Upscaling of Long-Term Uranium(VI) Desorption from Pore Scale Kinetics to Field-Scale Reactive Transport Models

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DOE Environmental Remediation Sciences Program, Fall PI meeting, Oak Ridge, TN, October 2006

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

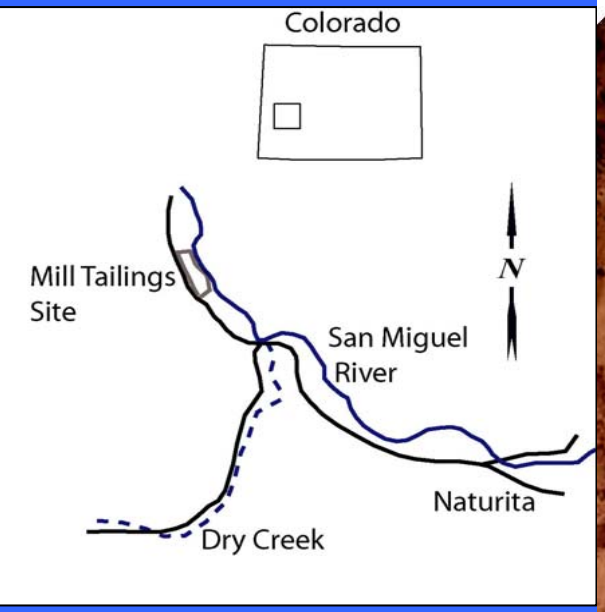
(Fine-grained porous media, 0.1 moles sites/m^3)

Modeling results and conceptual models for sorption

Predominant chemical species	Sorption as f(chemistry); K_d or surface complexation model	Retardation as f(chemistry); kinetic model; K_d or surface complexation model	Retardation under field conditions; kinetic model; K_d or surface complexation model	Retardation predictions under field conditions; K_d

Model Upscaling

Naturita, Colorado UMTRA Site



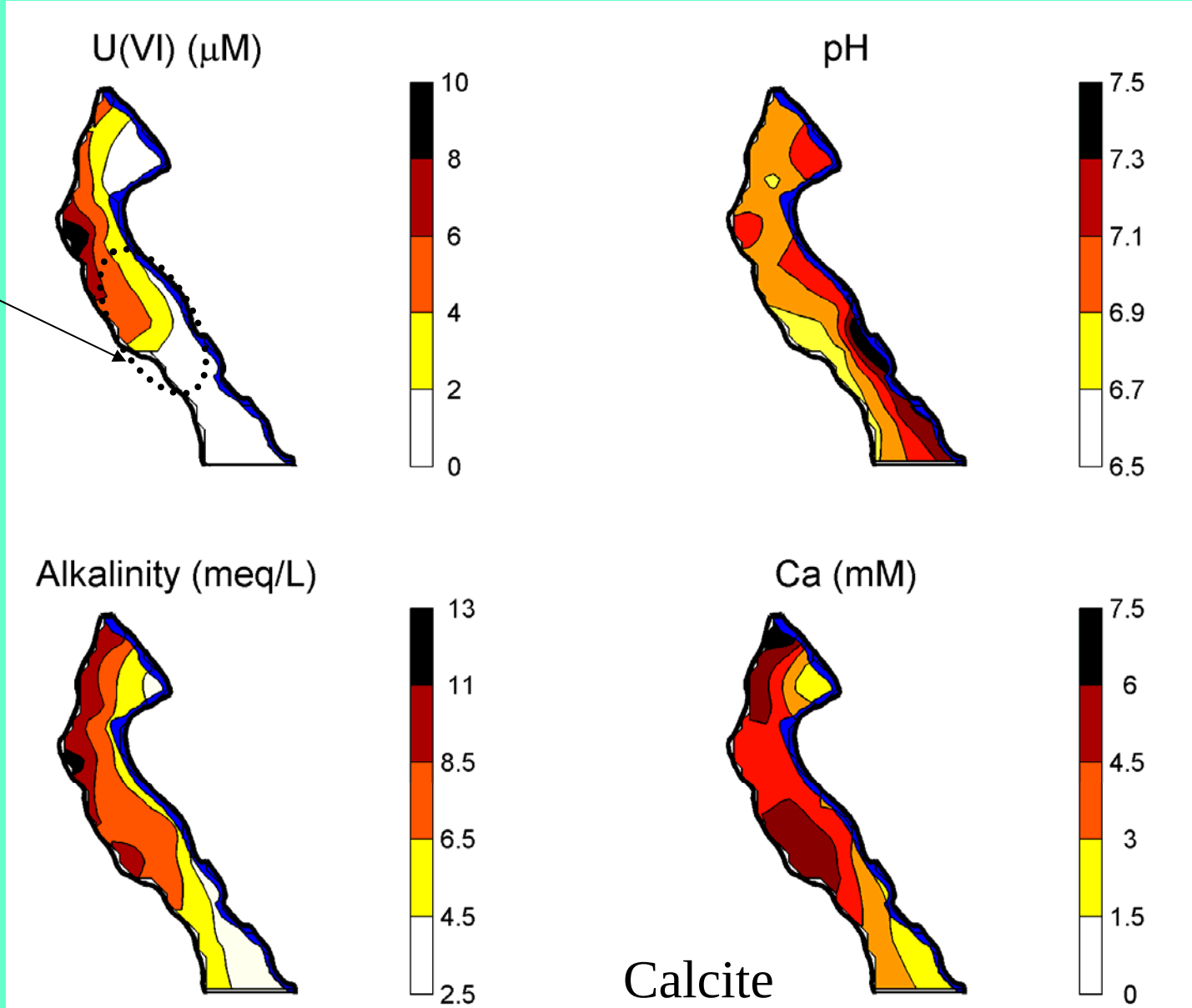
Aerial photo of uranium tailings, 1974

After completion of DOE surface reclamation, 1997

Installation of USGS wells, 1998

Concentration contour plots, Naturita aquifer, September 1999

1950, area of contamination



River water:

pH = 8.6
Alk = 2.3
Ca = 1.8
U(VI) = 0.01

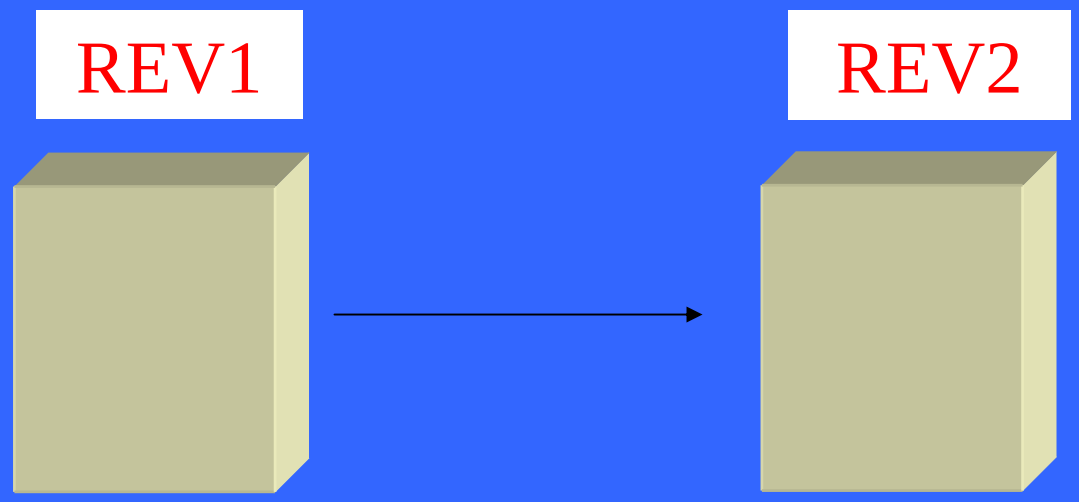
pCO_2 = 1-10%

Calcite control

Naturita UMTRA site: Alluvial Aquifer Sediment Texture

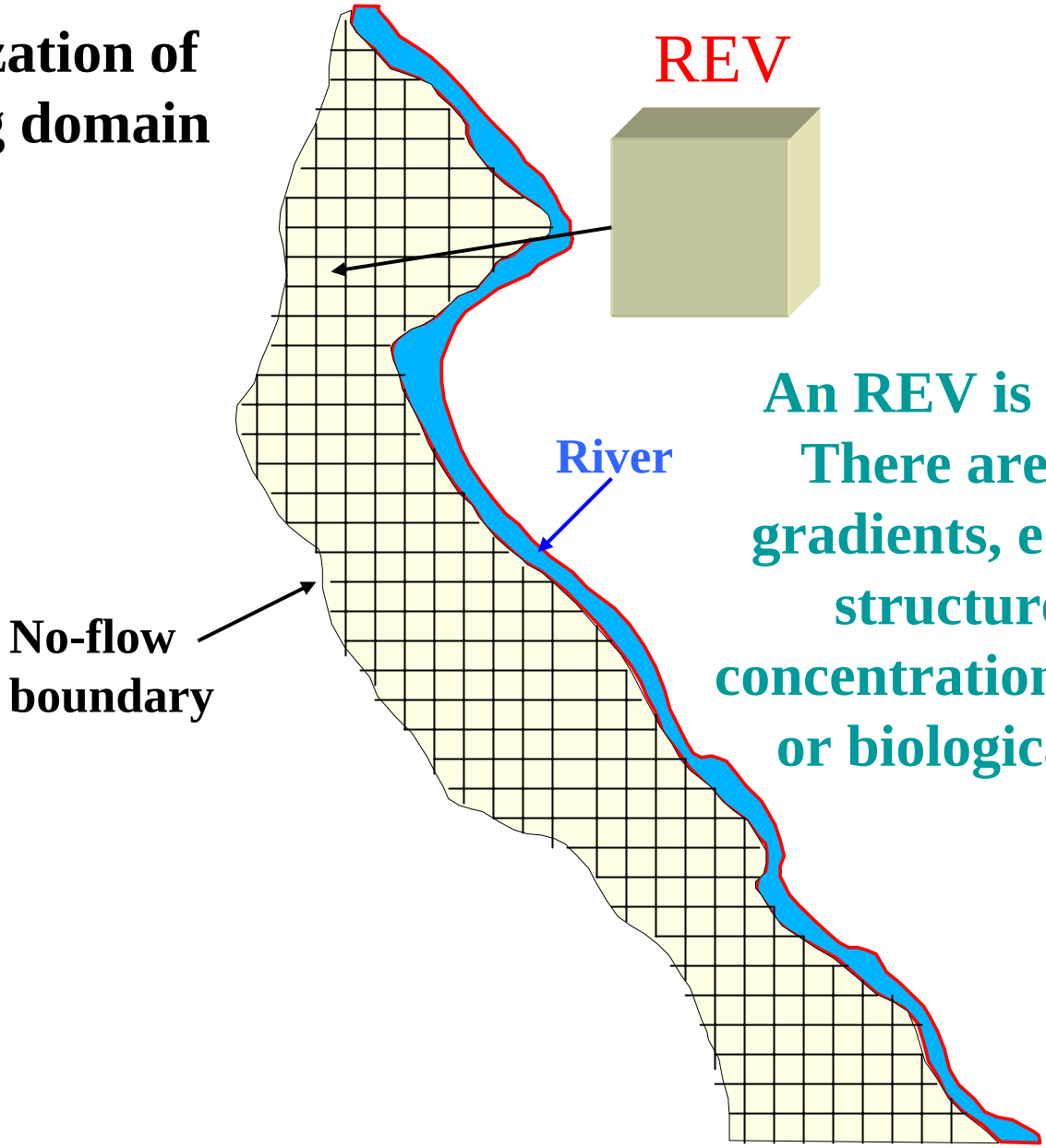
Continuum Models

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 <u>continuously</u> in space.



