Coupling Sorption to Soil Weathering During Reactive Transport: Impacts of Mineral Transformation and Sorbate Aging on Contaminant Speciation and Mobility

Lead Principal Investigator: Jon Chorover, University of Arizona

Co-Investigators: Karl Mueller, Penn State University
Peggy O'Day, University of California, Merced
R. Jeff Serne, Pacific Northwest National Laboratory
Carl Steefel, Lawrence Berkeley National Laboratory

Research Associates: Sunkyung Choi, UC Merced
Aaron Thompson, University of Arizona
Wooyong Um, PNNL

Graduate Students: Geoff Bowers, Penn State University
Nelson Rivera, UC Merced

The University of Arizona
Tucson Arizona
Arizona's First University.

UC Merced

Berkeley Lab
Ernest Orlando Lawrence Berkeley National Laboratory

PennState 1855

Pacific Northwest National Laboratory
Operated by Battelle for the U.S. Department of Energy

Project Objectives

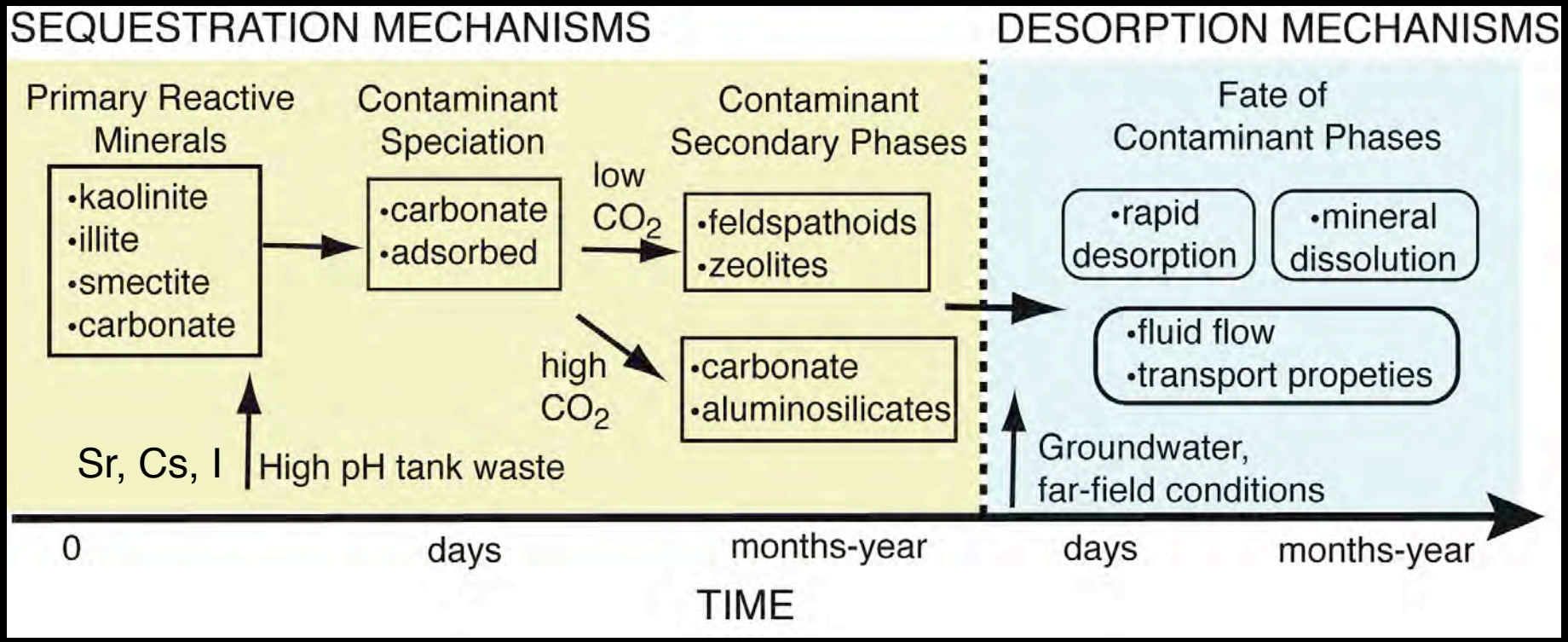
(1) Determine molecular-scale mechanisms responsible for time-dependent sequestration of co-contaminants (Cs, Sr, I) during reaction of waste-induced weathering fronts through sedimentary media.

(2) Examine the mechanism(s), rate, and extent of contaminant release from the sorbed state through bench-scale column experiments in saturated and unsaturated media.

(3) Develop a reactive transport model based on (1) and (2) that accurately simulates adsorption, aging, and desorption at the bench-scale, with transferability to field sites such as Hanford, and potentially applicability to other sites.

Project Conceptual Approach

Previous work → Current work



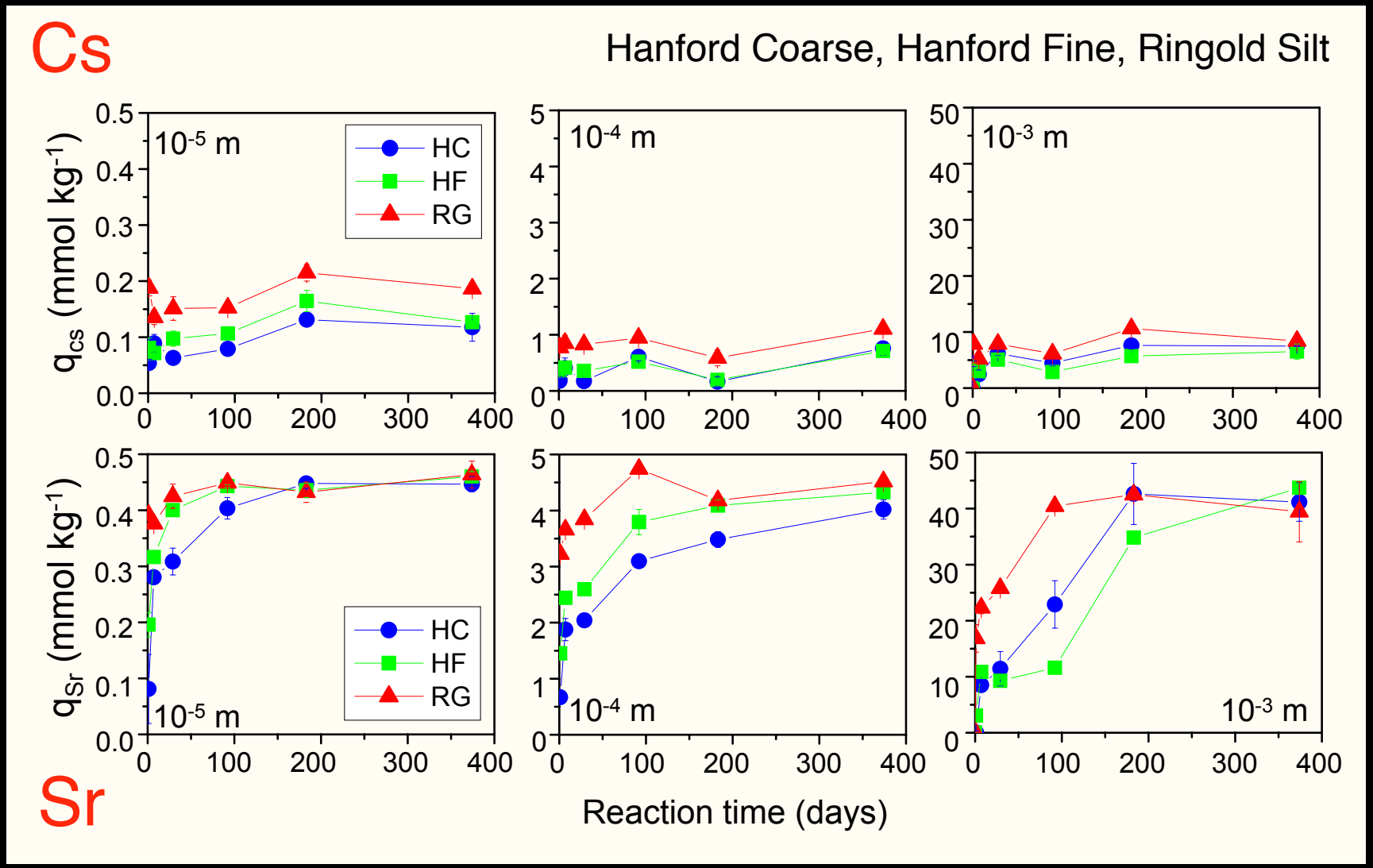
Batch experiments → Flow-through columns

