Significance of Microporosity to Reactive Transport Modeling at DOE Sites

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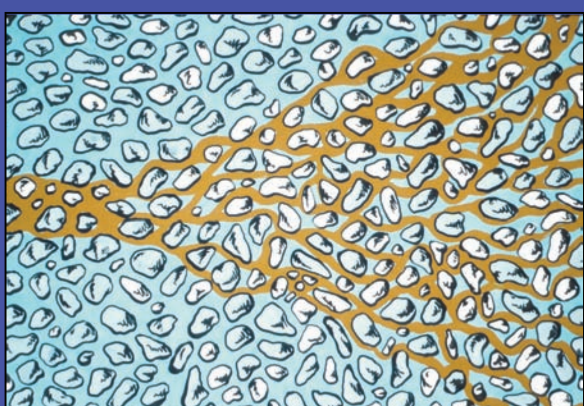
Uranium-Contaminated DOE Sites

Naturita UMTRA

Hanford 300 Area

Rifle UMTRA

Reactive Transport Modeling



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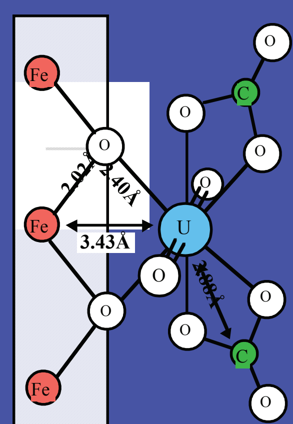

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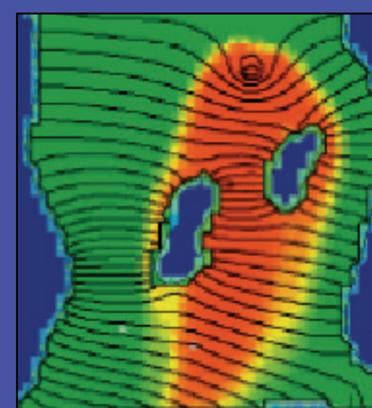
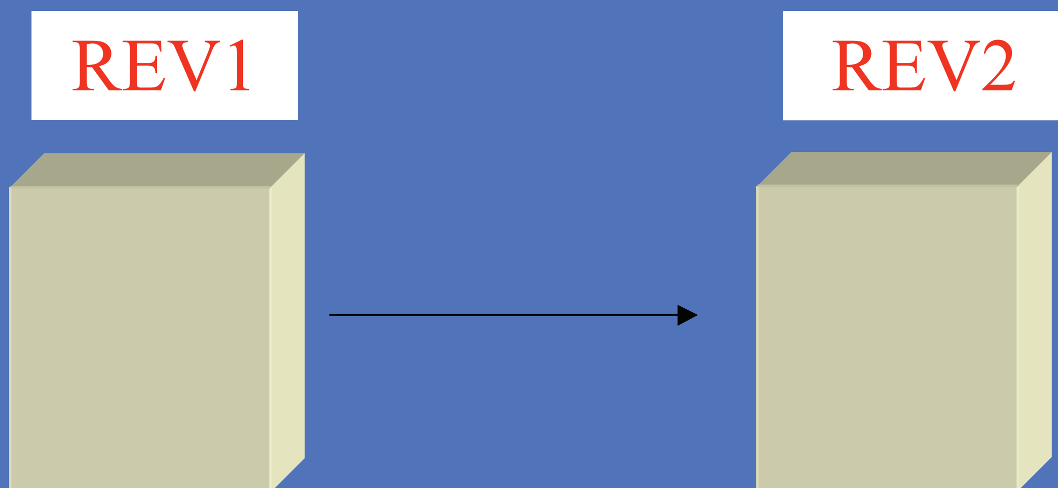
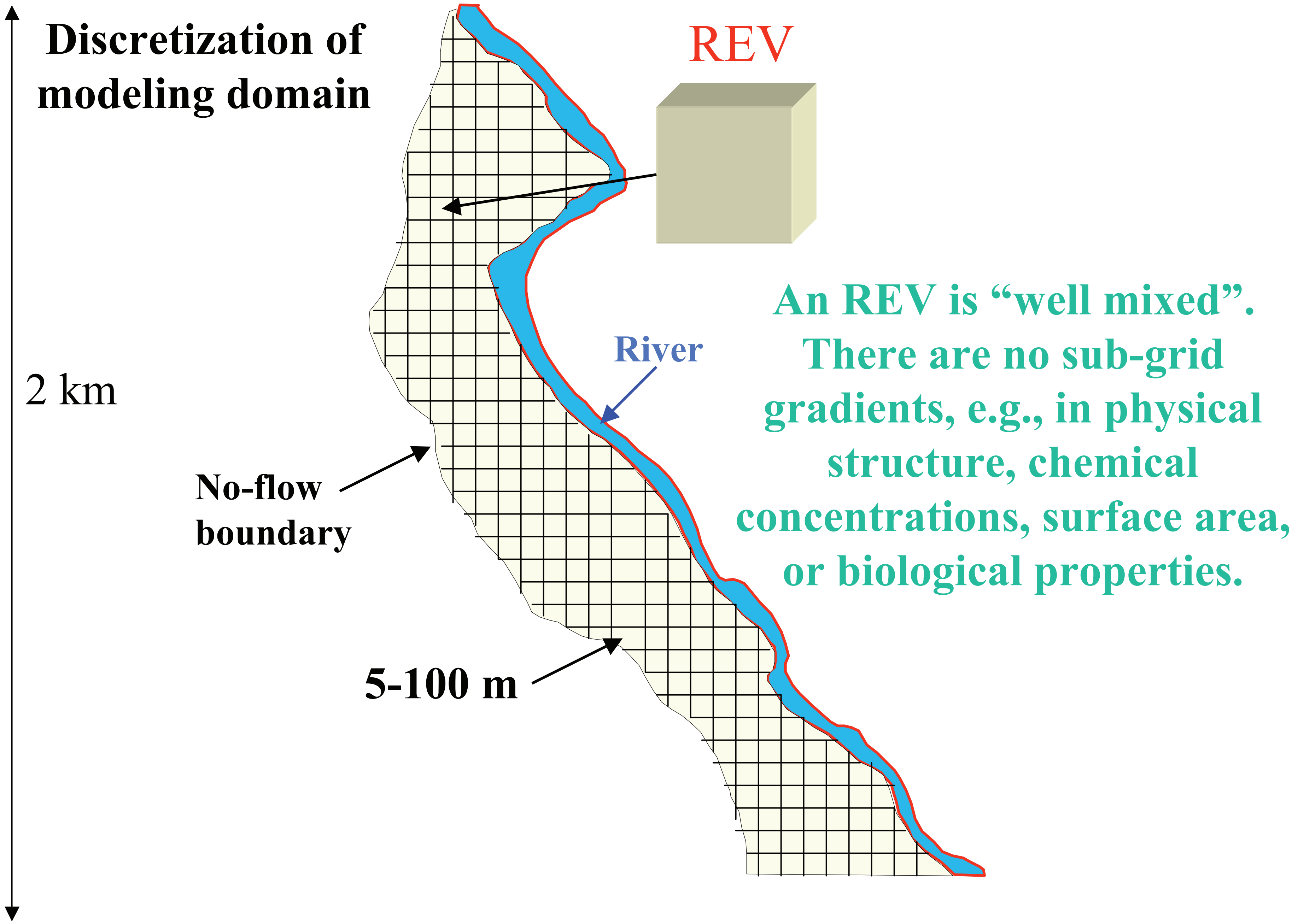


Reactive Transport Modeling: Continuum Models

Reactive transport models are commonly based on the *continuum* representation of porous media, in which the physical, chemical, and biological variables describing the system vary continuously in space.

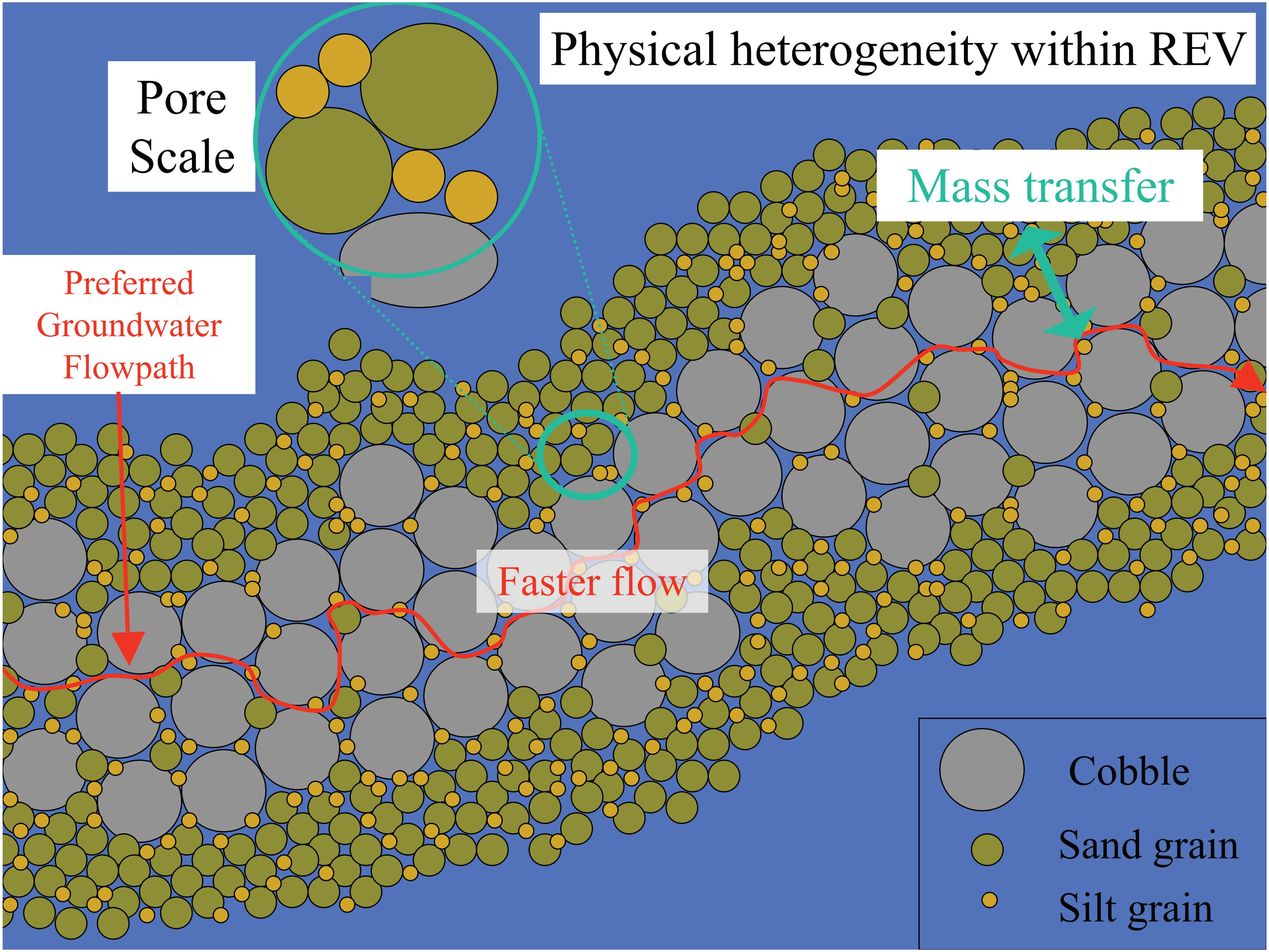


An REV has average values of physical, chemical, and microbiological variables


Discretization of modeling domain
2 km
No-flow boundary
5-100 m
REV
River
An REV is "well mixed". There are no sub-grid gradients, e.g., in physical structure, chemical concentrations, surface area, or biological properties.

