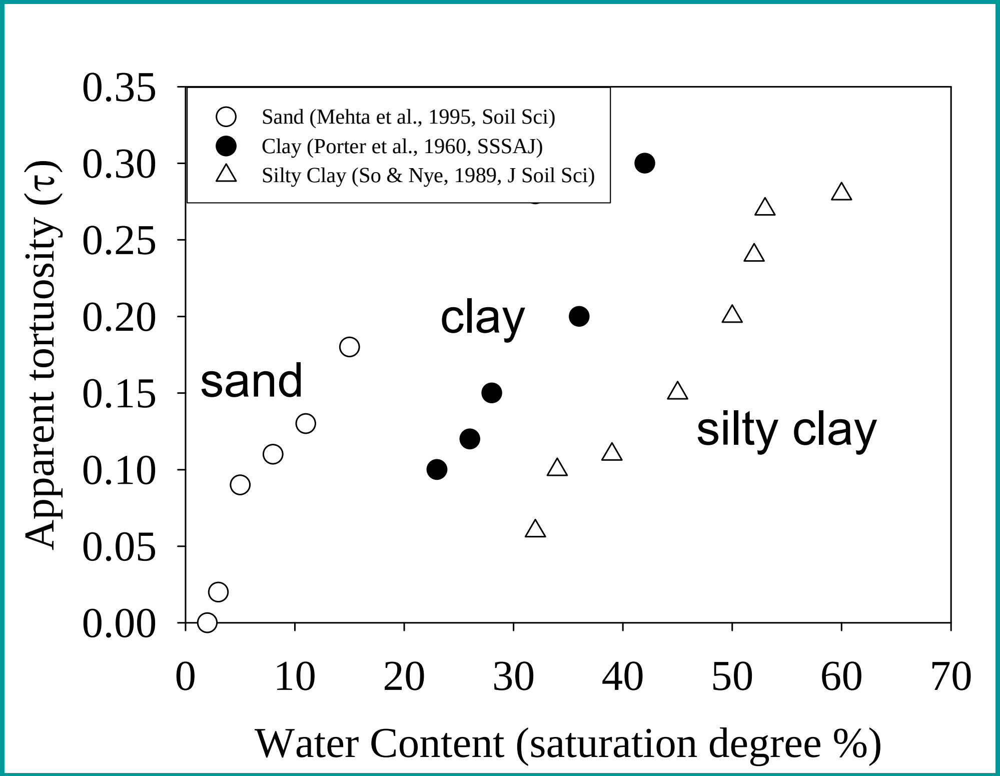
1) MD calculation for molecular diffusion coefficients.

2) Experiments?