- Model clays, sediments reacted with STWL (10^{-5} -10^{-3} m Sr, Cs, I)

Research Approach

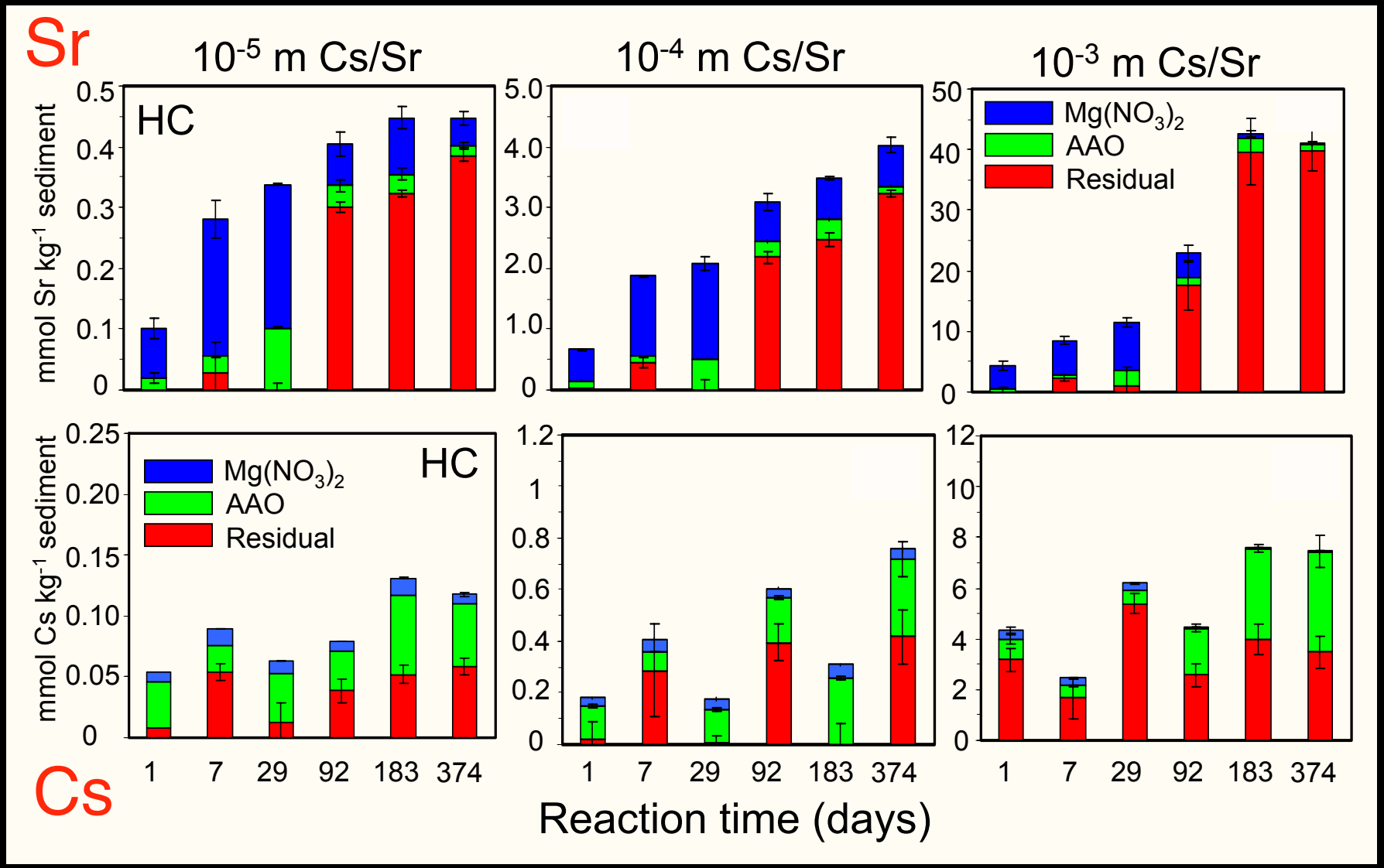
- Study of fundamental sorption, aging, and desorption processes using multi-faceted, bench-scale approach
- Novel applications of spectroscopic and imaging methods (synchrotron XAS/XRF/XRD, solid-state NMR, FTIR, SEM/TEM/EDS) to constrain molecular mechanisms
- Flow-through column experiments at different bench scales using aged media; saturated and unsaturated conditions
- Integration using reactive transport modeling with mechanistic and kinetic constraints
- Coordinated team effort among university and national lab groups; graduate and post-doctoral student training

