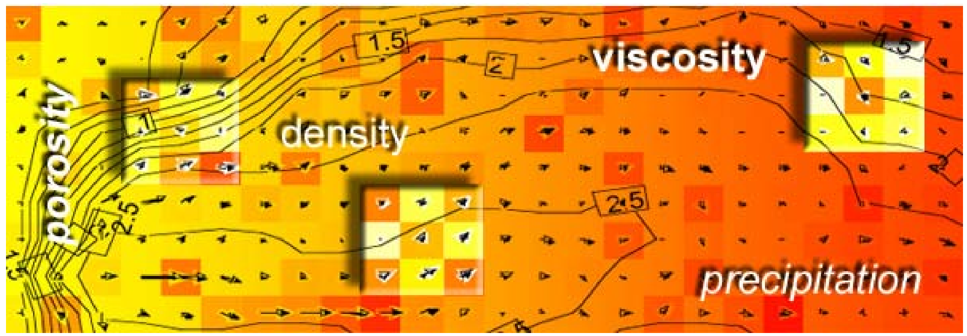
SAND2005-7298P

# Characterization and Mechanisms of Radionuclide Sorption in Soils

## JCN Y6464




**Project Review for**
**Advisory Committee on Nuclear Waste**
**and**
**U.S. Nuclear Regulatory Commission**

**November 15, 2005**
**Sandia National Laboratories**
**Albuquerque, New Mexico**

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company,
for the United States Department of Energy's National Nuclear Security Administration
under contract DE-AC04-94AL85000.

# Project History

**JCN W6811**
**Prediction of Radionuclide Sorption in Soils**
Completed June 2002
Deliverables:
    4 NUREG reports and numerous journal and book articles, and proceedings papers

**JCN Y6464**
**Characterization and Mechanisms of Radionuclide Sorption in Soils**
Started July 2002
Deliverables:
    Annual reports, due October 2003 and December 2004
    Topical reports, due March 2005, June 2005, and September 2005

# Research Objective

The major objective of this project is to provide a defensible, science-based understanding of radionuclide migration and retardation for assessing contaminant transport in the environment. Current PA models use simplified conceptual models for radionuclide retardation that are based on linear and reversible partition coefficients ($K_D$'s) measured for a specific set of experimental conditions, which usually are laboratory measurements of soil samples. Unfortunately, experience shows that this approach often fails to correlate with field measurement of actual transport. The reason is that the experimental $K_D$'s represent localized properties and are sometimes not applicable over time and at other locations considering the range of nonlinear geochemical phenomena and chemical conditions that can significantly affect radionuclide transport. Therefore it is critical to understand and model radionuclide retardation processes and mechanisms in soils.

- Generalization of chemical sorption models—beyond $K_D$ approach
- Evaluation of uncertainty in sorption parameters
- Characterization of sorption sites in soils
- Development of predictive tools including molecular modeling

# Research Tasks

- **Task 1** Preparation of a Work Plan
  - Completed July 2002
- **Task 2** Molecular Modeling of Radionuclides on Clay Minerals
  - Extension of Cs-Cl sorption models; emphasis on $UO_2^{2+}$ sorption
- **Task 3** Probabilistic Analysis of Sorption Parameters and Hydrologic Flow
  - Coupled chemistry and hydrology with reactive transport code; new emphasis on SCM models in GMS codes
- **Task 4** Characterization of Sorption on Soil Minerals at One or More Contaminant Sites
  - Extension of previous effort on Naturita site; recent emphasis on Cape Cod site (with USGS)
- **Task 5** Technical Support for Interagency MOU on Multimedia Environmental Modeling
  - Add-on task to represent NRC in interagency effort to describe state-of-the-art of reactive transport modeling

# Deliverables in FY04-FY05

## *NUREG Reports*

Altman, S.J., Reno, M.D., Rivers, M.L., and Cygan, R.T. (2005) Characterization of pore space and adsorption sites on aggregatre soil samples using synchrotron X-ray computerized microtomography. ***U.S. Nuclear Regulatory Commission Report***, NUREG/CR, p. 7-6. U.S. Nuclear Regulatory Commission, Washington D.C.

Criscenti, L.J., Eliassi, M., Cygan, R.T., Jové Colón, C.F., and Goldberg, S. (2005) Modeling adsorption processes: Issues in uncertainty, scaling, and prediction. ***U.S. Nuclear Regulatory Commission Report***, NUREG/CR, p. 6-12. U.S. Nuclear Regulatory Commission, Washington D.C.

Cygan, R.T., Siegel, M.D., and Criscenti, L.J. (2005) Proceedings of the international workshop on conceptual model development for subsurface reactive transport modeling of inorganic contaminants, radionuclides, and nutrients. ***U.S. Nuclear Regulatory Commission Report***, NUREG/CR, p. 5-2. U.S. Nuclear Regulatory Commission, Washington D.C.

Greathouse, J.A. and Cygan, R.T. (2005) Molecular dynamics simulation of uranyl(VI) sorption equilibria onto an external montmorillonite surface. ***U.S. Nuclear Regulatory Commission Report***, NUREG/CR, p. 5-6. U.S. Nuclear Regulatory Commission, Washington D.C.

Hammond, G.E. and Cygan, R.T. (2005) Geoquìmico: An interactive tool for comparing sorption conceptual models (surface complexation modeling vs. $K_D$). ***U.S. Nuclear Regulatory Commission Report***, NUREG/CR, p. 23. U.S. Nuclear Regulatory Commission, Washington D.C.

Jové Colón, C.F., Sanpawanitchakit, C., Xu, H., Cygan, R.T., Davis, J.A., Meece, D.M., and Hervig, R.L. (2005) A combined analytical study to characterize uranium soil and sediment contamination: The case of the Naturita UMTRA site and the role of grain coatings. ***U.S. Nuclear Regulatory Commission Report***, NUREG/CR, p. 6-3. U.S. Nuclear Regulatory Commission, Washington D.C.

# Deliverables in FY04-FY05

## *Journal Articles*

Altman, S.J., Rivers, M.L., Reno, M., Cygan, R.T., and McLain, A.A. (2004) Characterization of sorption sites on aggregate soil samples using synchrotron X-ray computerized microtomography. ***Environmental Science and Technology***, 39, 2679-2685.

Altman, S.J., Peplinski, W.J., and Rivers, M.L. (2005) Evaluation of synchrotron X-ray computerized microtomography for the visualization of transport processes in low-porosity materials. ***Journal of Contaminant Hydrology***, 78, 167-183.

Criscenti, L.J. (2004) Adsorption processes: At what spatial scale do we need to understand them? **Proceedings of the 11th International Symposium on Water-Rock Interaction, WRI-11**, 27th June – 2 July 2004, Saratoga Springs, NY. Eds. R. B. Wanty and R. R. Seal, A. A. Balkema Publishers, NY, p. 909-916.

Cygan, R.T., Liang, J.-J., and Kalinichev, A.G. (2004) Molecular models of hydroxide, oxyhydroxide, and clay phases and the development of a general force field. ***Journal of Physical Chemistry B***, 108(4), 1255-1266.

Greathouse, J.A. and Cygan, R.T. (2005) Molecular dynamics simulation of uranyl(VI) adsorption equilibria onto an external montmorillonite surface. ***Physical Chemistry Chemical Physics***, 7(20), 3580-3586.

Jové Colón, C.F., Sanpawanitchakit, C., Xu, H., Cygan, R.T., Davis, J.A., Meece, D.M., and Hervig, R.L. (2002) A combined analytical study to characterize uranium soil contamination: The case of the Naturita UMTRA site and the role of grain coatings. ***Geochimica et Cosmochimica Acta***, to be submitted.

# Task 2

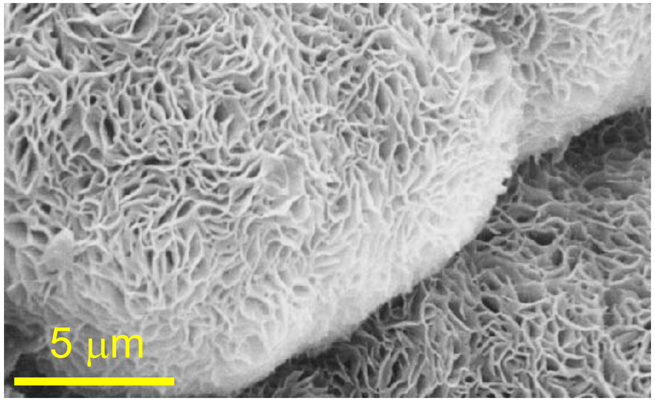
# Molecular Modeling of Radionuclides on Clay Minerals

**Jeffery A. Greathouse and Randall T. Cygan**

# Atomistic Simulation of Clay Minerals

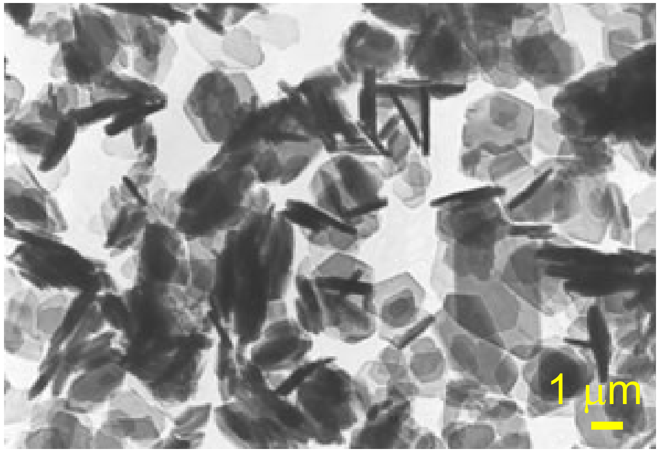
## Crystal structure models of layered minerals are typically unknown

- Nanocrystalline (cryptocrystalline) materials (less than 1 μm grain size)
- No large single crystals for X-ray diffraction refinements
- Hydrogen positions are often unknown (require neutron diffraction analysis) and control sorption process
- Complex chemistry with multicomponent systems, cation disorder, and vacancies
- Low symmetry (monoclinic or triclinic)
- Stacking disorder complicates structural analysis

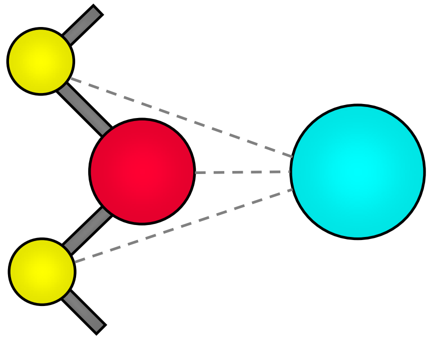



## Atomistic simulations of these minerals are non-trivial

- Require accurate empirical energy forcefield; quantum methods are too costly
- Large unit cells or simulation supercells are required (>100 atoms); precludes QM
- Significant electrostatic fields associated with layer structure
- Validation of models is difficult



# Clayff Forcefield Parameters for Modeling Clays and Hydrous Phases



Fully **flexible** model for exchange of momentum and energy among all species

$$E = \sum_i \sum_j (A_{ij}/r_{ij}^{12} - B_{ij}/r_{ij}^{6} + q_i q_j / r_{ij})$$

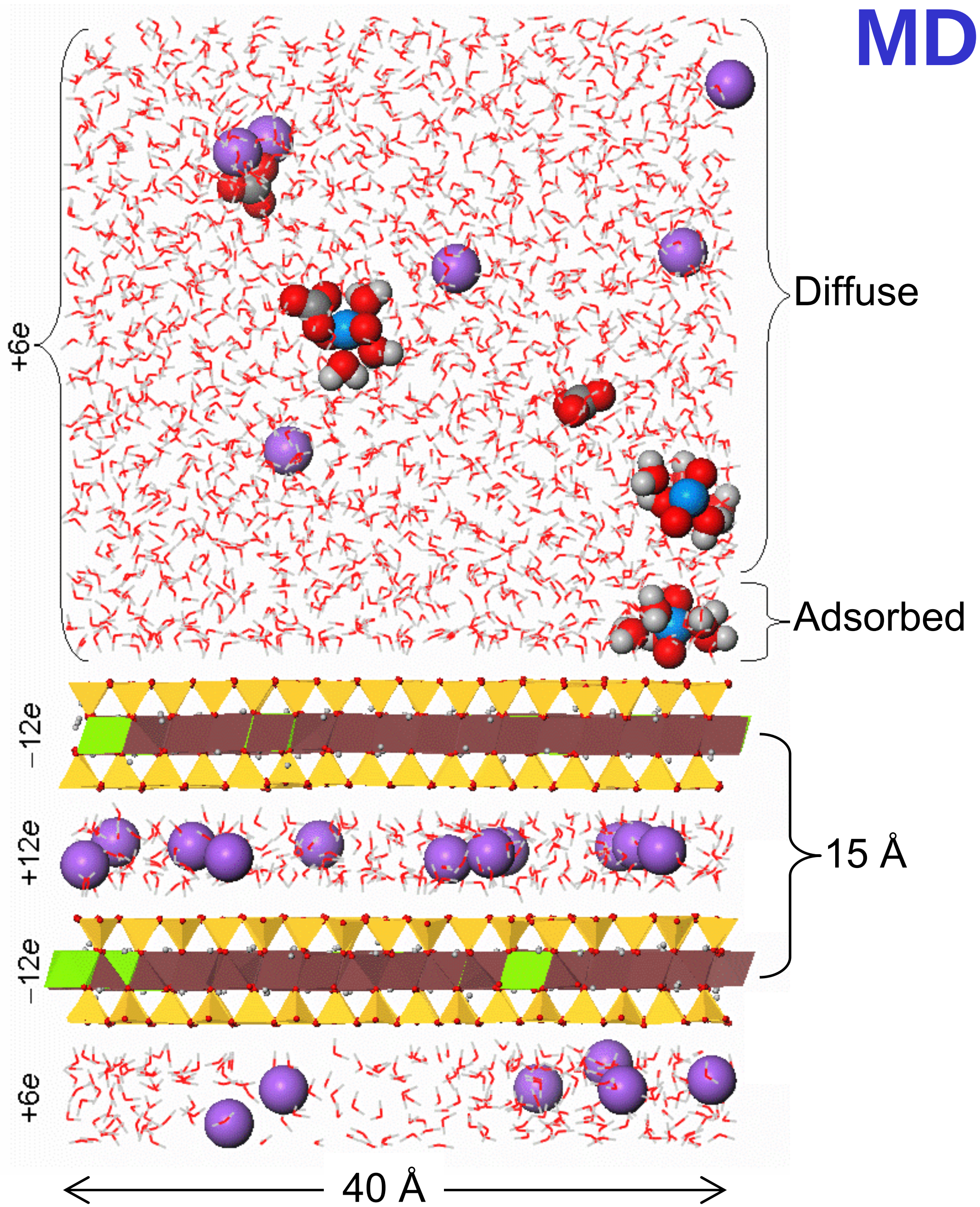
Short-range repulsion Van der Waals Coulombic

- SPC flexible water model and quantum-derived (ESP and Mulliken) partial charges
- Includes delocalization of charge at tetrahedral and octahedral substitution sites
- LJ terms parameterized from observed structures of simple oxides and hydroxides using GULP (Gale 1997)

**Input structures:** oxides, hydroxides, oxyhydroxides

quartz, corundum, diaspore, boehmite, gibbsite, brucite, goethite, lepidocrocite, portlandite, *etc.*

# MD Methods




## Aqueous region

- $[Na^+]$ = 0.162 M
- $[UO_2CO_3]$ = 0.081 – 0.162 M

## Clay

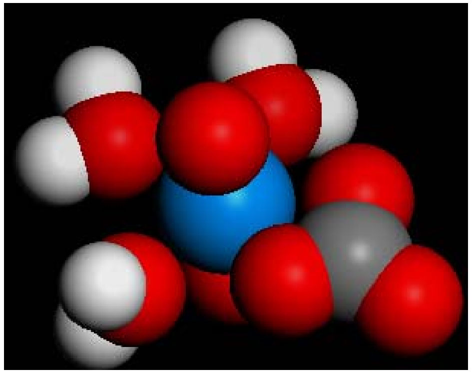
- Pyrophyllite (layer charge = 0)
- Montmorillonite (–0.375 *e* and –0.750 *e* per unit cell)

## MD Simulation

- LAMMPS software
- NVT, 300 K
- 3D Periodic Boundary Conditions
- Vacuum gap

# Simulation *versus* Experiment

| Property | Simulation | Experiment |
| --- | --- | --- |
| Unit cell data | Lattice constants (constant P simulation) | Diffraction |
| Local atomic coordination | Radial distribution functions | EXAFS |
| Interfacial structure | Atomic density profiles | X-Ray Scattering |
| Vibrational motion | Power spectra | IR/Raman |



# Forcefield Parameters

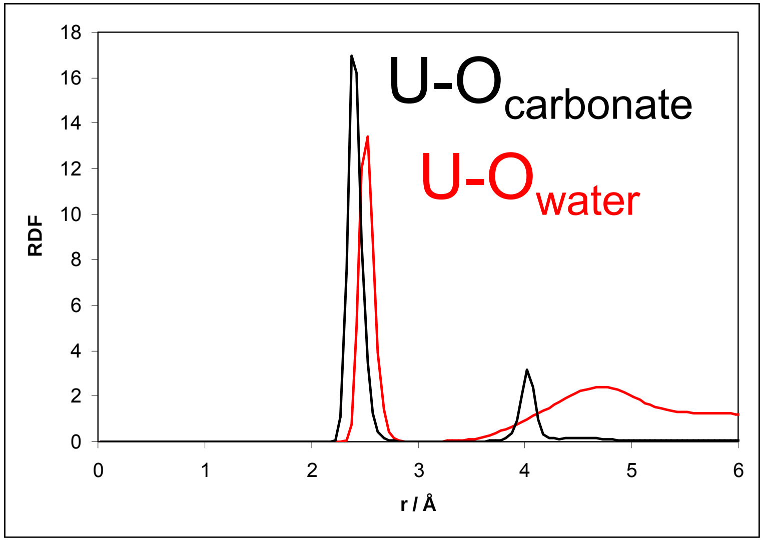
| Species | Atom | Charge / *e* |
|---|---|---|
| Water (Flexible SPC) | O | –0.82 |
| | H | 0.41 |
| Uranyl (Guilbaud & Wipff, 1996) | U | 2.50 |
| | O | –0.25 |
| Carbonate (CVFF) | C | 0.43 |
| | O | –0.81 |
| Clay (Cygan et al, 2004) | Si, Al, Mg | 2.10, 1.58, 1.36 |
| | O (surface) | –1.05 |

**Molecular flexibility for all polyatomics and clay**

# Analysis of MD Simulation

- Ten simulations (1.0 ns each) data averaging ⇒ 10 ns

- Radial Distribution Functions (RDF): U–O coordination numbers (first shell)