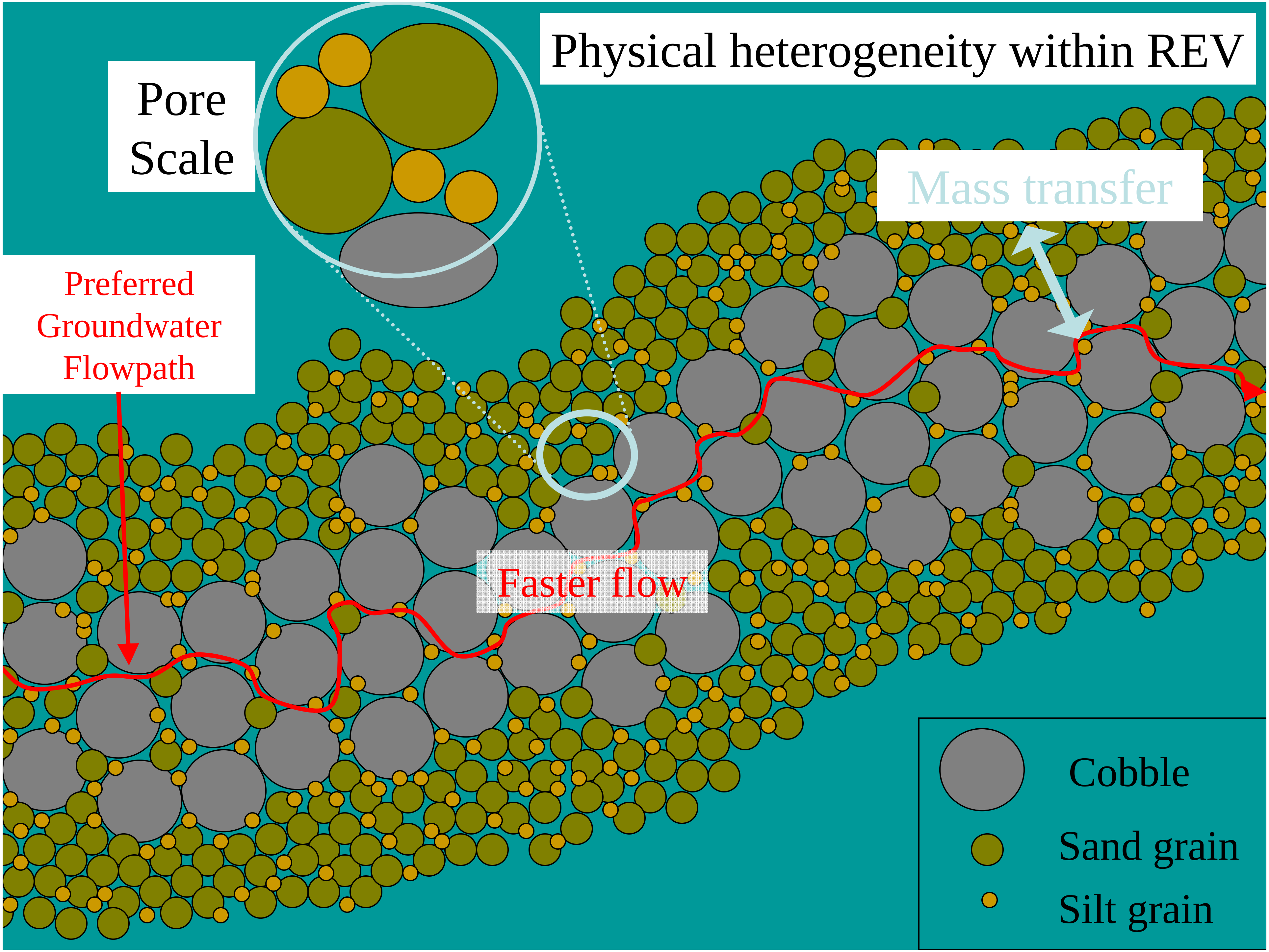
Apparent tortuosity:

1) Bulk-based tracer experiments (tritium), 2) direct intragrain pore connectivity measurements (NMR), 3) pore connectivity simulation, and others?

Effect of water content on mass transfer



Effects of water content on grain-scale mass transfer?