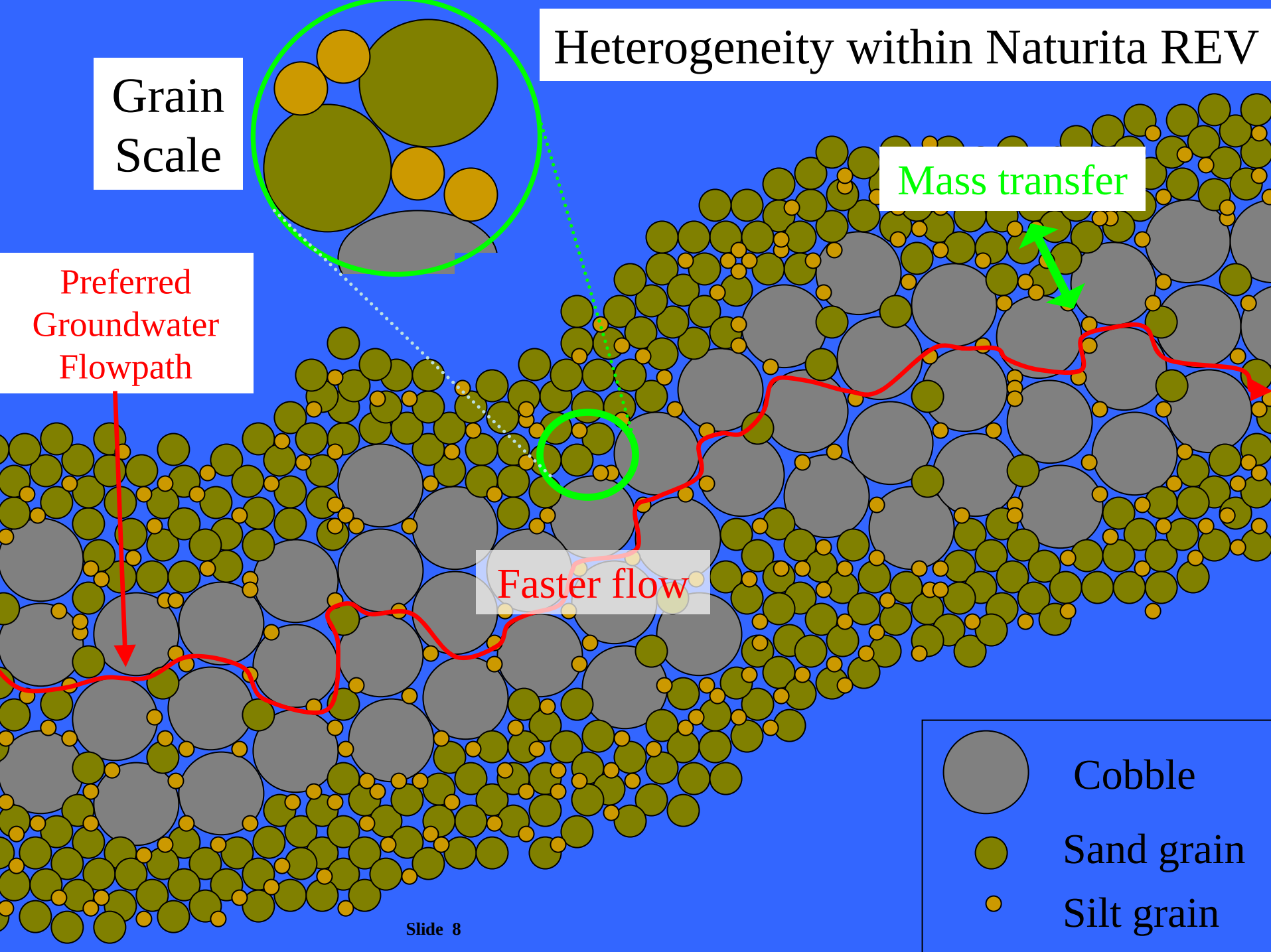
An REV has <u>average</u> values of physical, chemical, and microbiological variables

Discretization of modeling domain

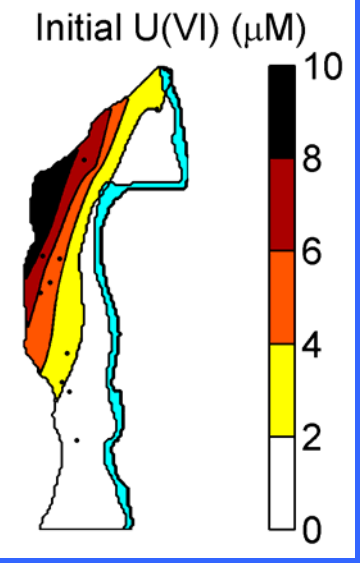


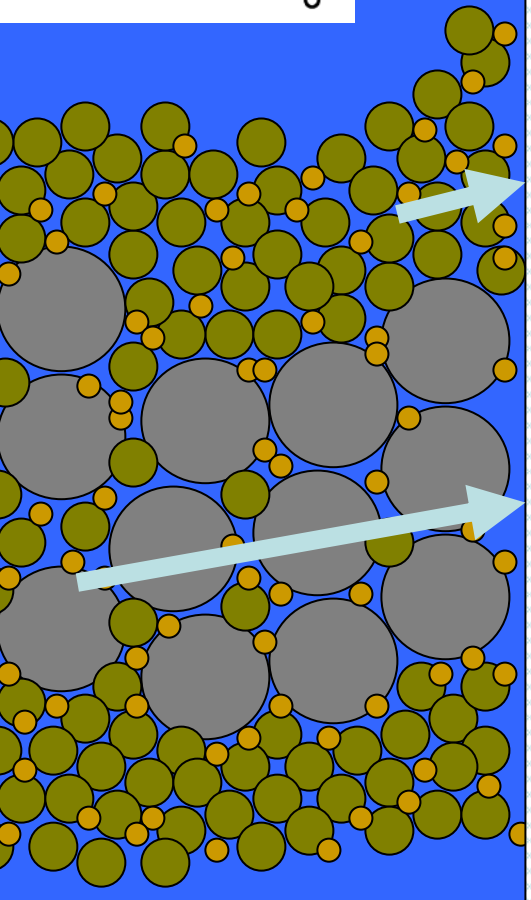
An REV is "well mixed". There are no sub-grid gradients, e.g., in physical structure, chemical concentrations, surface area, or biological properties.