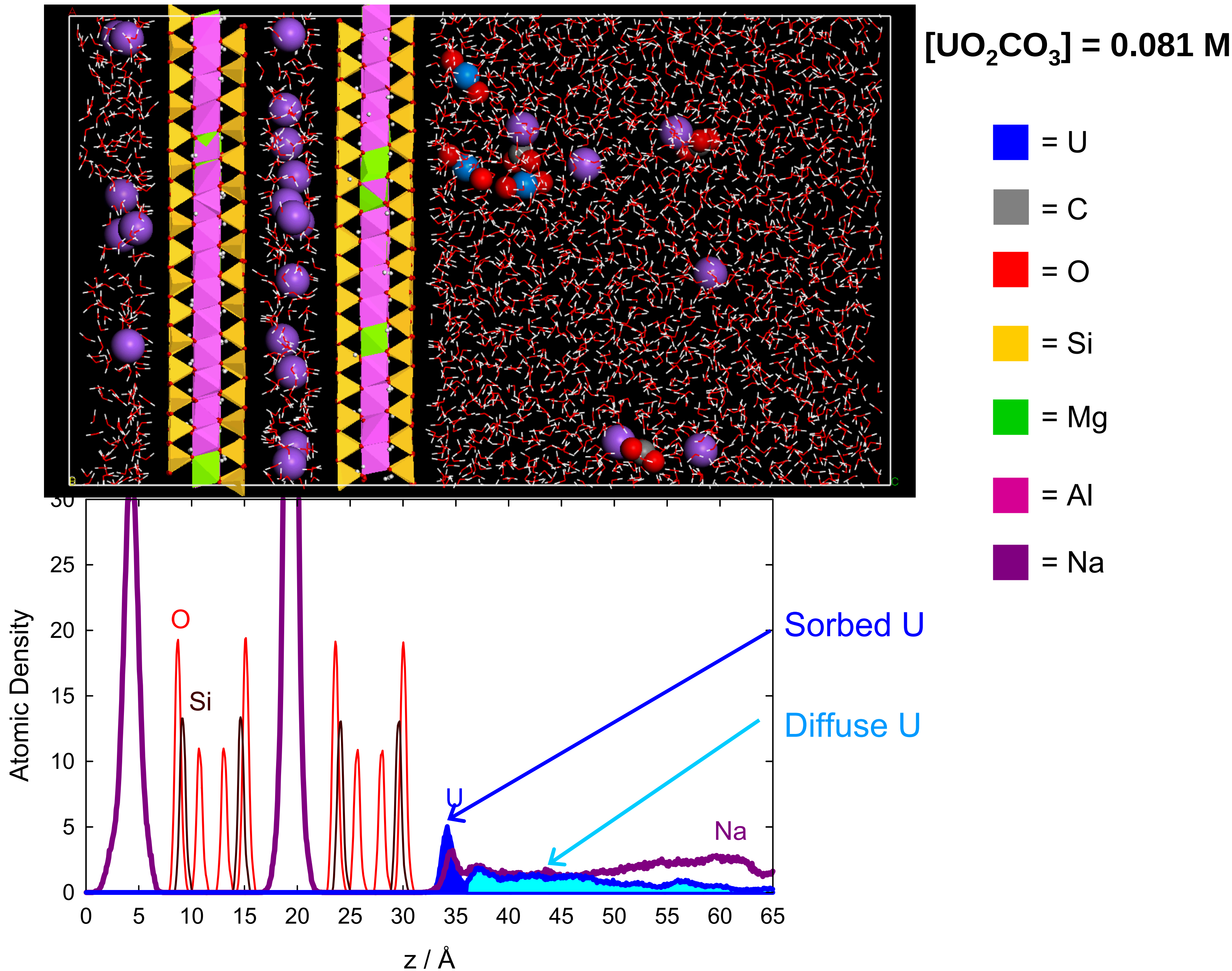

- Aqueous Speciation: $UO_2^{2+}$, $UO_2CO_3^0$, etc.

$$UO_2 + \text{clay} \rightarrow UO_2\text{-clay}$$

- Atomic density profiles: ion adsorption equilibria

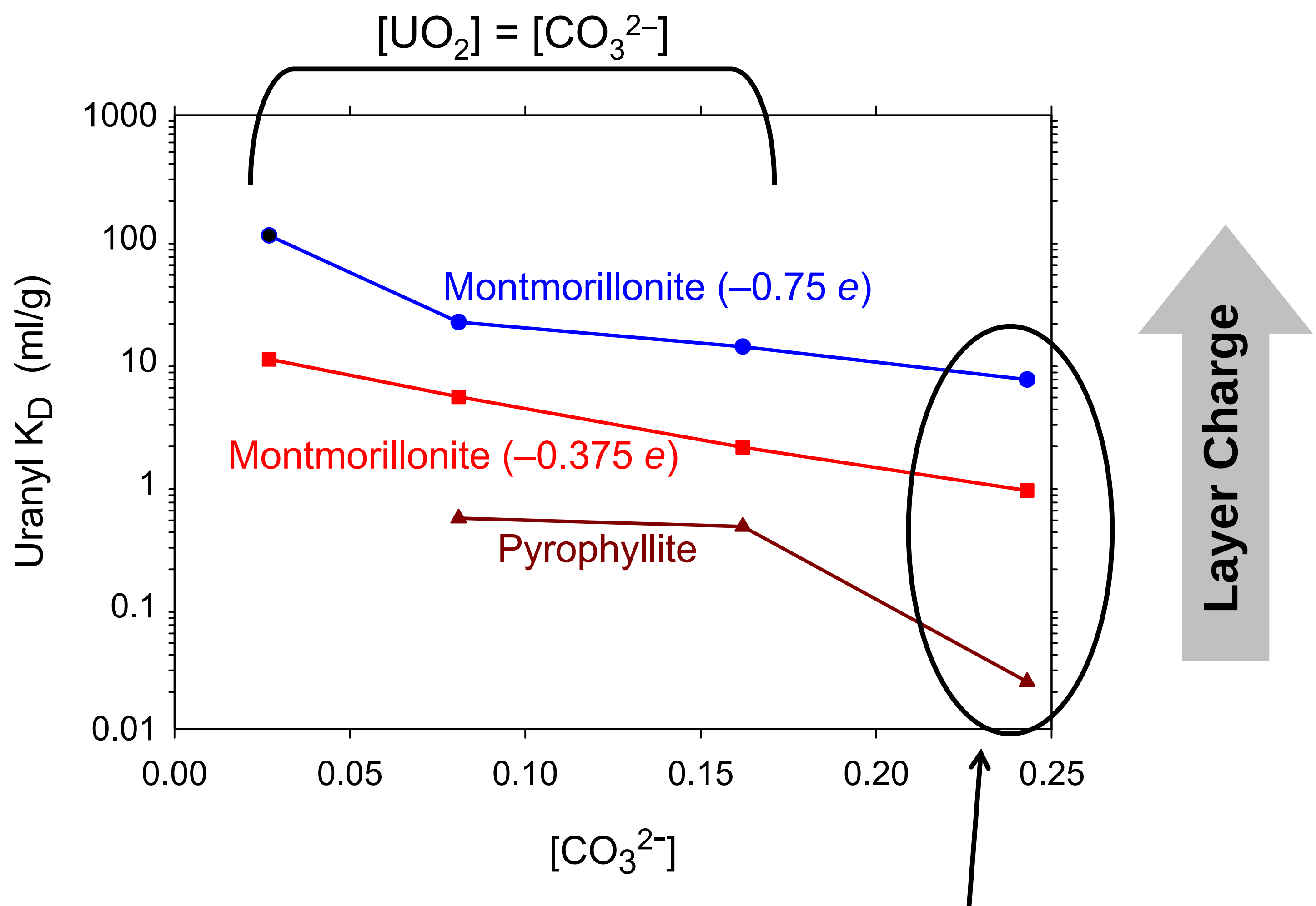
$$K = \frac{\%U_{\text{sorbed}}}{\%U_{\text{diffuse}}}$$

$$K_D = \left(\frac{\%U_{\text{sorbed}}}{\%U_{\text{diffuse}}}\right)\left(\frac{V_{\text{liquid}}}{m_{\text{clay}}}\right)$$



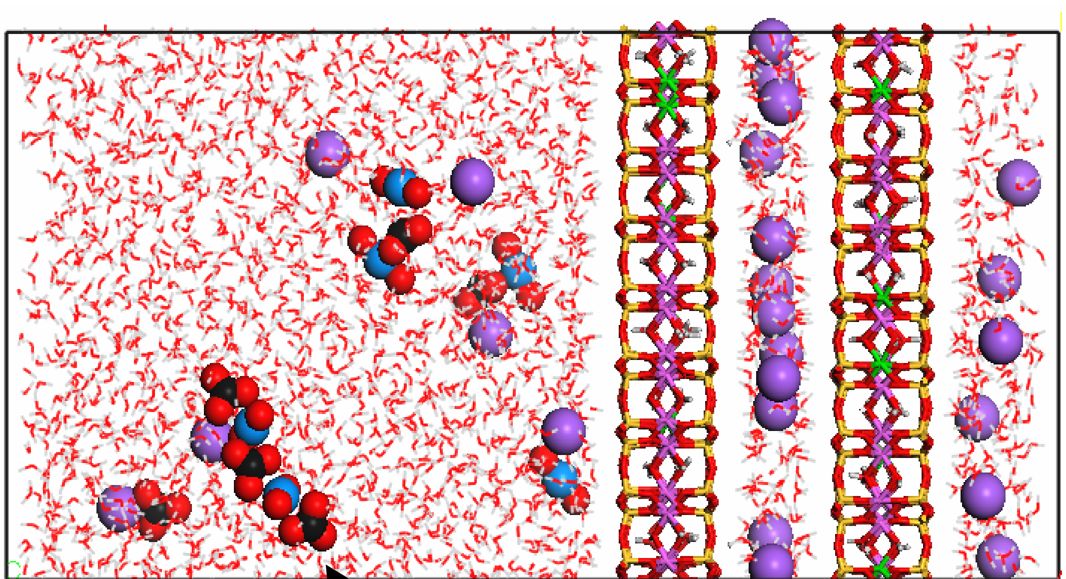
[$UO_2CO_3$] = 0.081 M
= U
= C
= O
= Si
= Mg
= Al
= Na
Atomic Density
z / Å
0
5
10
15
20
25
30
35
40
45
50
55
60
65
O
Si
U
Na
Sorbed U
Diffuse U

# Adsorption Equilibria



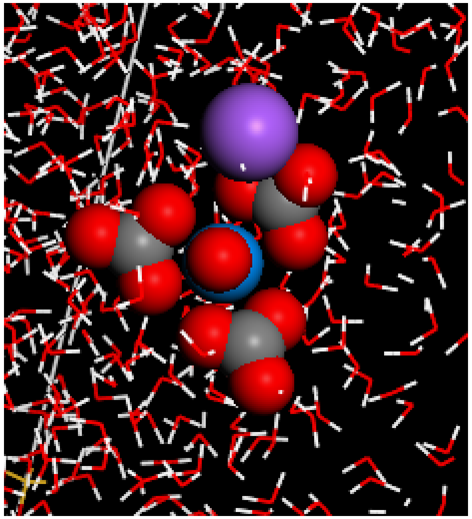

$[UO_2]$ = 0.162 M but $Na_2CO_3$ added to determine effect of additional carbonate

# Carbonato Complexes and Oligomers



$[(UO_2)_2(CO_3)_3]^{2-}$

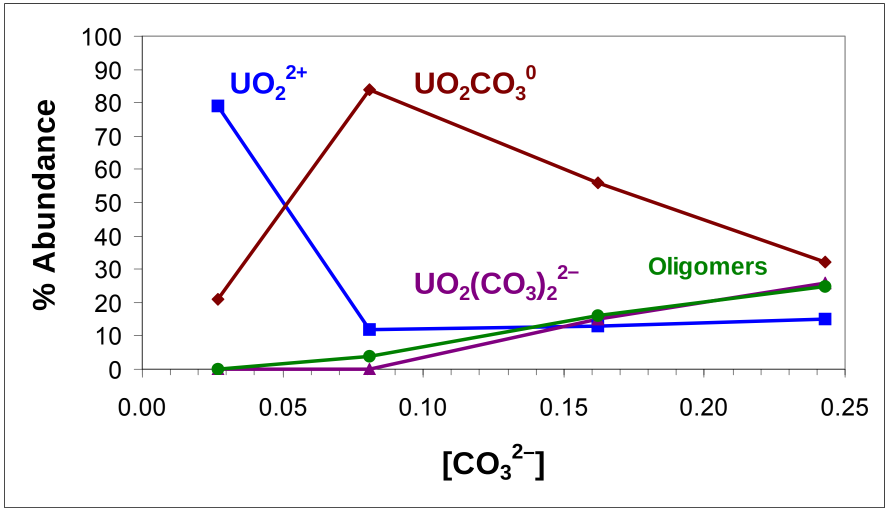
$[UO_2(CO_3)_3]^{4-}$



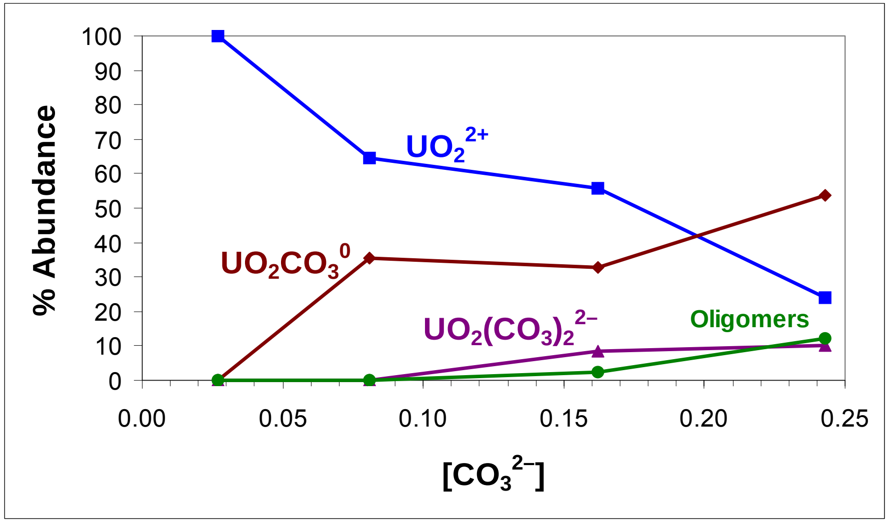
**High carbonate concentration hinders uranyl sorption**
Curtis et al, *App. Geochem*. **2004**; Fuller et al, *ES&T* **2003**.

# Uranyl Speciation in Diffuse Layer

## Pyrophyllite



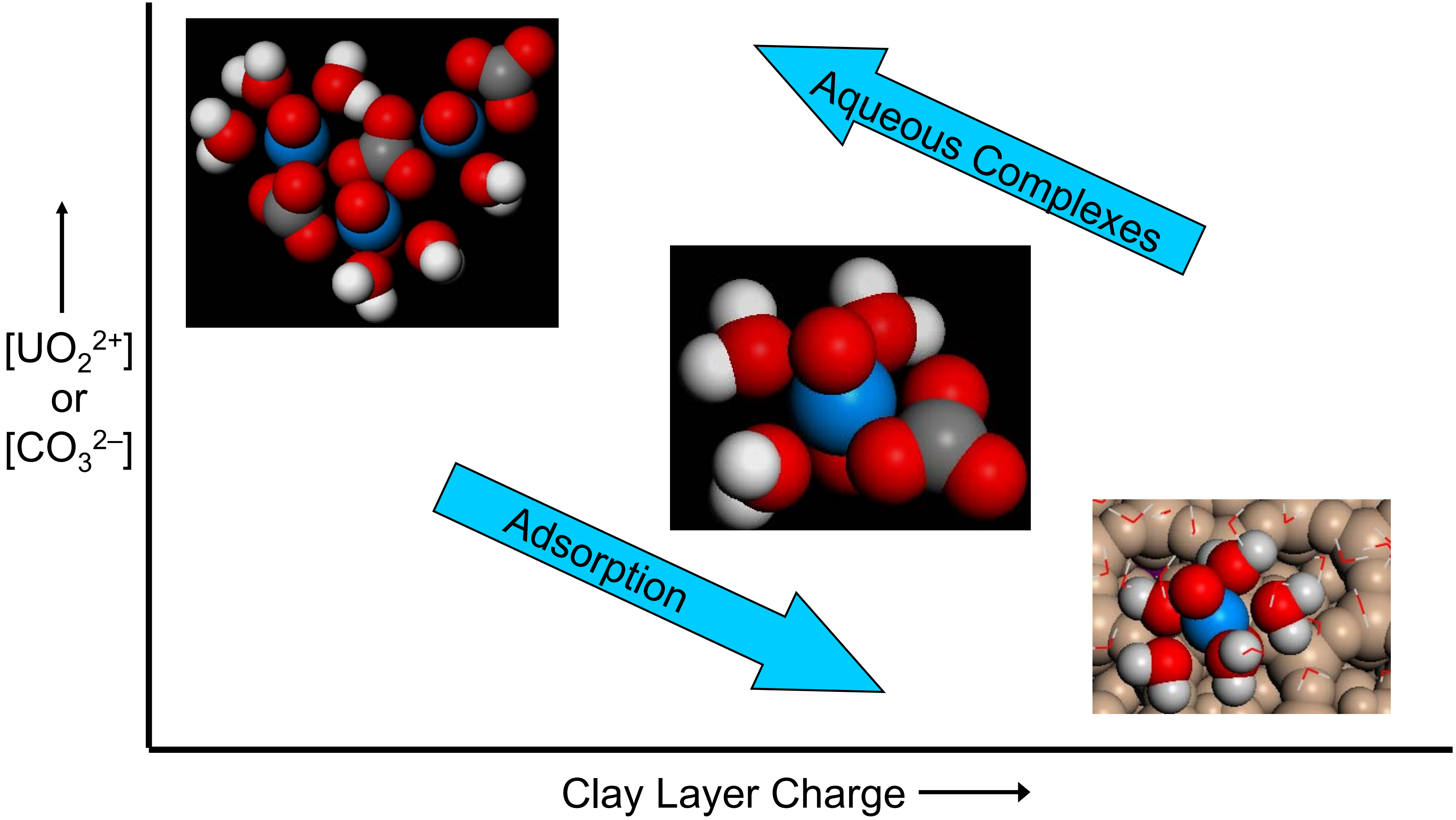

## Montmorillonite




0 → – 0.75

Layer Charge (*e* / clay unit cell)