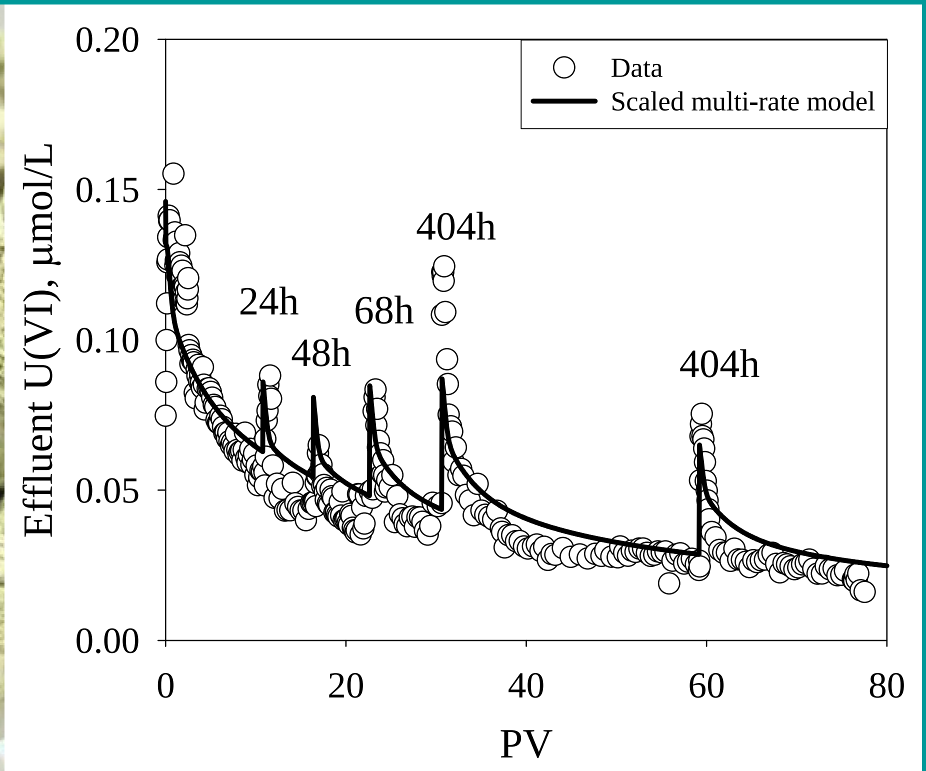

Physical heterogeneity within REV
Pore
Scale
Preferred
Groundwater
Flowpath
Mass transfer
Faster flow
Cobble
Sand grain
Silt grain

Proposed scaling approach

- Grain-scale mass transfer model for reactive, fine-grained materials
- Flow domain properties from tracer data of a large system: mobile/immobile porosity, mass transfer rate between flow domains
- Distribution of reactive, fine-grained materials in different flow domains within the REV based on their porosity ratio
- Volume-averaging of grain-scale mass transfer models in each flow domain
- Mass exchange between flow domains

Example of the scaling approach

NPP1-14 field-textured materials, SGW



Applicable under other geochemical conditions? other textured-sediments? field conditions?

Haggerty*: Series of 3 bench-scale experiments

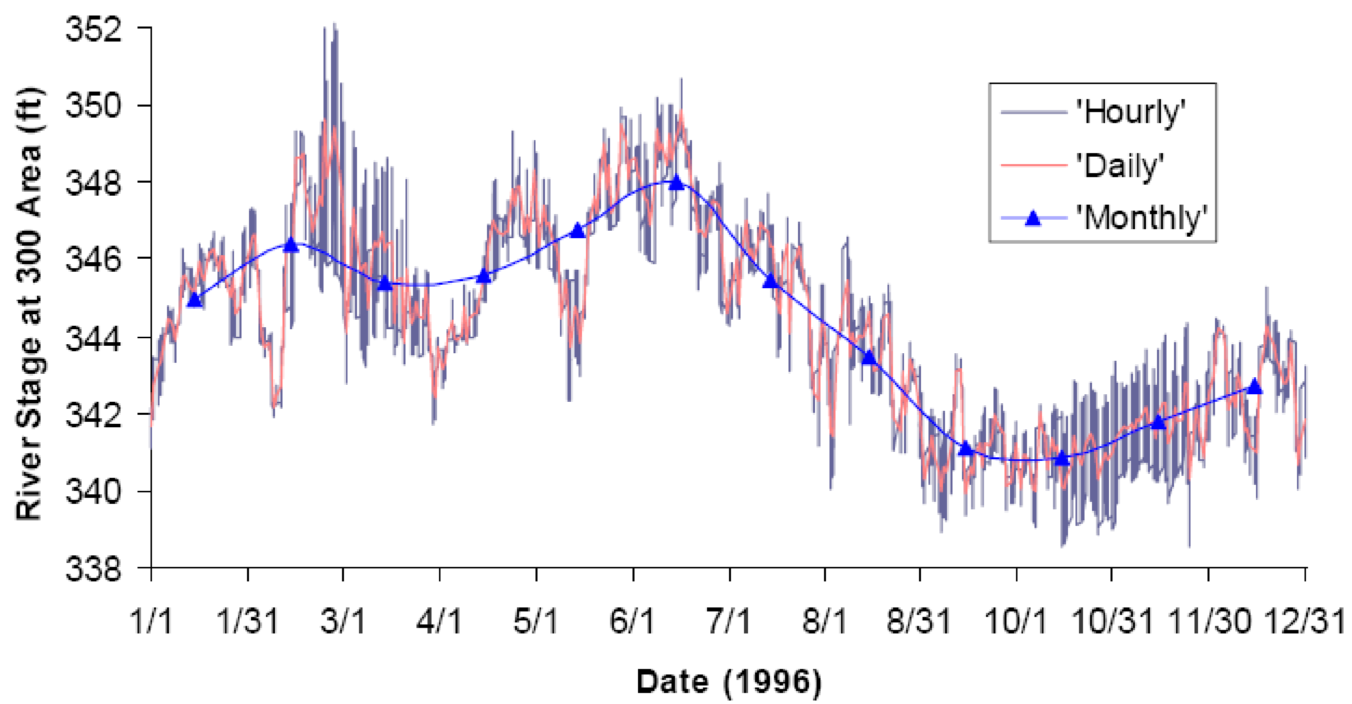
What are essential *intermediate-scale* processes