Batch Experiments: Cs & Sr Uptake on Hanford sediments reacted with STWL



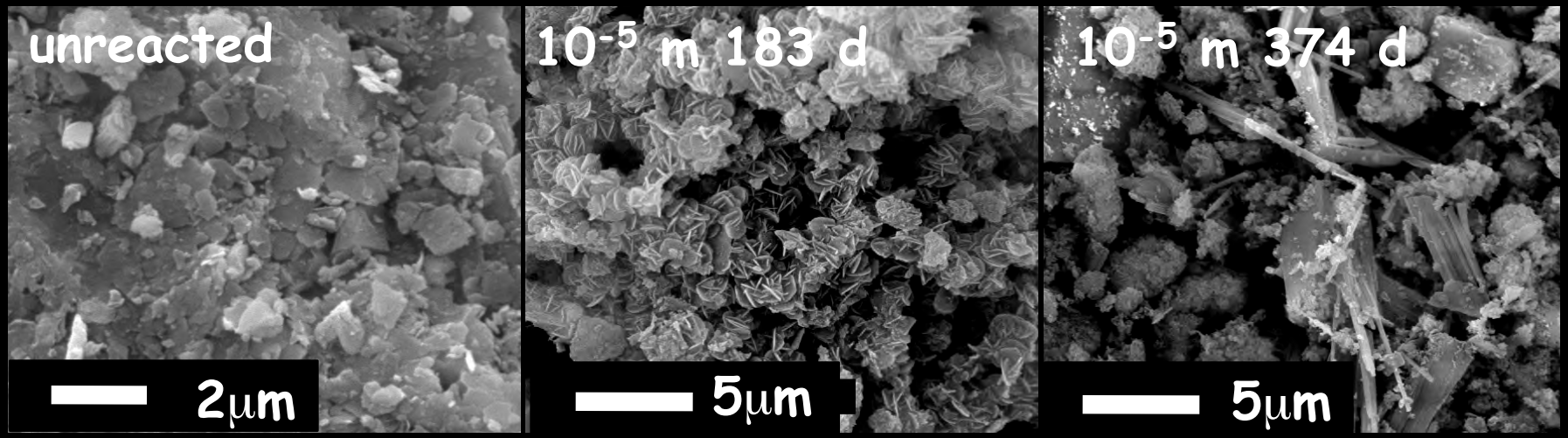
Chorover et al. (in prep.)

Batch Experiments: Sr & Cs extracted from reacted Hanford sediments

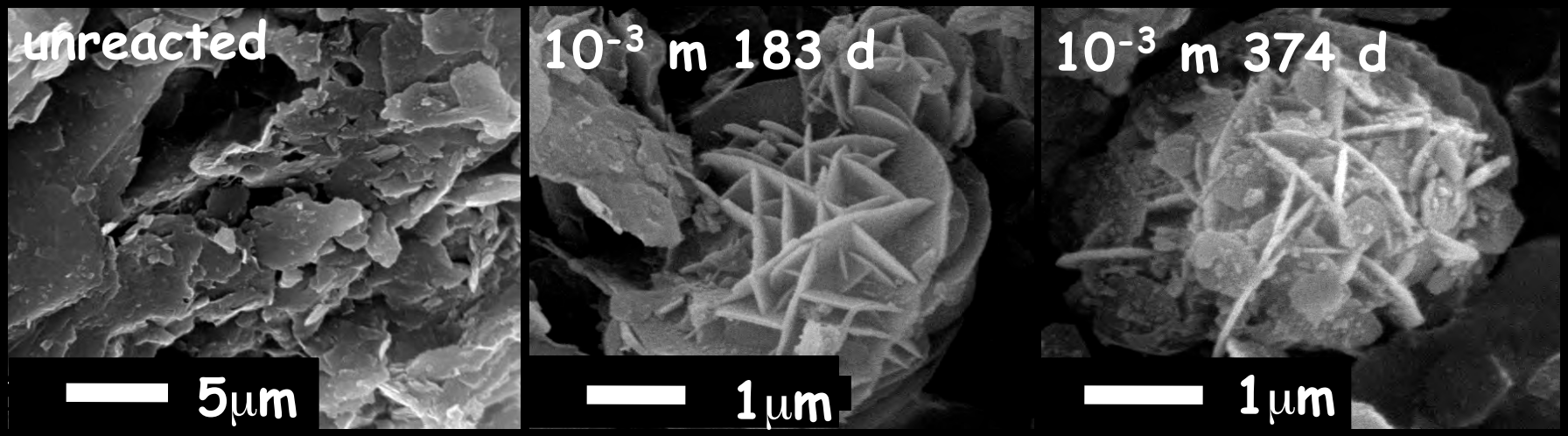


Chorover et al. (in prep.)