# Summary of Uranyl Adsorption and Complexation




= O   = C   = U   = H   = Clay

# Task 3

# Probabilistic Analysis of Sorption Parameters and Hydrologic Flow

## Modeling Adsorption Processes: Issues in Uncertainty, Scaling, and Prediction

**Louise J. Criscenti, Glenn E. Hammond, and Randall T. Cygan**

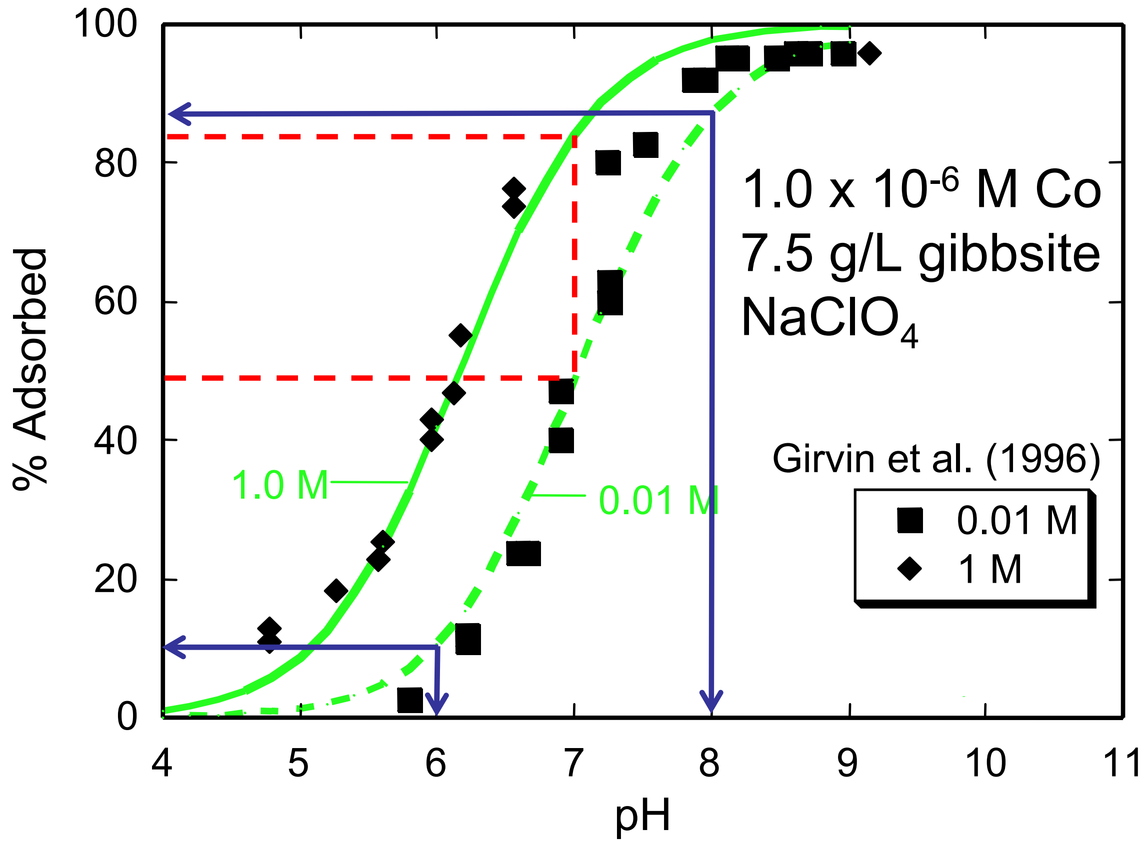
Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company,
for the United States Department of Energy's National Nuclear Security Administration
under contract DE-AC04-94AL85000.

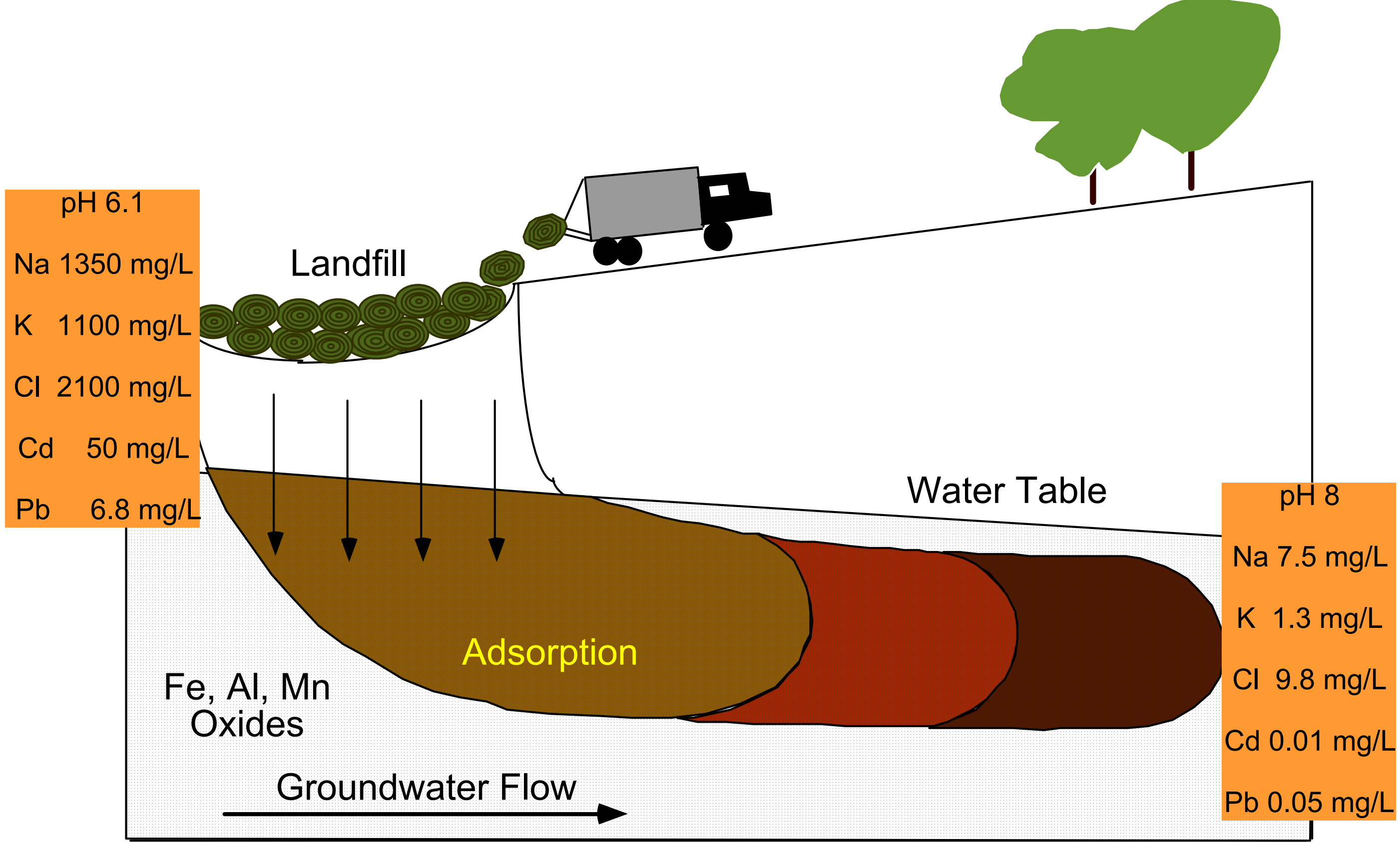
# Field-Scale Adsorption Processes: Why a $K_D$ Model is Insufficient

$$K_D = A_{(ads)}/A_{(aq)}$$

Determined at specific pH, I

Only applicable to measured system






## Reactive-Transport Model

Hydrology: Flow and Transport in Porous Media

Equilibrium Geochemistry:

Aqueous Speciation/Solubility

Adsorption -

$K_D$ ⟷ Surface Complexation

# What are the Uncertainties?

## Geochemical Conceptual Model

- Aqueous speciation scheme for each element
  (e.g., $Ca^{2+}$, $CaOH^{+}$, $CaCO_3^{o}$, $f_{CO2}$)
- Precipitation/dissolution of minerals
  (e.g., calcite, ferrihydrite)
- Equilibrium *versus* kinetic rate laws
- **Adsorption model and parameterization**

- Measurements of field geochemistry
  - Aqueous components
  - Modal distribution of minerals – **what minerals are adsorbing contaminants?**
  - Reactive surface area of solids

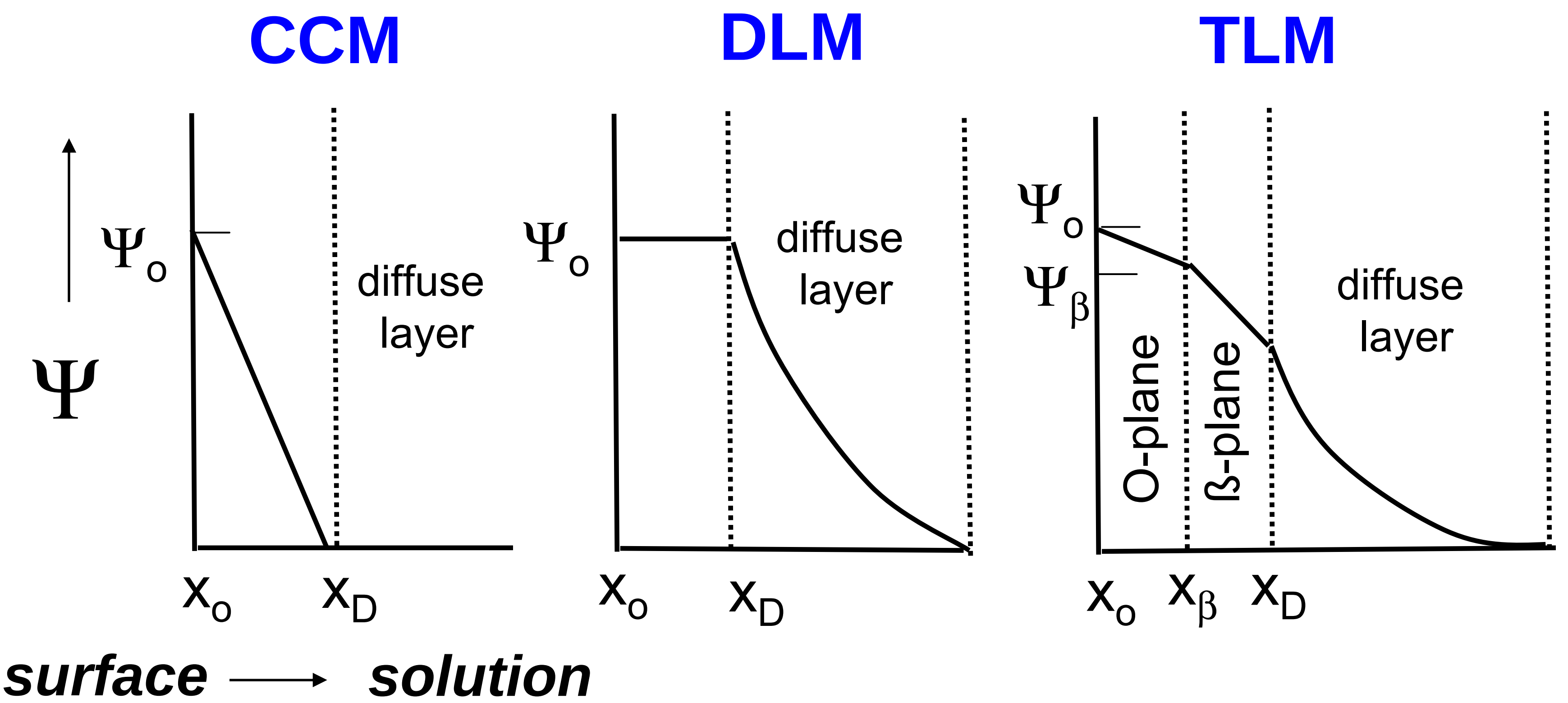
# Modeling the Solid-Water Interface
# Surface Complexation Models (SCM)

- Semi-empirical SCMs
  - Developed to fit bulk adsorption data to soils
    - General Composite Model (GCM)
- Single-Site Models
  - Developed to fit and predict bulk adsorption data to individual minerals
    - Constant Capacitance Model (CCM)
    - Diffuse Layer Model (DLM)
    - Triple Layer Model (TLM)
- Multi-site Models
  - Developed to fit and predict adsorption data to specific mineral surface sites
    - MUSIC, CD-MUSIC Models

# SCM Scaling Issues

- **Mineral/Water Interface**
  - In how much detail do we need to describe this interface?
- **Reaction Stoichiometries**
  - Can we extract acceptable reaction stoichiometries from bulk adsorption data?
  - Do we need to characterize the surface species using spectroscopic or molecular modeling techniques in order to write appropriate reactions?
- **Surface sites**
  - Can we use "average" surface site types to describe adsorption onto a mineral?
  - Can we use "average" surface site types to describe adsorption onto a soil?
- **What level of detail is needed for a *predictive* model of field processes?**

# Modeling the Mineral-Water Interface




$C_{CCM}$, $K^+$, $K^-$

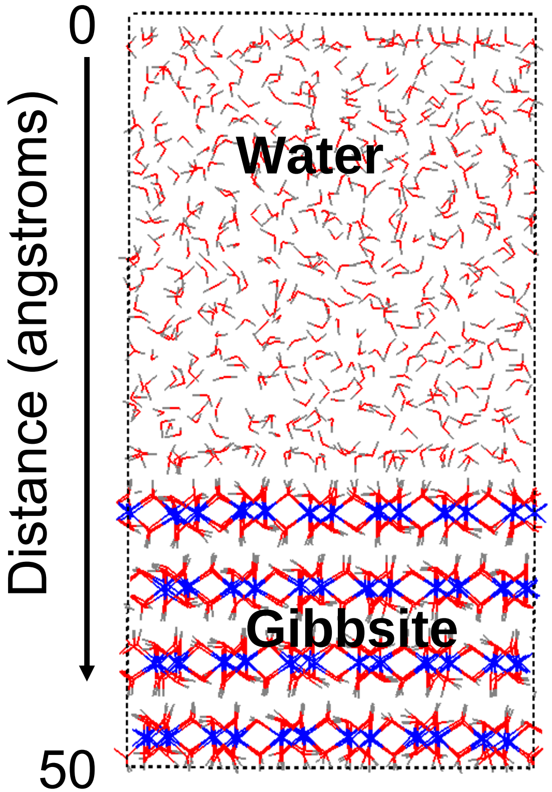
$K^+$, $K^-$

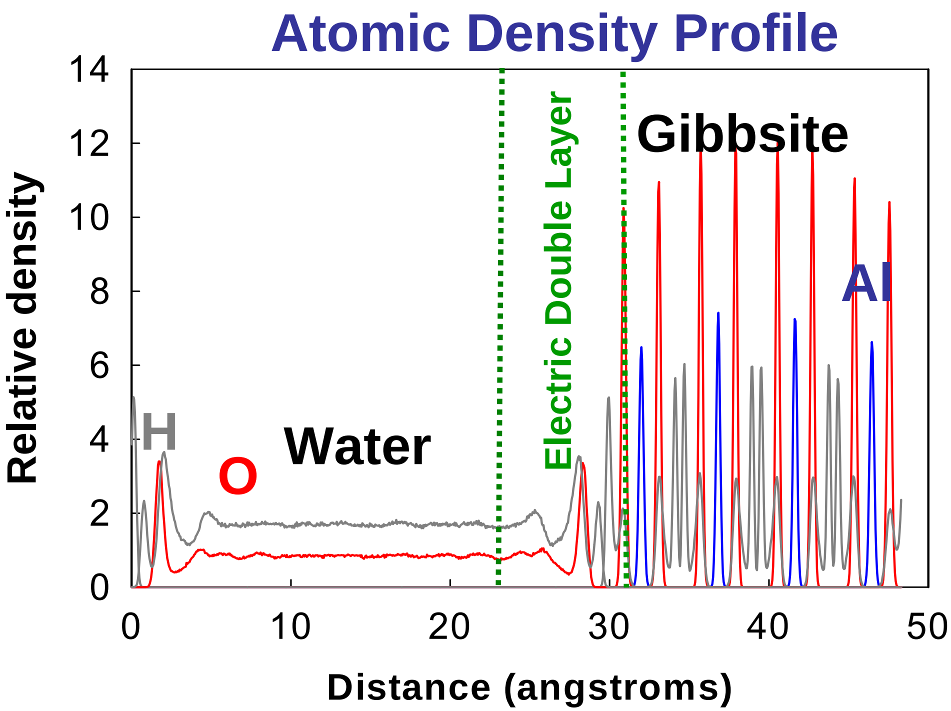
$C_1$, $C_2$, $K^+$, $K^-$, $K^M$, $K^L$

In how much detail do we need to describe the electric potential and charge distribution from the solid surface into bulk solution?