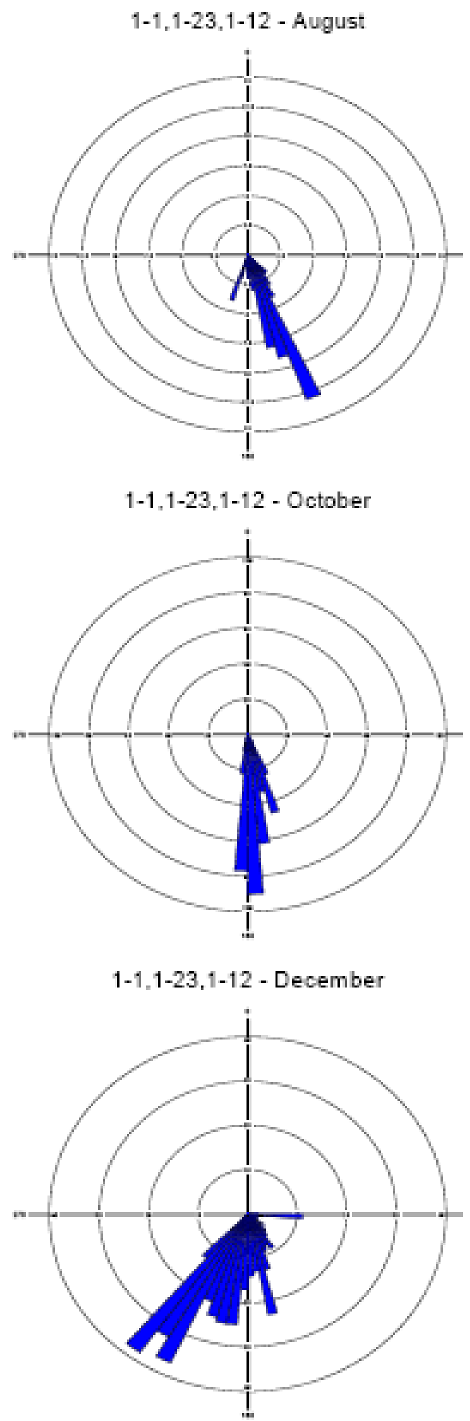
- *time-varying velocity*
- *vadose zone mass transfer*
- *intermediate-scale mass transfer (sm vs med length-scales)*

that must be included along with *chemistry* in reaction & multiscale mass transfer model?