SEM: Unreacted & reacted sediments



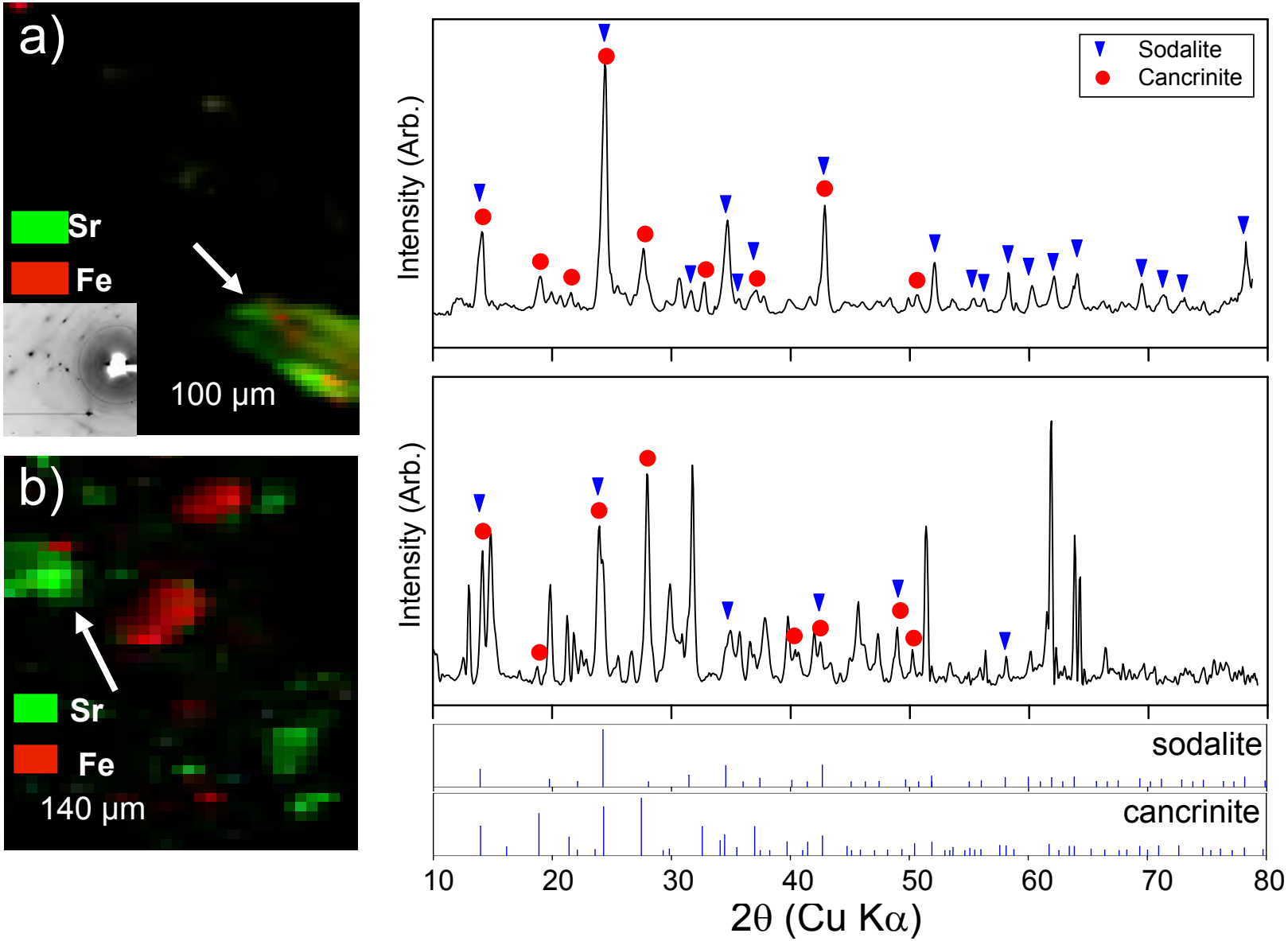
Hanford Coarse



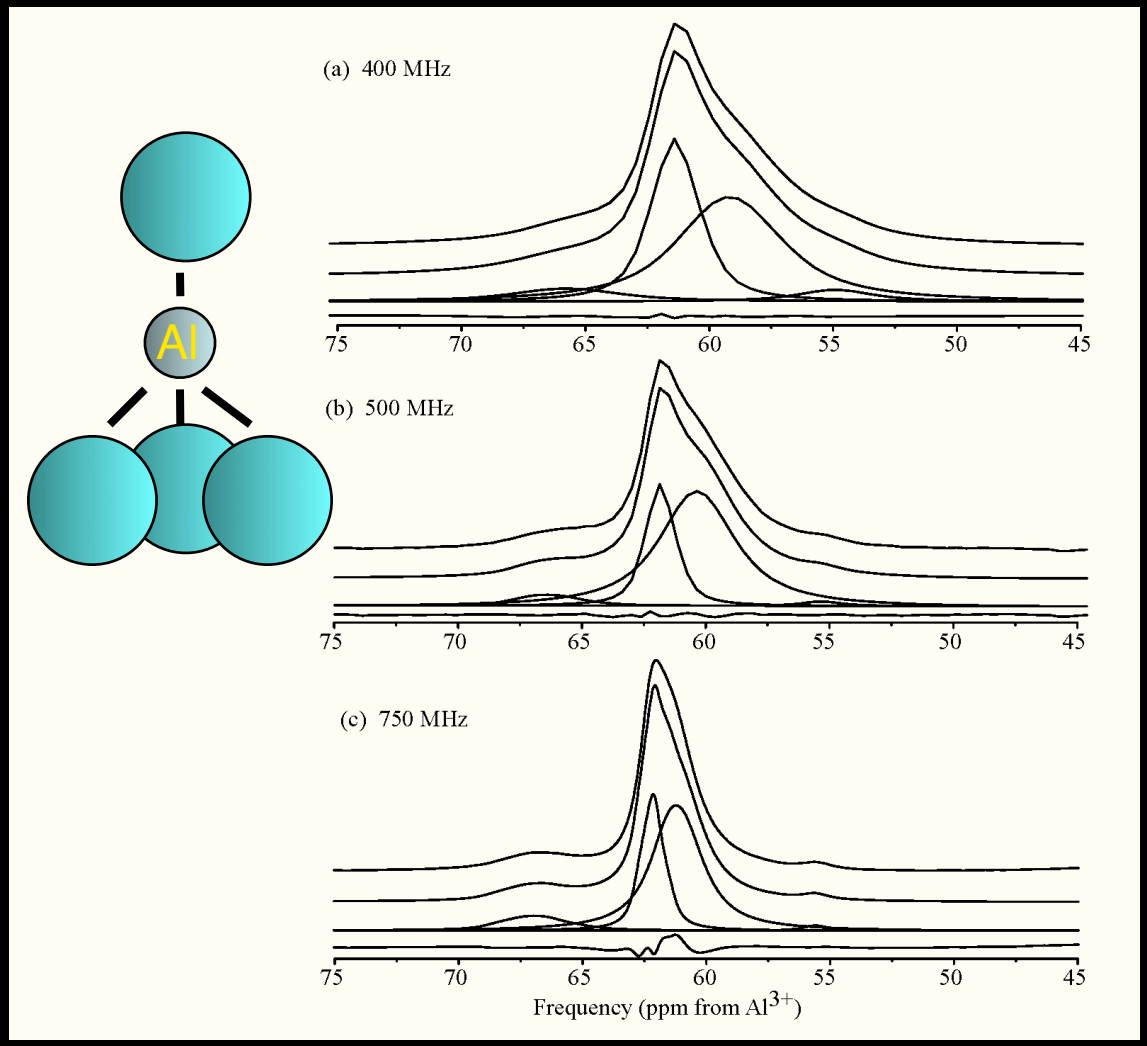
Ringold Silt

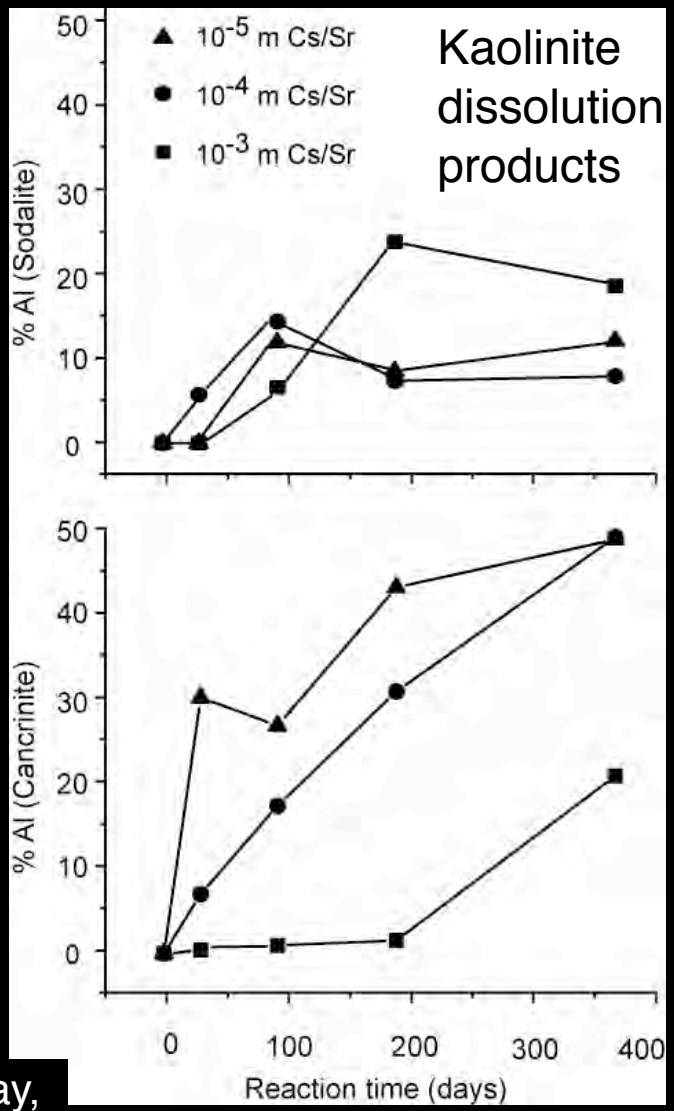
Chorover et al. (in prep.)