# Mineral-Water Interface: Determination through Molecular Dynamics

## $H_2O$ Structure at Gibbsite (001)




*Criscenti and Cygan, 2004*

# 1-D Simulations: Effects of Log K Uncertainty in SCM Geochemical Model

## Aqueous Components

| | | |
|---|---|---|
| $H^+$ | $UO_2^{2+}$ | $Cl^-$ |
| $Na^+$ | $Ca^{2+}$ | $NO_3^-$ |
| $K^+$ | $Fe^{3+}$ | $HCO_3^-$ |
| $Mg^{2+}$ | $Al^{3+}$ | $SO_4^{2-}$ |

## Aqueous Complexes

| | |
|---|---|
| $UO_2OH^+$ | $UO_2CO_3^o$ |
| $UO_2(OH)_2^o$ | $UO_2(CO_3)_2^{2-}$ |
| $UO_2(OH)_3^-$ | $UO_2(CO_3)_3^{4-}$ |
| $(UO_2)_2(OH)_5^+$ | $(UO_2)_2CO_3(OH)_3^-$ |

## Solid

**Low-Fe-Mg Smectite**

$Na_{.15}Ca_{.02}K_{.2}Mg_{.9}Fe_{.45}Al_{1.25}Si_{3.75}O_{10}(OH)_2$

## Surface Species

| | |
|---|---|
| $>AlOH$ | $>AlOH_2^+$ |
| $>AlO^-$ | $>AlOUO_2^+$ |

$$>AlO^- + H^+ = >AlOH$$

$$\log K = \frac{a_{>AlOH}}{a_{>AlO^-}\,a_{H^+}}$$

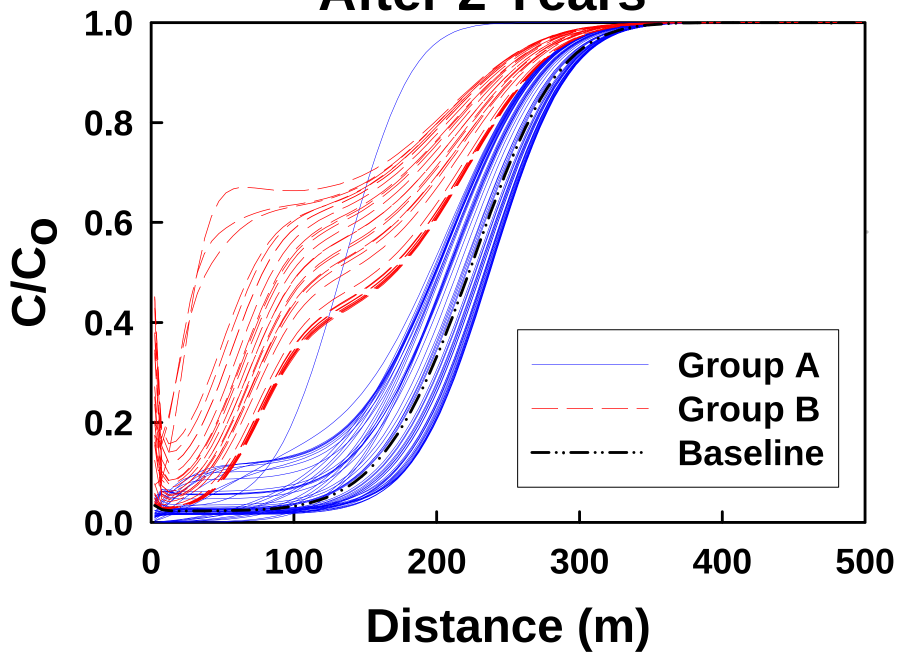
**Mean = 9.73**
**Std. Dev. = 1.5**

$$>AlOUO_2^+ + H^+ = >AlOH + UO_2^{2+}$$

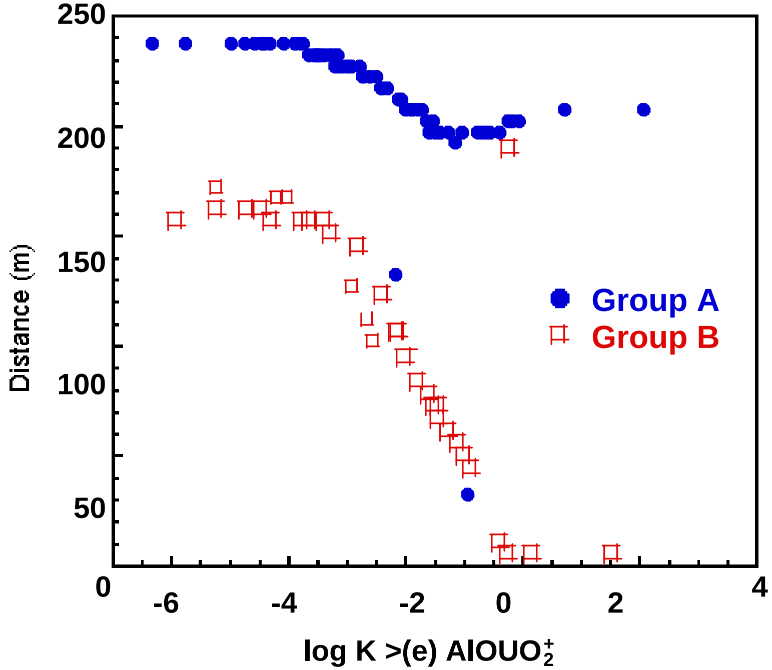
$$\log K = \frac{a_{>AlOH}\,a_{UO_2^{2+}}}{a_{>AlOUO_2^+}\,a_{H^+}}$$

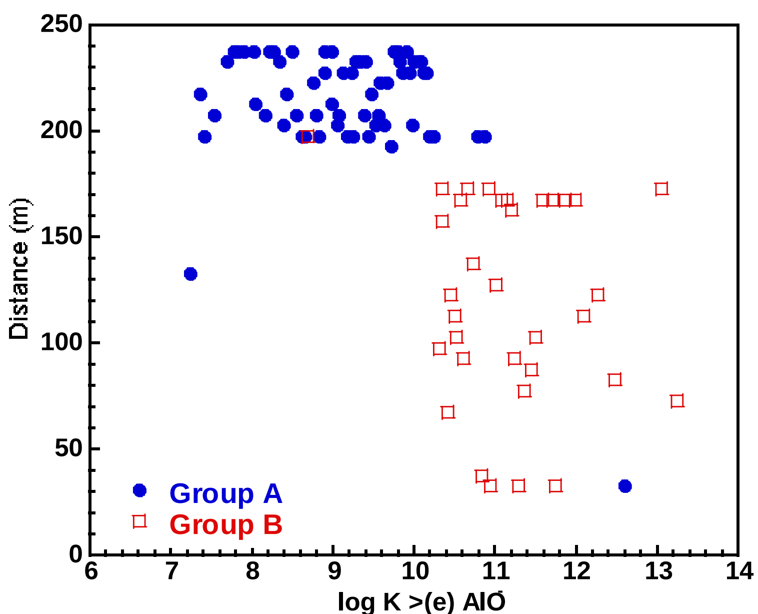
**Mean = -2.70**
**Std. Dev. = 1.5**

## Concentration Front After 2 Years




## 50% $C/C_o$ Distance vs. log K After 2 Years

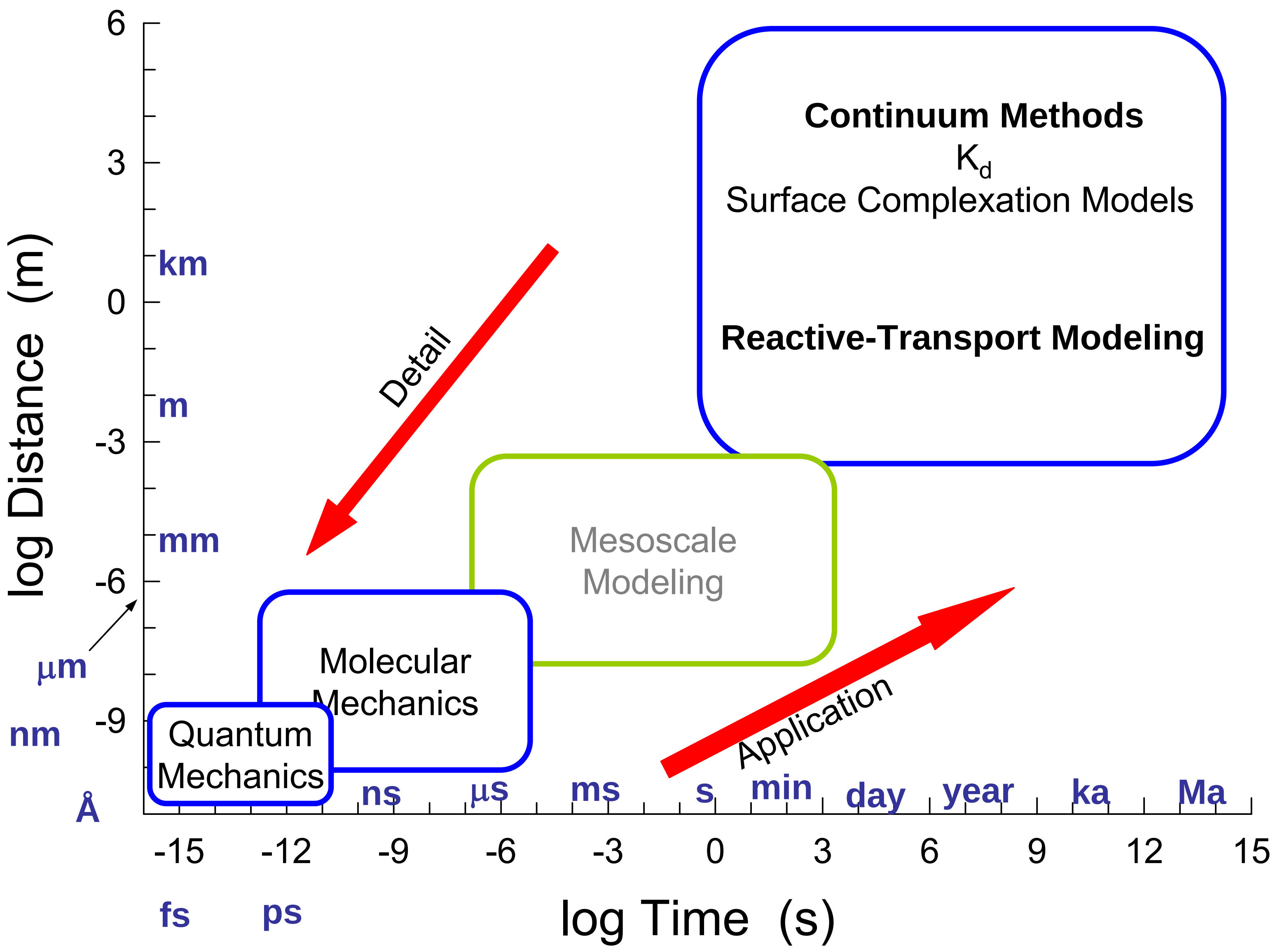



# Effects of Log K Uncertainty

**The difference between Group A and Group B behavior can be attributed to the *log* K >(e)AlO-.**

# Computer Simulation: x-t Array




After Cygan, 2001

# QM and MM → Continuum SCM Models

***QM and MM calculations help us address the following questions:***

- What level of detail is needed for a *predictive* model of field processes?
- For what geochemical questions can we “average” the properties of the mineral-water interface?
- What are the uncertainties associated with eliminating some of the finer details in a continuum model?

# Conclusions

- A key research area in reactive-process modeling is the development of adsorption models and internally-consistent parameter sets.
- The predictive capabilities of adsorption models *at any scale* have not been established.
- The adsorption model and parameter set used in a reactive-transport code can dominate the outcome of contaminant plume migration simulations.

# Geoquìmico: An Interactive Tool for Comparing Sorption Conceptual Models (Surface Complexation Modeling *versus* $K_D$)

# Motivation

- Existing subsurface geochemical transport models are often:
  - outdated in coding paradigm and limited to overly-simplistic sorption conceptual models
  - difficult to manage due to complexity of pre/post-processing and lack of support (not user-friendly)

- Newer, innovative tools are need to facilitate:
  - the utilization of state-of-the-art conceptual models
  - NRC–licensee concurrence
  - ease of use

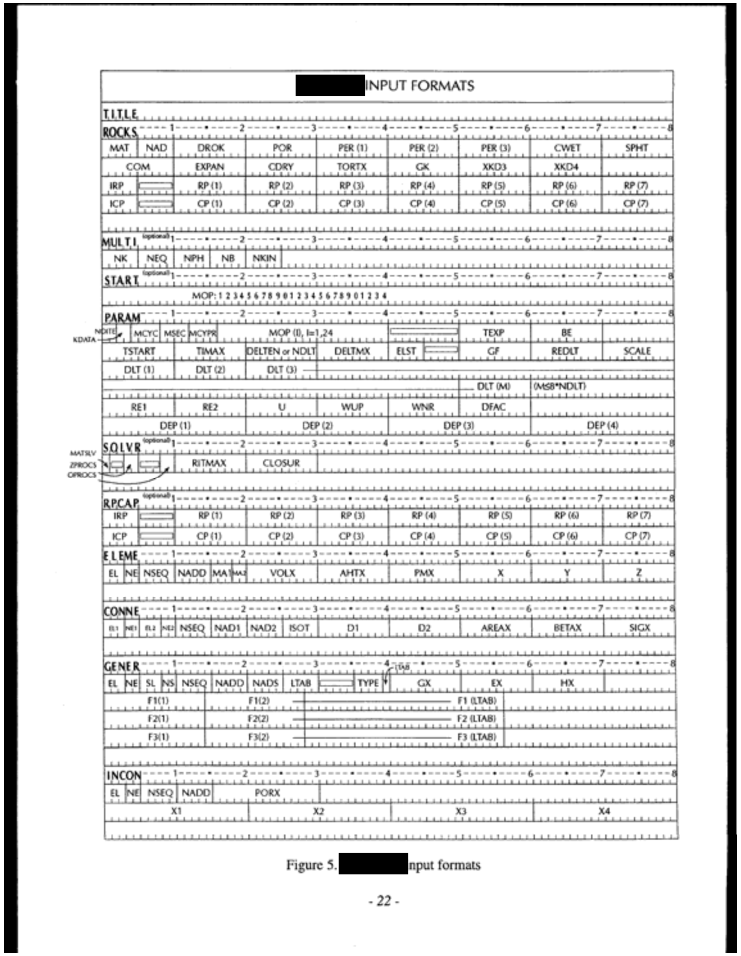
# Advantages of a User-Friendly Geochemical Transport Tool

- Provides framework for evaluating the validity of sorption conceptual models
- Aids licensees in the decision-making process by providing access to preconfigured, NRC-approved geochemical transport scenarios
- User-friendly graphical user interface facilitates modeling exercises
- Web-based programming provides platform independence and automated code maintenance

# Advantages of Simplified Web-Based Programs

- Less steep of a learning curve
  - Input is less complicated
- Data requirements more easily satisfied
- Faster turnaround
- Results are often more defensible
  - Parameter uncertainty may rule out the legitimacy of more sophisticated models
- Updates readily deployable
- Platform independence
- Graphical User Interface (GUI)

# Overly Complex Model Input

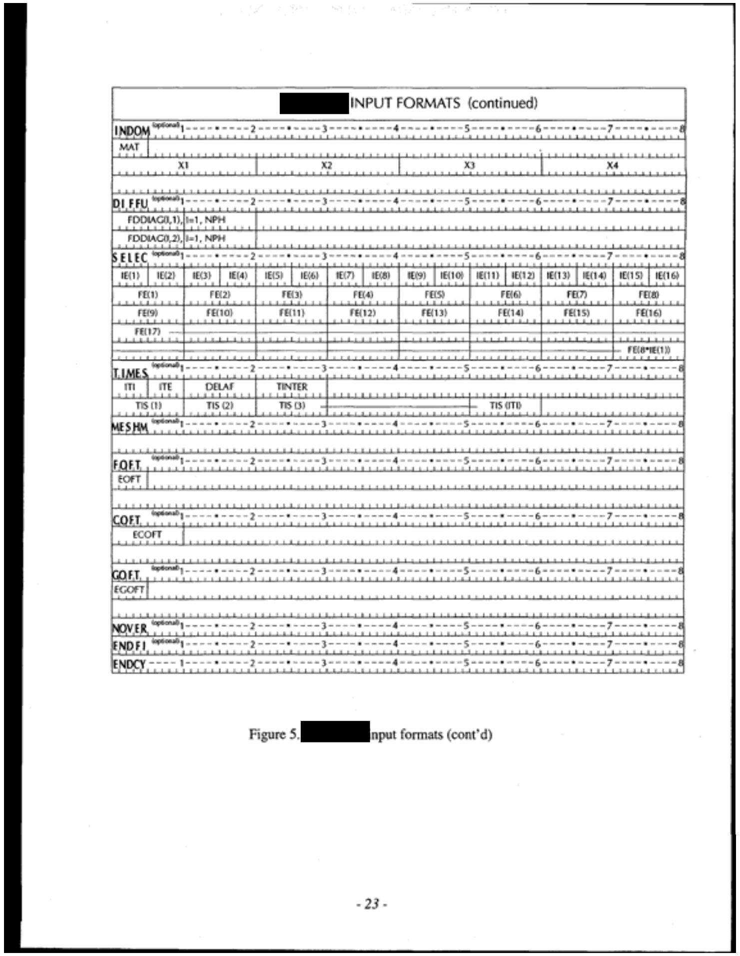


[redacted] INPUT FORMATS

TITLE
ROCKS
MAT | NAD | DROK | POR | PER (1) | PER (2) | PER (3) | CWET | SPHT
COM | EXPAN | CDRY | TORTX | GK | XKD3 | XKD4
IRP | RP (1) | RP (2) | RP (3) | RP (4) | RP (5) | RP (6) | RP (7)
ICP | CP (1) | CP (2) | CP (3) | CP (4) | CP (5) | CP (6) | CP (7)
MULTI (optional)
NK | NEQ | NPH | NB | NKIN
START (optional)
MOP: 1 2 3 4 5 6 7 8 9 0 1 2 3 4 5 6 7 8 9 0 1 2 3 4
PARAM
KDATA | NOITE | MCYC | MSEC | MCYPR | MOP (I), I=1,24 | TEXP | BE
TSTART | TIMAX | DELTEN or NDLT | DELTMX | ELST | GF | REDLT | SCALE
DLT (1) | DLT (2) | DLT (3)
DLT (M) | (M≤8*NDLT)
RE1 | RE2 | U | WUP | WNR | DFAC
DEP (1) | DEP (2) | DEP (3) | DEP (4)
SOLVR (optional)
MATSLV | ZPROCS | OPROCS | RITMAX | CLOSUR
RPCAP (optional)
IRP | RP (1) | RP (2) | RP (3) | RP (4) | RP (5) | RP (6) | RP (7)
ICP | CP (1) | CP (2) | CP (3) | CP (4) | CP (5) | CP (6) | CP (7)
ELEME
EL | NE | NSEQ | NADD | MA1 | MA2 | VOLX | AHTX | PMX | X | Y | Z
CONNE
EL1 | NE1 | EL2 | NE2 | NSEQ | NAD1 | NAD2 | ISOT | D1 | D2 | AREAX | BETAX | SIGX
GENER
EL | NE | SL | NS | NSEQ | NADD | NADS | LTAB | TYPE | ITAB | GX | EX | HX
F1(1) | F1(2) | F1 (LTAB)
F2(1) | F2(2) | F2 (LTAB)
F3(1) | F3(2) | F3 (LTAB)
INCON
EL | NE | NSEQ | NADD | PORX
X1 | X2 | X3 | X4

Figure 5. [redacted]nput formats

- 22 -



[redacted] INPUT FORMATS (continued)

INDOM (optional)
MAT
X1 | X2 | X3 | X4
DIFFU (optional)
FDDIAG(I,1), I=1, NPH
FDDIAG(I,2), I=1, NPH
SELEC (optional)
IE(1) | IE(2) | IE(3) | IE(4) | IE(5) | IE(6) | IE(7) | IE(8) | IE(9) | IE(10) | IE(11) | IE(12) | IE(13) | IE(14) | IE(15) | IE(16)
FE(1) | FE(2) | FE(3) | FE(4) | FE(5) | FE(6) | FE(7) | FE(8)
FE(9) | FE(10) | FE(11) | FE(12) | FE(13) | FE(14) | FE(15) | FE(16)
FE(17)
FE(8*IE(1))
TIMES (optional)
ITI | ITE | DELAF | TINTER
TIS (1) | TIS (2) | TIS (3) | TIS (ITI)
MESHM (optional)
FOFT (optional)
EOFT
COFT (optional)
ECOFT
GOFT (optional)
EGOFT
NOVER (optional)
ENDFI (optional)
ENDCY

Figure 5. [redacted]nput formats (cont'd)