* with assistance from J Istok lab

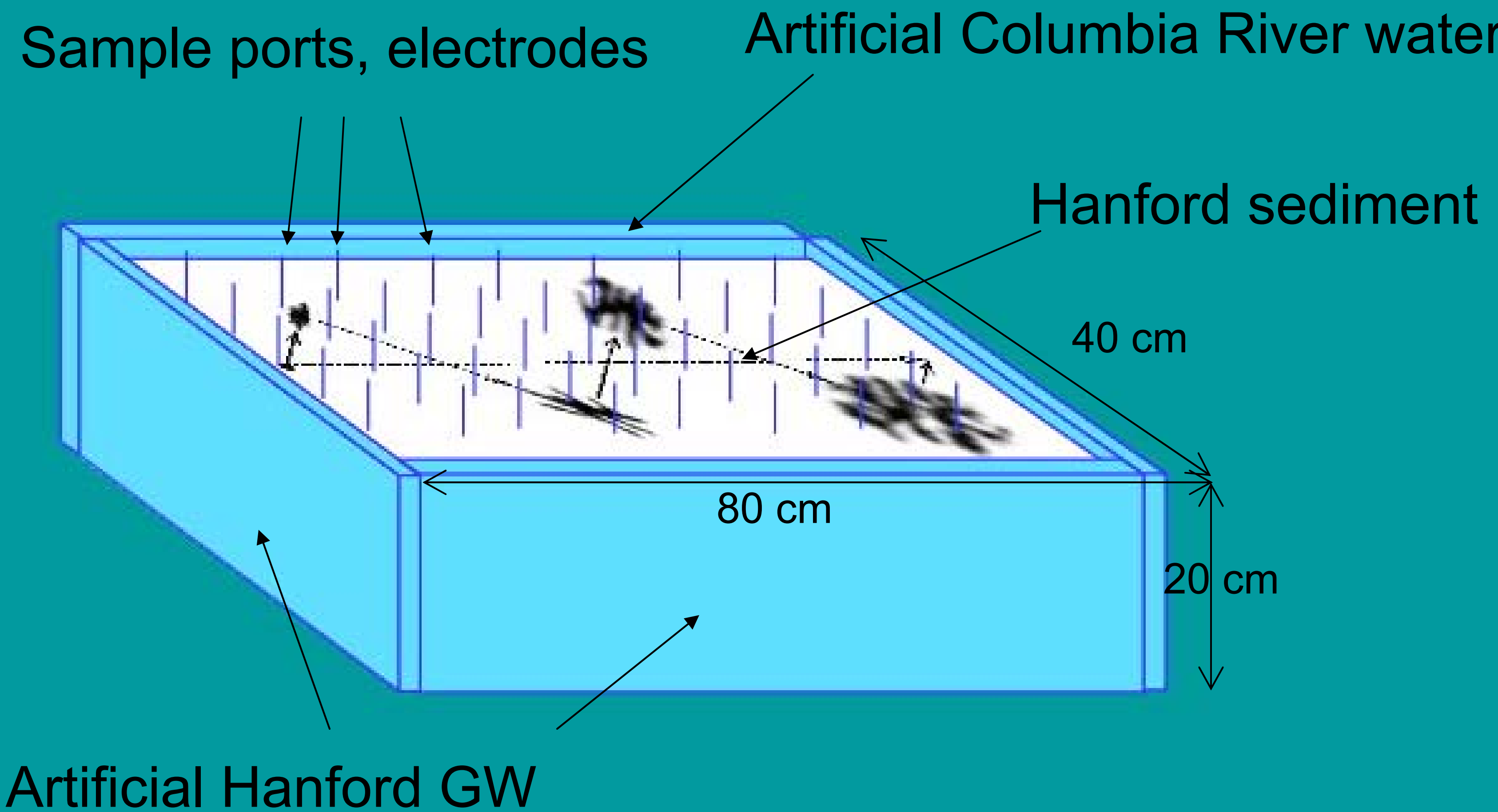
Changes in gradient & water table





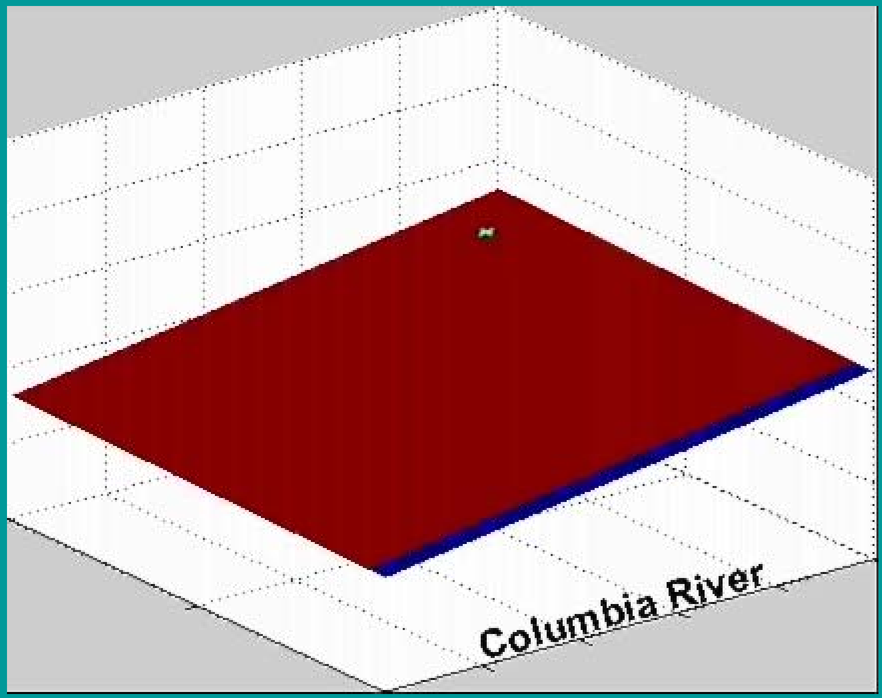
Zachara presentation, Nov. 2007

Sand box experiments



Sand box experiments

Artificial Hanford GW – high $CaCO_3$