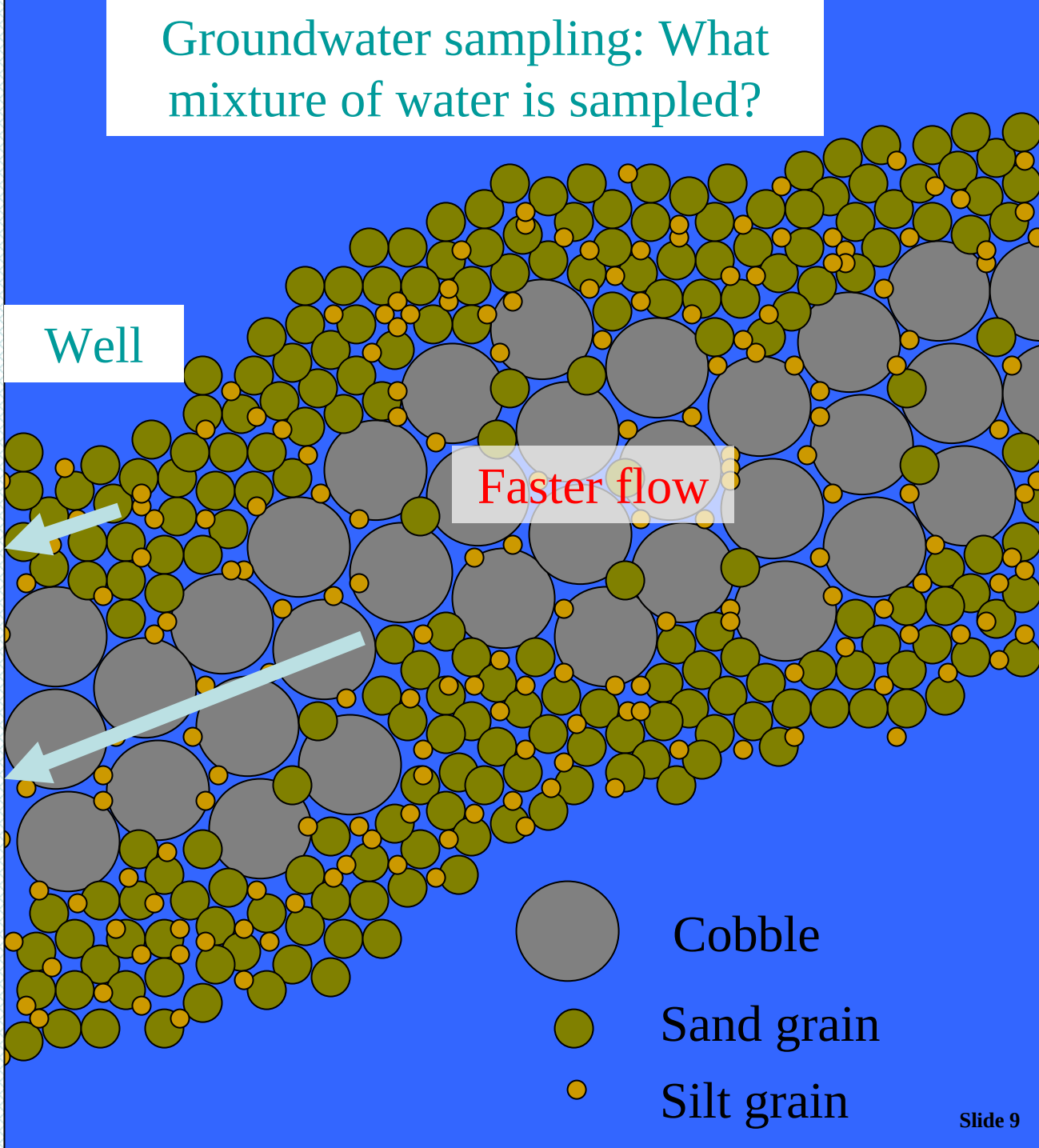
Heterogeneity within Naturita REV



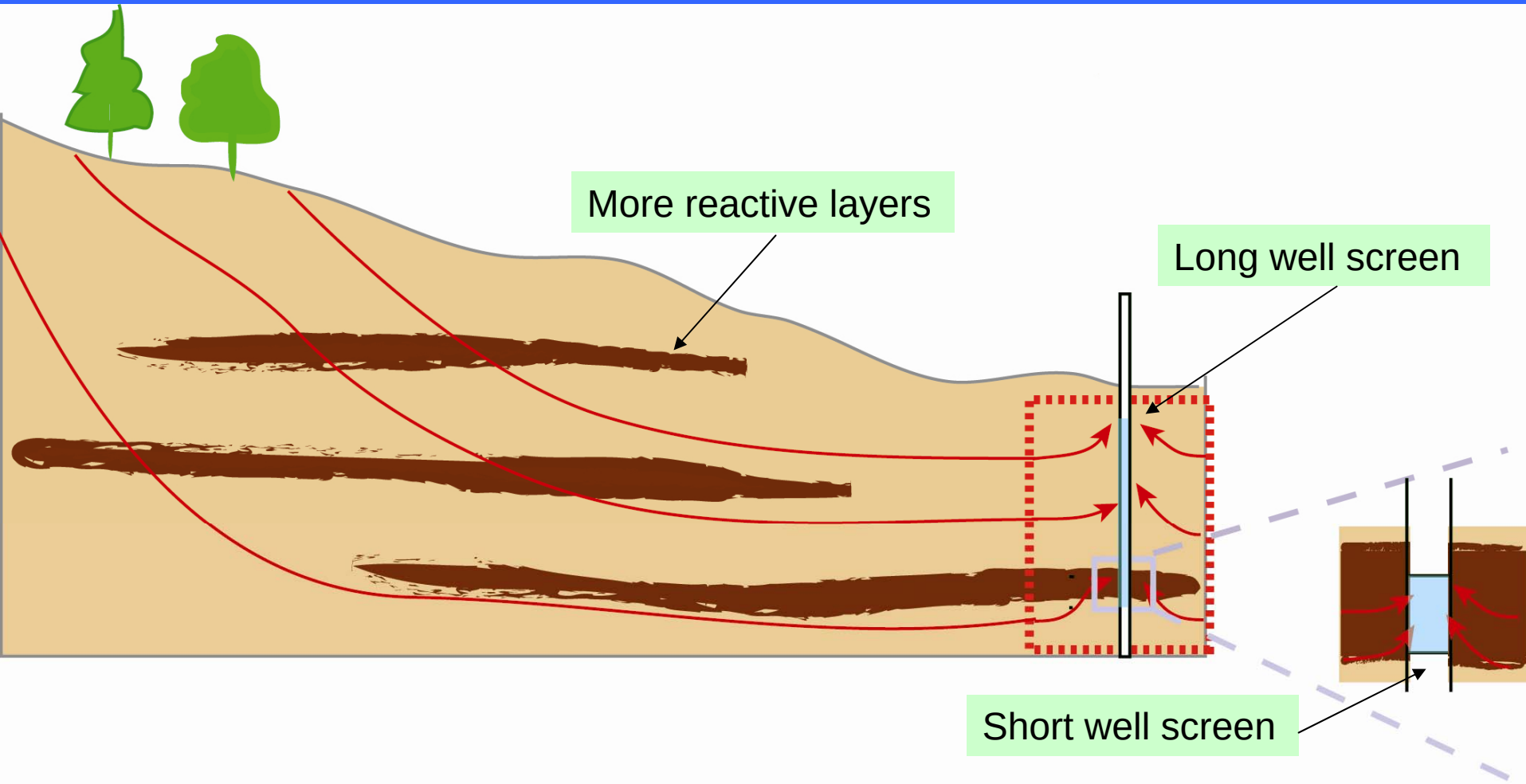
Groundwater sampling: What mixture of water is sampled?





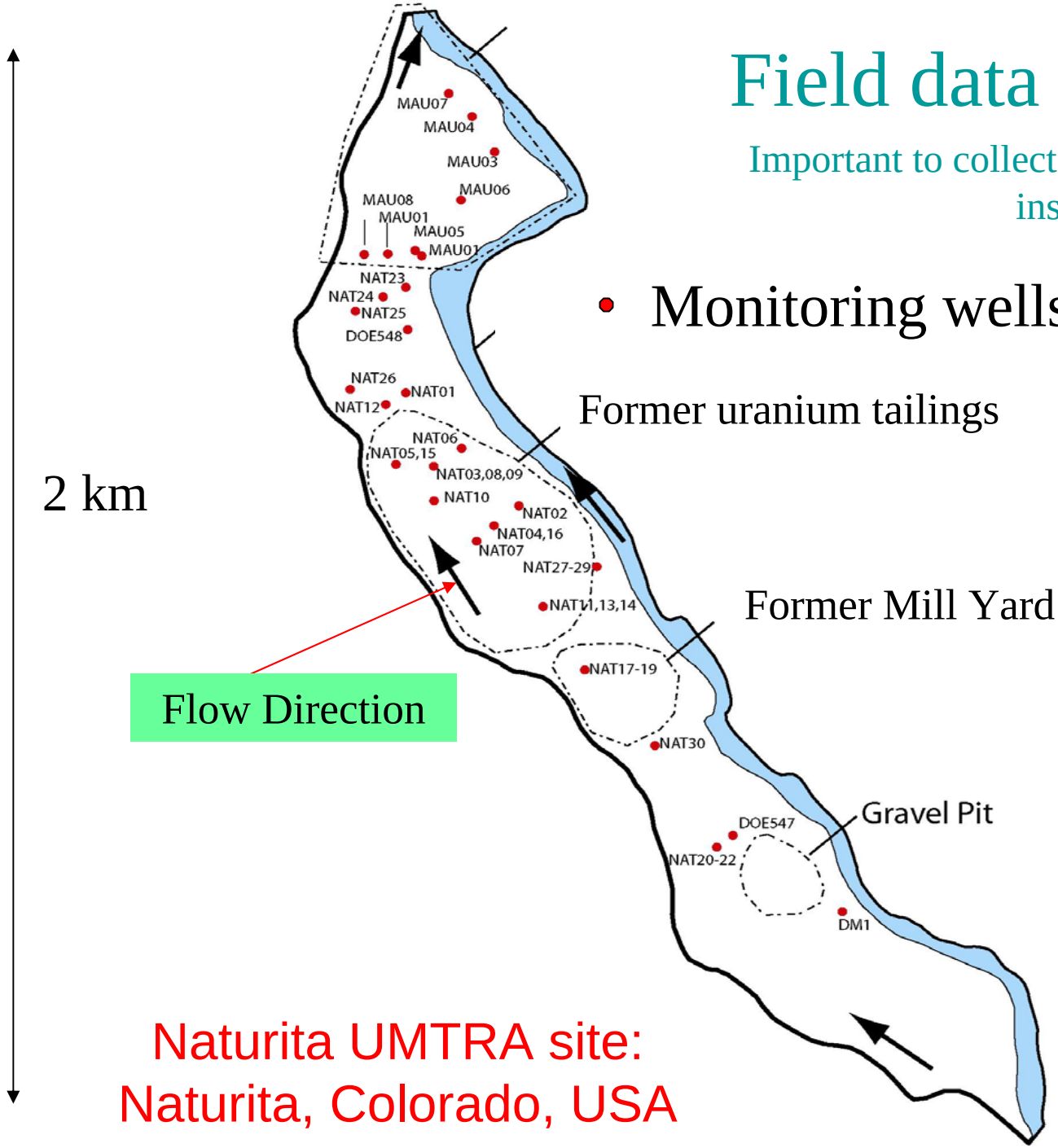


Scale of Observations



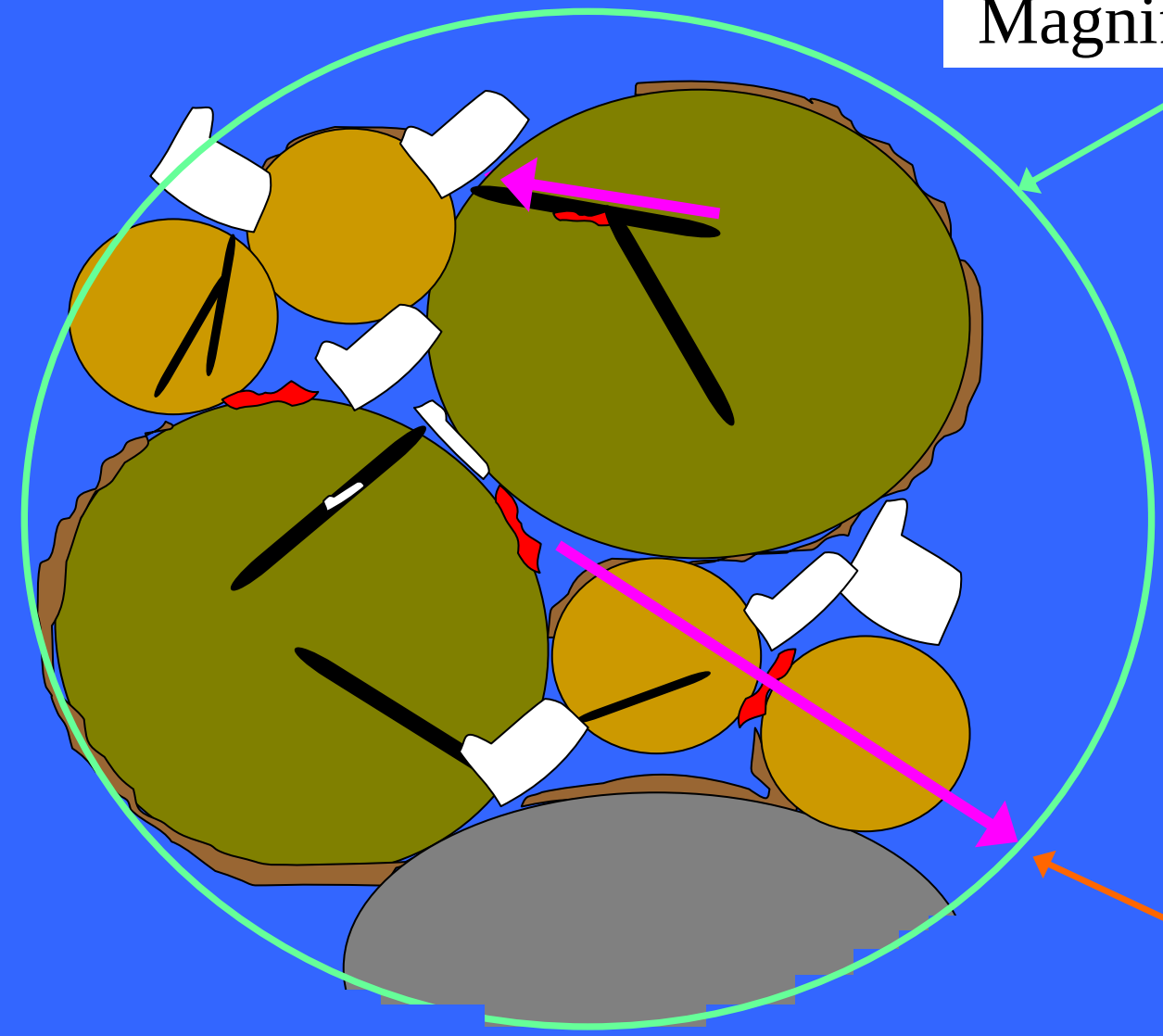
Field data are sparse!