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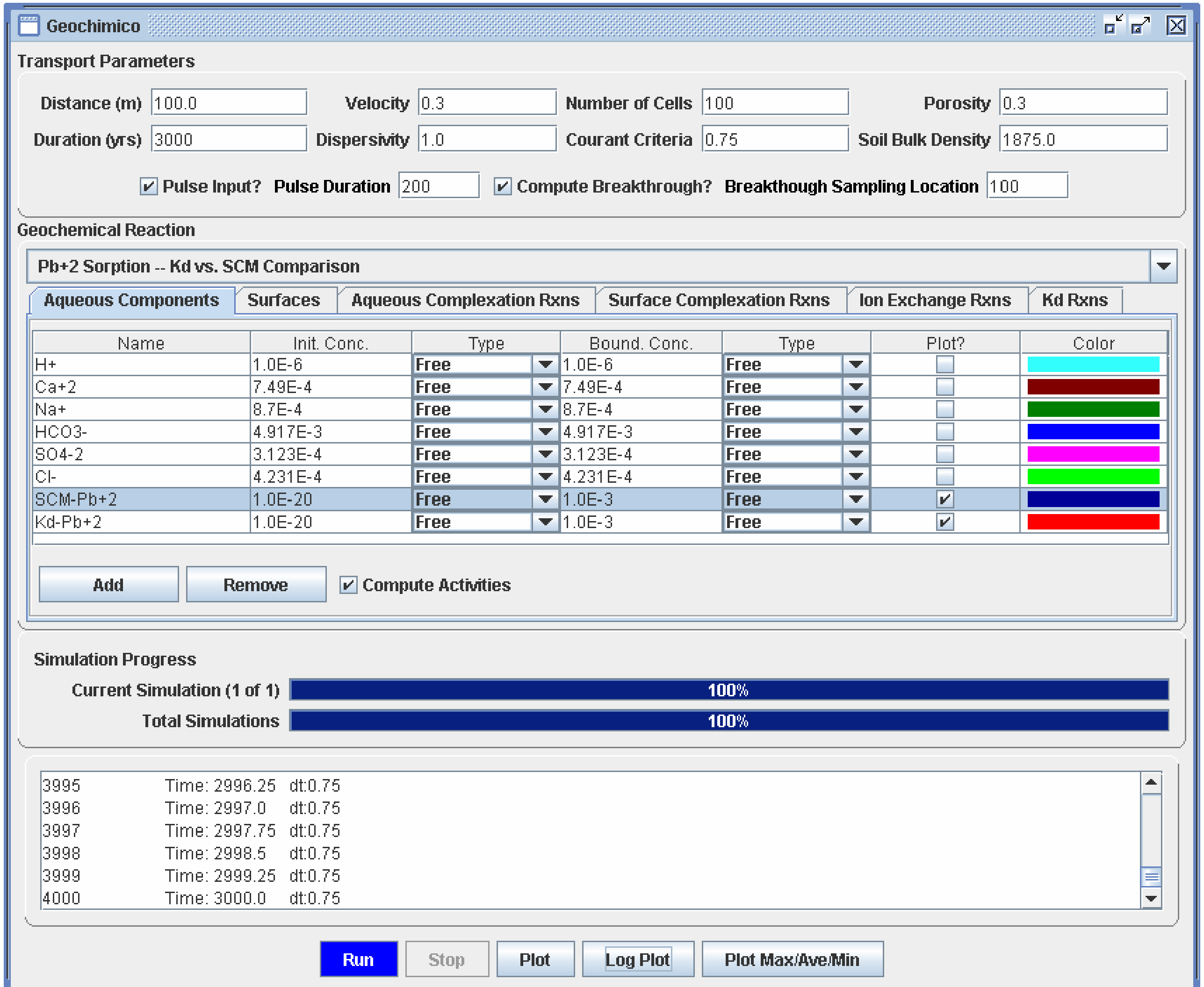
# Advantages/Disadvantages of Java

- Advantages
  - Object-oriented
  - Platform independent
  - Integrated GUI environment
  - Plethora of freely-available libraries
  - More robust to the every-day user
- Potential Disadvantages
  - Java is 1.5X-3X slower than C (better than 10X-20X from late 90’s)
  - Legacy codes limit acceptance within scientific computing

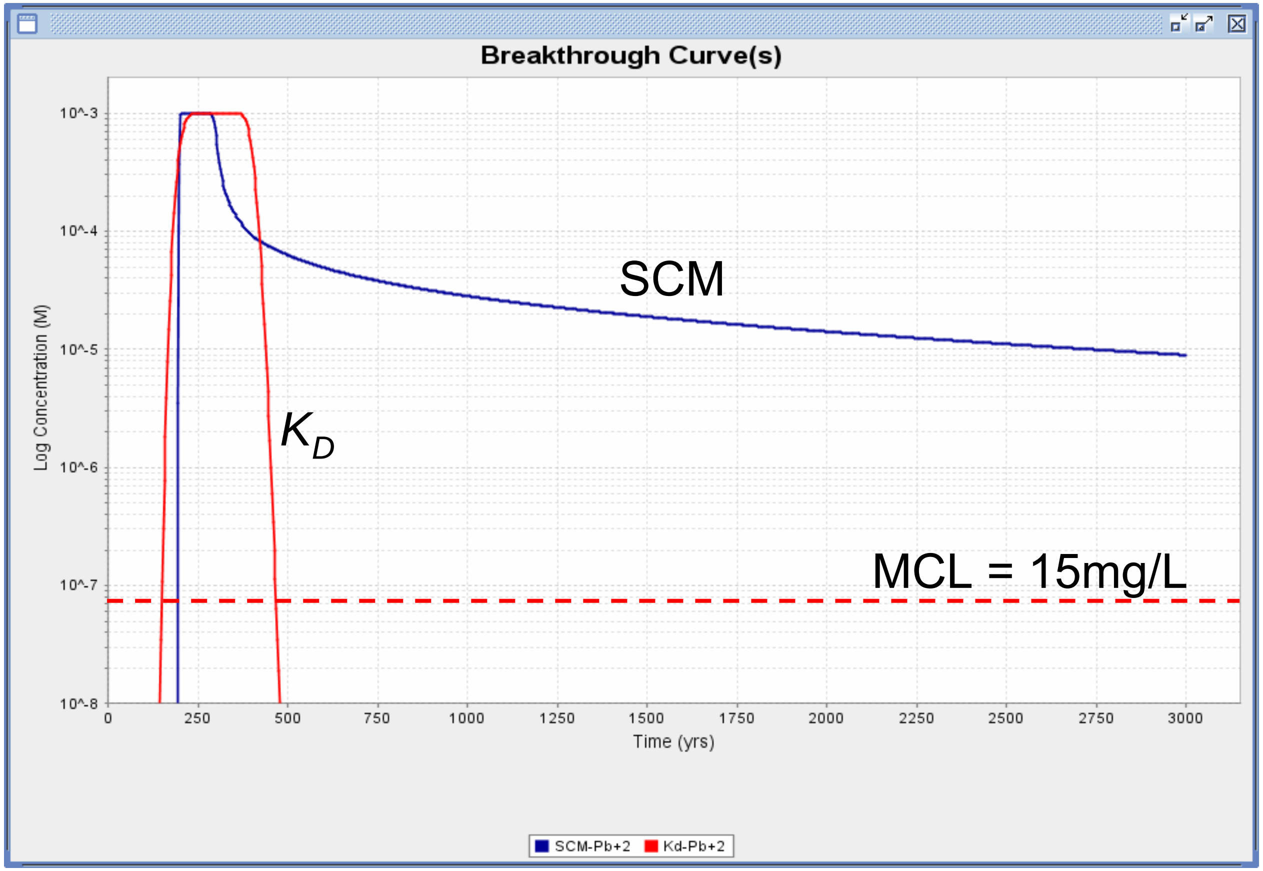
# Geoquímico


Geochimico
Transport Parameters
Distance (m) 100.0
Velocity 0.3
Number of Cells 100
Porosity 0.3
Duration (yrs) 3000
Dispersivity 1.0
Courant Criteria 0.75
Soil Bulk Density 1875.0
Pulse Input? Pulse Duration 200
Compute Breakthrough? Breakthough Sampling Location 100
Geochemical Reaction
Pb+2 Sorption -- Kd vs. SCM Comparison
Aqueous Components
Surfaces
Aqueous Complexation Rxns
Surface Complexation Rxns
Ion Exchange Rxns
Kd Rxns
Name
Init. Conc.
Type
Bound. Conc.
Type
Plot?
Color
H+ 1.0E-6 Free 1.0E-6 Free
Ca+2 7.49E-4 Free 7.49E-4 Free
Na+ 8.7E-4 Free 8.7E-4 Free
HCO3- 4.917E-3 Free 4.917E-3 Free
SO4-2 3.123E-4 Free 3.123E-4 Free
Cl- 4.231E-4 Free 4.231E-4 Free
SCM-Pb+2 1.0E-20 Free 1.0E-3 Free
Kd-Pb+2 1.0E-20 Free 1.0E-3 Free
Add
Remove
Compute Activities
Simulation Progress
Current Simulation (1 of 1) 100%
Total Simulations 100%
3995 Time: 2996.25 dt:0.75
3996 Time: 2997.0 dt:0.75
3997 Time: 2997.75 dt:0.75
3998 Time: 2998.5 dt:0.75
3999 Time: 2999.25 dt:0.75
4000 Time: 3000.0 dt:0.75
Run
Stop
Plot
Log Plot
Plot Max/Ave/Min

# Geoquímico Capabilities

- 1D transport using finite volume formulation
- Geochemical reaction
  - Aqueous complexation
  - Sorption
    - surface complexation
    - ion exchange
    - linear $K_D$
- Preconfigured geochemical schemes
- Uncertainty analysis (e.g. random surface site conc.)
- Web-based Java user interface

# Example of $Pb^{2+}$ Breakthrough Based on $K_D$ and SCM Sorption Models



# Future Directions for Geoquímico

1. Development of uranium sorption scenarios
2. Total component concentration plotting capability
3. Support of non-standard distributions (e.g. log-normal) for uncertainty analysis
4. Sorption of tertiary or secondary species
5. Ability to save/load geochemical transport scenarios
6. Statistical analysis module for uncertainty runs

# TASK 4
# Characterization of Soil Aggregate Samples and Intergranular Materials from the Naturita UMTRA Site
## (and Cape Cod Toxics Research Site)

Susan J. Altman, Carlos Jové Colón, and Randall T. Cygan

November 15, 2005

# Purpose

- **Evaluate methods for characterizing soil aggregate samples**
  - **Destructive (SEM-EDS, SIMS, HRTEM, M-SXRF, and M-XANES)**
  - **Non-destructive (CMT)**
- **Examine association of uranium (or cesium as a proxy for uranium) adsorption with mineral phases**
- **Characterize iron-bearing minerals (beyond XRD)**

**Traditional Approach**

- Measure bulk distribution coefficients ($K_D$)
- Measures the average effect
- Leads to overestimate of plume advance in models
- Leads to understatement of the difficulty in removing contaminants in models

**Alternative to the $K_D$ approach**

- Account for variation in adsorptive properties for different minerals in the substrate
- Account for reversibility/irreversibility of the adsorptive process
- Leads to more accurate models
- Need more detailed information on the substrate

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# Multiscale Experimental Work Is Complimentary

- Microbeam study
  - Identifies important minerals and sorbing phases
  - Determine compositions of these minerals
  - Shows associations of iron and uranium on samples
- Computerized Microtomography (CMT) study
  - Allows for examination of entire aggregate
  - Estimates mass fraction iron in different portions of the sample
  - With knowledge of mineralogy of the samples, can determine the mass fraction of the different iron-bearing minerals
  - Nondestructive
  - Could be coupled with transport experiments

Sandia National Laboratories

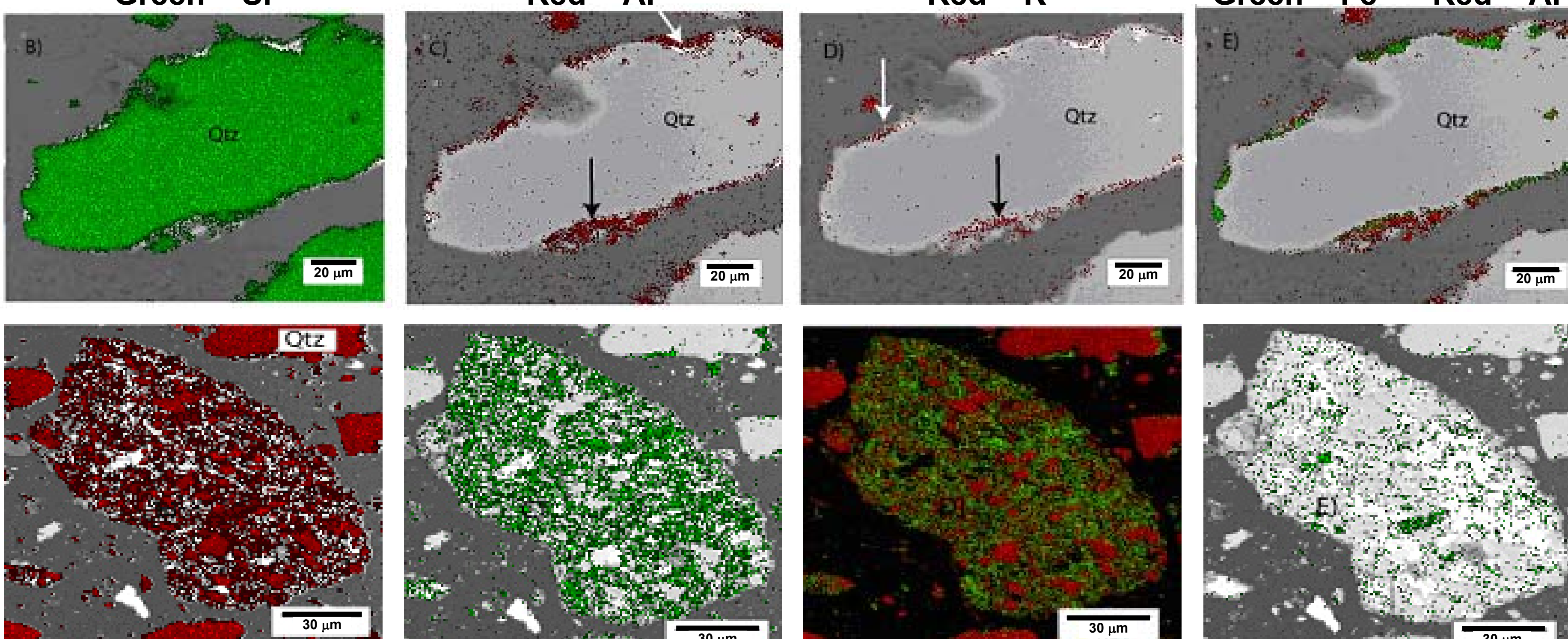
# Microanalytical Techniques

- Scanning Electron Microscopy – Energy Dispersive Spectrometry (SEM-EDS)
  - Polished epoxy mounts of untreated composite samples
  - Sandia National Laboratories
  - Carlos F. Jové Colón, David M. Meece, James A. Davis
- Secondary Ion Mass Spectrometry (SIMS)
  - Polished epoxy mounts of untreated composite samples
  - Arizona State University
  - Richard L. Hervig, Carlos F. Jové Colón, Charoen Sanpawanitchakit
- High Resolution Transmission Electron Microscopy (HRTEM)
  - Ion-milled, sand-size grains and fine-grained segregated granular fractions from untreated samples
  - Carbonate-free uranium treated sample (no sample prep)
  - Department of Earth and Planetary Sciences, University of New Mexico
  - Huifang Xu, Carlos F. Jové Colón, Randall T. Cygan
- Micro-Synchrotron X-Ray Fluroescence (M-SXRF)
  - Carbonate-free uranium treated sample
  - Brookhaven National Laboratory (National Synchrotron Light Source beamline X-26A)
  - Carlos F. Jové Colón, Charoen Sanpawanitchakit
- Micro-X-Ray Adsorption Near-Edge Spectroscopy (M-XANES)
  - Carbonate-free uranium treated sample
  - Brookhaven National Laboratory (National Synchrotron Light Source beamline X-26A)
  - Carlos F. Jové Colón, Charoen Sanpawanitchakit

Jové Colón, C. F., C. Sanpawanitchakit, H. Xu, R. T. Cygan, J. A. Davis, D. M. Meece, and R. L. Hervig (in review), A Combined Analytical Study to Characterize Uranium Soil Contamination: The Case of the Naturita UMTRA Site and the Role of Grain Coatings, U. S. Nuclear Regulatory Commission, NUREG/CR-?? Washington, D. C.