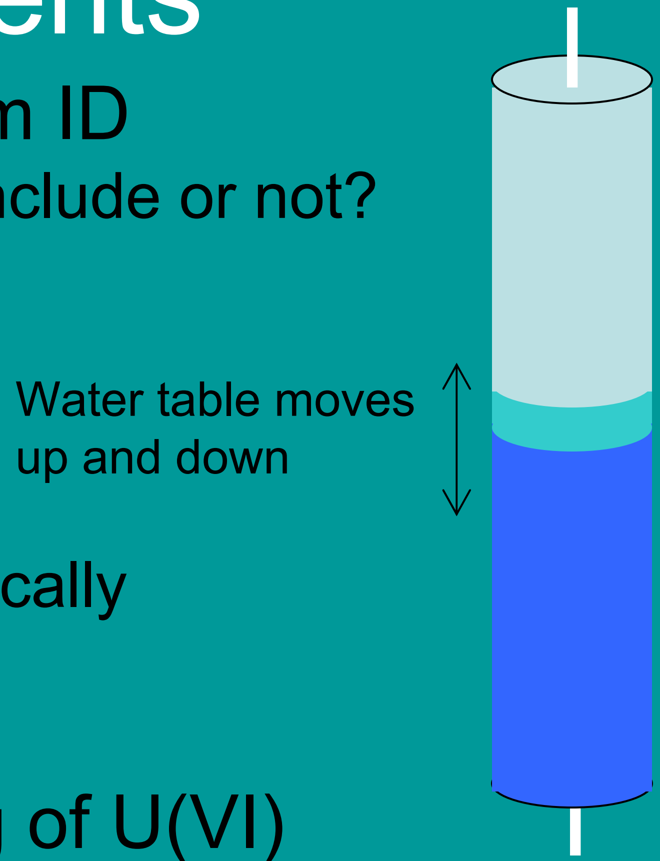


Artificial Columbia River – low CaCO3

- Time-varying boundaries
  - Hanford sediment
  - artificial CR &
  - Hanford waters
- U(VI) injection at SPP conc.
- Do we see the essential features of 300 Area?