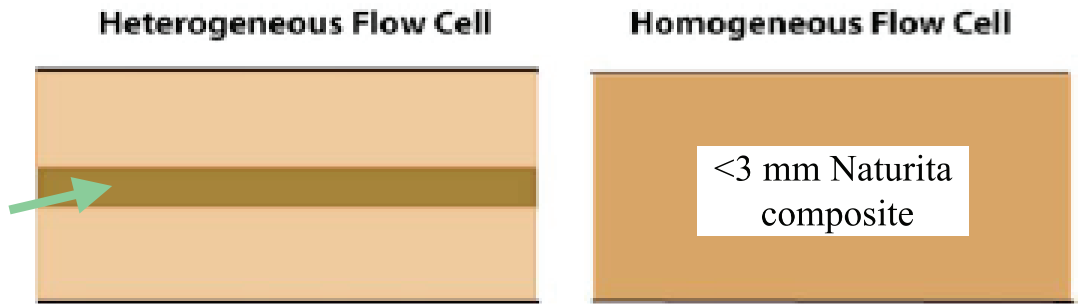
Naturita UMTRA site: Alluvial Aquifer Sediment Texture

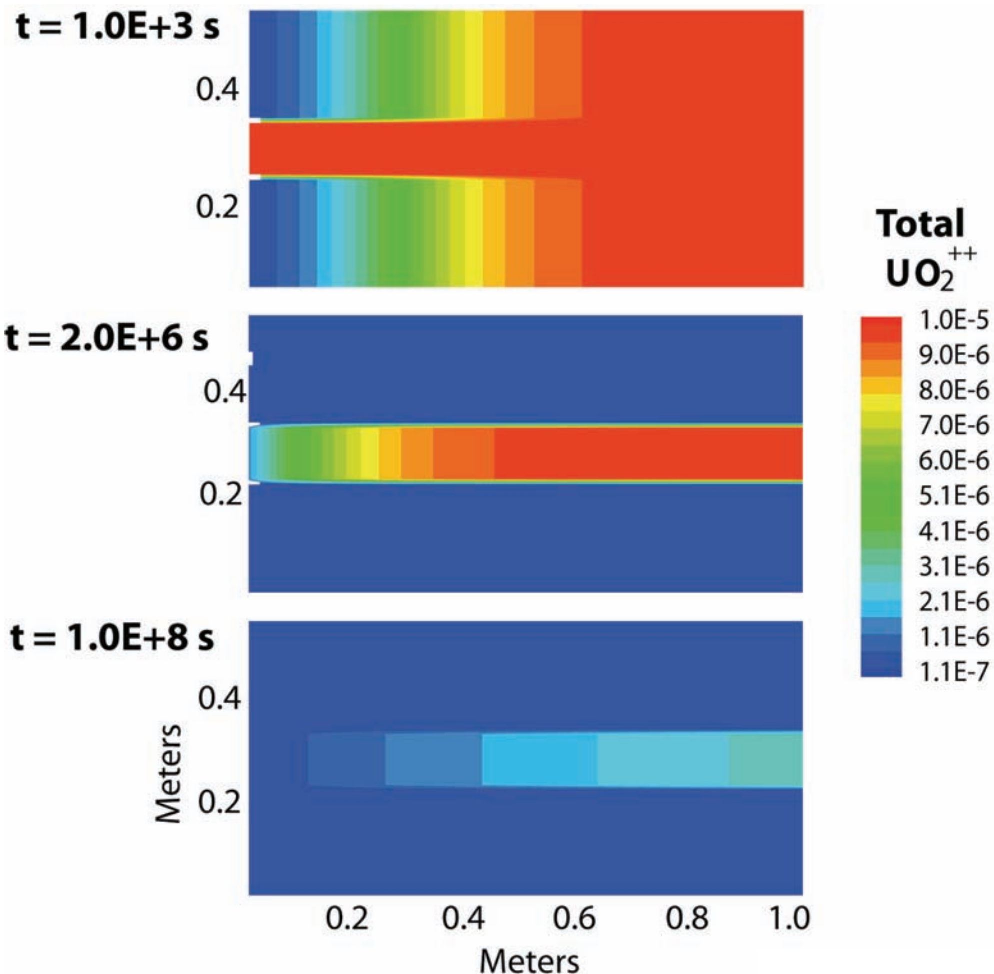
50% cobbles, >6.4 cm;
15% <3mm,
~85% of U(VI) sorption

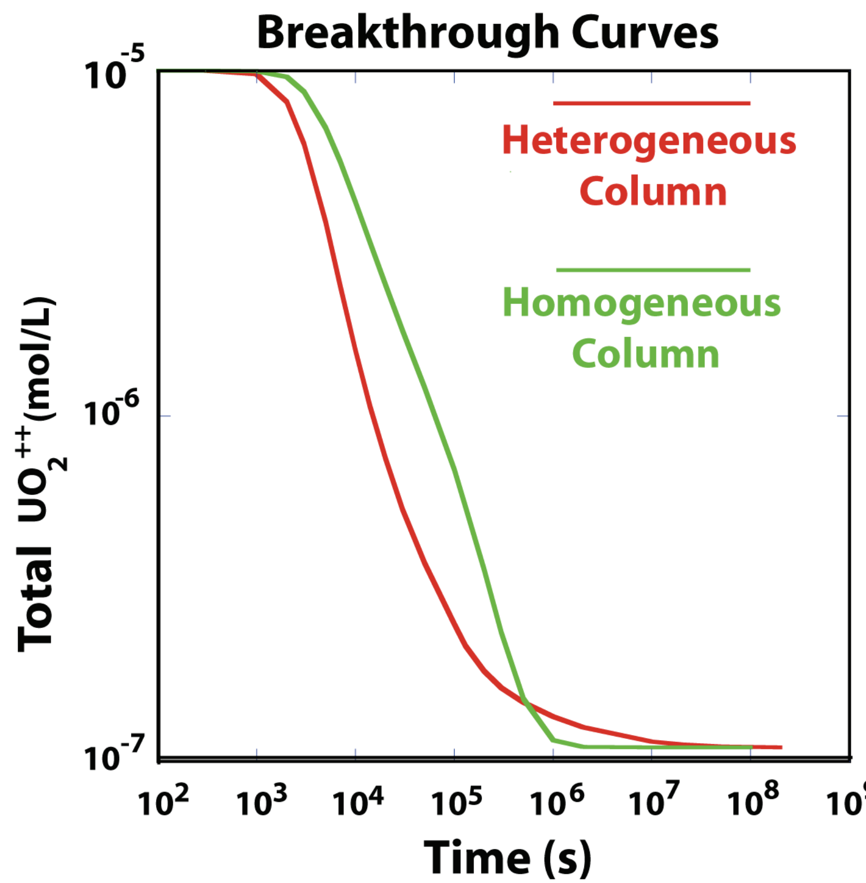

Physical heterogeneity within REV
Pore Scale
Preferred Groundwater Flowpath
Mass transfer
Faster flow
Cobble
Sand grain
Silt grain

Effect of Subgrid Physical Heterogeneity with Local Chemical Equilibrium

Layer of fine-grained sediment



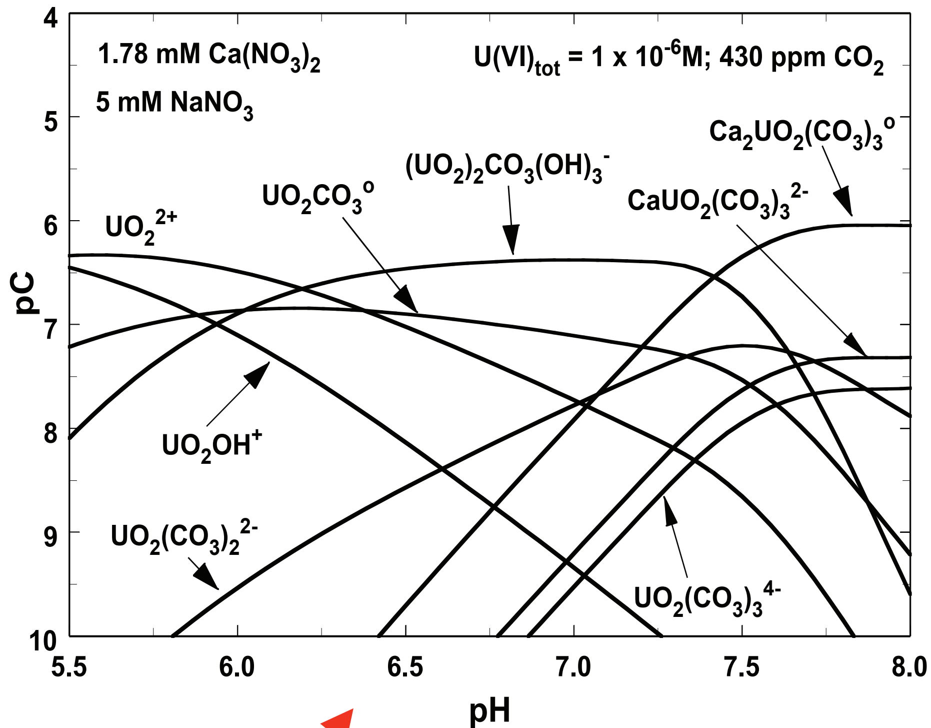




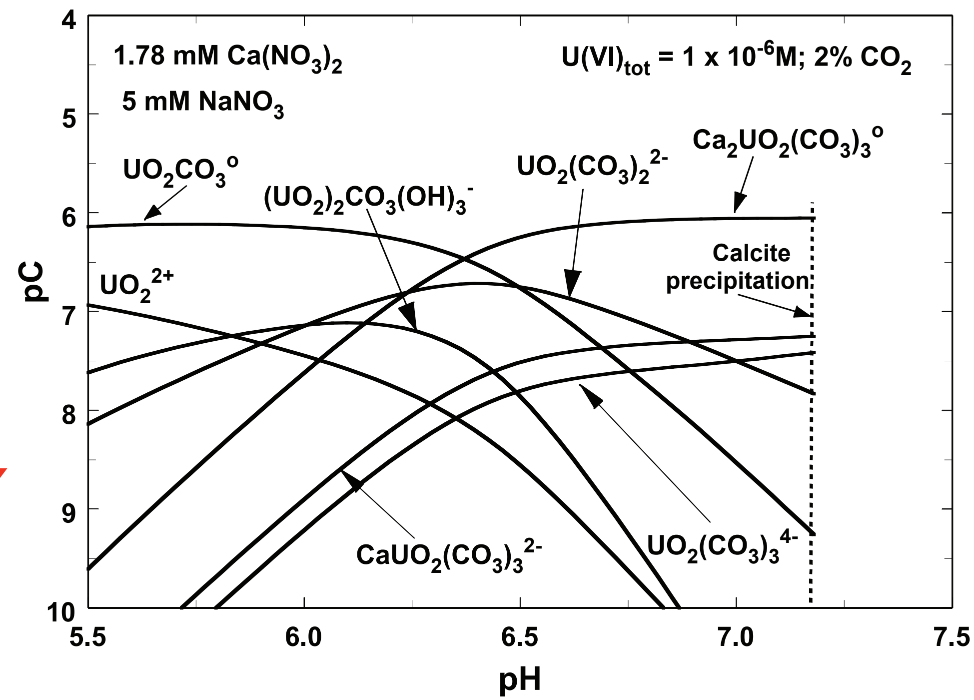
RTM simulations by L. Li and C. Steefel

Importance of $Ca_2UO_2(CO_3)_3^0$ aqueous species at all 3 DOE sites

Naturita; Rifle: pH 7
Hanford: pH 7.5-8

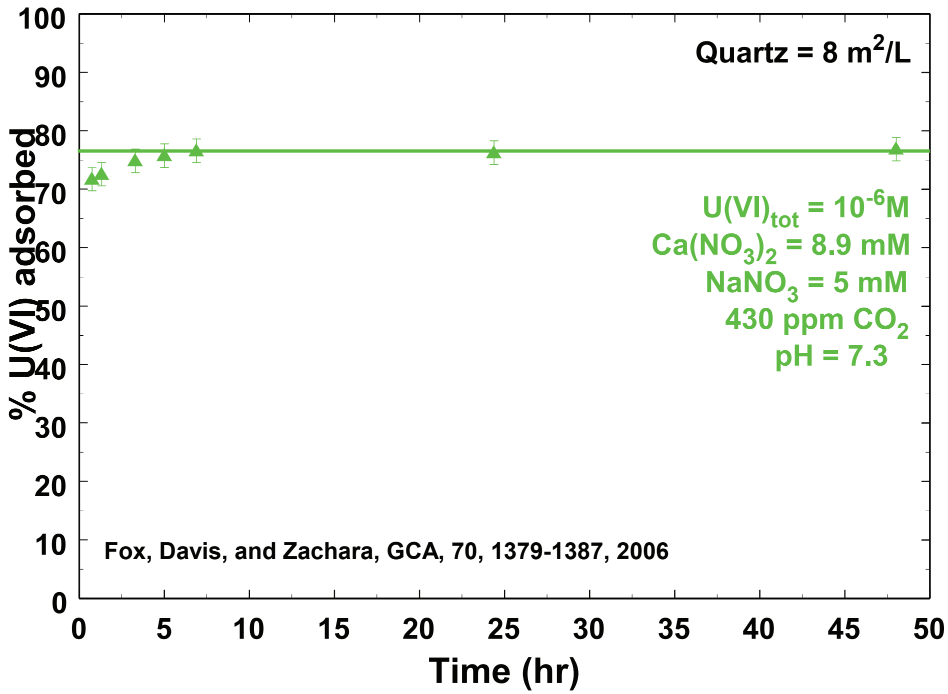


At equilibrium with 430 ppm CO_2



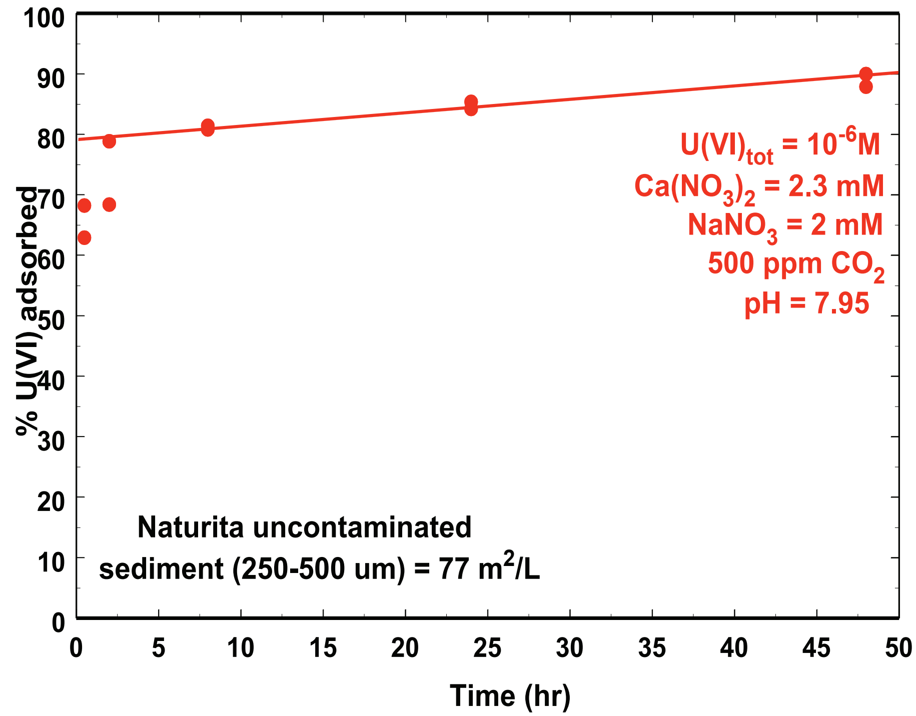
At 2% pCO_2 typical of groundwater conditions at all 3 sites