Important to collect sediments as wells are installed



Naturita UMTRA site:
Naturita, Colorado, USA

Magnified Grain Scale



Concentration gradients (e.g., H^+, U(VI), PO_4^{3-}, HCO_3^-)$_p$

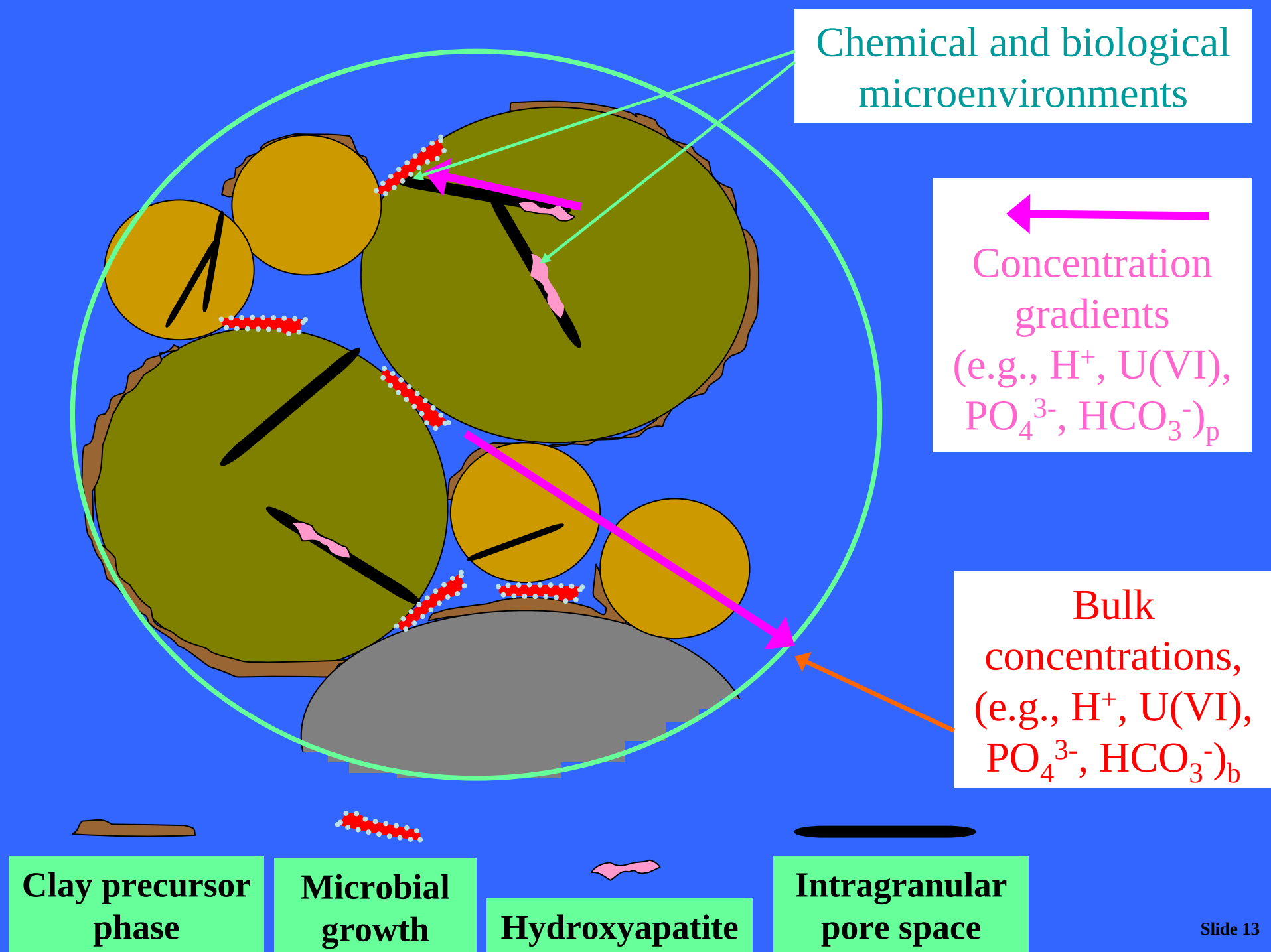
<u>Temporally</u>-variant bulk concentrations, (e.g., H^+, U(VI), PO_4^{3-}, HCO_3^-)$_b$

Clay precursor phase

Calcite

Iron oxide precipitate

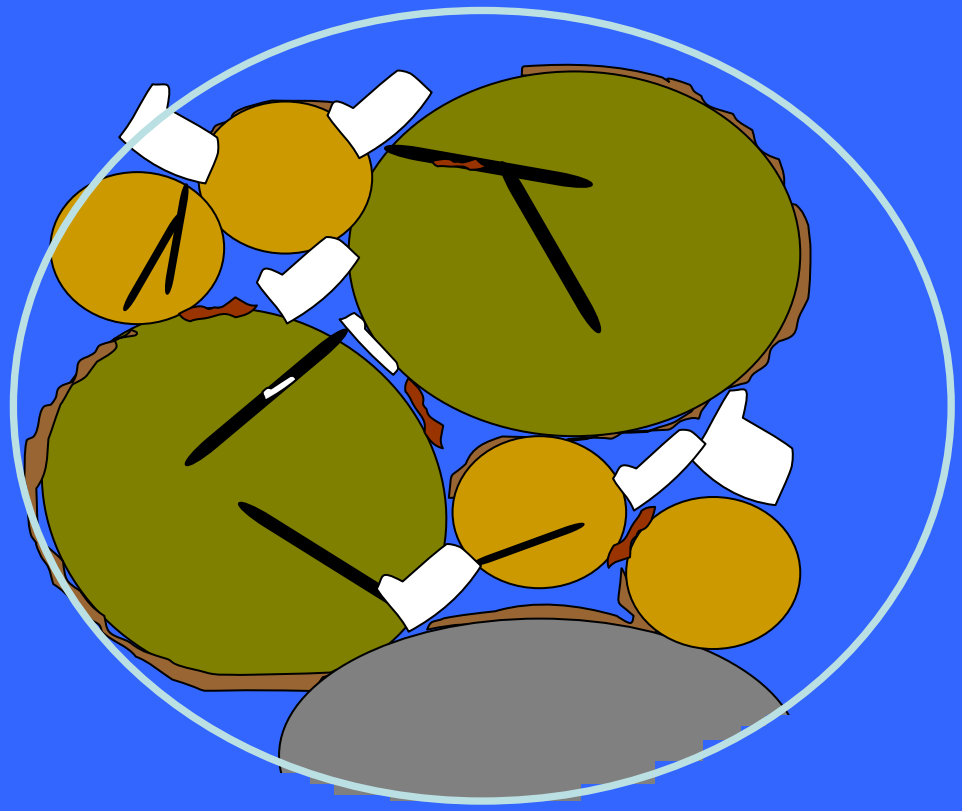
Intragranular pore space


Chemical and biological microenvironments
Concentration gradients (e.g., H^+, U(VI), PO_4^{3-}, HCO_3^-)$_p$
Bulk concentrations, (e.g., H^+, U(VI), PO_4^{3-}, HCO_3^-)$_b$
Clay precursor phase
Microbial growth
Hydroxyapatite
Intragranular pore space

Upscaling: Single Minerals to Mixed Mineral Assemblages

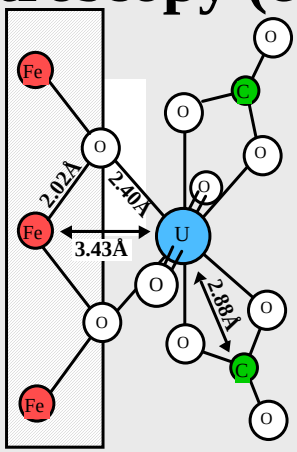
Concept of Mineral Component Additivity (Honeyman, 1984):

$$\text{Adsorbed } U(VI)_{sediment} = U_{quartz} + U_{feldspars} + U_{calcite} + U_{iron\ oxides} + U_{illite} + U_{humics\ and\ bacterial\ surfaces}$$



Model Upscaling

Spectroscopy (e.g., EXAFS)



Batch studies

Modeling

Identification of chemical species: surface complexes, precipitates

- Bond distances and coordination number
- Neighboring atoms
- Generally resolved to one to three species

Modeling

K_d values

Sorption isotherms

Surface Complexation Models:

- CD-Music
- Extended Triple Layer (Sverjensky)
- Semi-mechanistic models

Solid Solutions

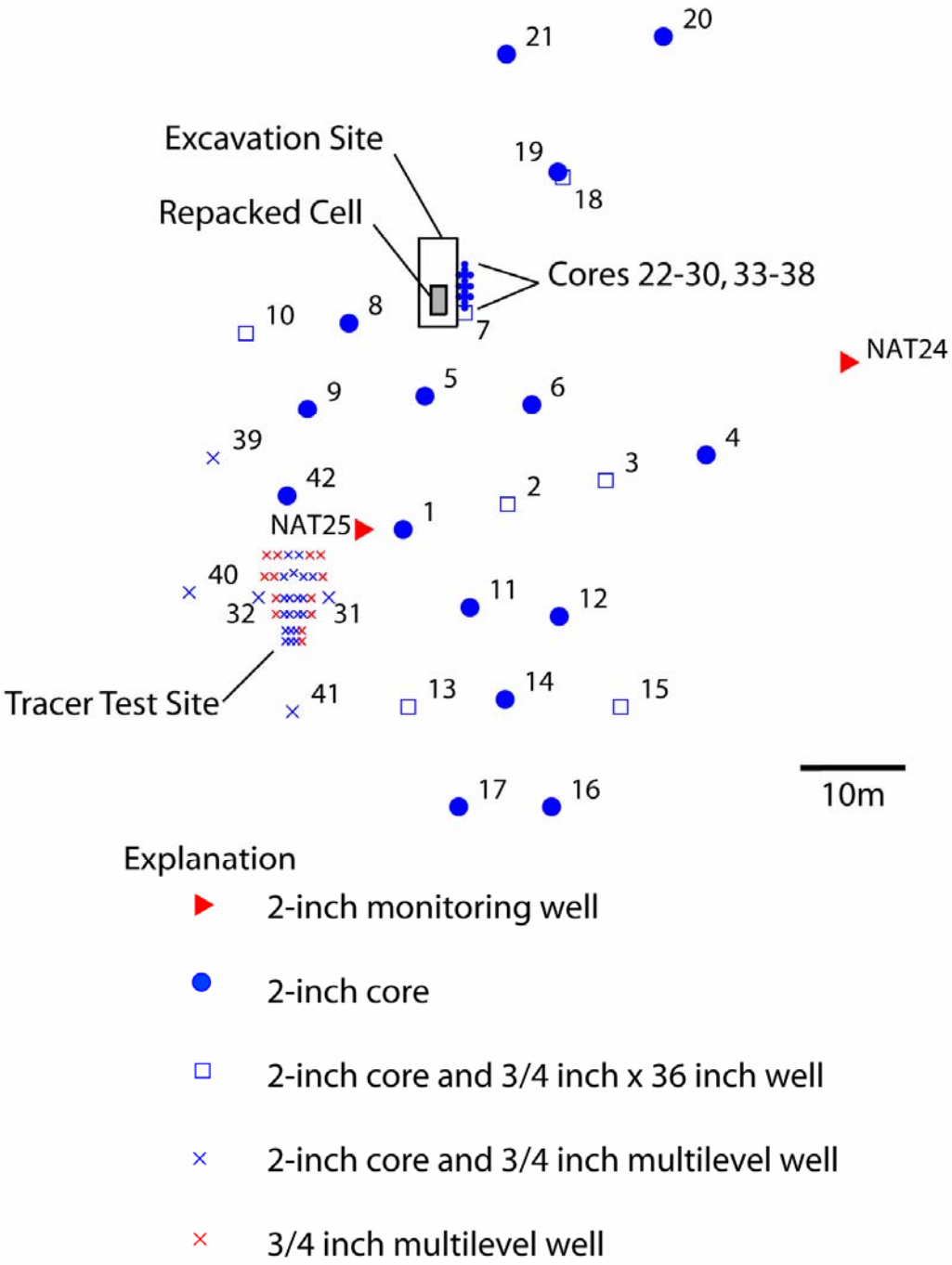
Need for multiscale experiments!