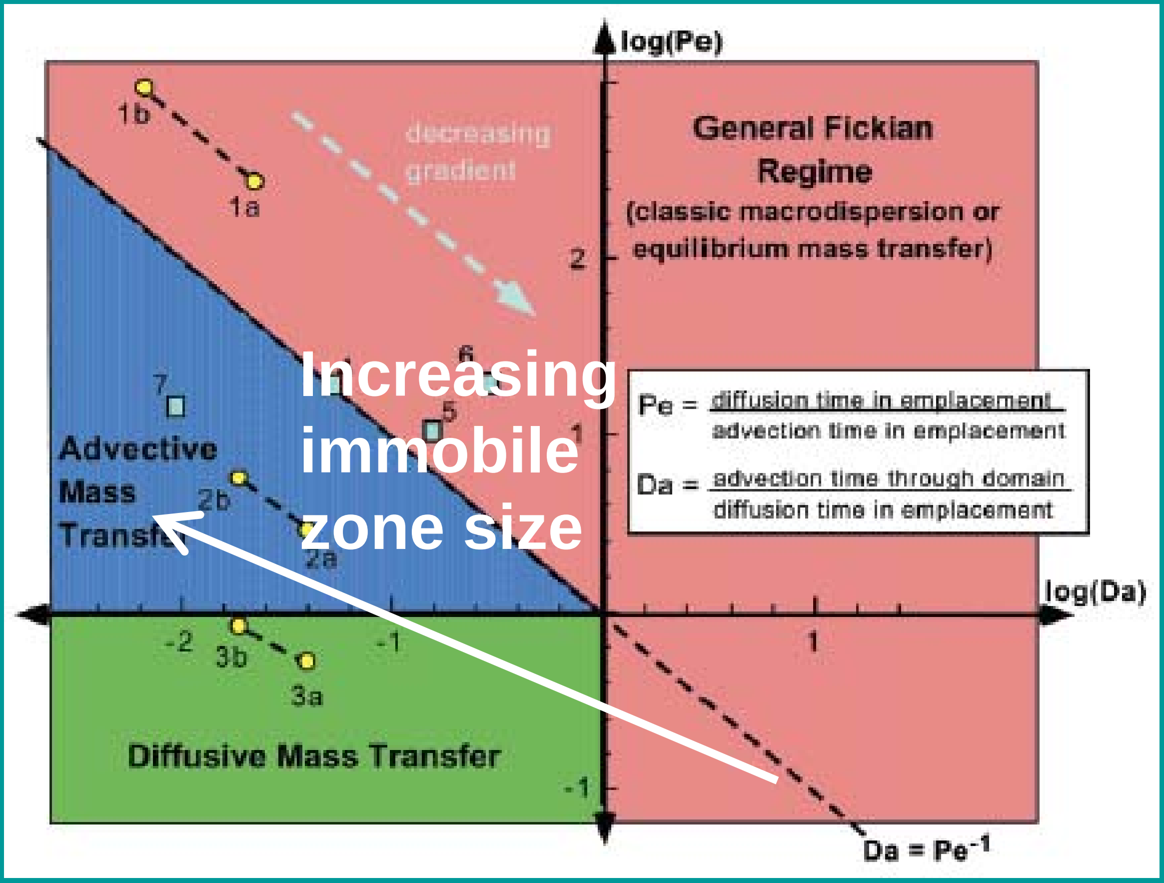
Fluctuating water table experiments

- column 50? cm long, 10? cm ID
  - question re: >2 mm fraction include or not? Capillarity scaling issue.
- water flows from top or bottom
- instruments:
  - sample ports every 5 cm vertically
  - water content
  - electrical conductivity
- measure long-term leaching of U(VI)
- post-mortem analysis of U(VI) spatial distribution (budget-dependent)



Mass Transfer Scale & Process

- motivation:
  - movie 1
  - movie 2
  - movie 3



Zinn et al., 2004
DOE grant DE-FG02-ooER15030

Intermediate-scale, long-term desorption/dissolution exps

- 2 saturated columns <2mm size and same grain size distribution
  - 1 homogenized
  - 1 heterogeneous
    - zones with larger sizes
    - embedded zones with smaller sizes
- measure long-term leaching of U(VI)
- post-mortem analysis of U(VI) spatial distribution (budget-dependent)
- ?post-mortem flow-path analysis with water-soluble epoxy or fluorescent microspheres?