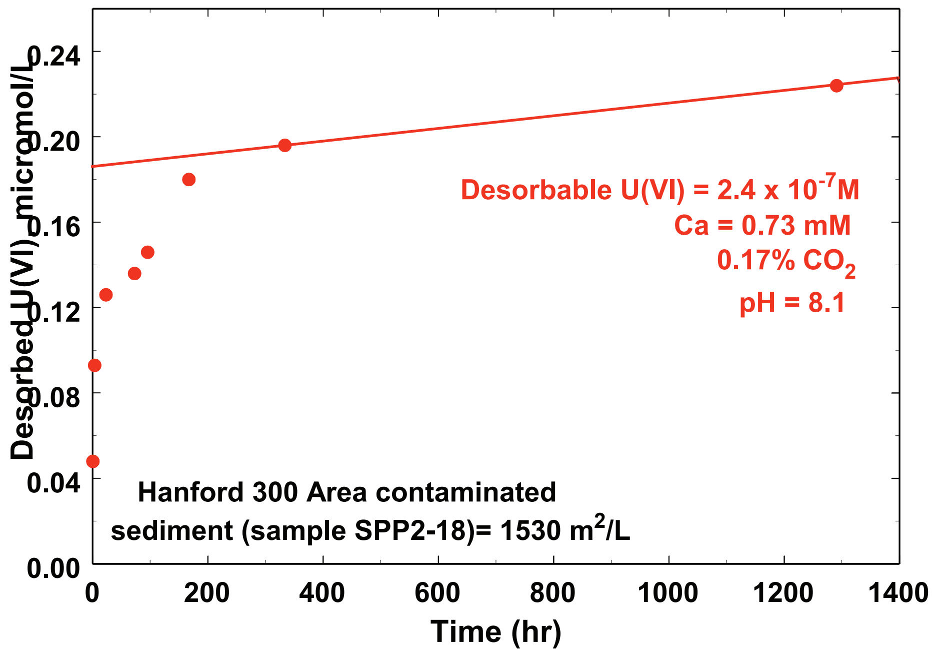
Fox, Davis, and Zachara, 2006, GCA



Adsorption/desorption of U(VI) reaches equilibrium quickly in well-stirred batch reactors with non-porous single mineral phase with $Ca_2UO_2(CO_3)_3{}^0$ as the predominant aqueous species

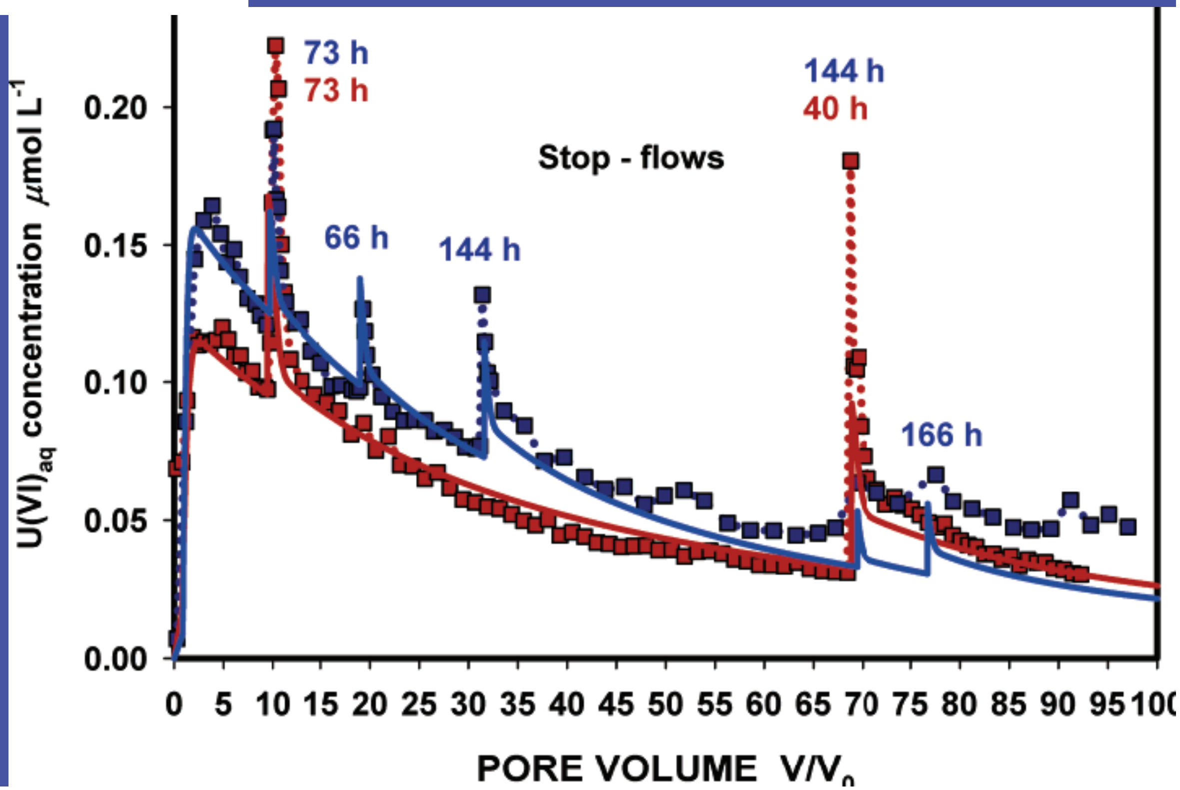
Adsorption/desorption of U(VI) approaches equilibrium slowly in well-stirred batch reactors with aquifer sediments from all 3 DOE sites with $Ca_2UO_2(CO_3)_3{}^0$ as the predominant aqueous species, taking weeks to months to reach a steady-state U(VI) concentration (Example: Naturita *adsorption*)





Desorption of U(VI) approaches equilibrium very slowly in well-stirred batch reactors with Hanford aquifer sediments (sample SPP2-18) (Bond, Davis, and Zachara, 2008)

Flow interruption in column experiments with sample SPP2-18 show that the rate of U(VI) desorption is rate-limited (Qafoku et al, ES&T, 2005)



Nanoporosity and surface areas of Hanford sample NPP1-16 (<2 mm)

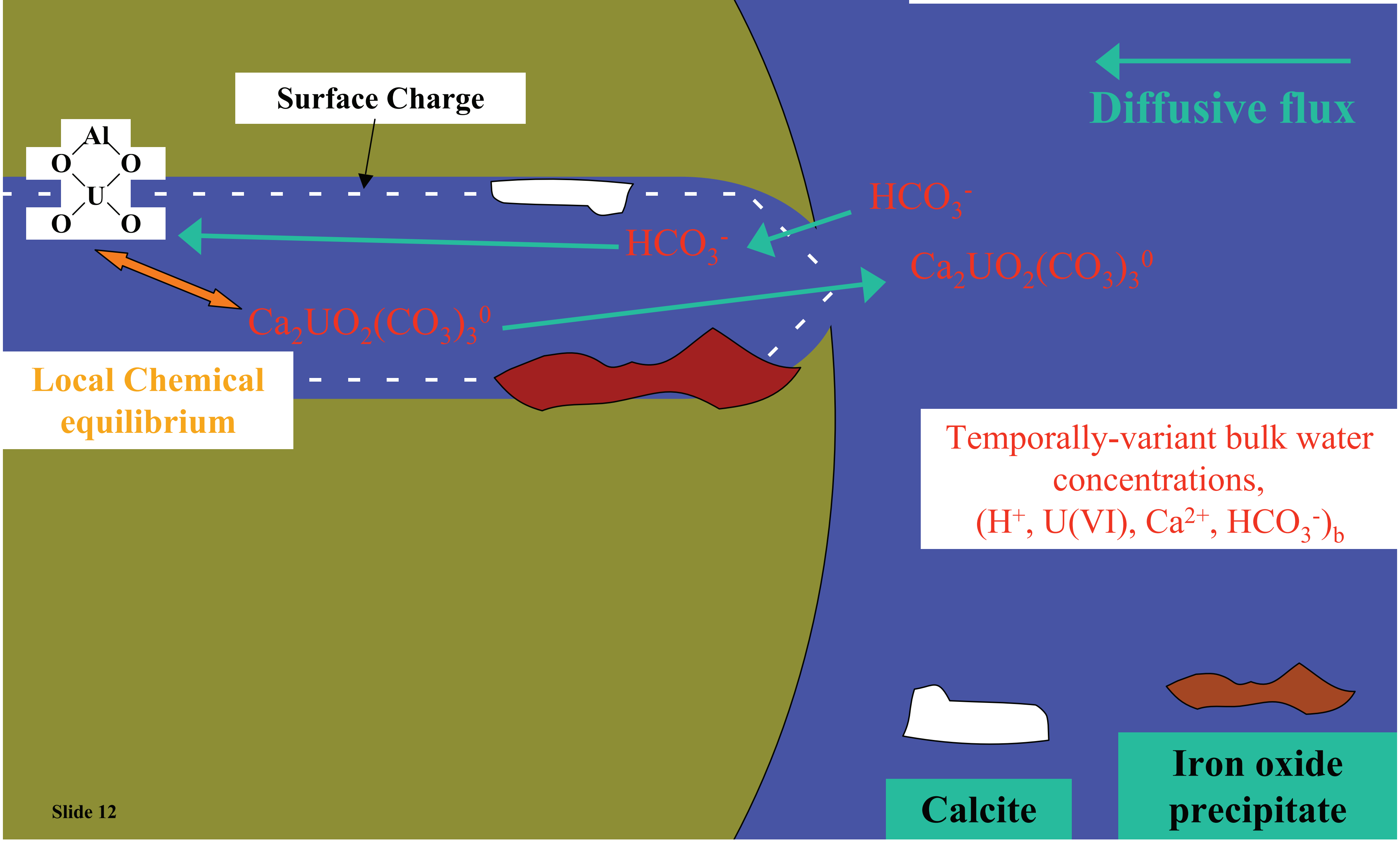
Hg porosimetry:

Porosity (pore size <300 nm): 12.6%
Surface area in pores <300 nm = 12.5 m^2/g

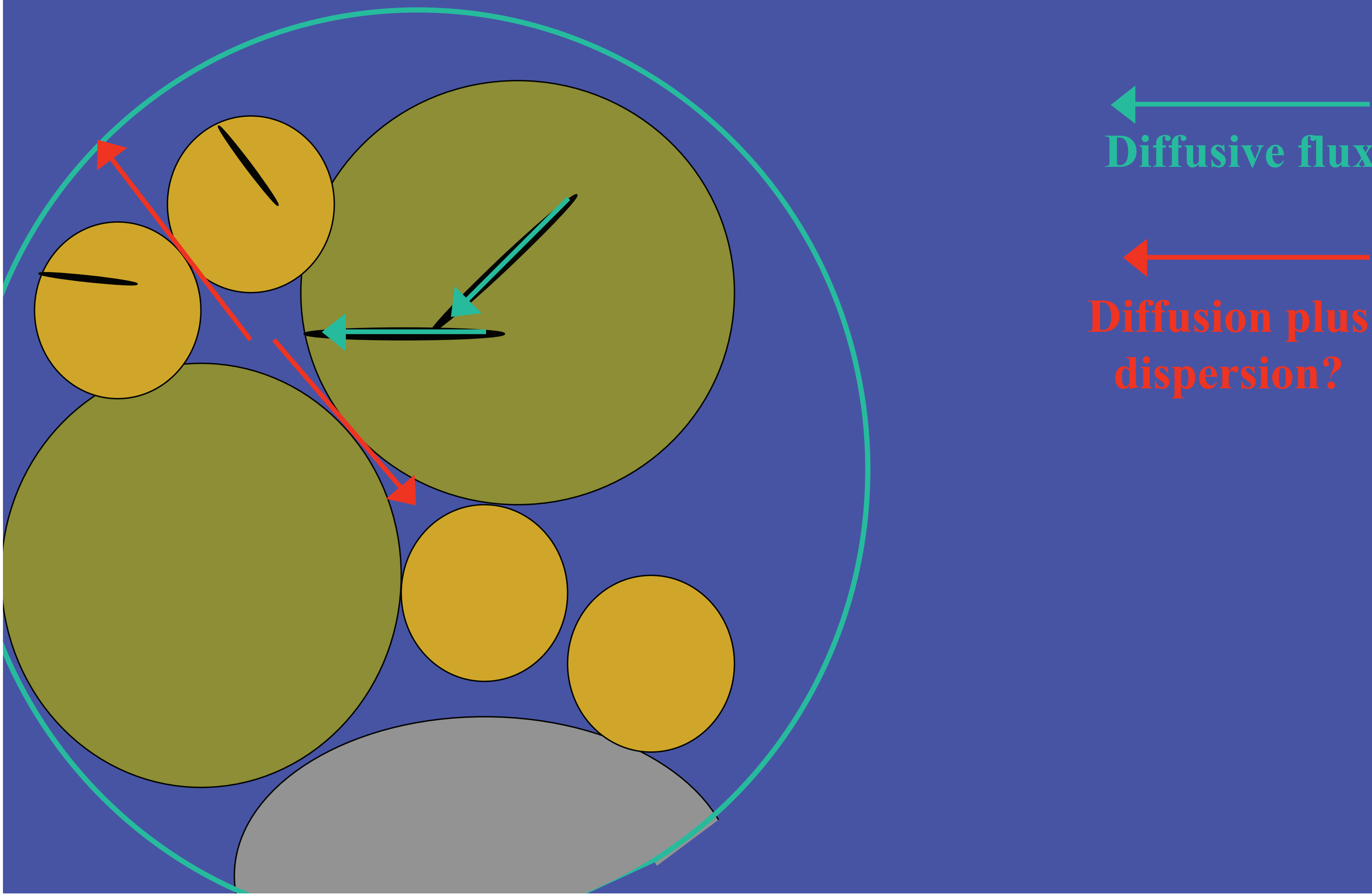
N_2 gas adsorption/desorption (BET):