Synchrotron X-ray Micro-XRF & XRD: Hanford Sediments (aged 1 year)



^{27}Al MAS NMR at High-Fields: Kinetics of Clay Weathering

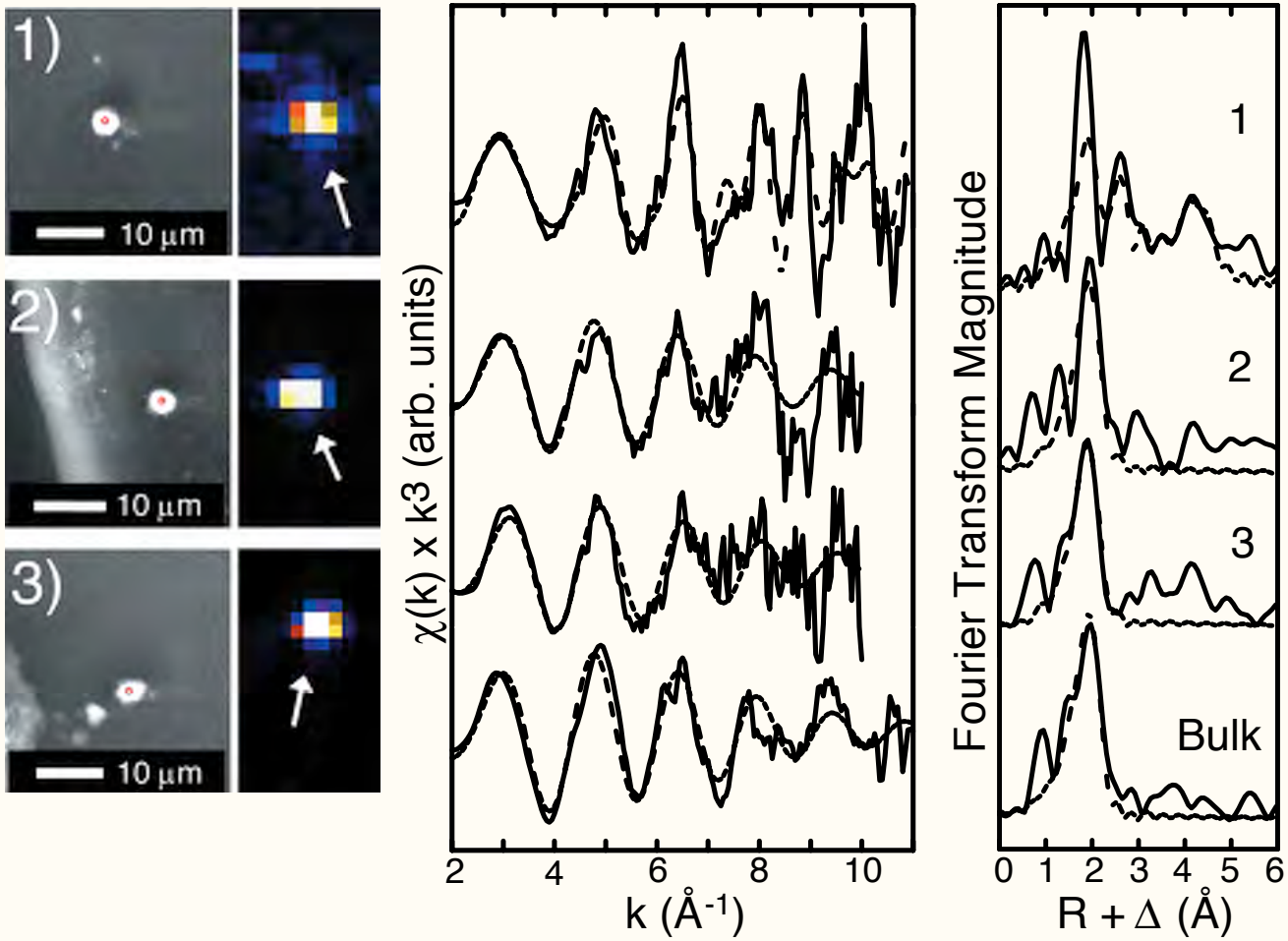




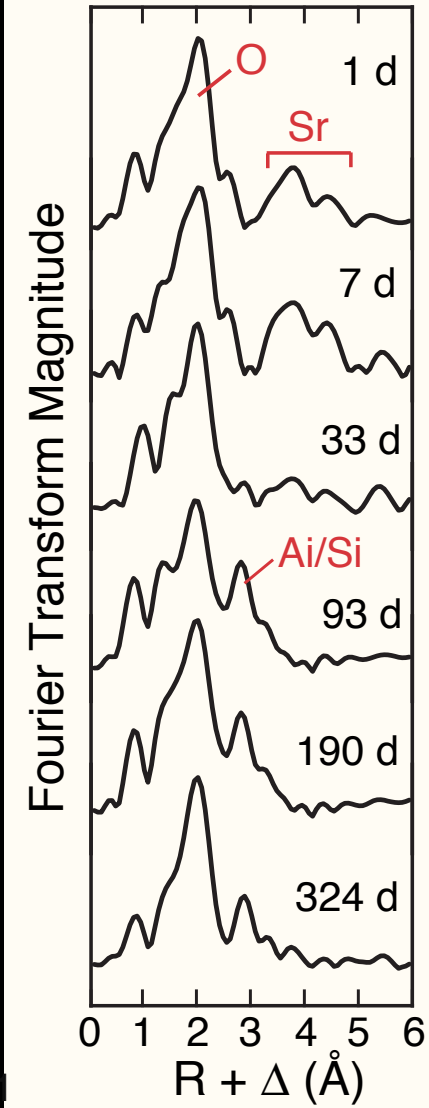
G. S. Crosson, S. Choi, J. Chorover, M. K. Amistadi, P. A. O'Day, and K. T. Mueller, J. Phys. Chem. B 110, 723-732 (2006).