# Scanning Electron Microscope with Energy Dispersive Spectroscopy (SEM-EDS)

Green = Si | Red = Al | Red = K | Green = Fe | Red = Al




Red = Si | Green = Al | Green = Al | Red = Si | Green = K

- Coating thicknesses ranging from ~10 - ~15 µm
- Al- and Fe-rich coatings observed
- Aggregates with porous texture held together by clays
- Uranium below the detection limit

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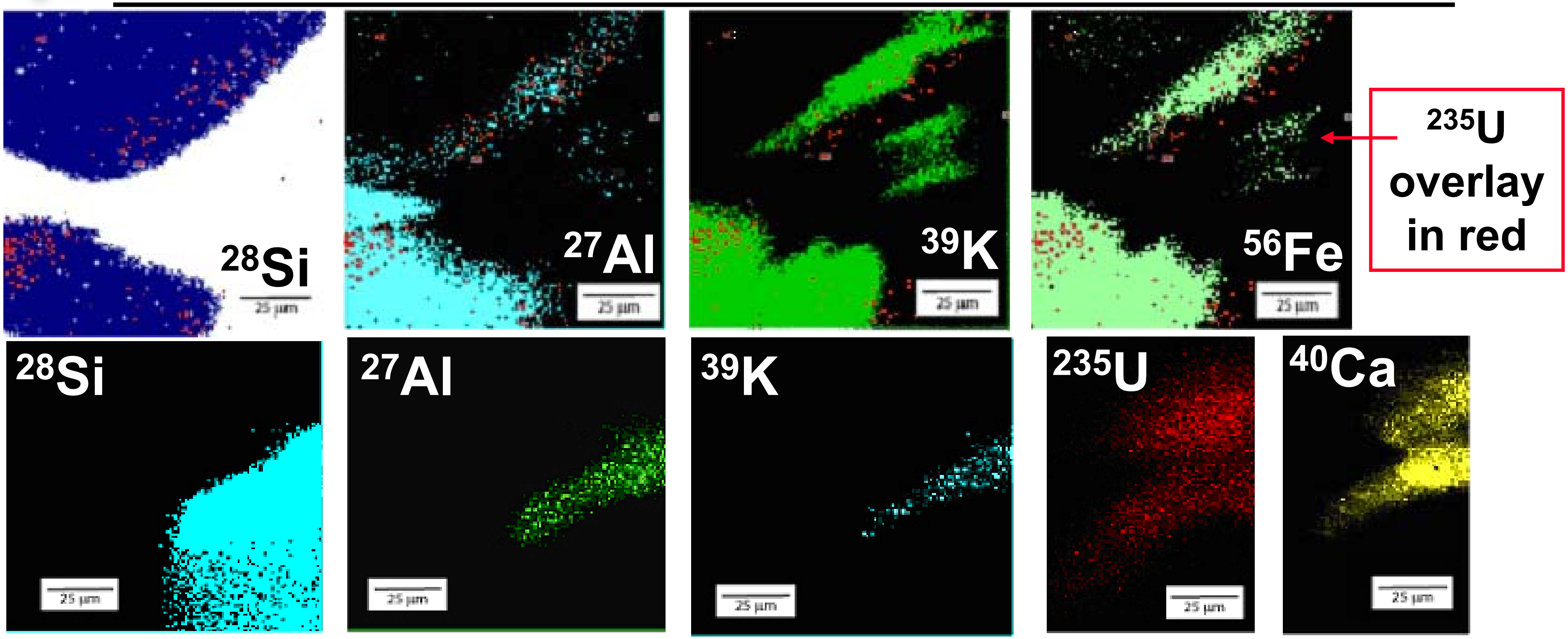
# Secondary Ion Mass Spectrometry




- Substrate grains are quartz
- No clear evidence of uranium association with any particular phase
  - Uranium associated with Al (probably a clay) (upper sample)
  - Uranium probably associated with carbonate (lower sample)
  - Close to the detection limit for uranium
- Suggestion that $^{238}$U diffuses deep within the clay coating
- Al-rich coatings are up to ~ 10 $\mu$m thick

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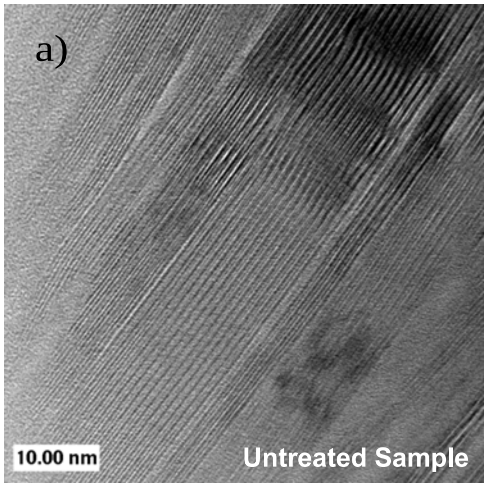
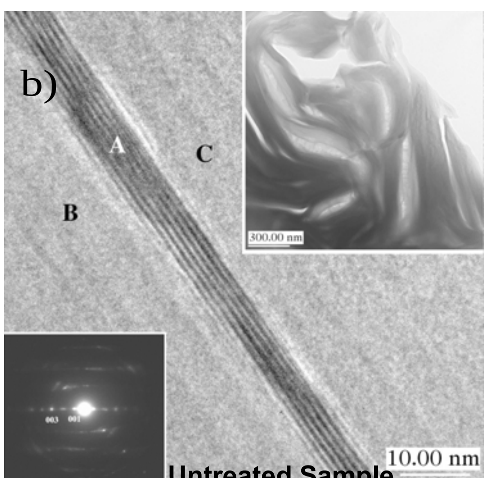
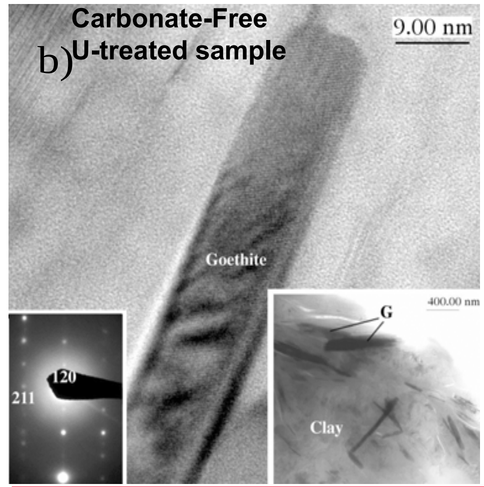
# Transmission Electron Microscopy

**Interlayered illite/smectite (dominate the clay phase)**

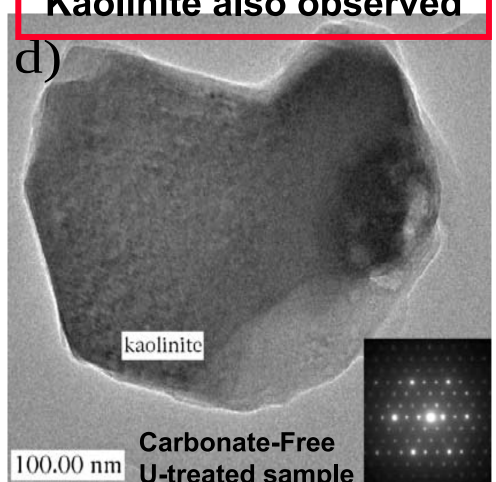


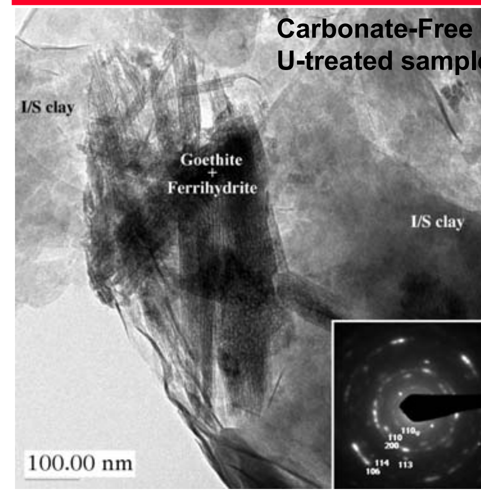

**Close co-existence of Fe-(oxy)hydroxides and clay**

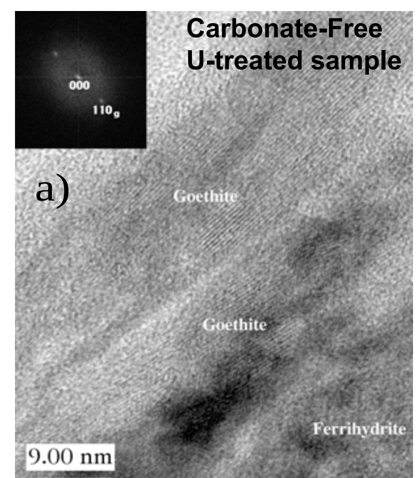



**Kaolinite also observed**



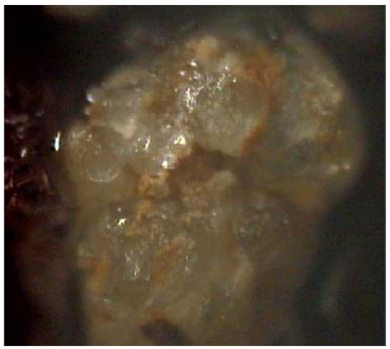

**Close co-existence of Fe-(oxy)hydroxides (e.g., goethite, ferrihydrite)**



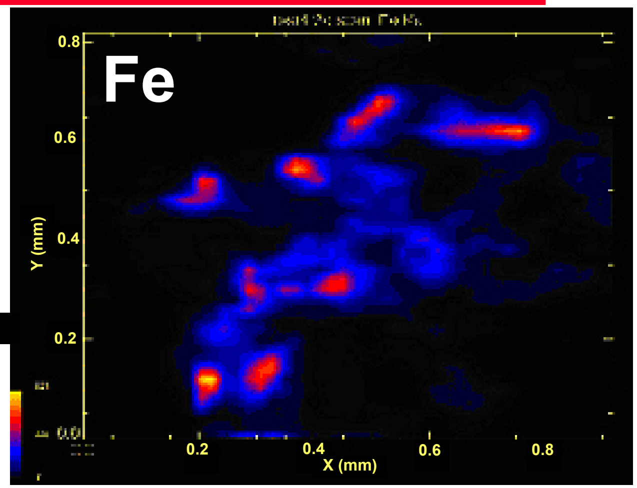



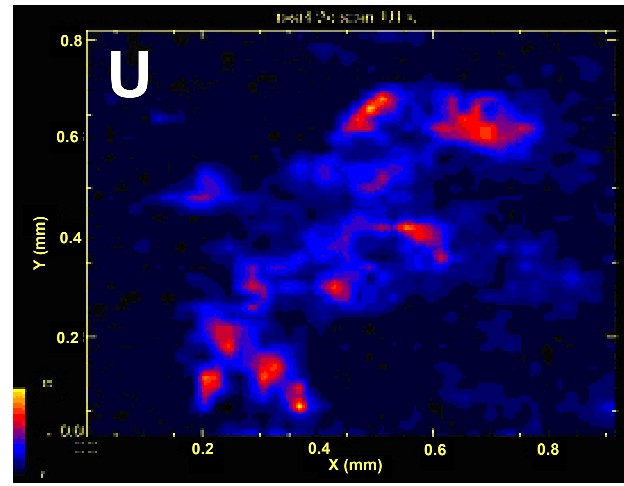
# Micro Synchrotron X-Ray Fluorescence and Micro X-Ray Near-Edge Spectroscopy

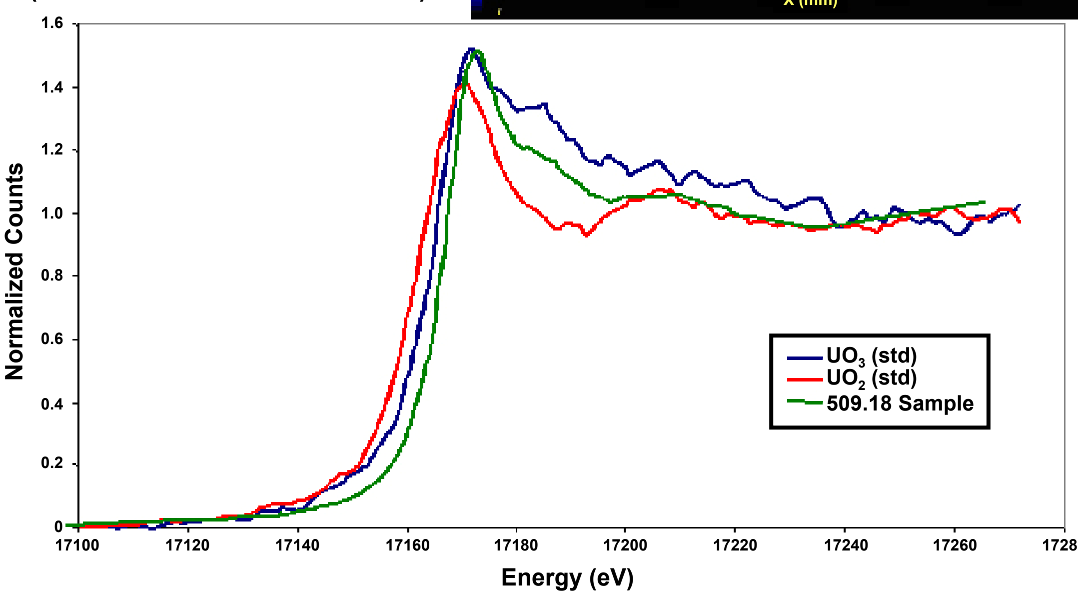
## Uranium-Treated Carbonate-Free Sample



**Optical Image**
(same scale as M-SXRF results)




- **Spatial correlation between Fe and uranium**
- **Fe-(oxy)hydroxides are the main sink for uranium**
- **Local redox state of uranium in Fe-rich areas is $U^{6+}$**

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# Suite of Techniques with Different Spatial Resolutions and Sensitivities Provide Comprehensive Characterization

| Technique | Untreated Composite Sample | Carbonate-Free $U^{6+}$ Treated Sample |
|---|---|---|
| SEM-EDS | • Presence of Fe-rich and Al-Si rich (clay) coatings<br>• Fe-rich phases present as small scattered particles in the clay layer | --- |
| SIMS | • Presence of uranium in the Al-Si clay layer<br>• No clear association between Fe and U (due to limitations of technique) | --- |
| HRTEM | • Clays are dominantly mixed layer illite/smectite | • Large population of Fe-(oxy)hydroxide phases with a nanoporous nature<br>• Fe-bearing layers are highly heterogeneous (hematite, goethite, ferrihydrite)<br>• Fe-rich particles contain areas of ferrihydrite homogeneously transforming to goethite |
| M-SXRF | --- | • Close association of U and Fe-rich domains |

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# Synchrotron Source X-Ray Microtomography

Susan J. Altman, Marissa D. Reno, Angela A. McLain, Mark Rivers, Randall T. Cygan

Altman, S. J., W. J. Peplinski, and M. L. Rivers, Evaluation of synchrotron X-ray computerized microtomography for the visualization of transport processes in low-porosity materials, *J. Contam. Hydrol*., *78*(*3*), 167-183, 2005.

Altman, S.J., Rivers, M.L., Reno, M.D., McLain, A.A., and Randy Cygan R. T. Characterization of sorption sites on aggregate soil samples using synchrotron X-ray CMT, *Environ. Sci. Technol*., *39*(8), 2679-2685, 2005.

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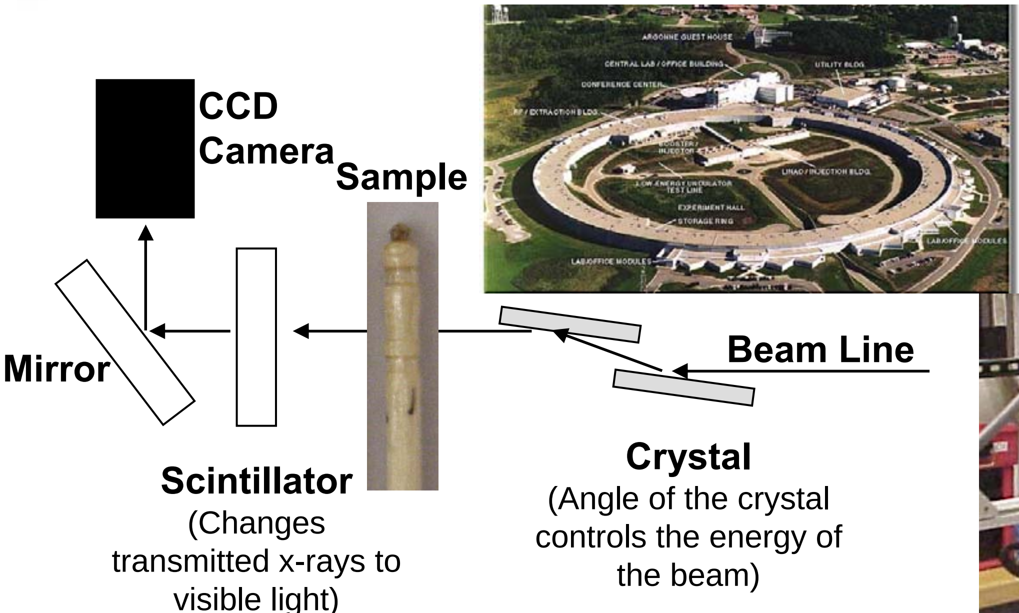
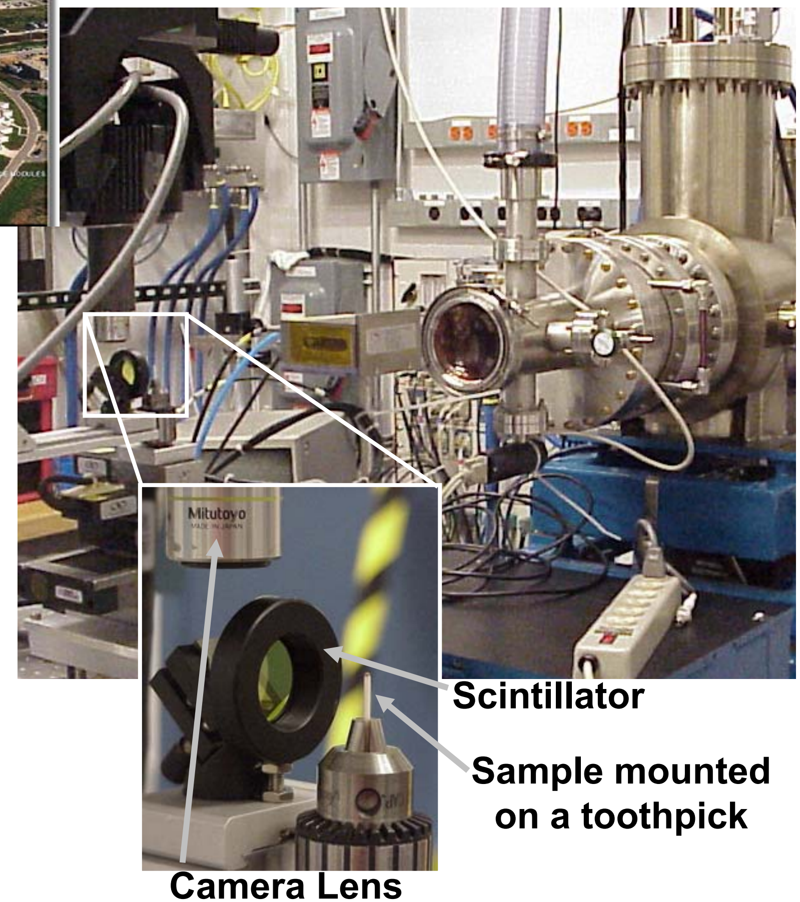
# Data Acquisition at the Advanced Photon Source