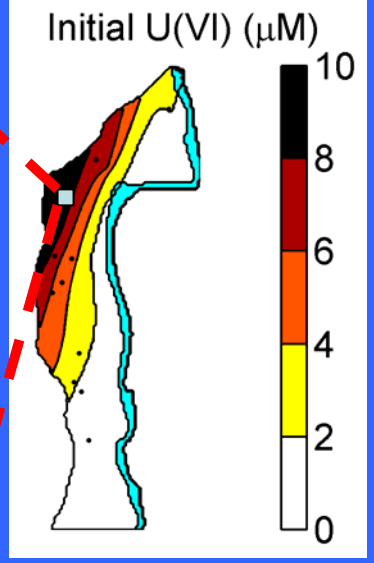
Batch/column

Intermediate-scale studies

Field-scale predictions

Goal: Develop scientifically defensible approaches for upscaling reactive transport models through a detailed understanding of U(VI) desorption processes across spatial scales



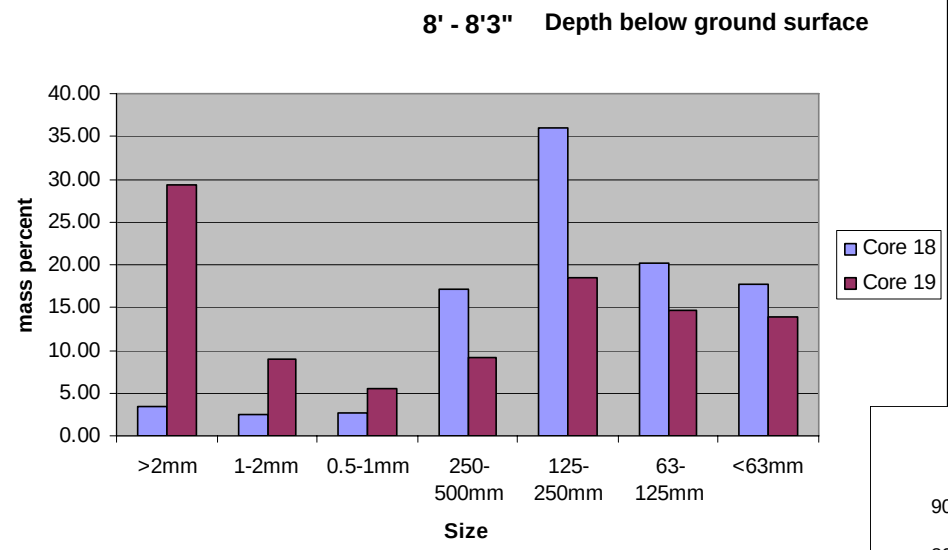


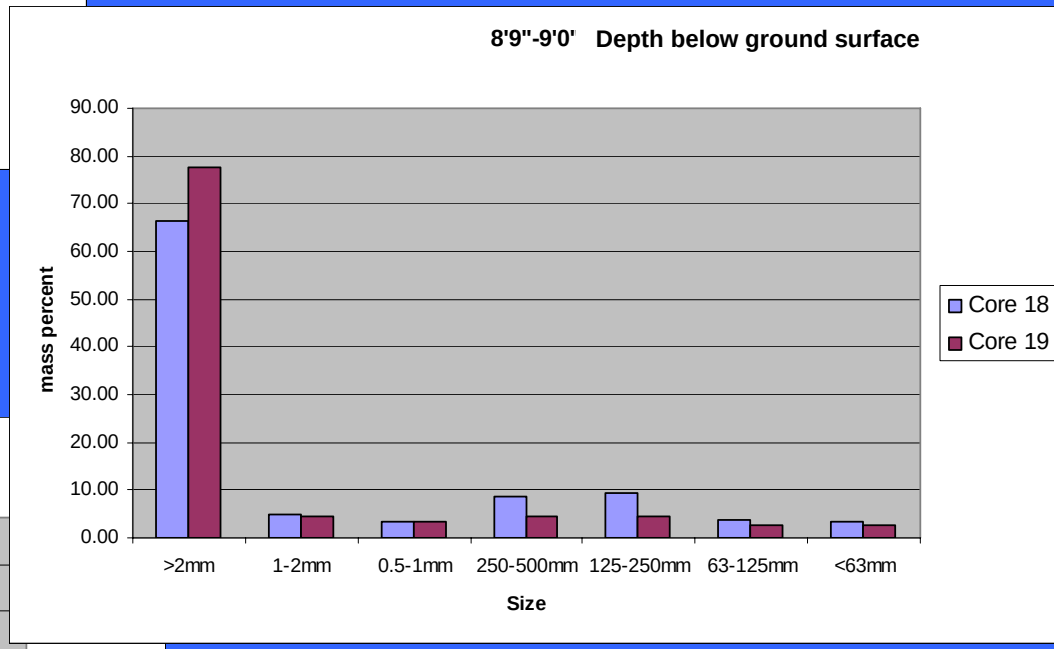
Field Activities:
March – October 2006

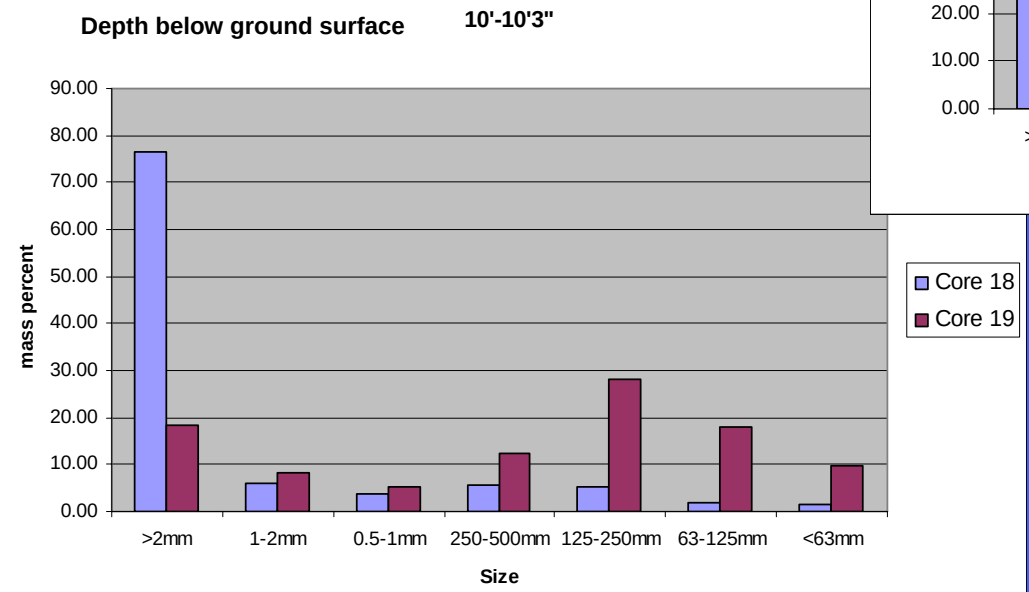
1. Excavate 15 yd^3 below water table
2. Sieve to <4 mm (field cell) and 2 yd^3 <2 mm (lab experiments)
3. Install reaction cell/tracer test site at excavated site
4. Install separate tracer test site (10 m scale)
5. Coring for geostatistical statistics

USGS geoprobe used to collect cores of subsurface material and install multilevel sampling wells at tracer test site

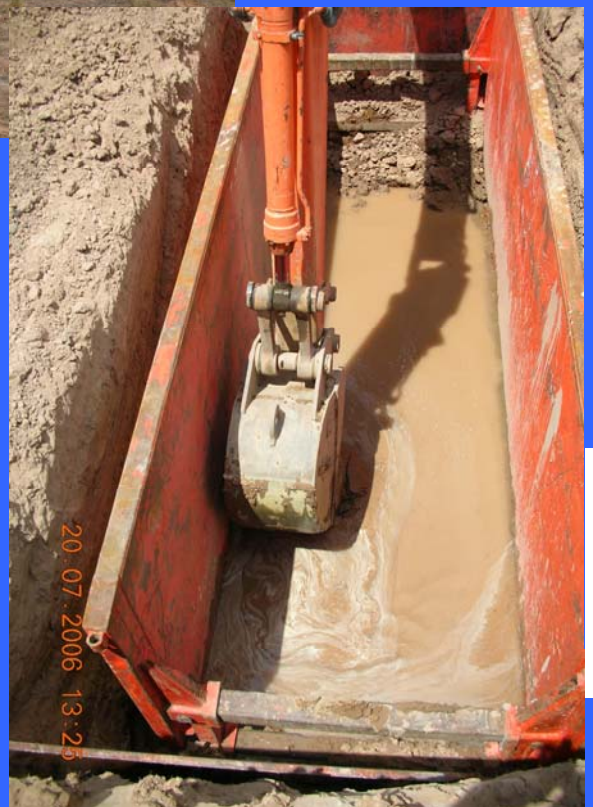
Heterogeneity in grain size distribution for two cores separated horizontally by 0.5 m







Excavation of subsurface material below the water table



20 grab samples collected during excavation for characterization

5 Days – 12 people sieving all day in 100 degree heat!

<2 mm sediments in 12 drums

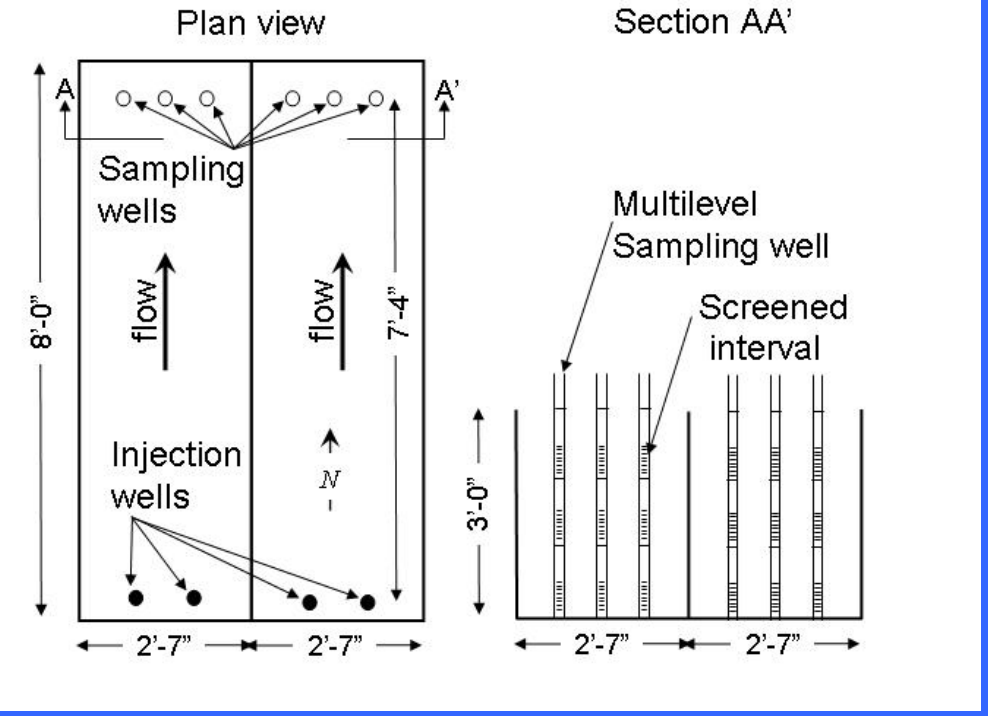
Intermediate-scale 2-D and 3-D tanks

Batch/column

Tank construction in progress at CSM

Mixing and sieving sediments to smaller size fractions

Reaction cell for tracer tests with known sediment structure and properties



Packed with well-mixed <4 mm sieved subsurface materials

Packed with two layers of well-mixed <4 mm sieved subsurface materials with middle layer of cobbles

Filling one side of cell with well-mixed <4 mm sieved subsurface materials

Emplacing layer of cobbles in one side of cell

Finished!