Sr-XAS: Kaolinite reacted with STWL

Micro-EXAFS: Neoformed particles at 33 d



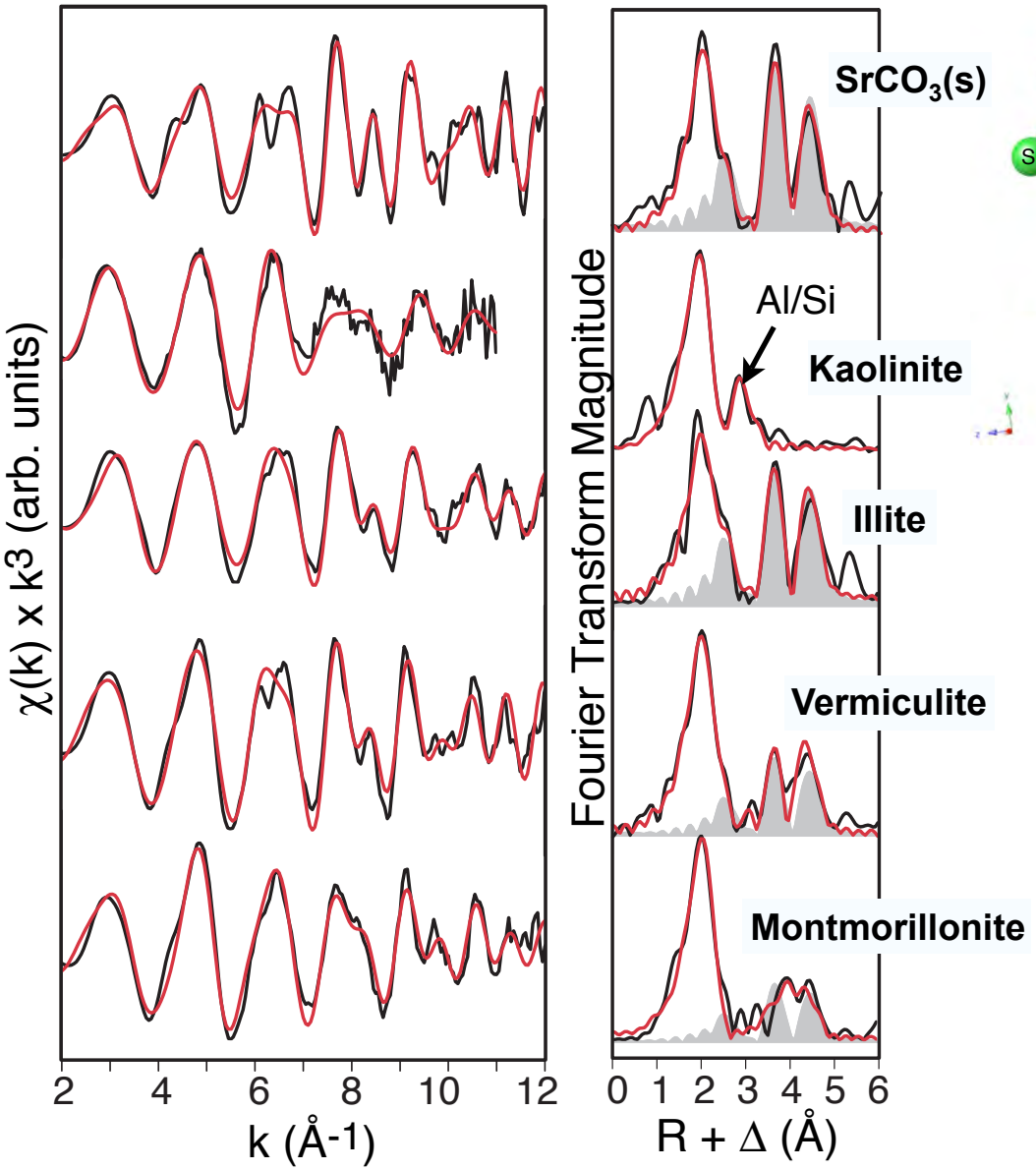
Bulk EXAFS

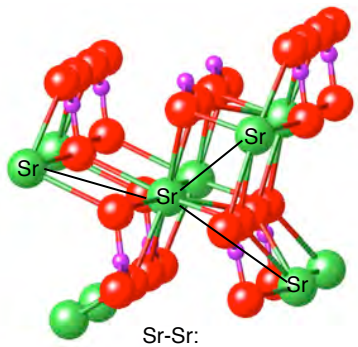


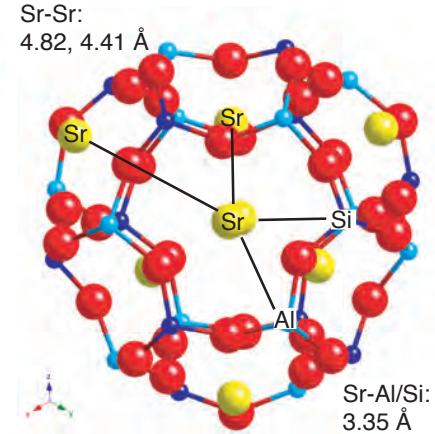
S. Choi, P. A. O'Day, N. Rivera, K. T. Mueller, M. A. Vairavamurthy, S. Seraphin, J. Chorover, Env. Sci. Tec. 40, 2608-2614 (2006)

Figure 1

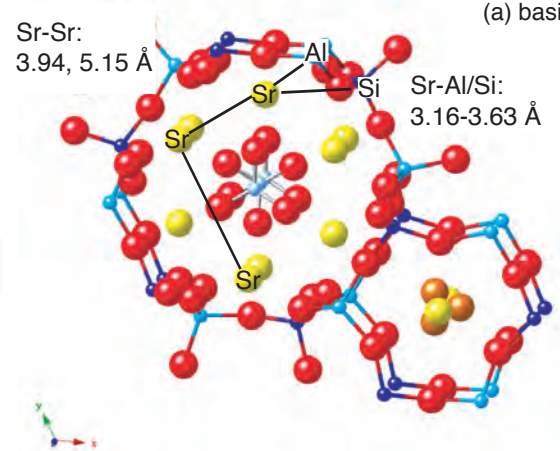
Bulk Sr EXAFS : Model clays (aged 1 year)