Porosity (pore size <300 nm): 10.9%
Surface area in pores <300 nm = 29.9 m^2/g
Total surface area of sample = 30.7 m^2/g

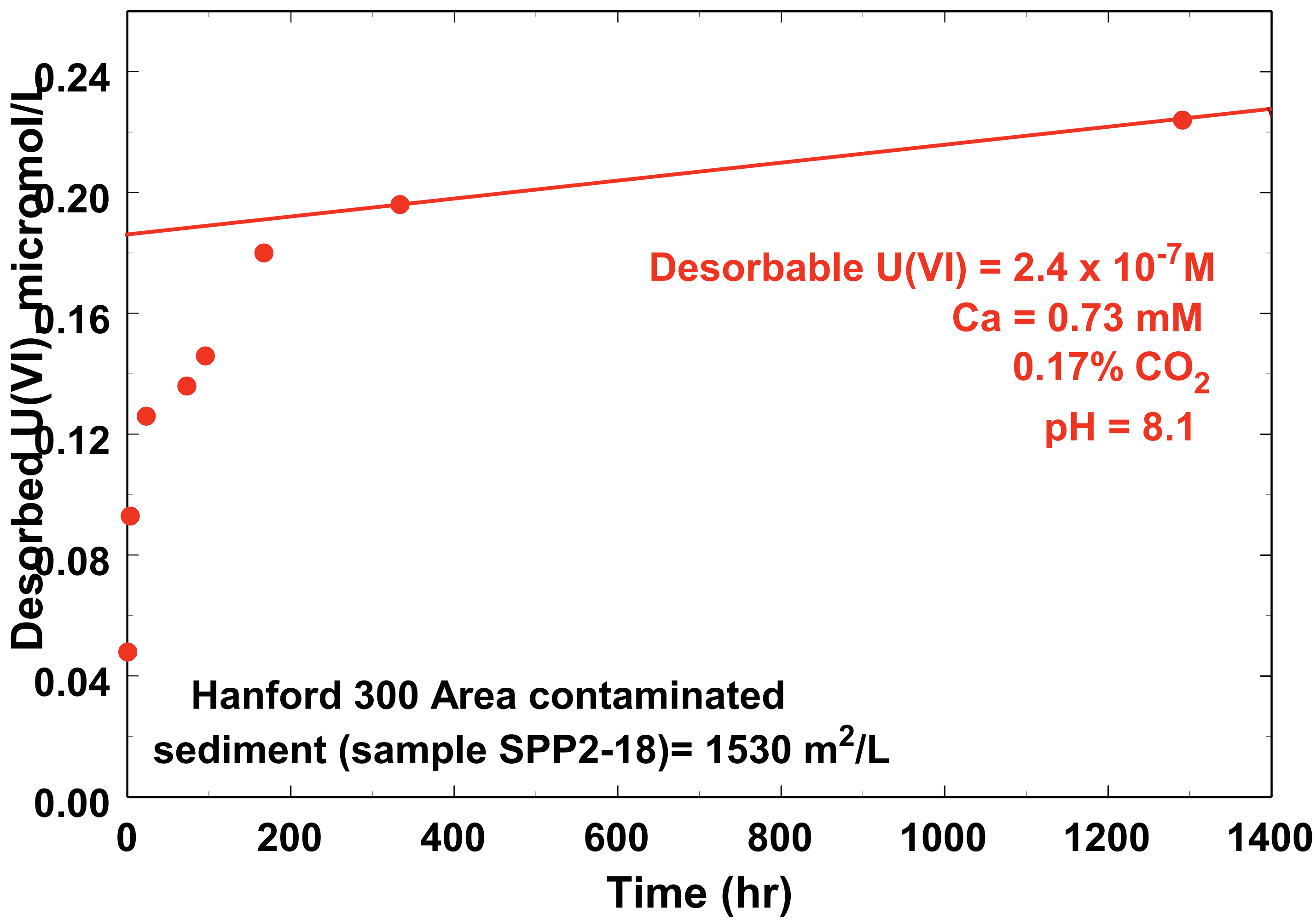
Magnified Particle Scale Showing Intraparticle Pore



Column Experiment: Pore Scale



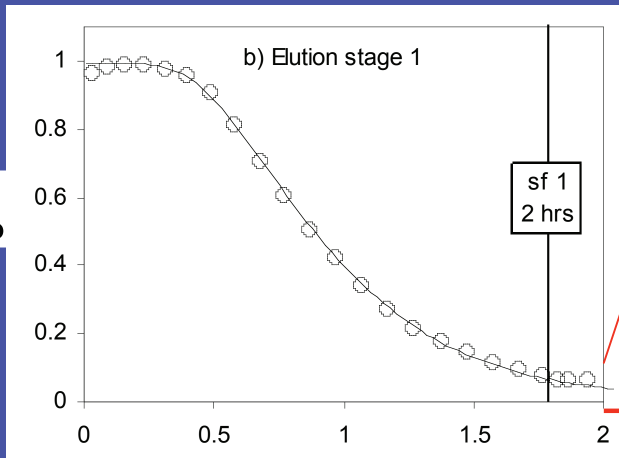
Approximately 50% of U(VI) desorbs from intragranular porosity??

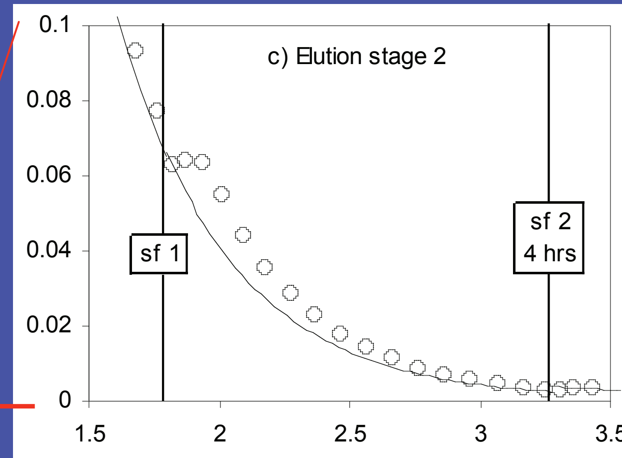


Bond, Davis, and Zachara, 2008, Adsorption in Geomedia II

Advection, dispersion, and diffusion of tritium out of a column packed with Hanford sample NPP2-4

C/C$_o$

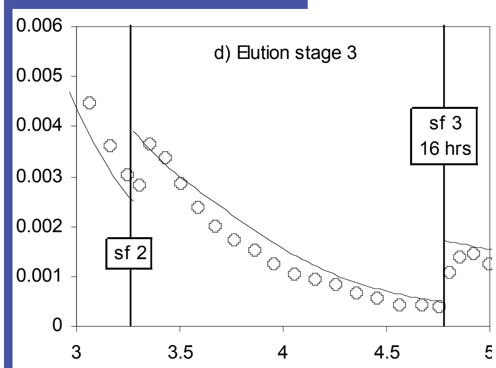


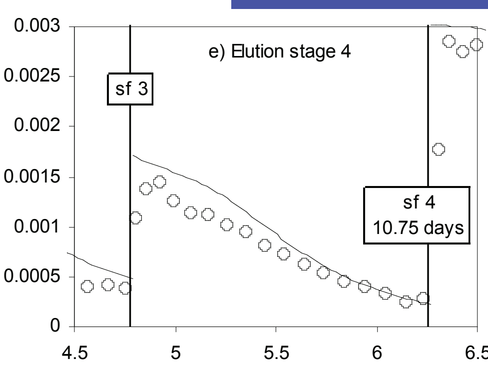


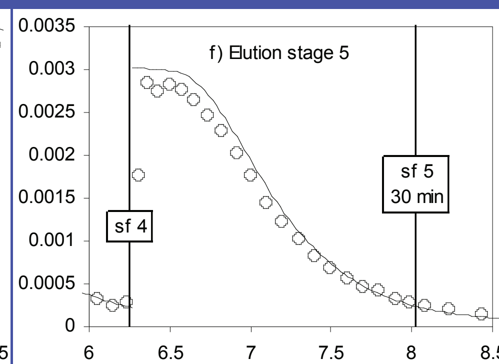
Pore volumes

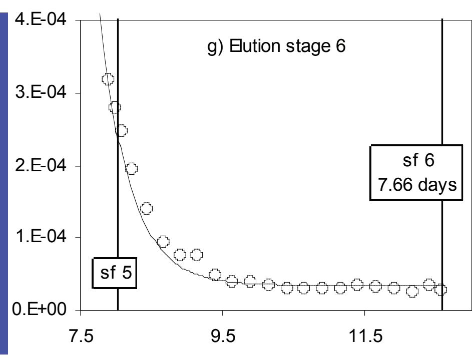
Procedure: Pack sample in column; let sit for 4 months in water with high HTO

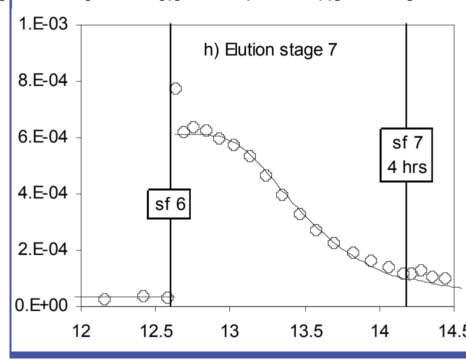
Solid curve shows model with HTO diffusion from two immobile zones with a total intragranular porosity of 1.05%