Site with multi-level samplers for natural-gradient and forced-gradient tracer tests

The Team

Concluding Remarks

- Have started an upscaling study of U(VI) desorption processes at the Naturita UMTRA site

  Collected and sieved a large composite sample for intermediate- and lab-scale experiments

  Installed a reaction cell/tracer test site with known sediment structures and materials that were composited and will be characterized

  Installed a separate field tracer test site

  Collected many closely-spaced cores for geostatistical analyses of properties

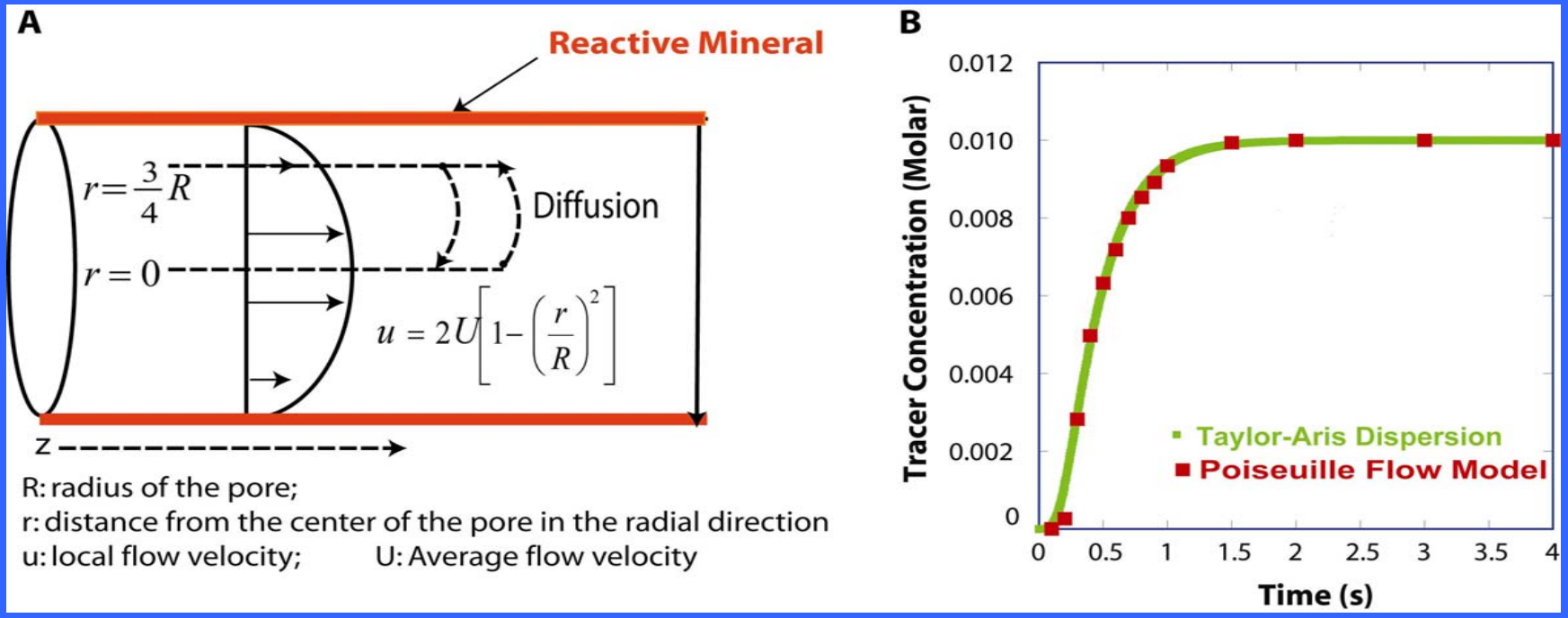
- Hypothesis: Physical heterogeneity can cause sub-grid concentration gradients that are not accounted for in reactive transport models based on the single continuum approach

- Hypothesis: Solute concentrations measured from monitoring wells may be derived from a mixture of waters of differing concentrations from subsurface regions of physical and chemical heterogeneity, and the mixed concentration does not accurately represent chemical equilibria in the system or the actual rates of reactions

- Goal: Develop scientifically defensible approaches for upscaling reactive transport models through a detailed understanding of U(VI) desorption processes across spatial scales

Uranium DRIVE IN
BE MORE
BIPEDAL
WE
HAVE
DIESEL
25.07.2006 07:02

Transport in a Single Pore

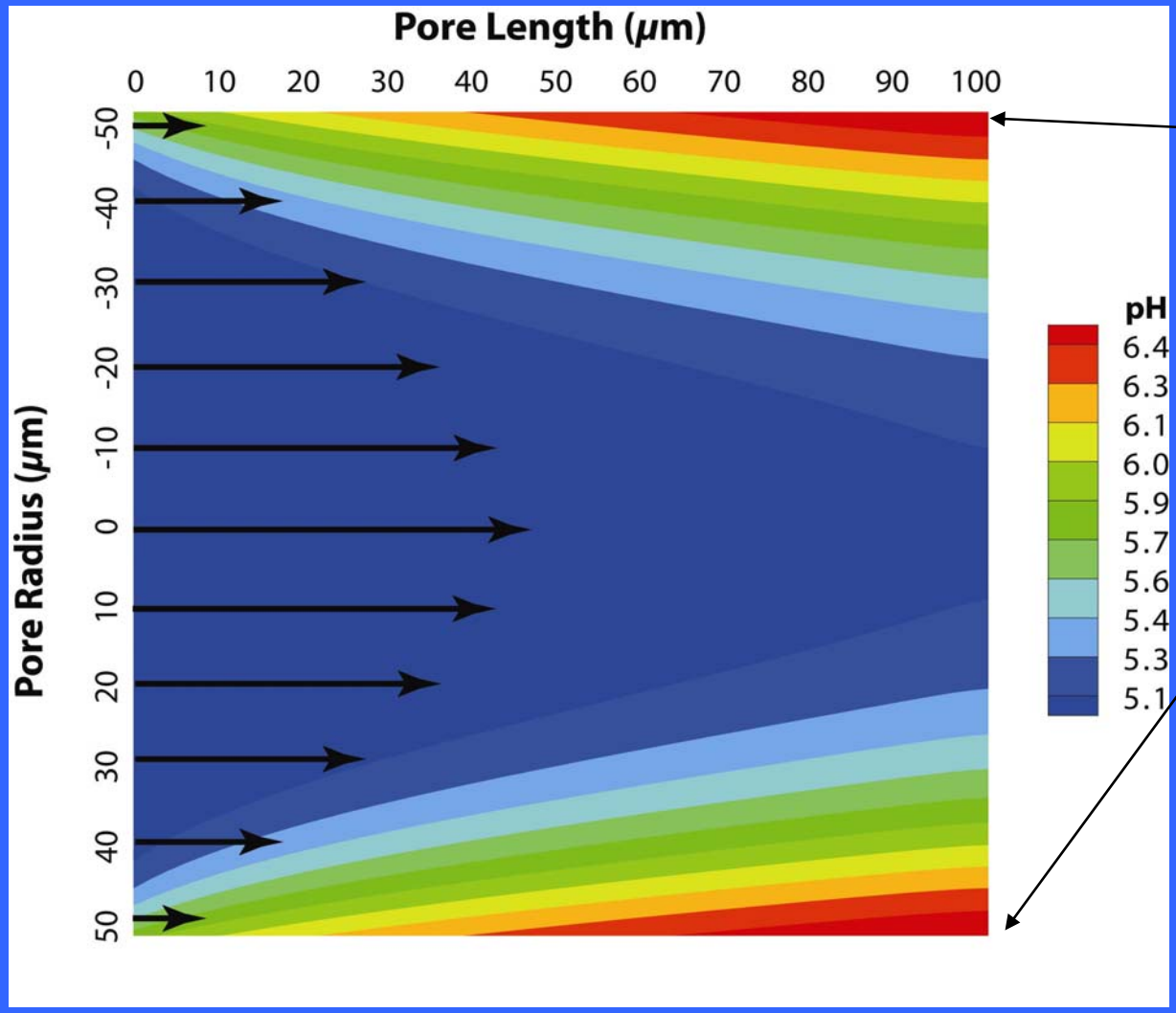


Velocity field from Poiseuille's Law: Analogue of flow heterogeneity

Verify 2D axisymmetric flow and transport using analytical solution for Taylor-Aris dispersion

Numerical results for reactive flow in a single pore in calcite (pH perturbation)

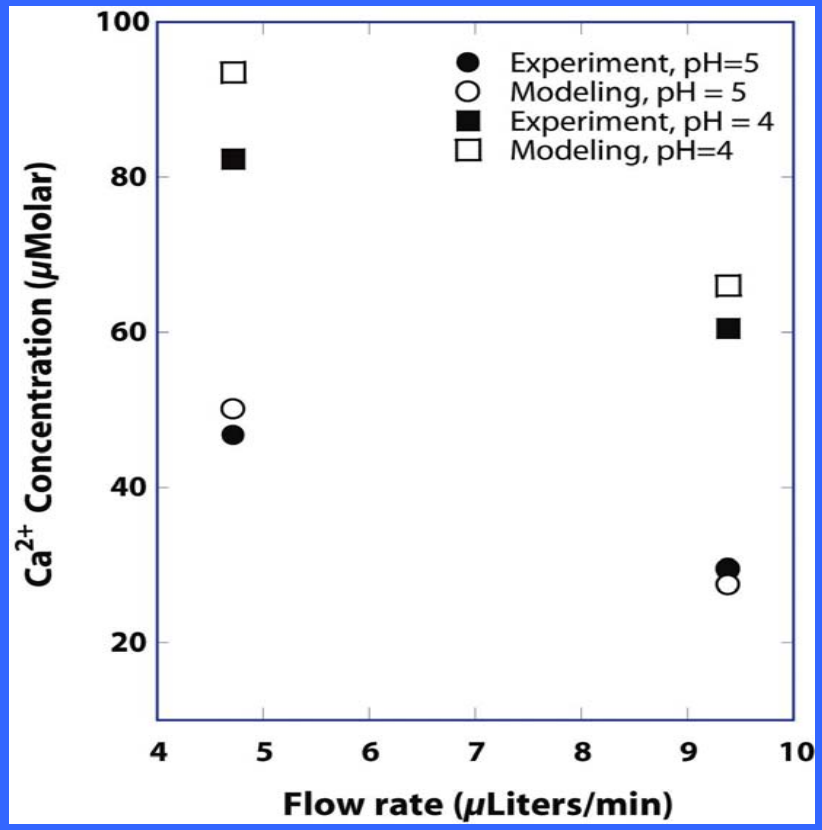
Axisymmetric cylindrical geometry for pore, with dissolution only at pore walls