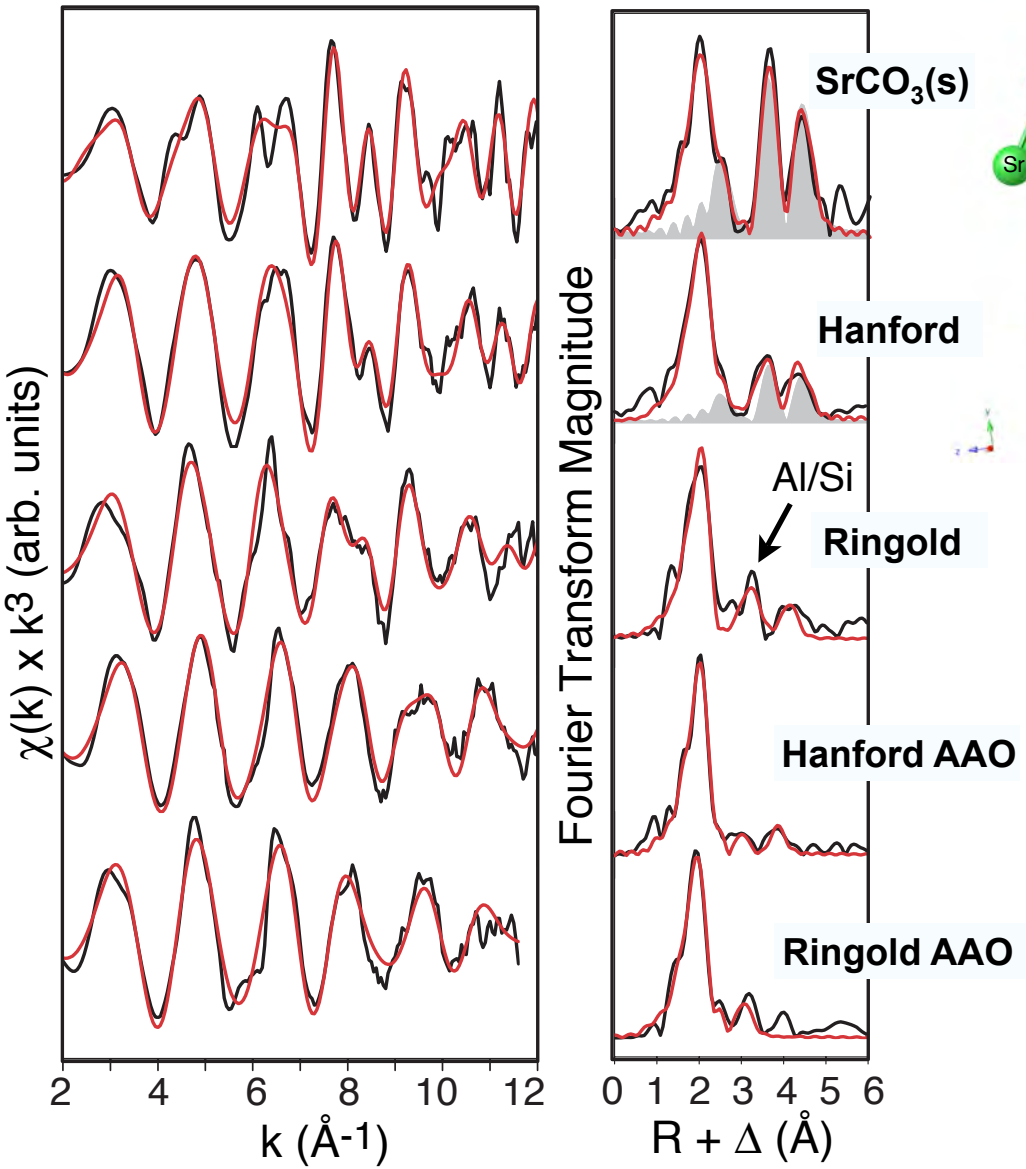
(a) basic sodalite

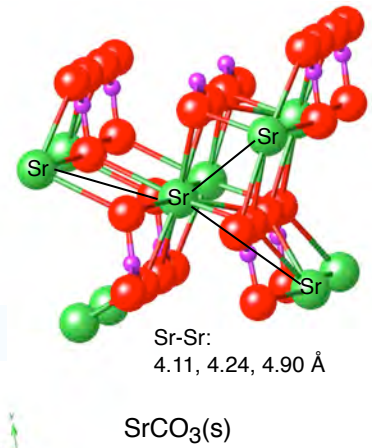


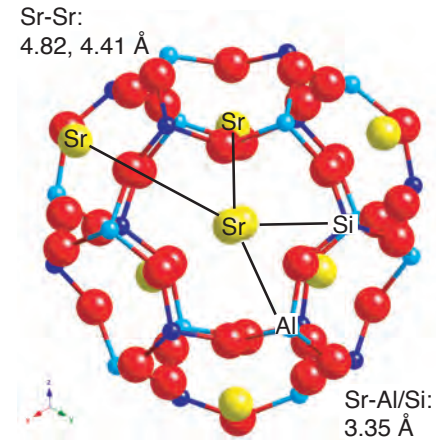
(b) nitrate cancrinite

Choi et al. (in prep.)

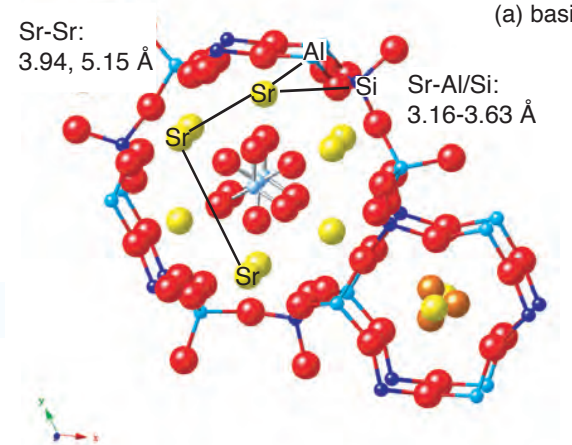
Bulk Sr EXAFS: Hanford Sediments, reacted and AAO extracted (aged 1 year)







(a) basic sodalite



(b) nitrate cancrinite

Choi et al. (in prep.)

Summary of Batch Results: Model Clays & Hanford Sediments

- Molecular mechanisms of Sr & Cs sorption change with time and system composition
- Rate of formation of secondary aluminosilicate limited by Si supply from dissolution of primary minerals
- Sr (& Cs) dehydration and irreversible sequestration with aging in feldspathoid minerals; more recalcitrant Sr than Cs in sediments after 1 year
- Larger fraction of adsorbed Cs but less total uptake than Sr
- Competition between carbonate and feldspathoid/zeolite phases for Sr
- Carbonate precipitation not kinetically limited and is easily reversed

Work In Progress: Contaminant Desorption Studies

(1) Age Hanford Sediments for 6 and 12 mo in simulated waste solutions (presence and absence of CO_2) leading to sequestration of Sr, Cs and I in neo-formed aluminosilicates.

(2) Couple flow-through desorption experiments using different sized columns and different influent chemistries with reactive transport modeling (program CRUNCH).