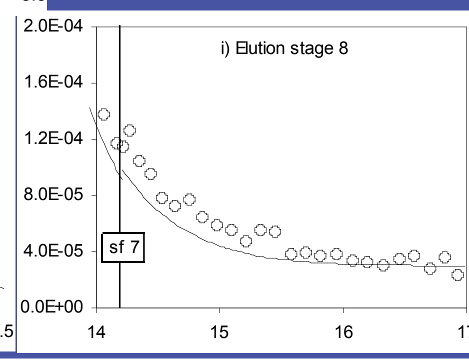




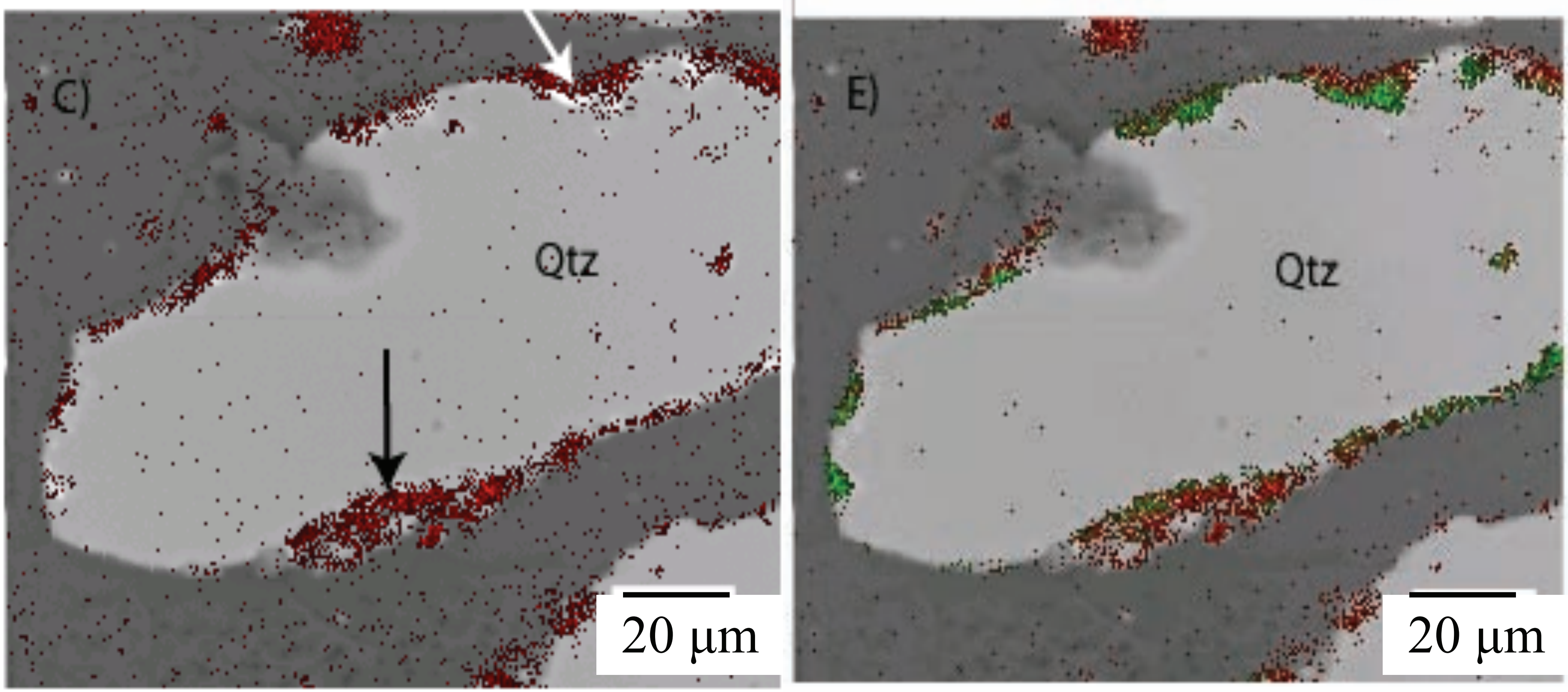








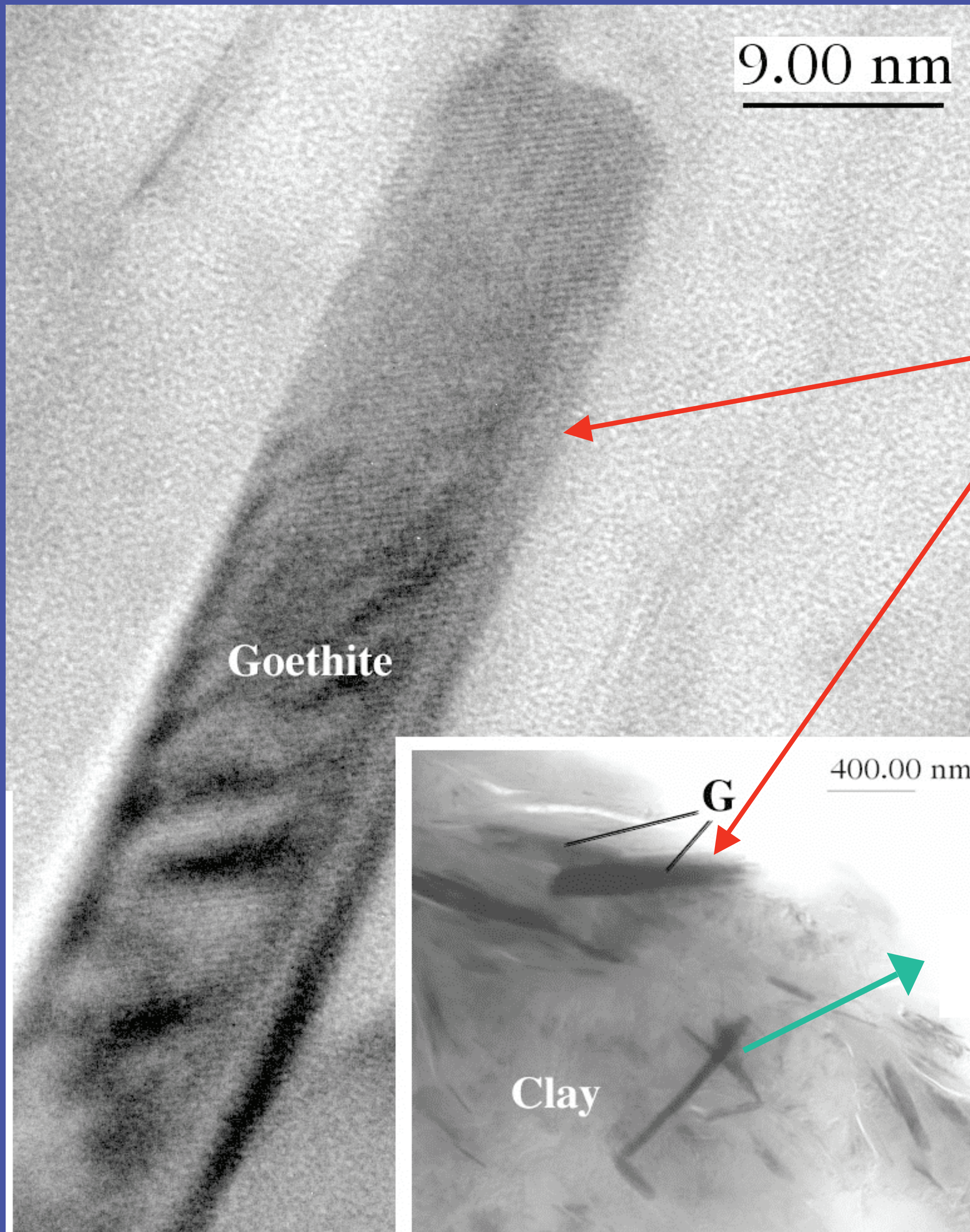
Grain coatings: Another type of microporosity?



Relative abundances of Al and Fe in grain coatings (µm thickness)

Naturita sediment quartz grain coatings

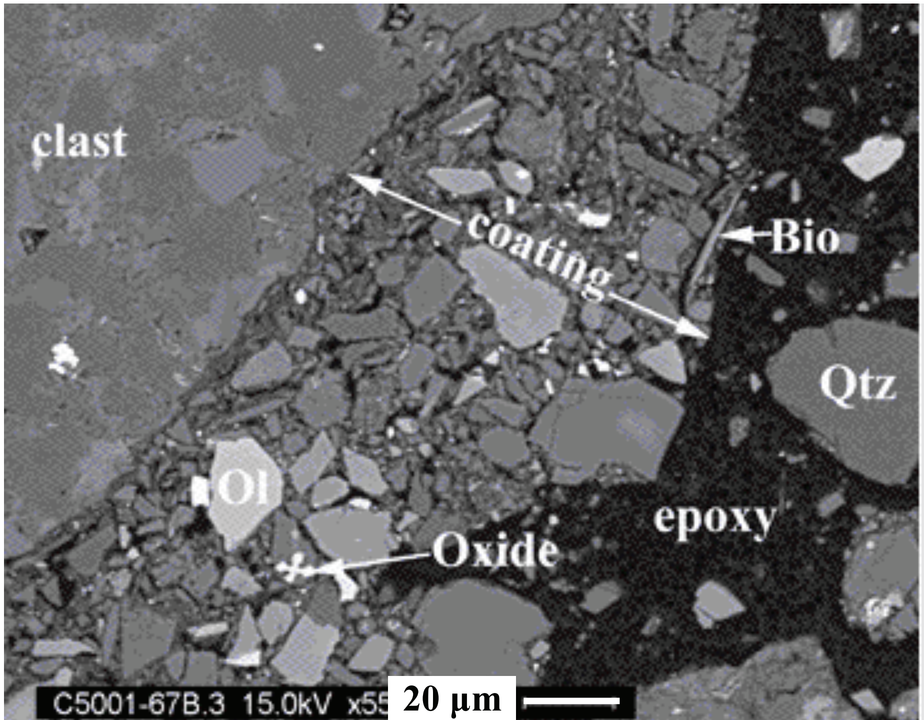
Naturita sediment grain coatings

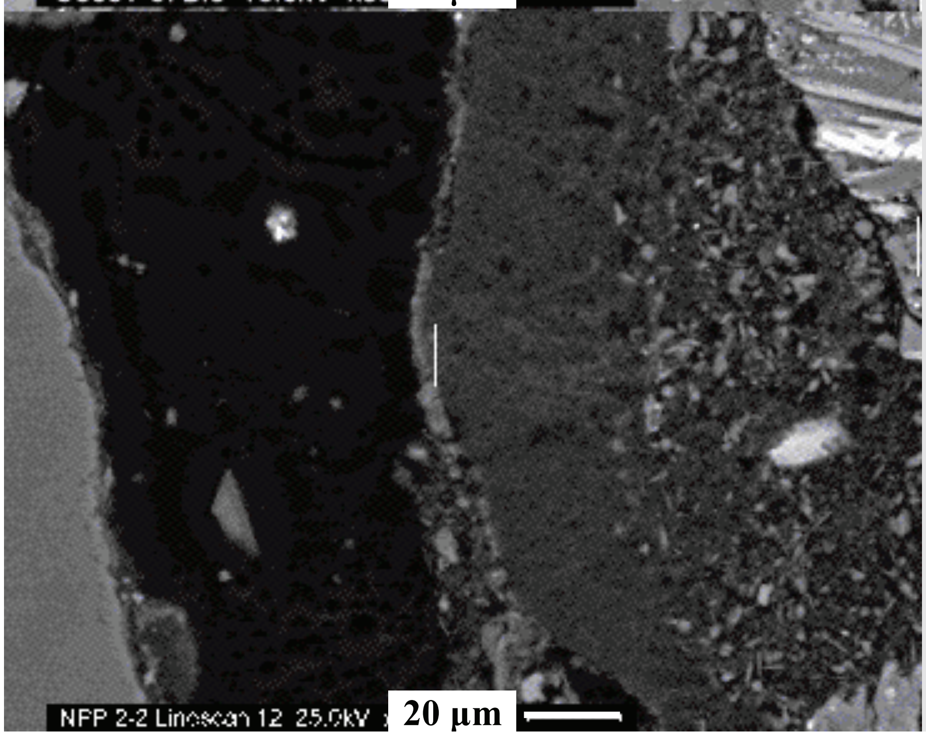


Bright-field TEM images showing needle-like goethite (G) crystals immersed in illite/smectite clay matrix.

U(VI) diffusive flux

Davis et al., GCA, 68, 3621 (2004)





Hanford uncontaminated vadose zone sample: C5001-67B

Coating consists of micron-sized mineral fragments.

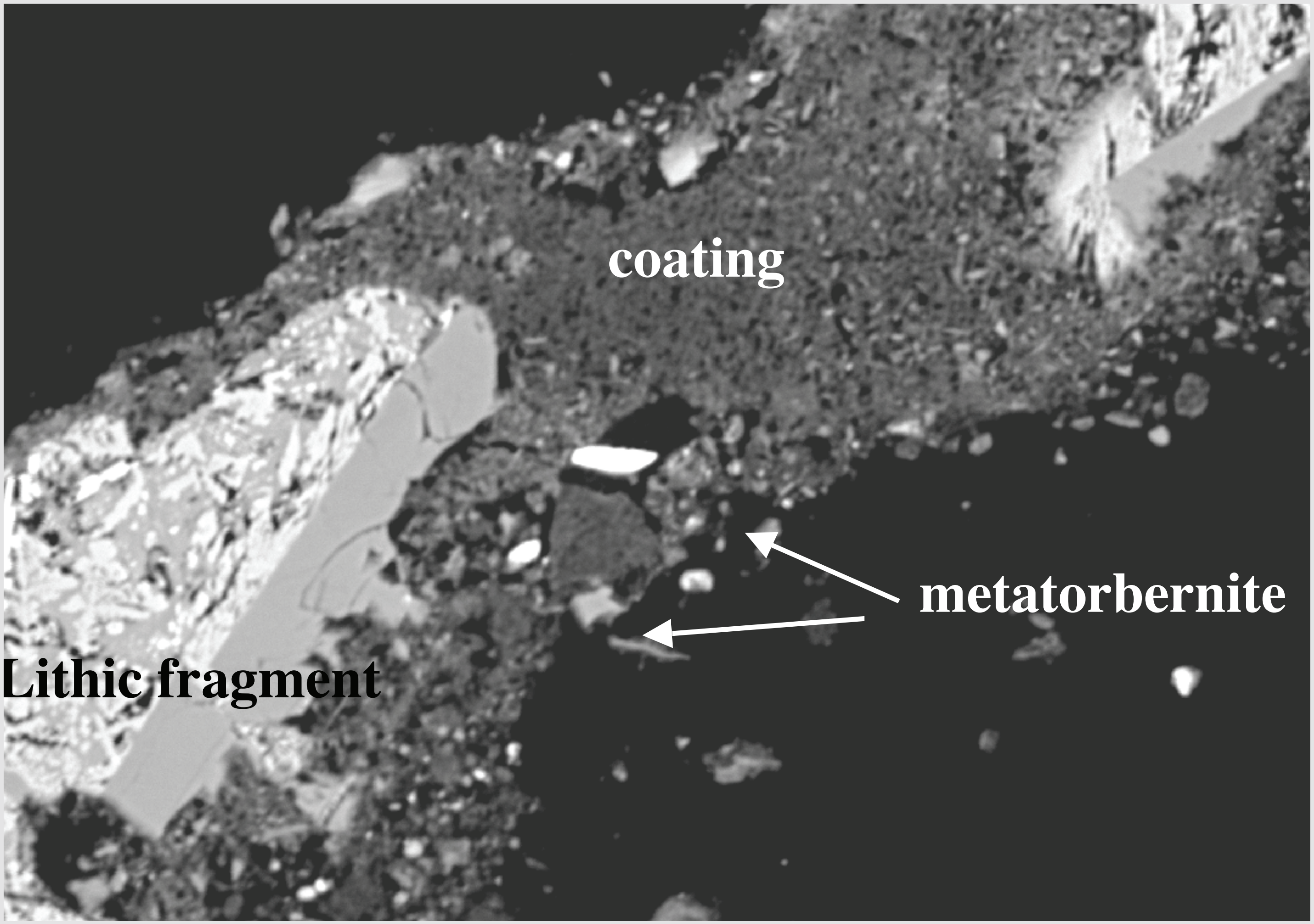
Hanford contaminated vadose zone sample: NPP2-2