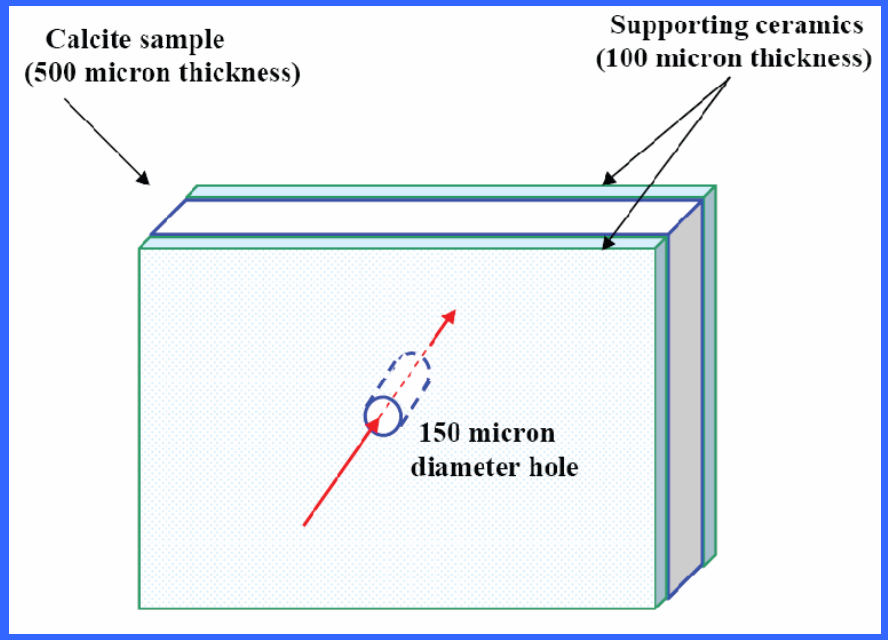


Effluent pH from flux-weighted average

When gradients are present, effective rate < rate adjacent to mineral

Comparison of Experimental and Modeling Results

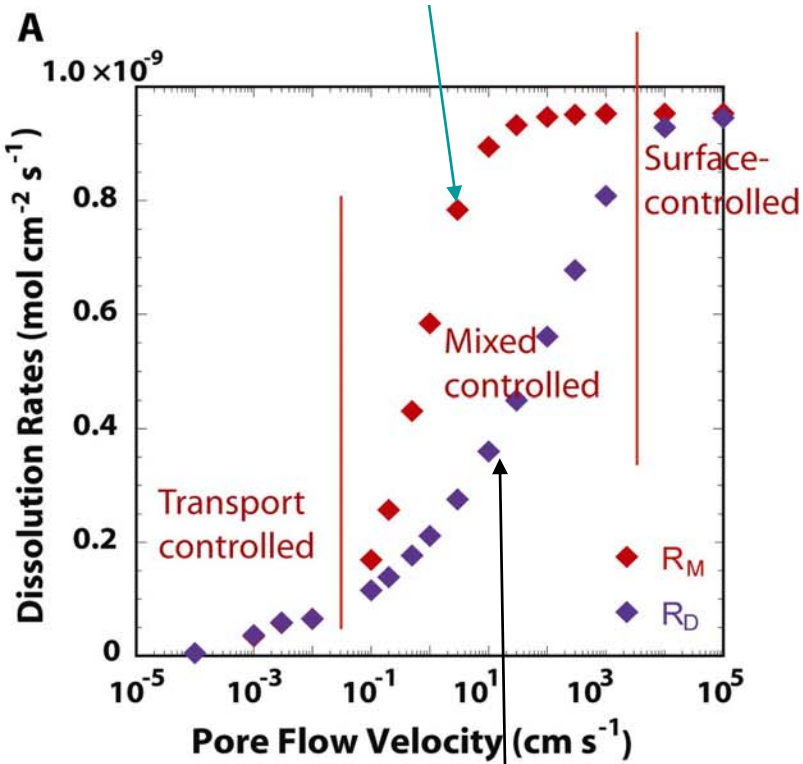


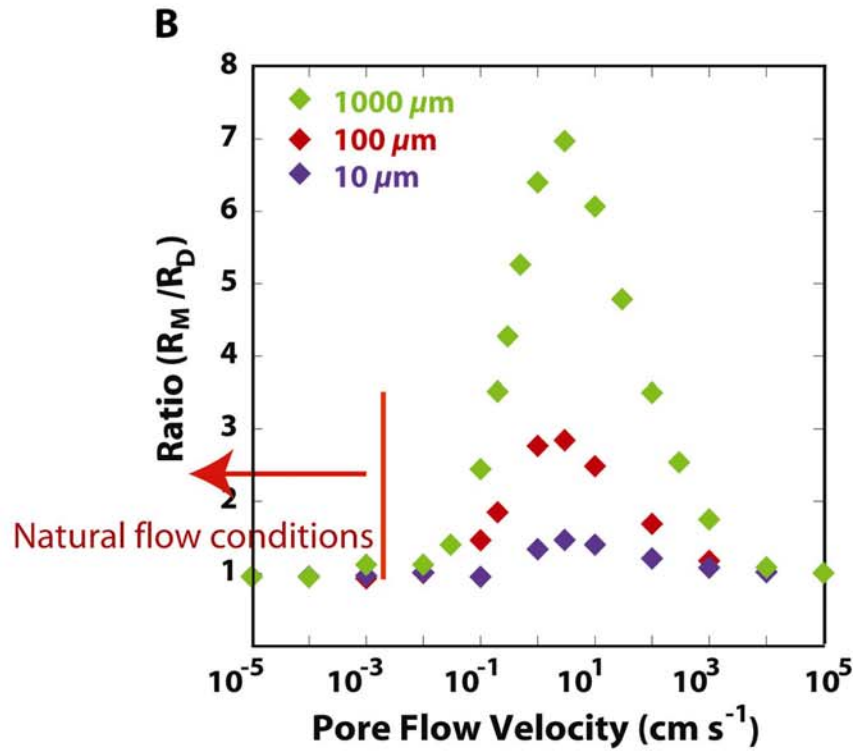


Single pore is drilled in a crystal of Iceland spar

Scale Dependence of Effective Rates

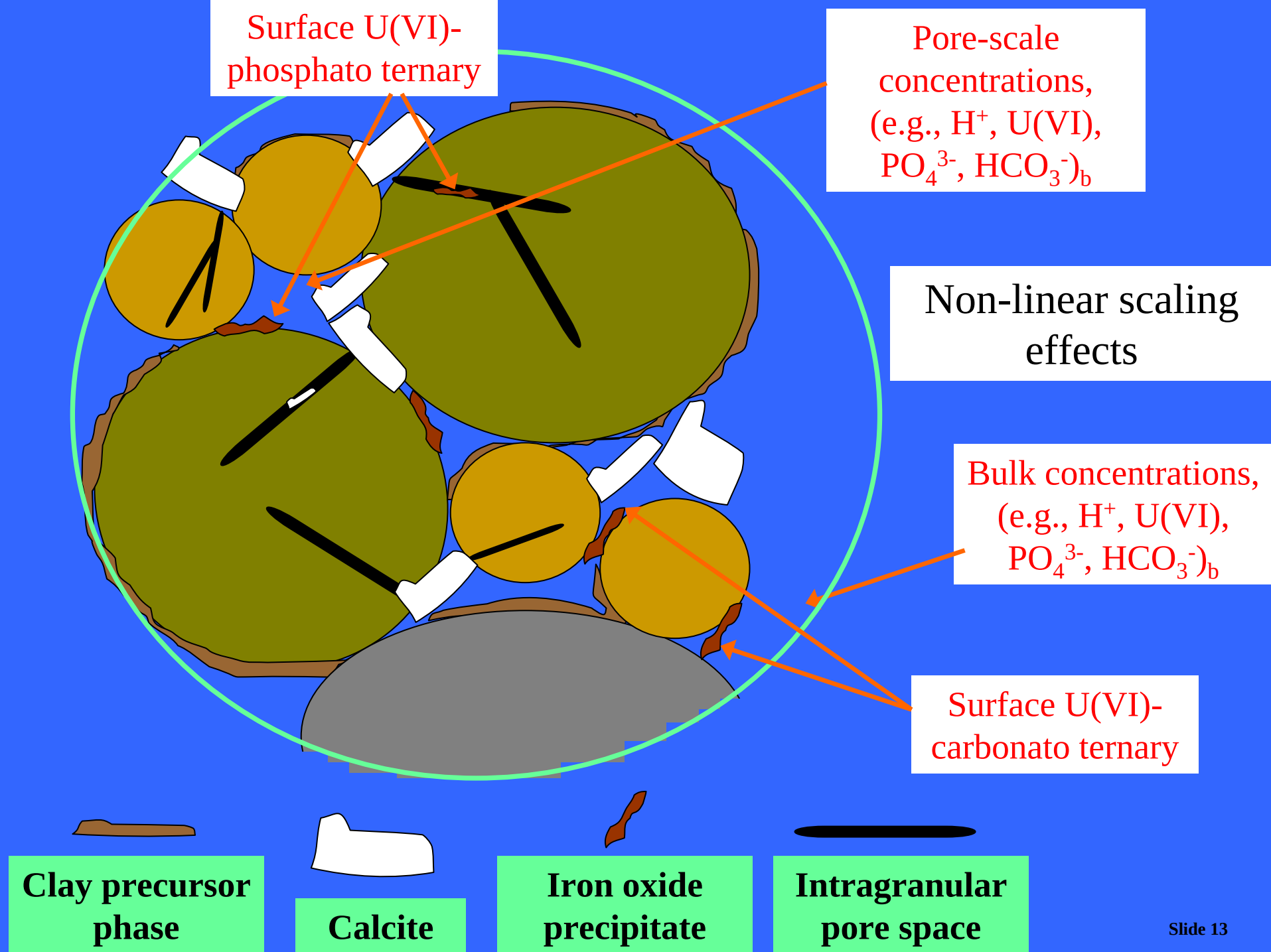
Rates for well-mixed pore



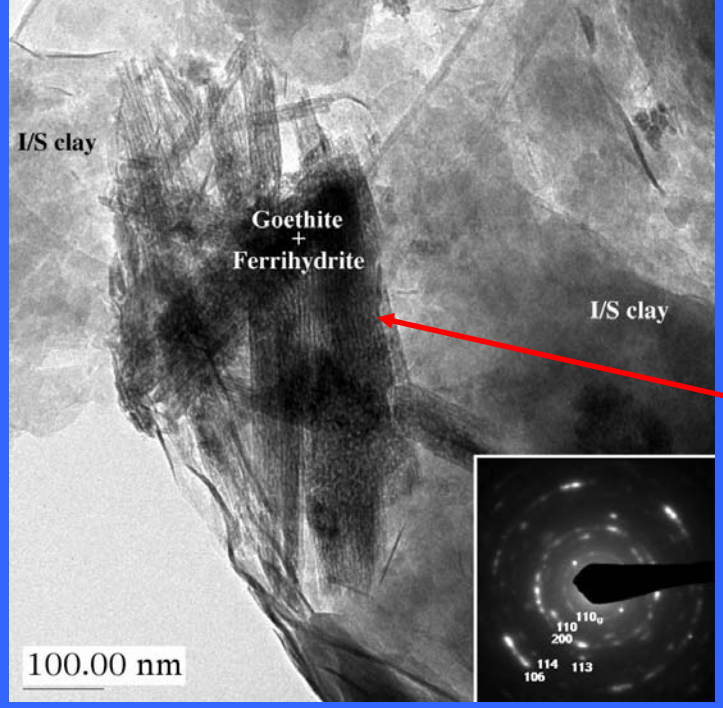


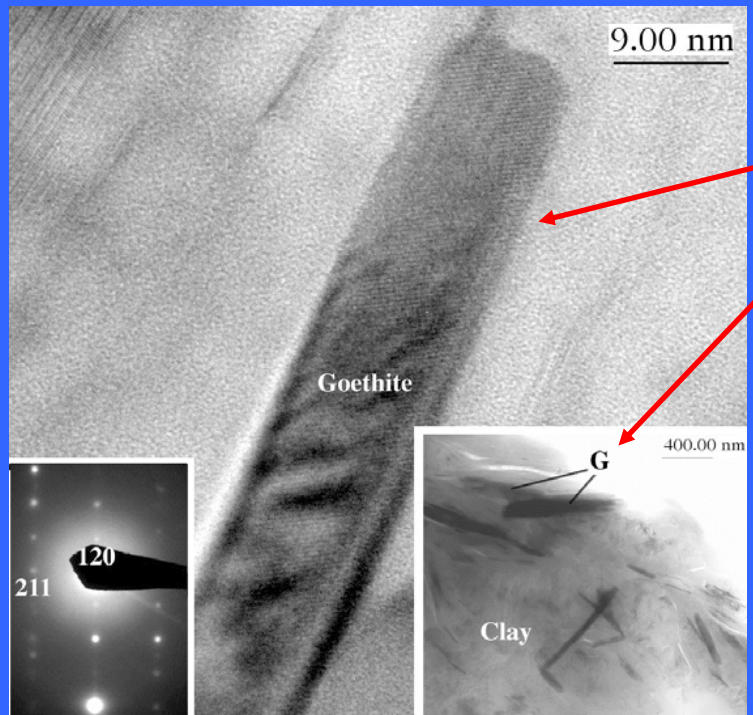
Rates for pore using realistic diffusion

Ratio of rate with complete mixing versus effective rate where gradients may be present


Surface U(VI)-phosphato ternary
Pore-scale concentrations, (e.g., H^+, U(VI), PO_4^{3-}, HCO_3^-)$_b$
Non-linear scaling effects
Bulk concentrations, (e.g., H^+, U(VI), PO_4^{3-}, HCO_3^-)$_b$
Surface U(VI)-carbonato ternary
Clay precursor phase
Calcite
Iron oxide precipitate
Intragranular pore space