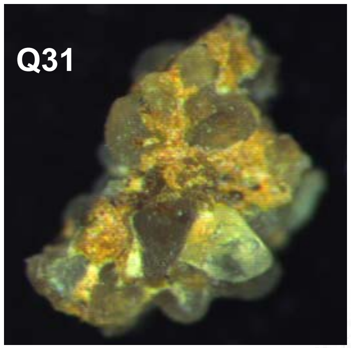



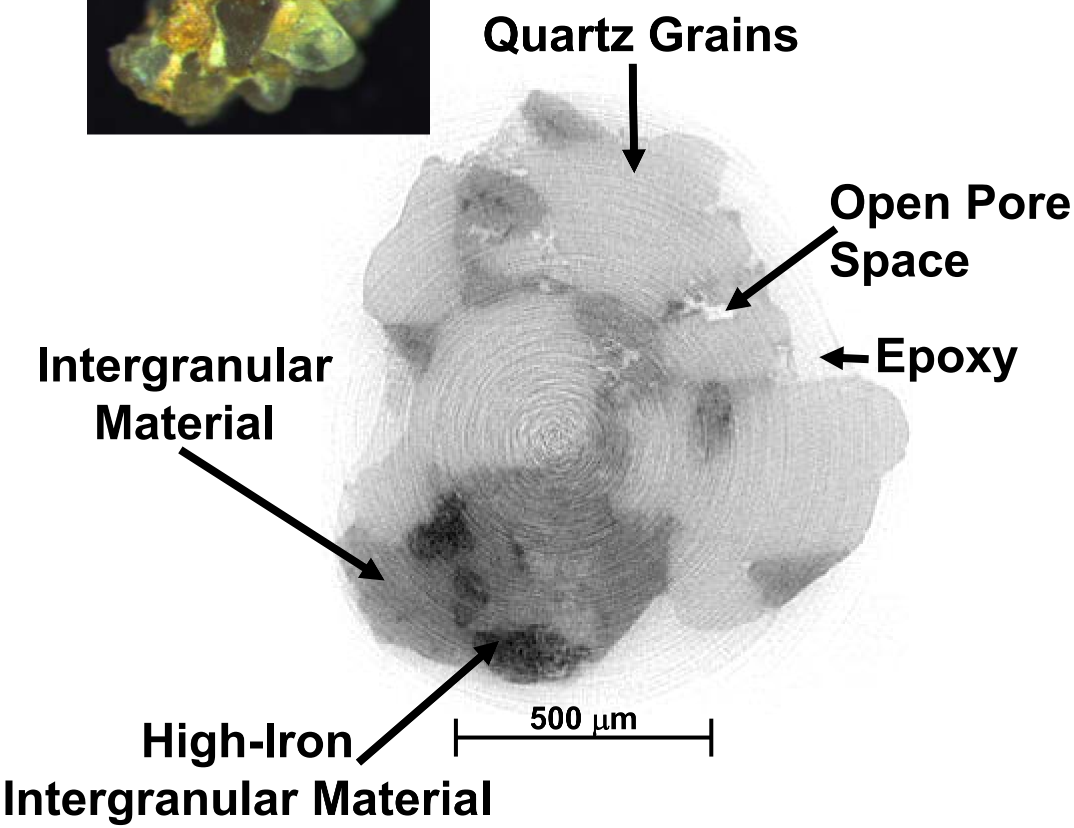

$$\frac{I}{I_o} = \exp(-\mu x)$$

- $I_o$ = Source Intensity (at X = 0)
- $I$ = Measured Intensity
- $x$ = Distance X-rays travel through the material (L)
- $\mu$ = Linear absorption coefficient (1/L)

Output at each pixel of a CT image

# CMT Images Allow for Visualization of Different Materials within the Aggregate

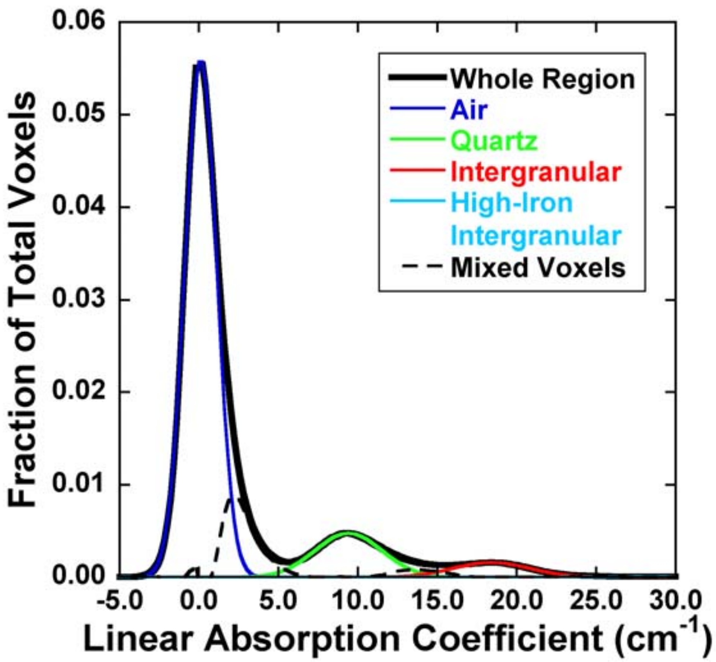


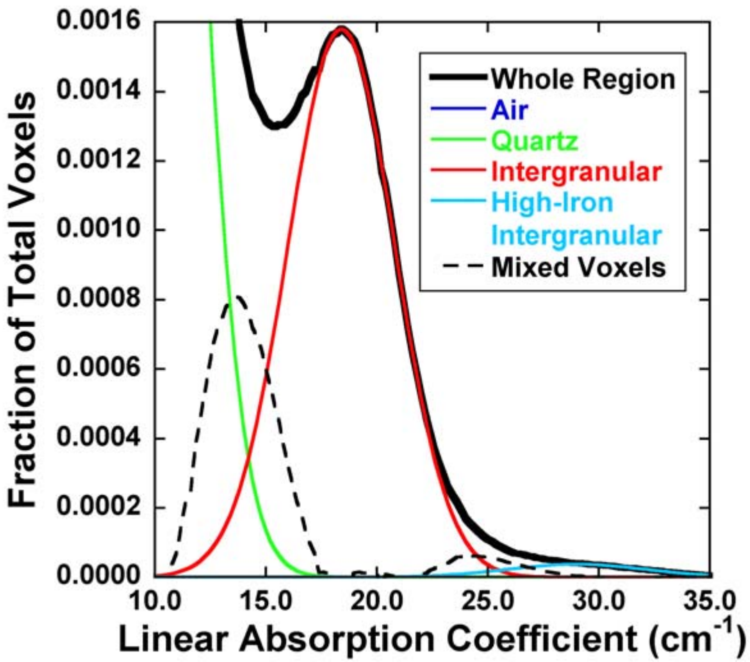




- CMT allows for qualitative differentiation of different portions of the aggregate grain
  - Air
  - Quartz grains
  - Intergranular Material
- Open pore space can be visualized
- Tree-ring structures are a product of from the reconstruction process – source of noise
- Voxel size = 3.9 microns on a side
- Dark = higher linear absorption coefficient (greater X-ray absorption)

# Histograms μ Values Allow for Quantitative Distinction of Different Materials

- Noise appears to be random (can be defined by Gaussian Distribution)
- Distinct distributions for air/epoxy, quartz, and intergranular material
- Certain portion of the voxels have "mixed values"
  - Voxels that overlap two substances
  - X-Ray refraction

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# With Mean μ Values Can Calculate $f_{Fe}$, $f_{Fe\text{-}Oxide}$, and $f_{Clay}$

## Four Equations

$$(f_{Fe-Oxide})(f_{Fe_{Fe-Oxide}}) + (f_{Clay})(f_{Fe_{Clay}}) = f_{Fe}$$

$$(f_{Fe-Oxide}) + (f_{Clay}) = 1$$

$$\sigma = \frac{(f_{Fe-Oxide})\mu}{\rho_{Fe-Oxide}} + \frac{(f_{Clay})\mu}{\rho_{Clay}}$$

$$f_{Fe} = M + \sigma B$$

## Four Unknowns

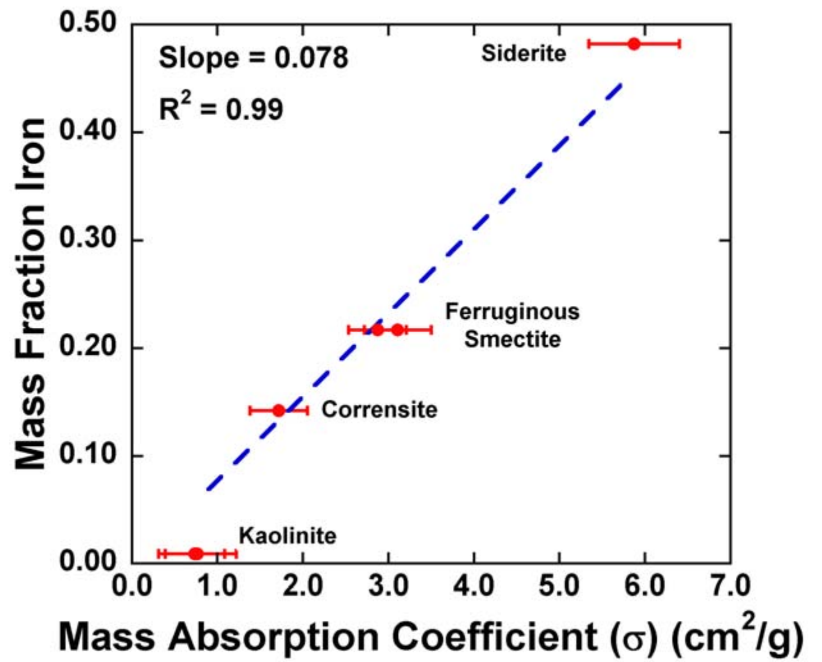
$\sigma$

$f_{Fe\text{-}Oxide}$

$f_{Clay}$

$f_{Fe}$

**Use mineral standards to derive a relations ship between mass fraction iron and mass absorption coefficient ($\sigma = \mu/\rho$)**

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# Linear Absorption Coefficient Calculations

Ferrihydrite

$Fe_5O_7OH \bullet 4H_2O$

$\rho = 3.8 \text{ g cm}^{-3}$

Goethite

$Fe^{+3}O(OH)$

$\rho = 3.8 \text{ g cm}^{-3}$

Clays (layered smectite/illite)

$\rho = 3.8 \text{ g cm}^{-3}$

$K_{0.31}Ca_{0.11}(Al_{1.41}Fe_{0.59})(Si_{3.42}Al_{0.53})O_{10}(OH)_2 \bullet 7H_2O$

$K_{0.5}Ca_{0.2}(Al_{1.41}Fe_{0.11}Mg_{0.45})(Si_{3.42}Al_{0.53})O_{10}(OH)_2 \bullet 7H_2O$

Knowns:

$f_{Fe_{Fe\text{-}Oxide}} = 0.53 \text{ or } 0.63$

$f_{Fe_{Clay}} = 0.01 \text{ or } 0.08$

$\rho_{Fe\text{-}oxide} = 3.8 \text{ or } 4.3 \text{ g cm}^{-3}$

$\mu$ (from histogram data)

B (from regression)

M = 0

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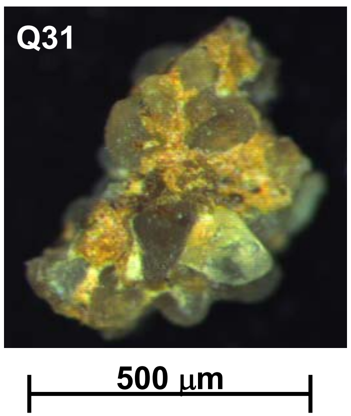
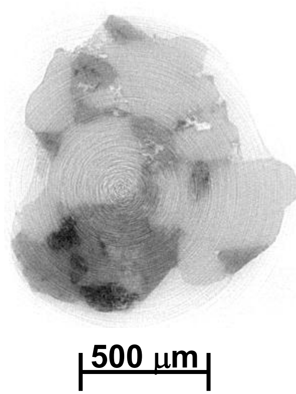
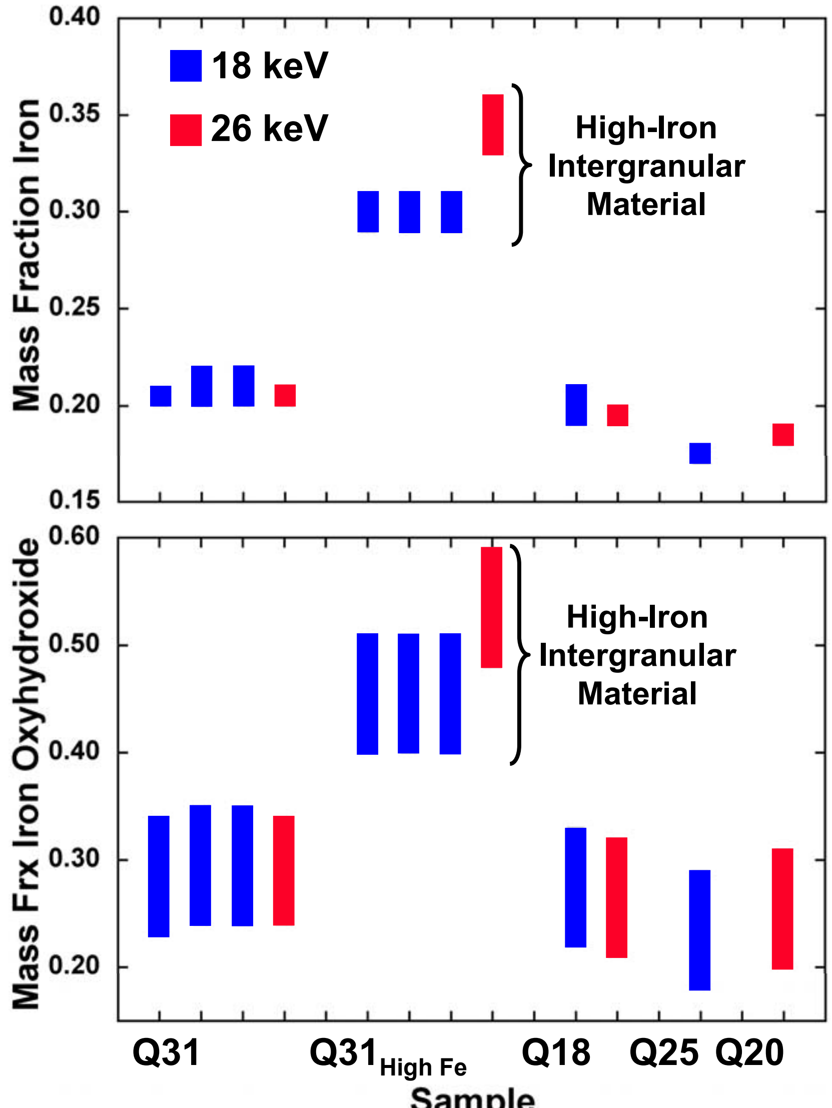
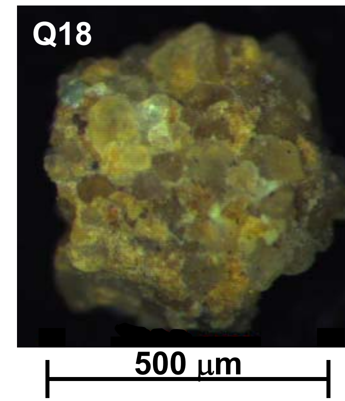
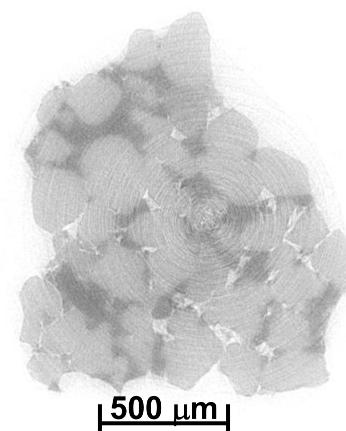
# Calculated Mass Fraction Iron and Mass Fraction Iron Oxyhydroxide



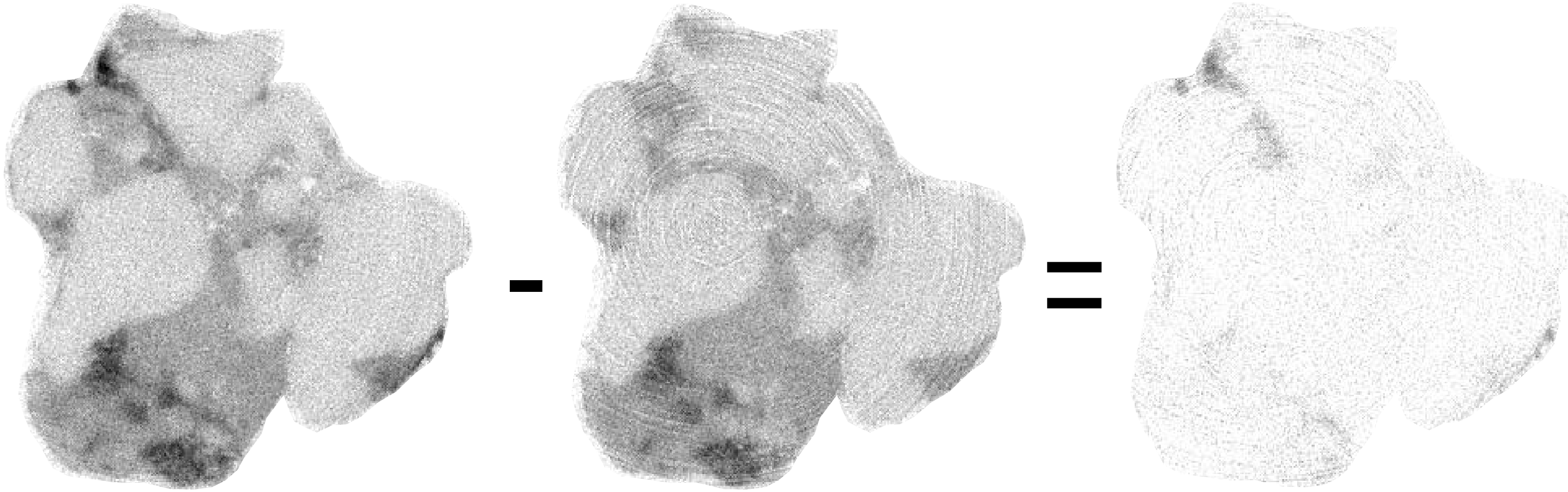



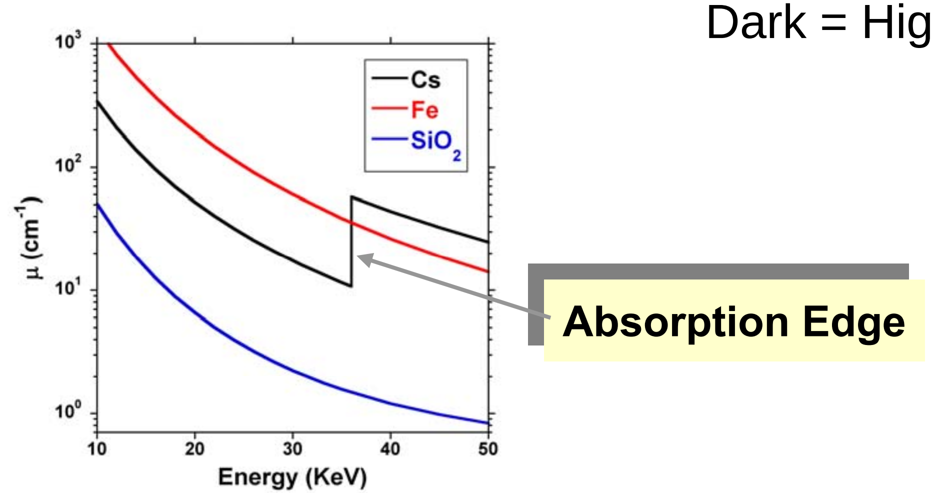



# Cesium Adsorption Observed on Intergranular Materials



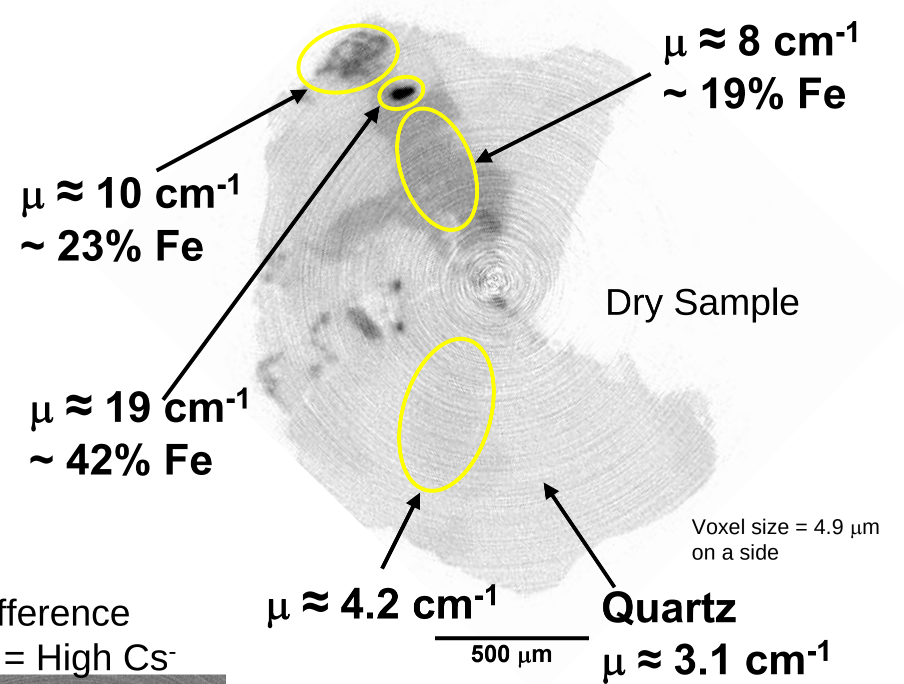
Above Cs Absorption Edge - Below Cs Absorption Edge = Difference