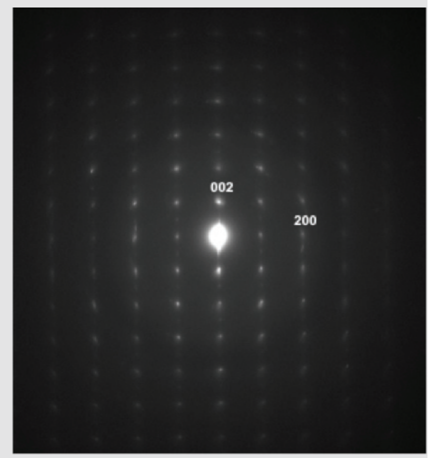
Coating has much finer texture, with a fine-grained clay coating several microns thick at the outer ridge of the grain. Probably influenced by infiltration of low and high pH pond water containing high concentrations of Al and Si.

Stubbs et al., 2008

Hanford contaminated vadose zone sample: NPP2-2

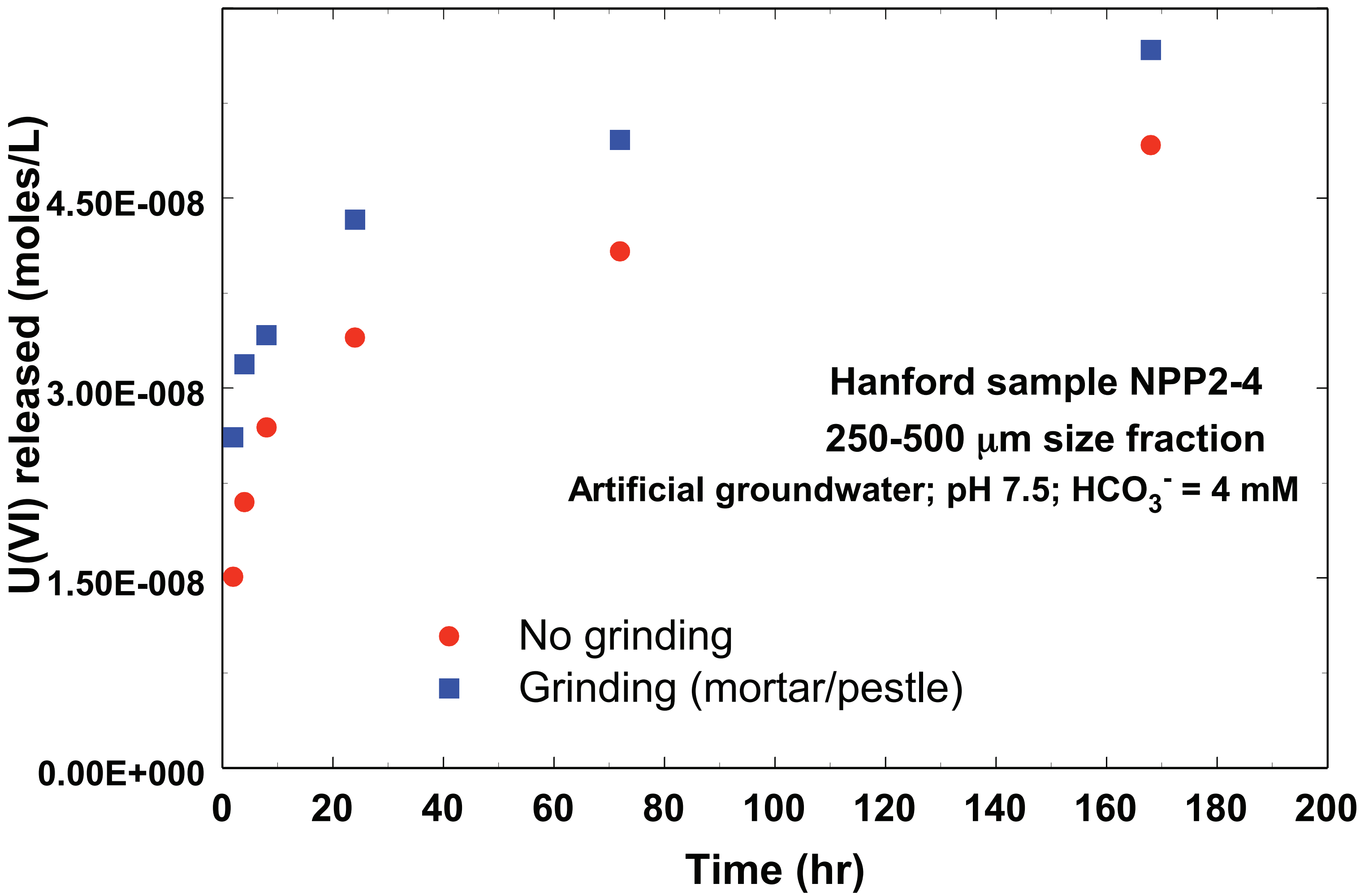
Metatorbernite precipitate [$Cu(UO_2)_2(PO_4)_2 \cdot 8H_2O$] is encapsulated within coatings on contaminated grains

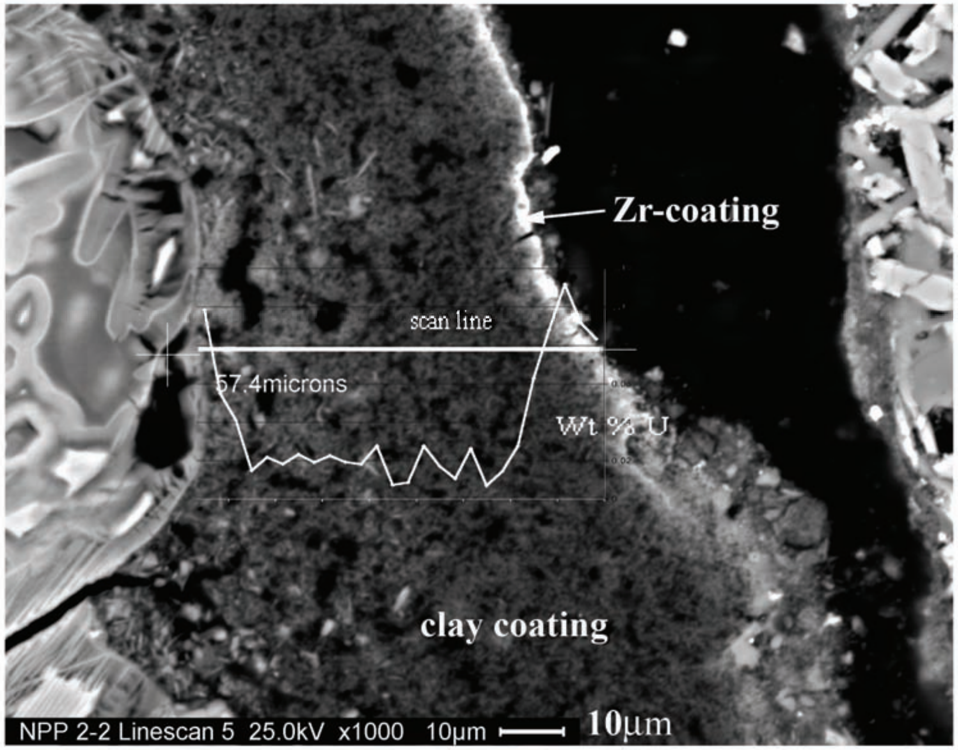


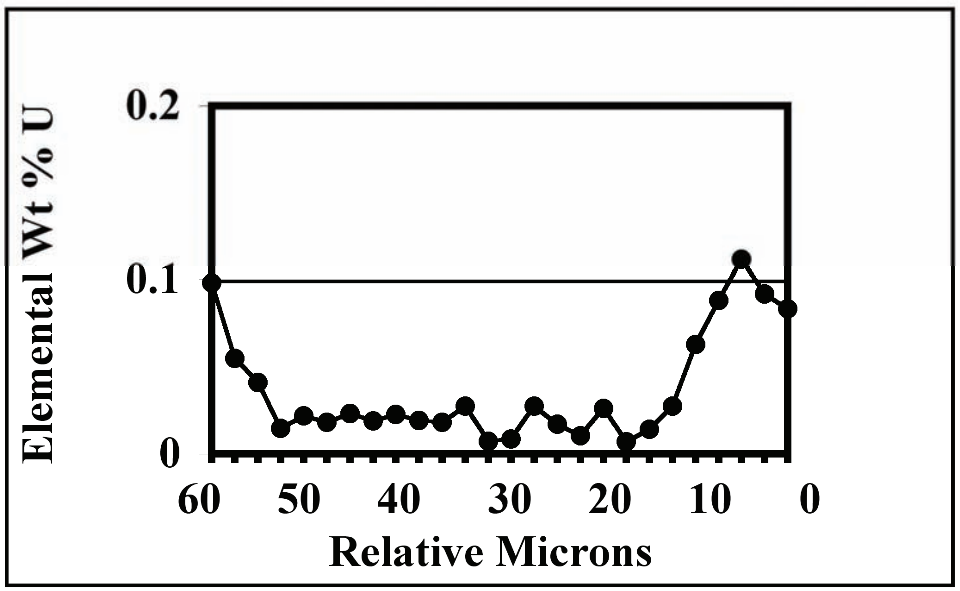


Stubbs et al., 2008

Hanford contaminated vadose zone sample: NPP2-4







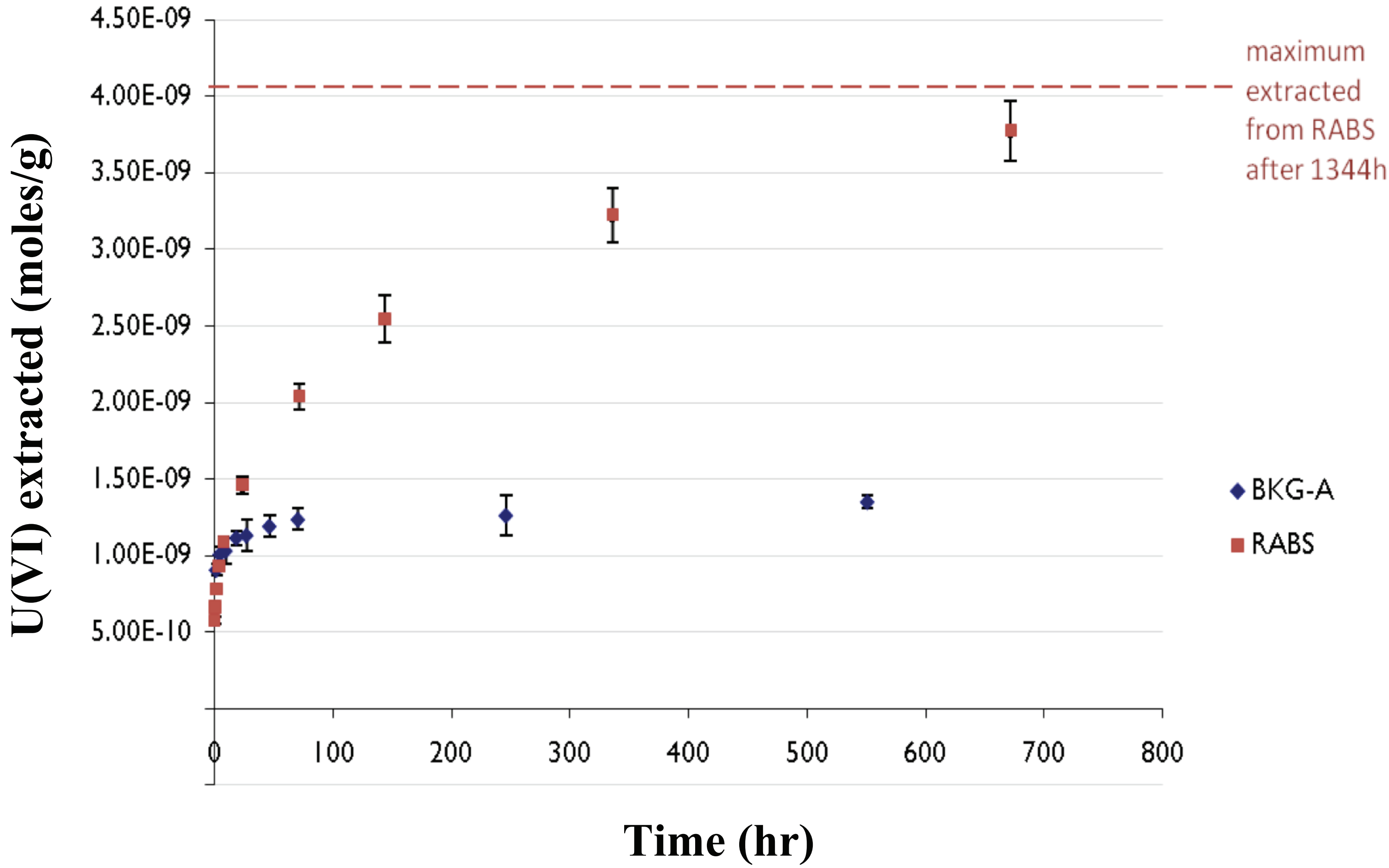
Hanford contaminated vadose zone sample: NPP2-2

Backscattering image of a 60 µm wide, fine-grained clay coating. Outer edge of coating contains very high concentrations of Zr and U, presumably from cladding waste. Electron microprobe WDS linescans show gradients in U concentration across the coating.