Naturita sediment grain coatings

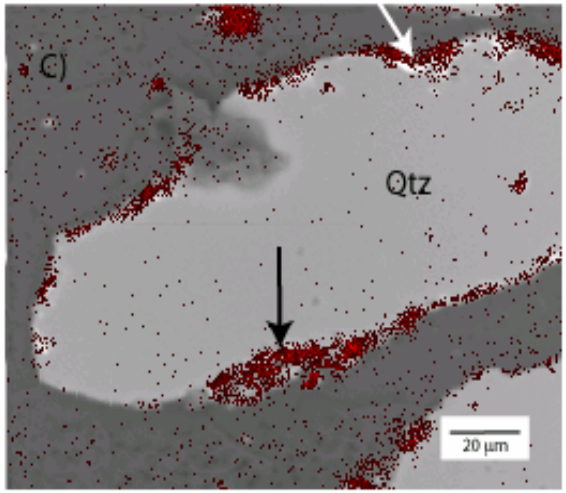




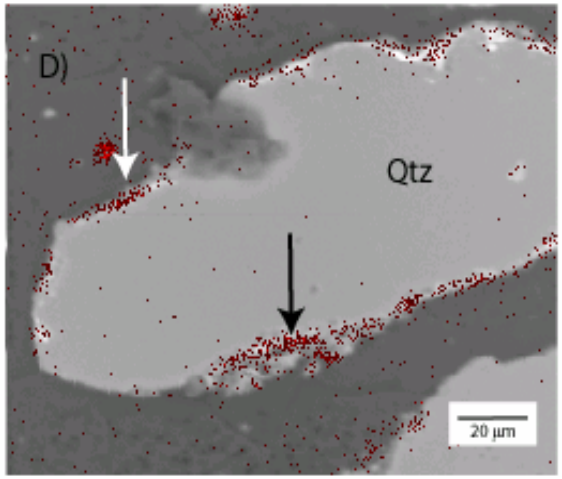
a) Low-magnification TEM image showing rafts of goethite and ferrihydrite immersed in surface coating of illite/smectite (I/S) clay.

b) Bright-field TEM images showing needle-like goethite (G) crystals immersed in I/S clay matrix.

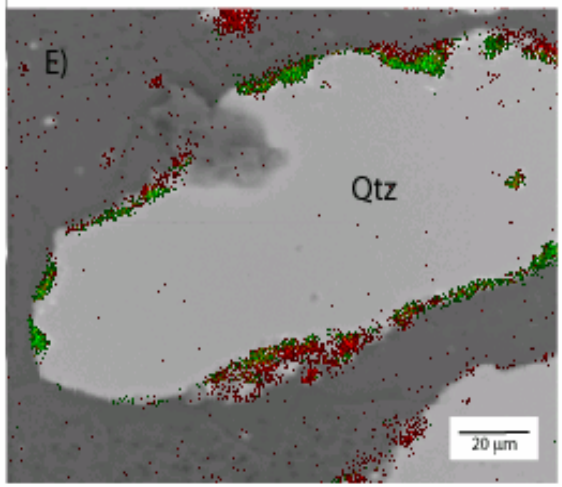
Jove-Colon et al., 2006, GCA, submitted



Combined BSEI and X-ray map of Al (red). Al possibly delineates predominant amounts of clay (arrows) present at the grain rim area.



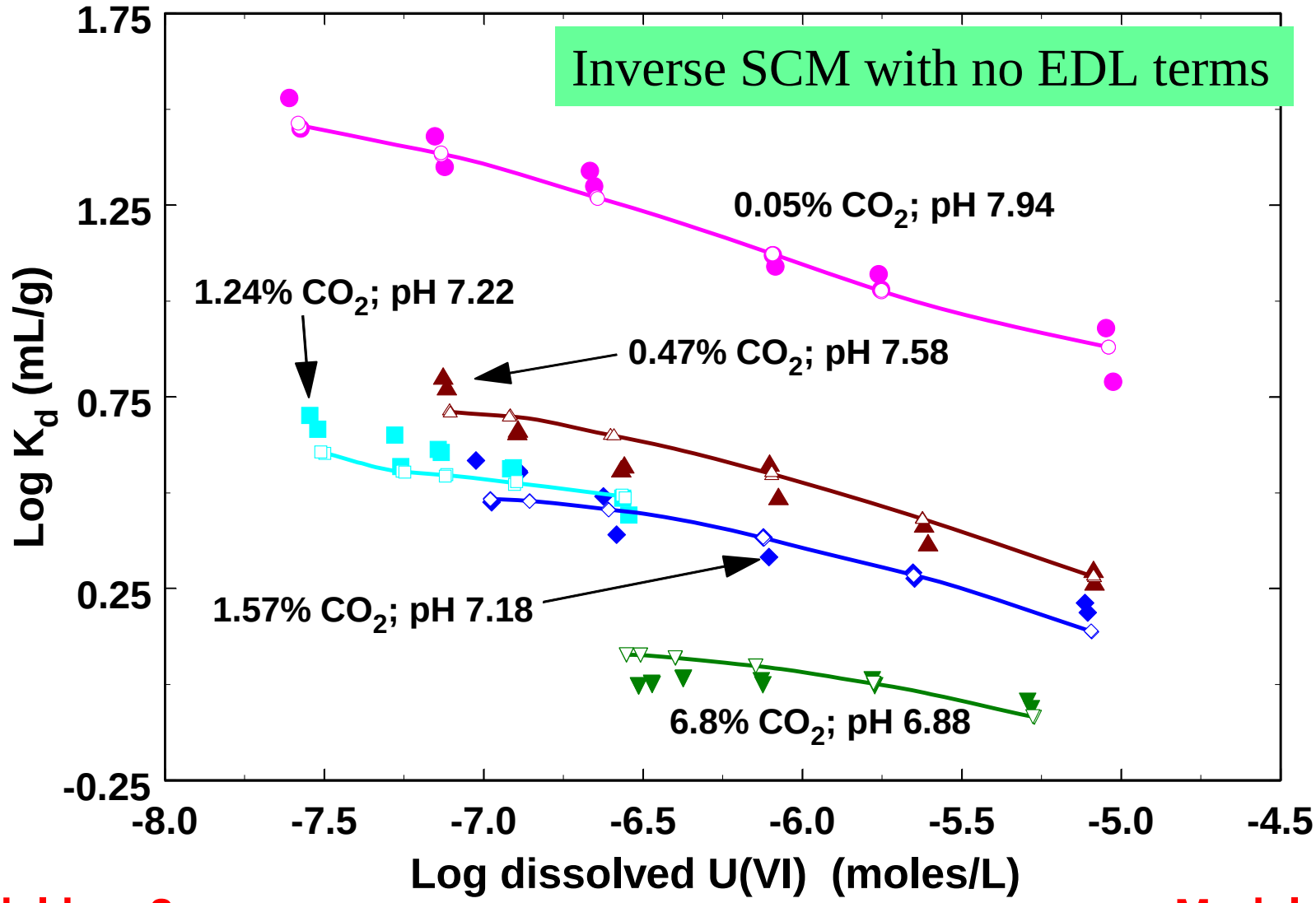
Combined BSEI and X-ray map of K (red). The apparent correlation of K and AL delineates the possible presence of an outer clay (arrows) bordering the quartz grain.



Combined X-ray map of Al (red) and Fe (green). Notice the presence of Fe (probably as an oxi-hydroxide) underlying the Al (Clay?) rim.

Naturita aquifer sediment is predominantly, quartz, feldspar, and calcite, with minor amounts of other mineral phases

Images from Jove-Colon et al., 2006, GCA, submitted.



Model has 2 surface reactions:

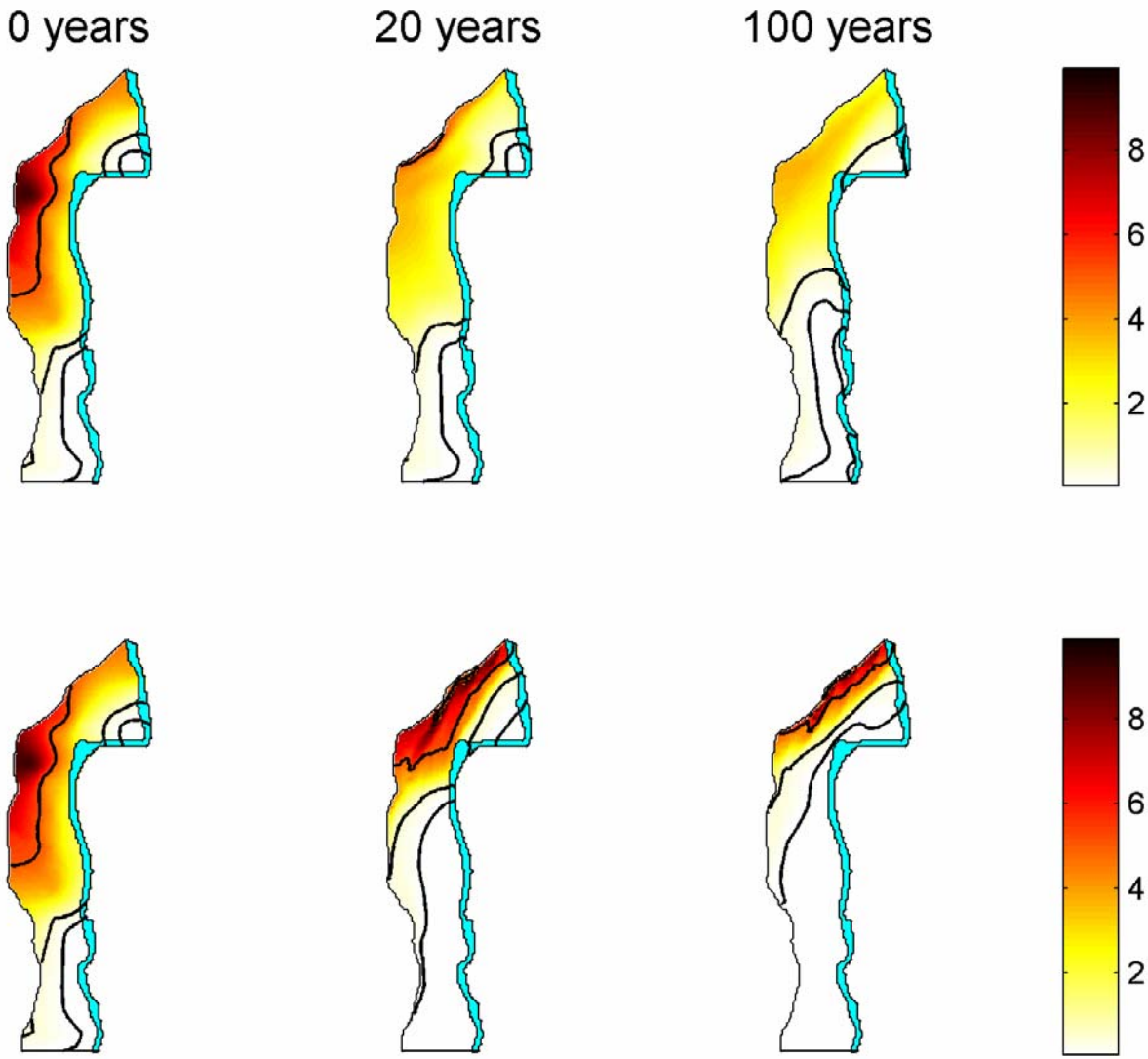
$$\equiv SOH + UO_2^{2+} = \equiv SOUO_2^{+} + H^{+}$$

$$\equiv SOH + UO_2^{2+} = \equiv SOUO_2OH + 2H^{+}$$

Model has 3 site types

Davis et al., 2004, GCA, 68, 3621-3641

Simulated U(VI) concentrations, μM



SCM

Constant K_d = 0.26mL/g