Dark = High Cs

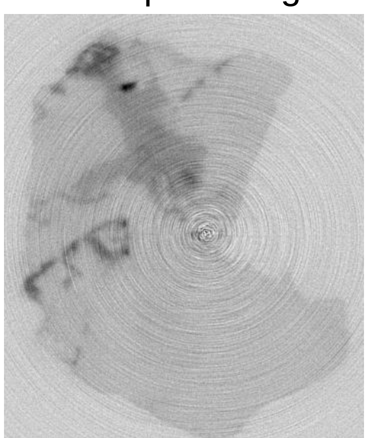


# Cape Cod Aggregates Appear to be More Heterogeneous

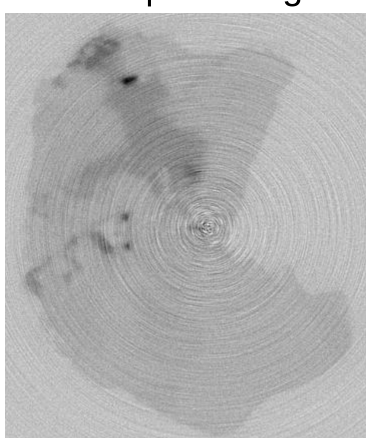
| Potential Coatings or Intergranular Material | % Fe |
|---|---|
| Hydrous ferric oxide | 63 or less |
| Hematite | 70 |
| Goethite | 63 |
| Magnetite | 72 |
| Ferrihydrite | 54 – 73 |



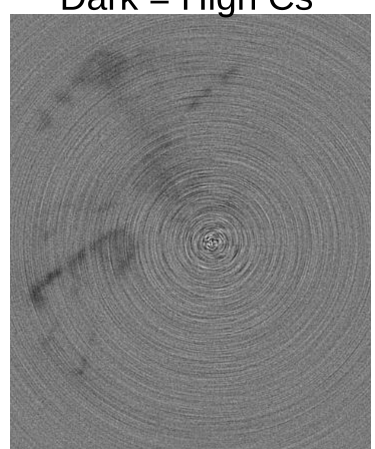

Above Cs Absorption Edge

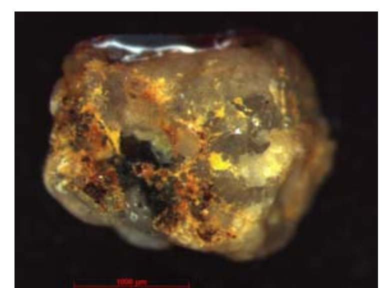


Below Cs Absorption Edge



Difference Dark = High Cs$^{-}$





# Next Steps

- Finish evaluation of Cape Cod samples
- Determine surface areas for each effective adsorbing phase from CMT data
- Develop more explicit surface complexation models to account for all adsorbing phases
- Compare those modeling results with $K_D$ and generalized composite surface complexation modeling approach

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# Task 5

# Technical Support for Interagency MOU on Multimedia Environmental Modeling

## Summary of the Federal Interagency Workshop on Reactive Transport Modeling

**Malcolm D. Siegel, Louise J. Criscenti, and Randall T. Cygan**

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company,
for the United States Department of Energy's National Nuclear Security Administration
under contract DE-AC04-94AL85000.

# Summary of the Federal Interagency Workshop on Reactive Transport Modeling

- Activity identified in the May 2003 Phase 2 Proposal for Working Group 3
  - Organize and convene a Federal Workshop on "Conceptual Model Development for Subsurface Reactive Transport Modeling of Inorganic Contaminants, Radionuclides, and Nutrients"
- Workshop hosted by Sandia National Laboratories
  - April 20 – 22, 2004 in Albuquerque, NM
  - Financed by registration fee, travel support from ERDC, NRC, DOE, USGS, and EPA
- Attended by more than 70 engineers and scientists
  - Federal agencies, academia, international
  - 17 invited presentations
  - 4 breakout sessions

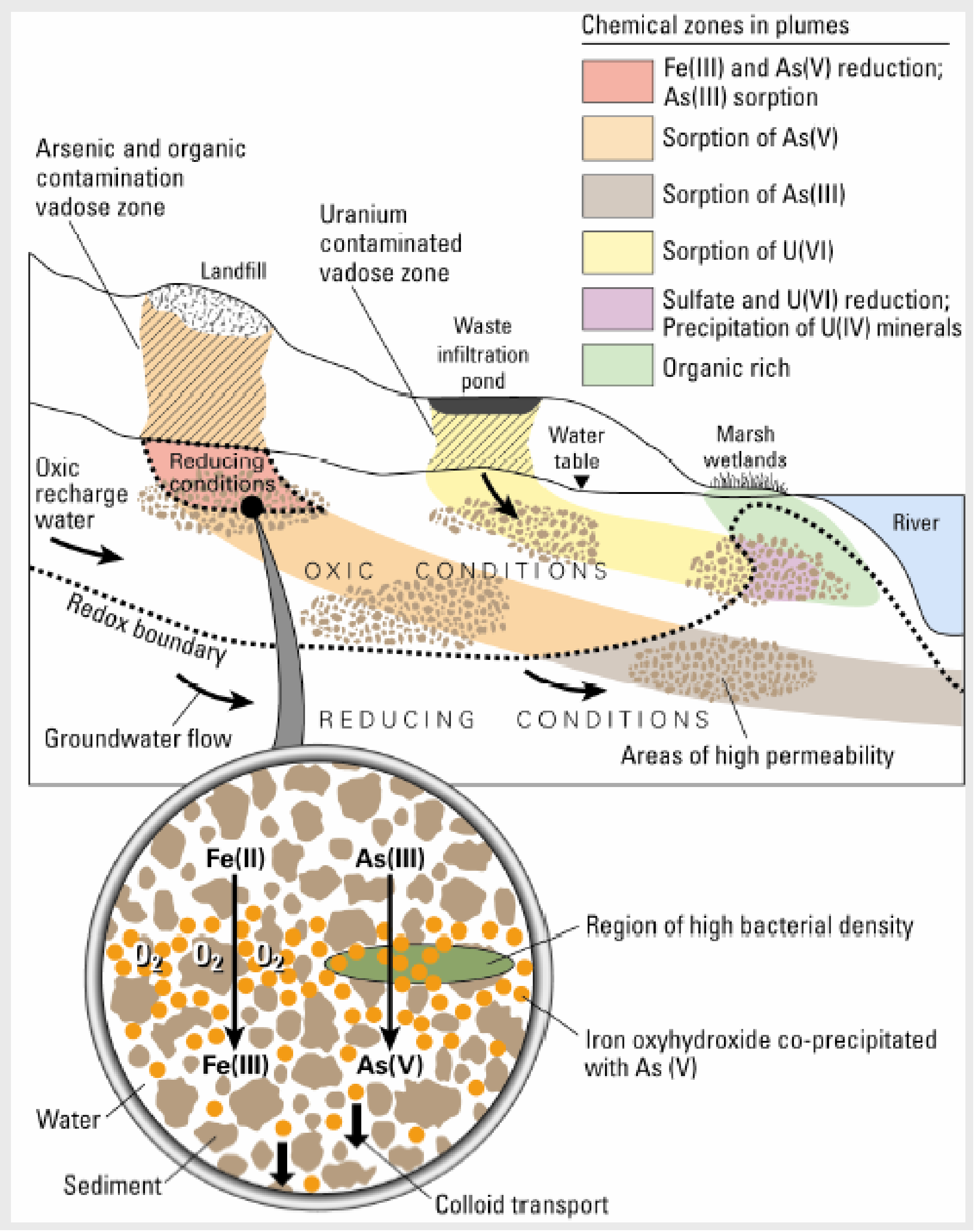
# Workshop Objectives

- Confirm key agency needs and goals for field-scale subsurface reactive transport modeling
- Assess and show by example the state-of-the-art in modeling processes controlling field-scale migration of inorganic solutes
- Evaluate the state-of-the-art to define
  - Where advances are needed in scientific understanding
  - New approaches for developing conceptual models
  - Improved methods for assessing field-relevant reaction parameters
  - Useful targets for new model development

# Complexity of Subsurface Environment

- Macroscale
- Microscale
- Atomic scale

"Constant $K_D$ won't work!"



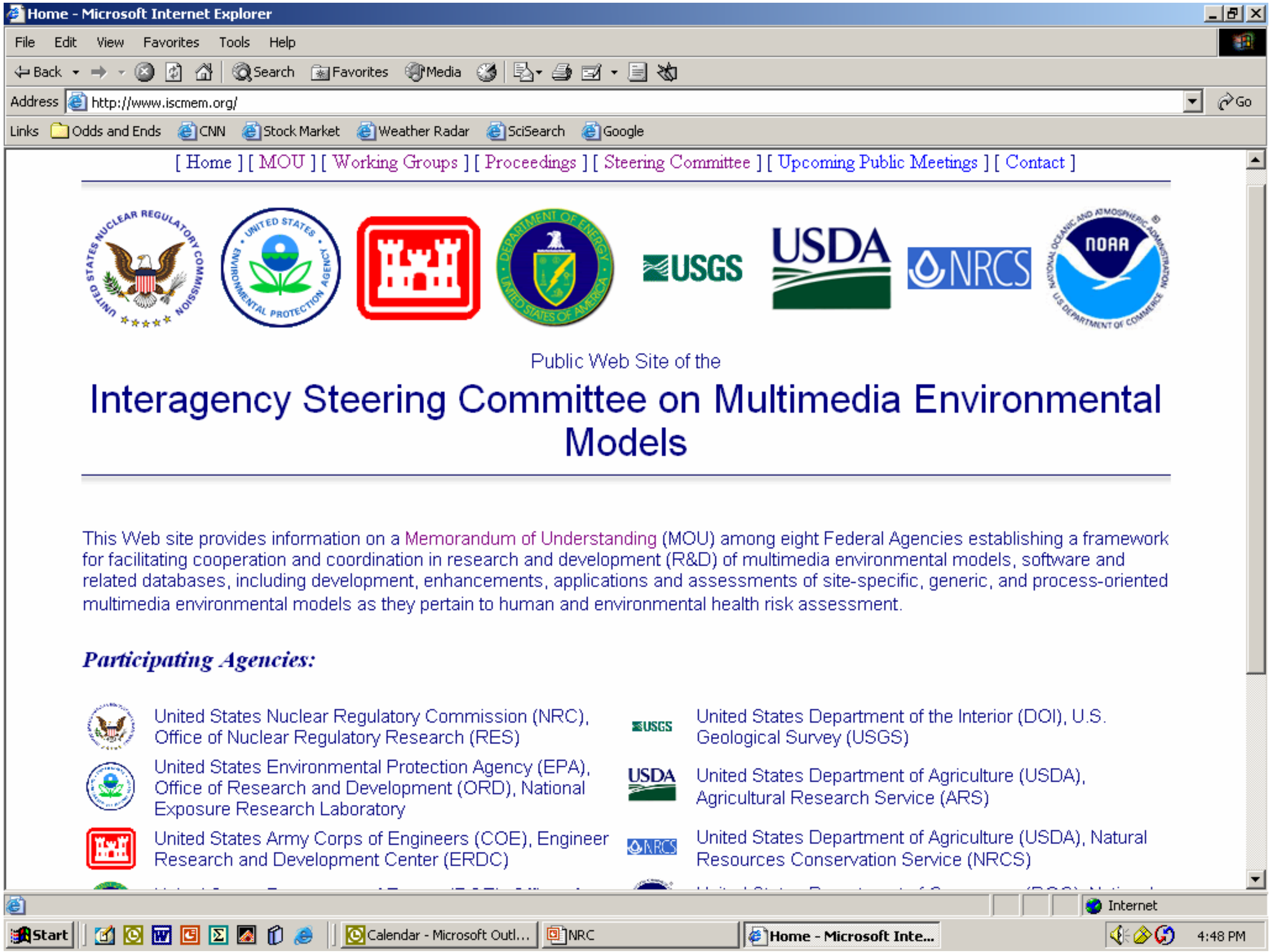
# Breakout Session Summaries
# Sorption and Ion Exchange Processes

- **Panel Recommendations**
  Publish a guidance document on conceptual models for sorption
  Develop a database for sorption model parameters
  Investigate applying surface complexation modeling to sorption in fracture rock systems and within the vadose zones

- **Unresolved Question**
  Conditional (Generalized Composite) or unconditional (Component Additivity) constants or $K_d$ more cost effective?

- **Field Site**
  Support long-term research at field site(s) for the purpose of developing and testing reactive transport models
  Select site for
  - ✓ Balance between complexity and tractability
  - ✓ A range of observable length scales of physical/chemical heterogeneity
  - ✓ Hydrologic and chemical transients to test system response
  - ✓ Spectrum of measurable biogeochemical processes operating in the system

# MOU Working Groups Public Web Pages



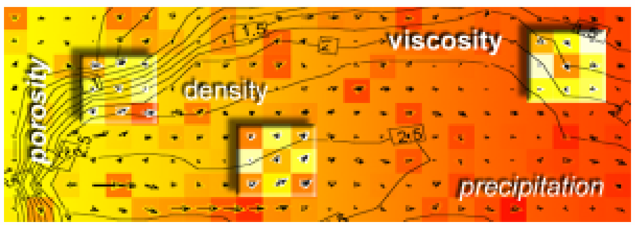

- Coordination for content of public web pages
- Public documents for multimedia environmental models
- Publication of phase two proposal for reactive transport modeling

# MOU Working Groups Public Web Pages

www.iscmem.org

Conceptual Model Development for Subsurface Reactive Transport Modeling of Inorganic Contaminants, Radionuclides, and Nutrients

*U.S. Federal Interagency Workshop*




April 20 – 22, 2004

*La Posada de Albuquerque*
Albuquerque, New Mexico

Sandia National Laboratories
A Department of Energy National Laboratory

## Web Page Design

U.S. FEDERAL INTERAGENCY WORKSHOP

Conceptual Model Development for Subsurface Reactive Transport Modeling of Inorganic Contaminants, Radionuclides, and Nutrients

Abstracts and presentations from the interagency workshop are provided below. The workshop was held in downtown Albuquerque on April 20-22, 2004 at the La Posada, and was sponsored by the Working Group on Subsurface Reactive Solute Transport of Federal Interagency Steering Committee on Multimedia Environmental Models.

**Description of Workshop**
The workshop was organized along two dimensions: applications and processes. The applications were introduced during the first day and were followed throughout the workshop. The technical review sessions were organized by processes: Physical/Coupling; Sorption; Redox/Microbiology; Precipitation/Dissolution. The breakout sessions were organized by the same topics. During the breakout sessions, we identified research projects on the corresponding process that are directly relevant to agency applications. During the final plenary session we pulled it all together by listing the research topics that will provide the greatest benefit to the most applications.

**Participants**
Seventy-four individuals representing numerous government laboratories, research universities, and private industries attended the workshop. Participants

**Summary Reports from Breakout Sessions**
Physical/Coupling Report
Sorption Report
Redox/Microbiology Report
Precipitation/Dissolution Report

***Reactive Transport Modeling and Simulation***

Initial Remarks and Goals of Workshop
**Jim Davis**
U.S. Geological Survey
Presentation

Geochemistry, Groundwater and Pollution: Learning by Modeling

# Post-Workshop Activities

- Publication of Working Group #3 workshop abstracts, presentation, and summaries on web
- Publication of Working Group #3 workshop proceedings as NUREG report (Cygan *et al*., 2005)
- Publication of workshop summary article in ***Eos*** (Davis *et al*. 2004)
- Organizing special issue of ***Vadose Zone Journal***; highlight reactive transport modeling and workshop topics (Goldberg and Cygan, Eds., 2006)
- Currently organizing Organics Subgroup

Davis, J.A., Yabusaki, S.B., Steefel, C.I., Zachara, J.M., Curtis, G.P., Redden, G.D., Criscenti, L.J., and Honeyman, B.D. (2004) Assessing conceptual models for subsurface reactive transport of inorganic contaminants. ***Eos, Transactions of the American Geophysical Union***, 85(44), 449-455.

Cygan, R.T., Siegel, M.D., and Criscenti, L.J. (2005) Proceedings of the international workshop on conceptual model development for subsurface reactive transport modeling of inorganic contaminants, radionuclides, and nutrients. ***U.S. Nuclear Regulatory Commission Report***, NUREG/CR, p. 5-2. U.S. Nuclear Regulatory Commission, Washington D.C., in press.

# Future Studies

- Compare SCM models: Will the component additivity model work?
  - Use three important phases from Naturita (e.g., quartz, ferrihydrite, clay)
  - Perform $UO_2^{2+}$ adsorption experiments; fit data using different SCM complexity
  - Perform $UO_2^{2+}$ adsorption experiments on groups of 2 or 3 minerals at a time
  - Use fitted log *K*s and surface complexes from previous experiments to “predict” adsorption to mineral assemblages
  - Assess relative ability of each model to make predictions—How much information is lost when we use simpler models?
  - Determine impact of surface protonation scheme on $UO_2^{2+}$ adsorption and SCM
- Complete development of Geoquímico
  - Expand component plotting capability
  - Support non-standard distributions for uncertainty analysis
  - Develop statistical analysis for uncertainty simulations
- Develop CMT method for determination of effective surface areas
  - Derive algorithm for surface area from 3D data describing important sorbing phases
  - Compare mineral mixtures with soil samples
  - Incorporate results into SCM models