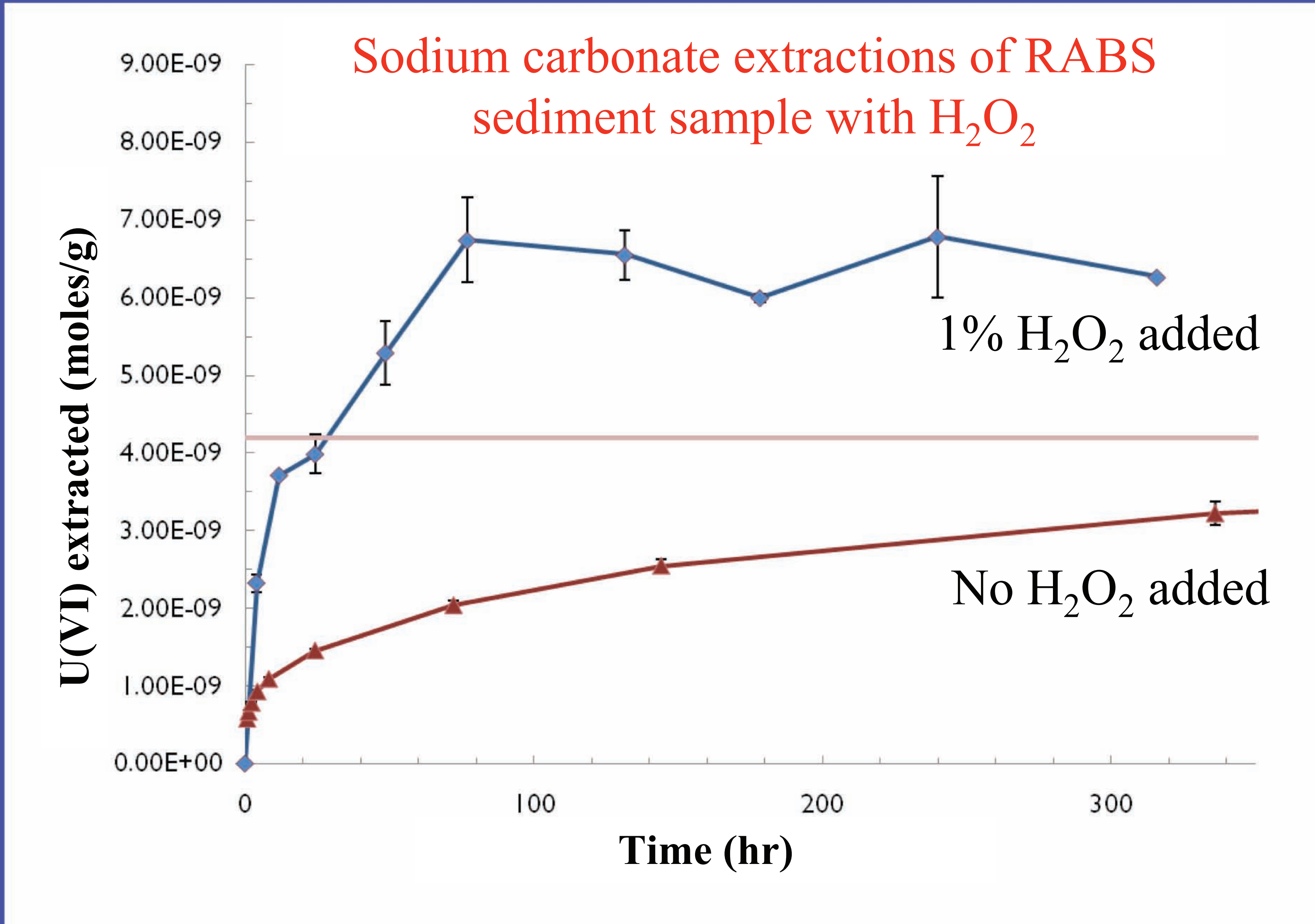
Stubbs et al., 2008

Zones of Natural Bioreduction in Rifle Aquifer Sediments

Sodium carbonate extractions of Rifle sediment samples (BKG-A and RABS)

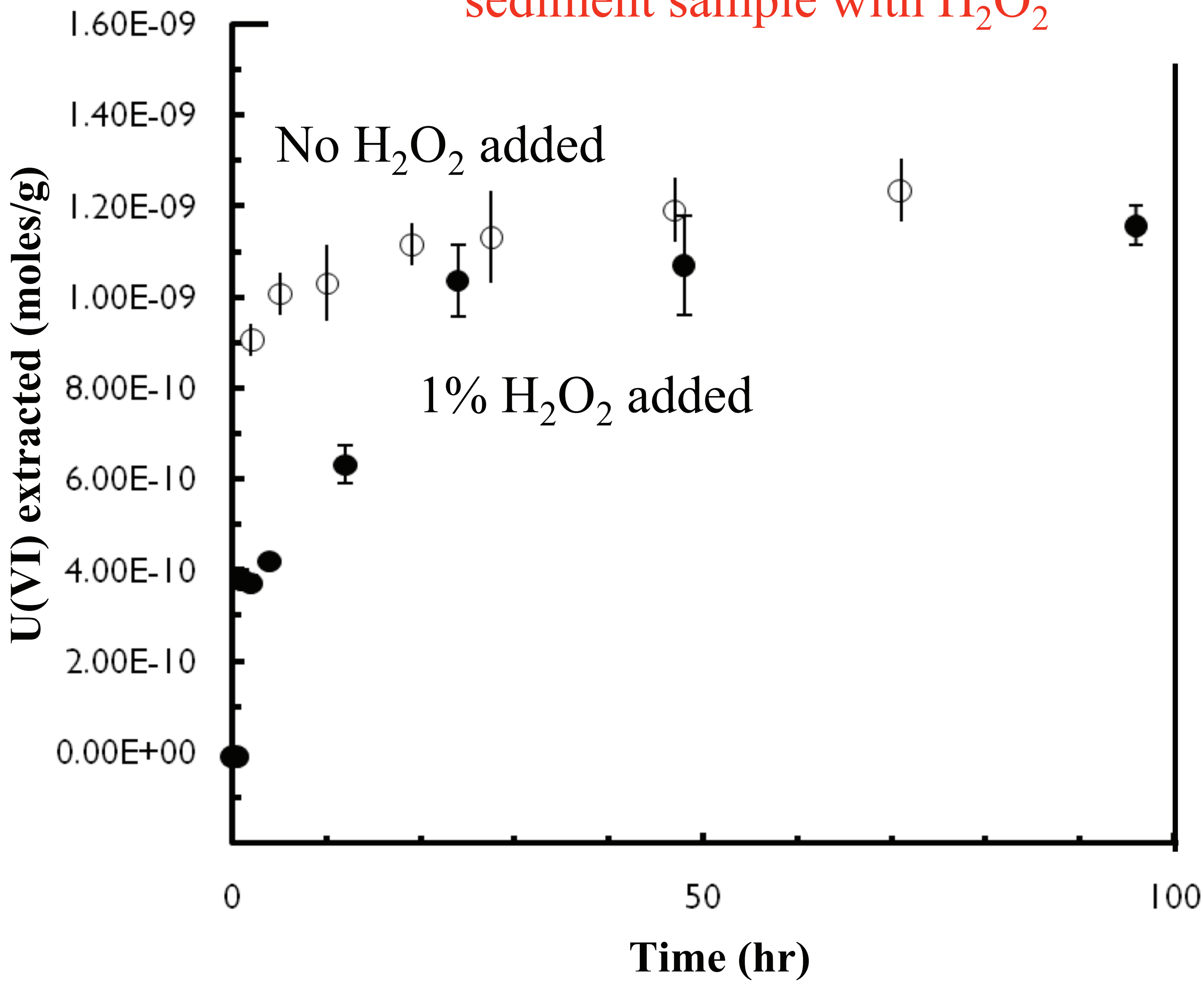


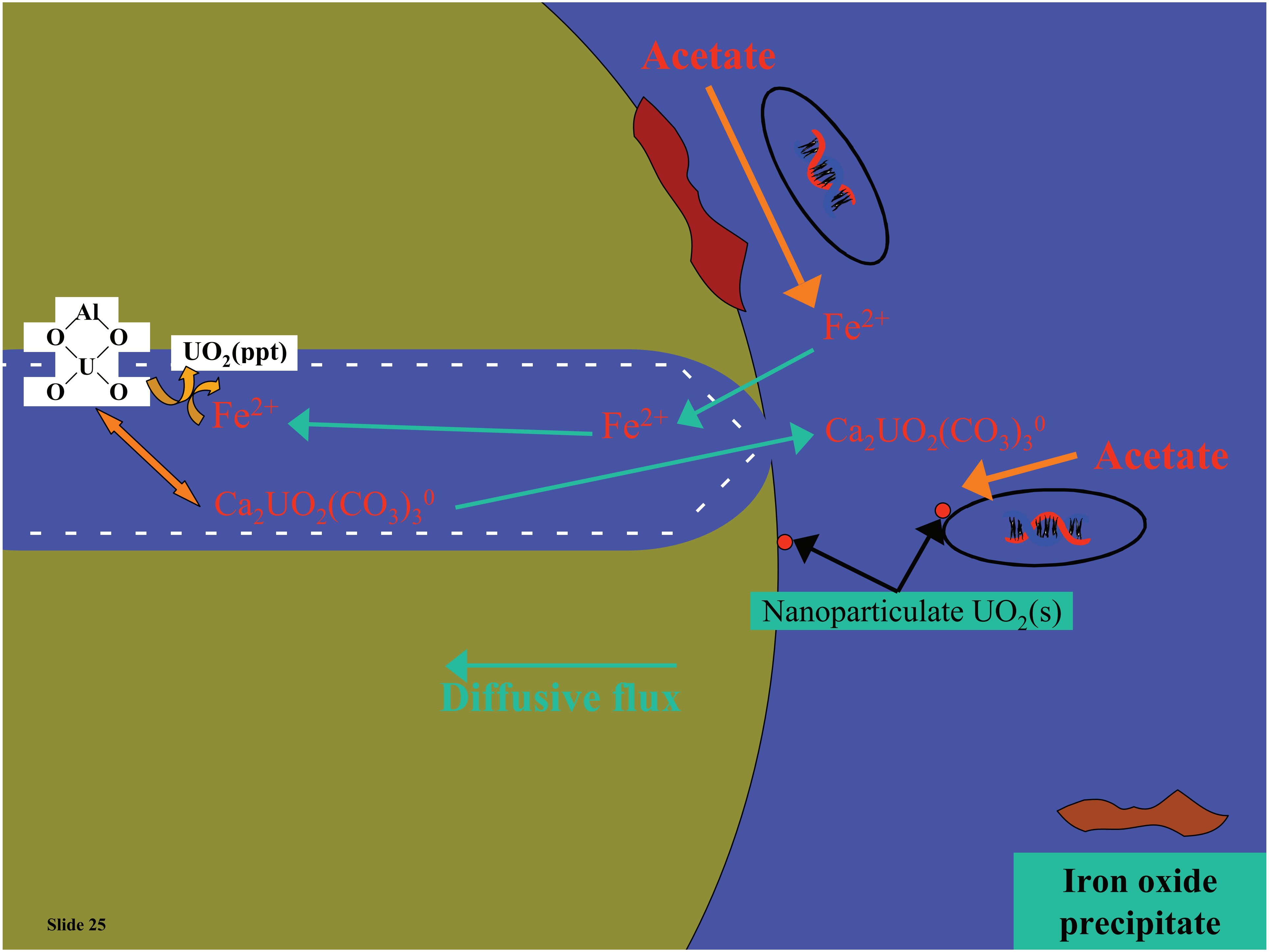
50 g/L air-dried sediment
Extractions performed in air; pH 9.4; 17.2 mM total carbonate

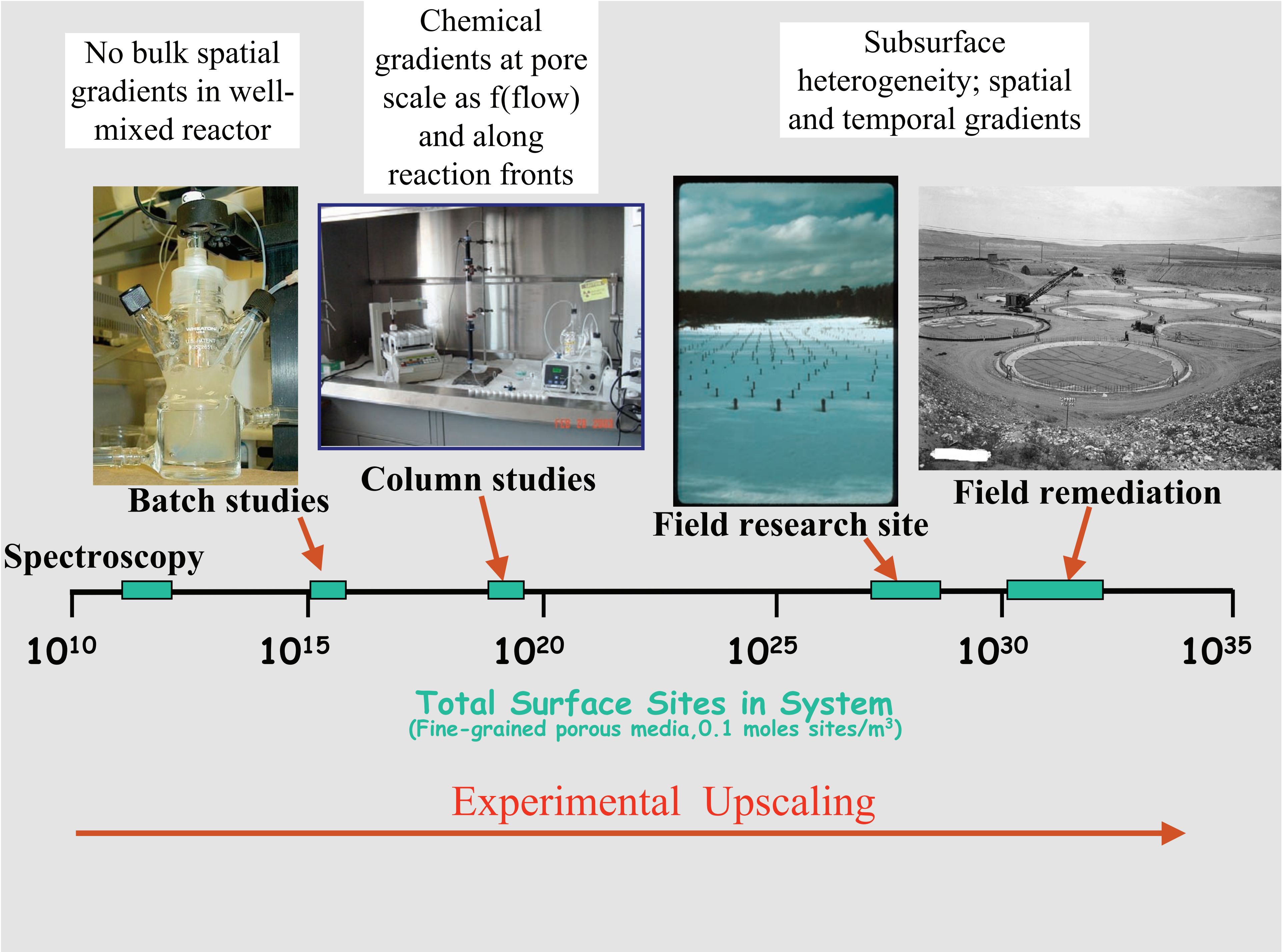


RABS total U = 1.76E-8 moles/g

Sodium carbonate extractions of BKG-A sediment sample with H_2O_2

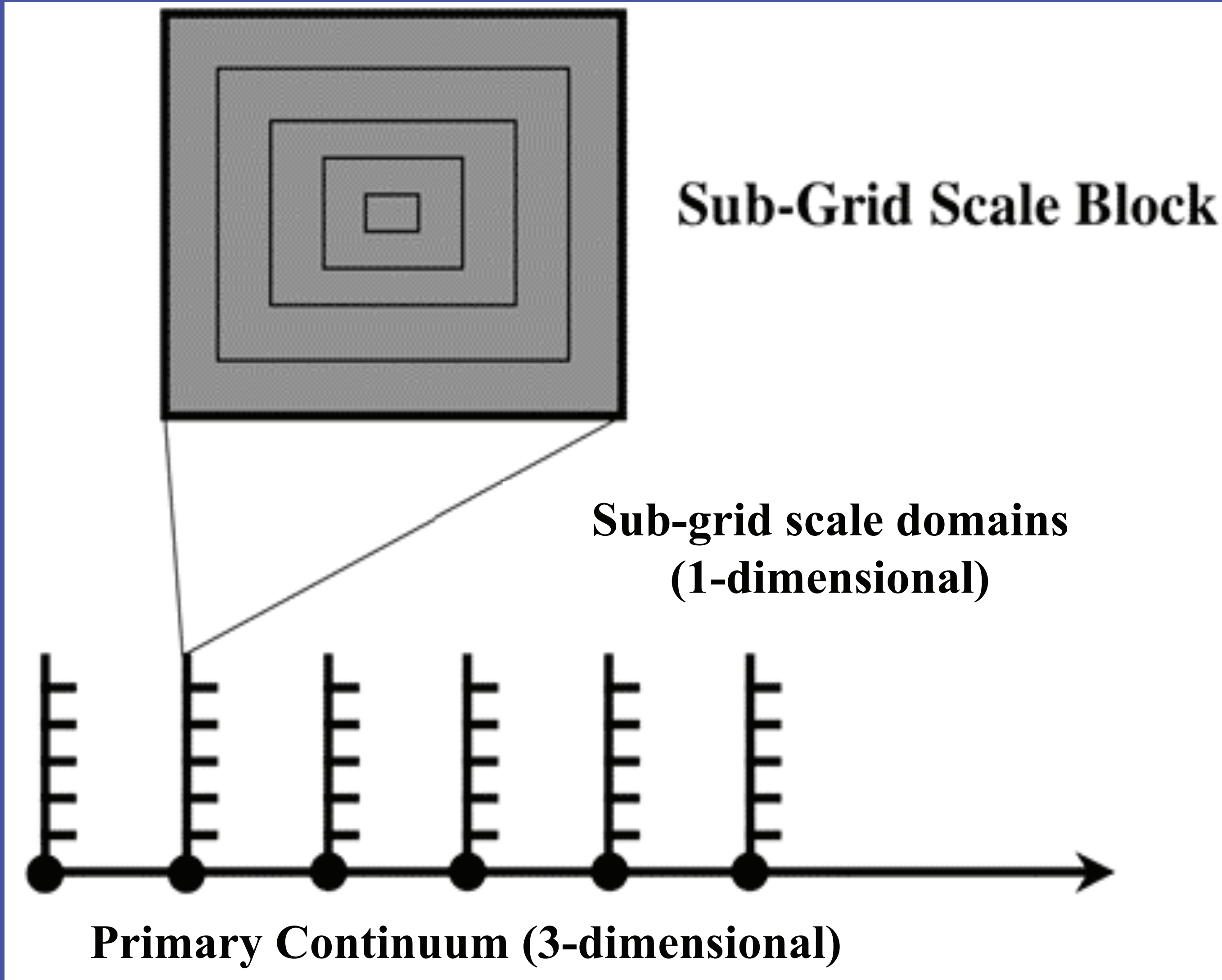



Acetate
Fe2+
Al
O O
U
O O
UO2(ppt)
Fe2+
Fe2+
Ca2UO2(CO3)3 0
Ca2UO2(CO3)3 0
Acetate
Nanoparticulate UO2(s)
Diffusive flux
Iron oxide precipitate



No bulk spatial gradients in well-mixed reactor
Chemical gradients at pore scale as f(flow) and along reaction fronts
Subsurface heterogeneity; spatial and temporal gradients
Batch studies
Column studies
Field research site
Field remediation
Spectroscopy
10^{10}
10^{15}
10^{20}
10^{25}
10^{30}
10^{35}
Total Surface Sites in System
(Fine-grained porous media,0.1 moles sites/m^3)
Experimental Upscaling

Multiscale Continuum Models



Lichtner and Kang, Water Resources Research, 43, W12S15, 2007

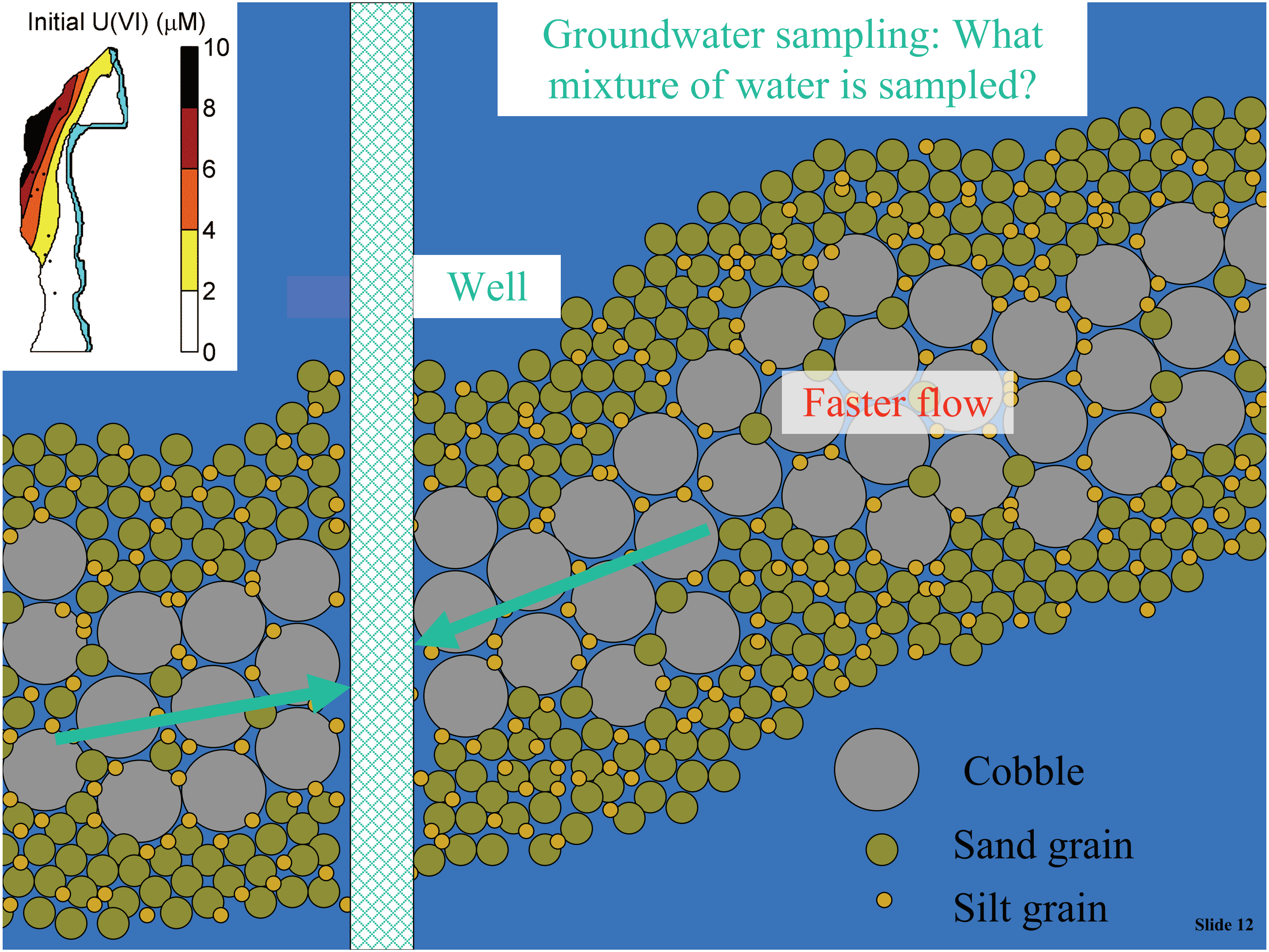
Conclusion

One of the largest problems for single continuum RTM at the field scale is heterogeneities of physical, chemical, and biological properties at the sub-grid scale and the *non-linear* scale dependence of coupled processes. Intragranular pore space and mineral grain coatings may be an important physical regime for many U-contaminated sites.

<u>Research Priorities:</u>

1) Multiscale continuum models (requires high performance computing)
2) Multiscale experimental studies
3) Methods for field characterization of significant parameters
4) Improved but simplified conceptual models for coupled processes (e.g., sorption and aqueous speciation)
5) Better understanding of parameter and conceptual model uncertainties

Groundwater sampling: What mixture of water is sampled?



Batch/column **Intermediate-scale studies** **Field-scale predictions**

Need for multiscale experiments!