Simulated field desorption solutions:

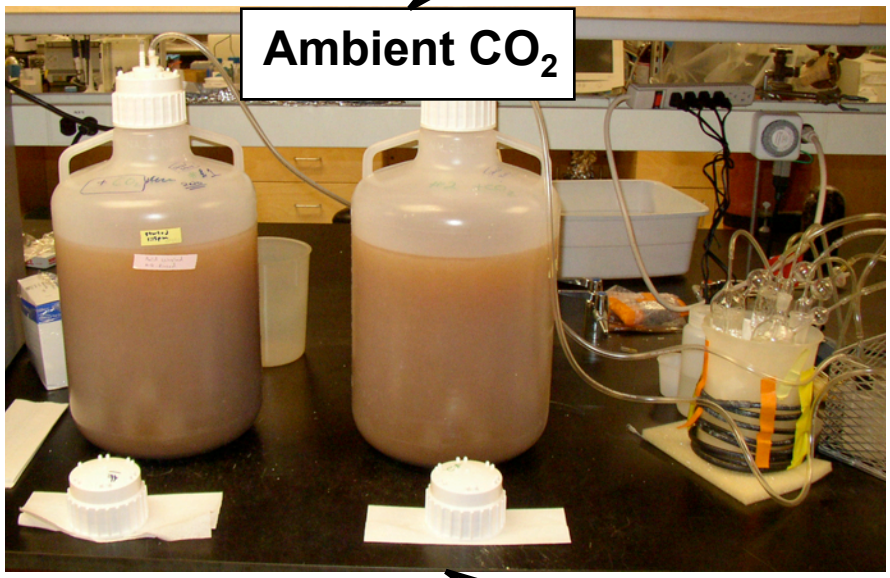
- *Neutralized high salinity (NHS)*
- *Background pore water (BPW)*

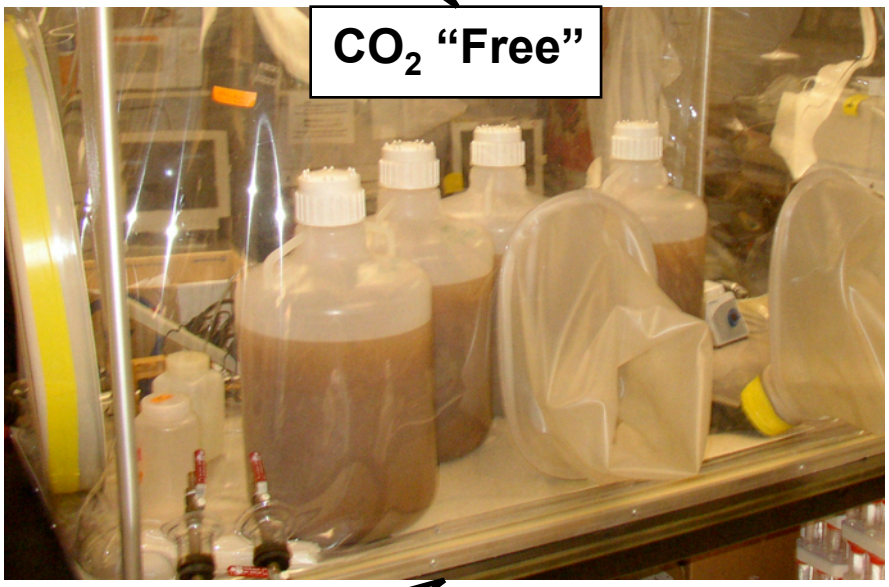
Batch reactors: Simulated contact of tank waste with Hanford sediments

High contaminant
10^{-3} m Sr, Cs, 10^{-5} m I

Low contaminant
10^{-5} m Sr, Cs, 10^{-7} m I

400g sediment per treatment

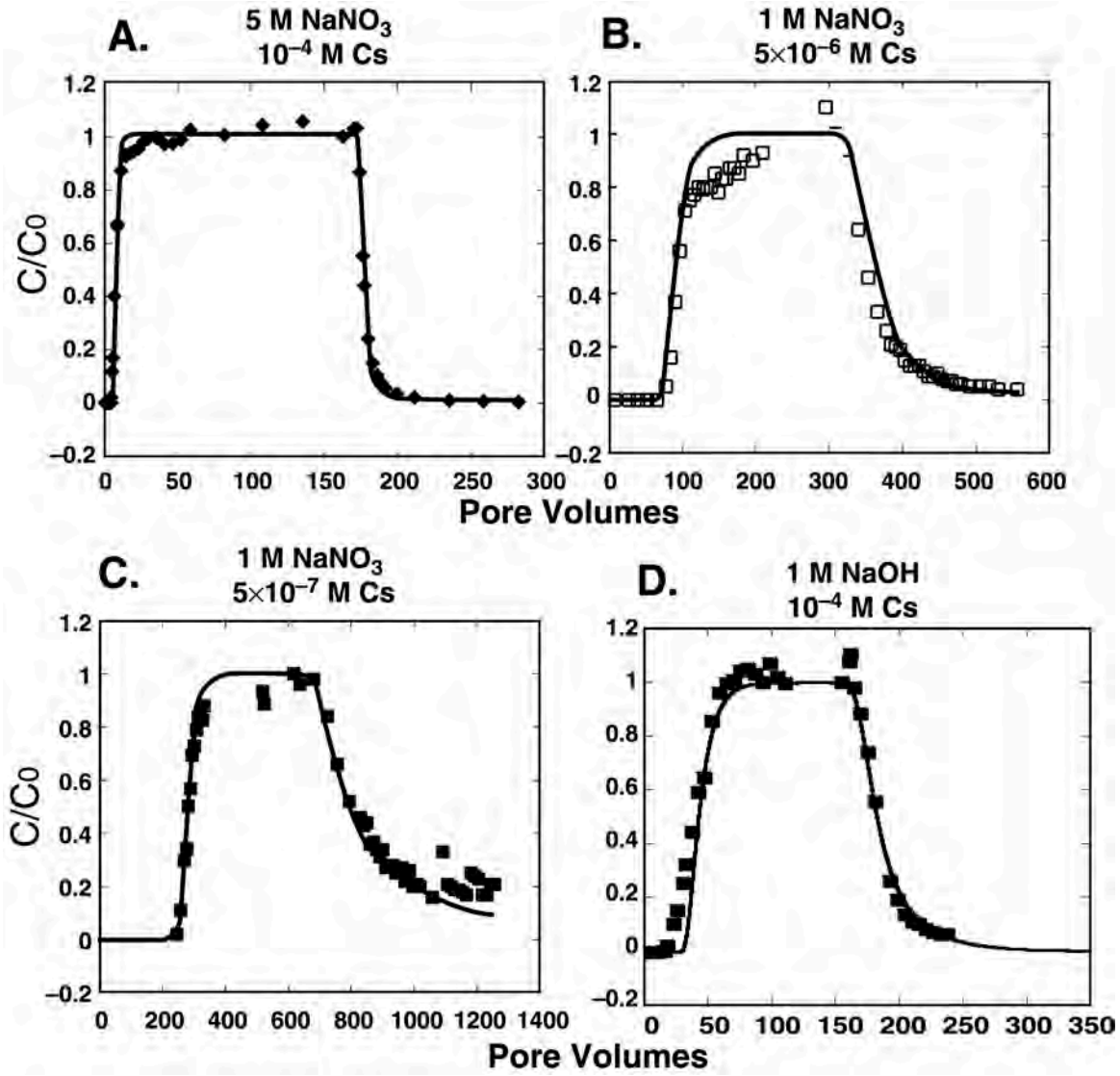




6 month aging

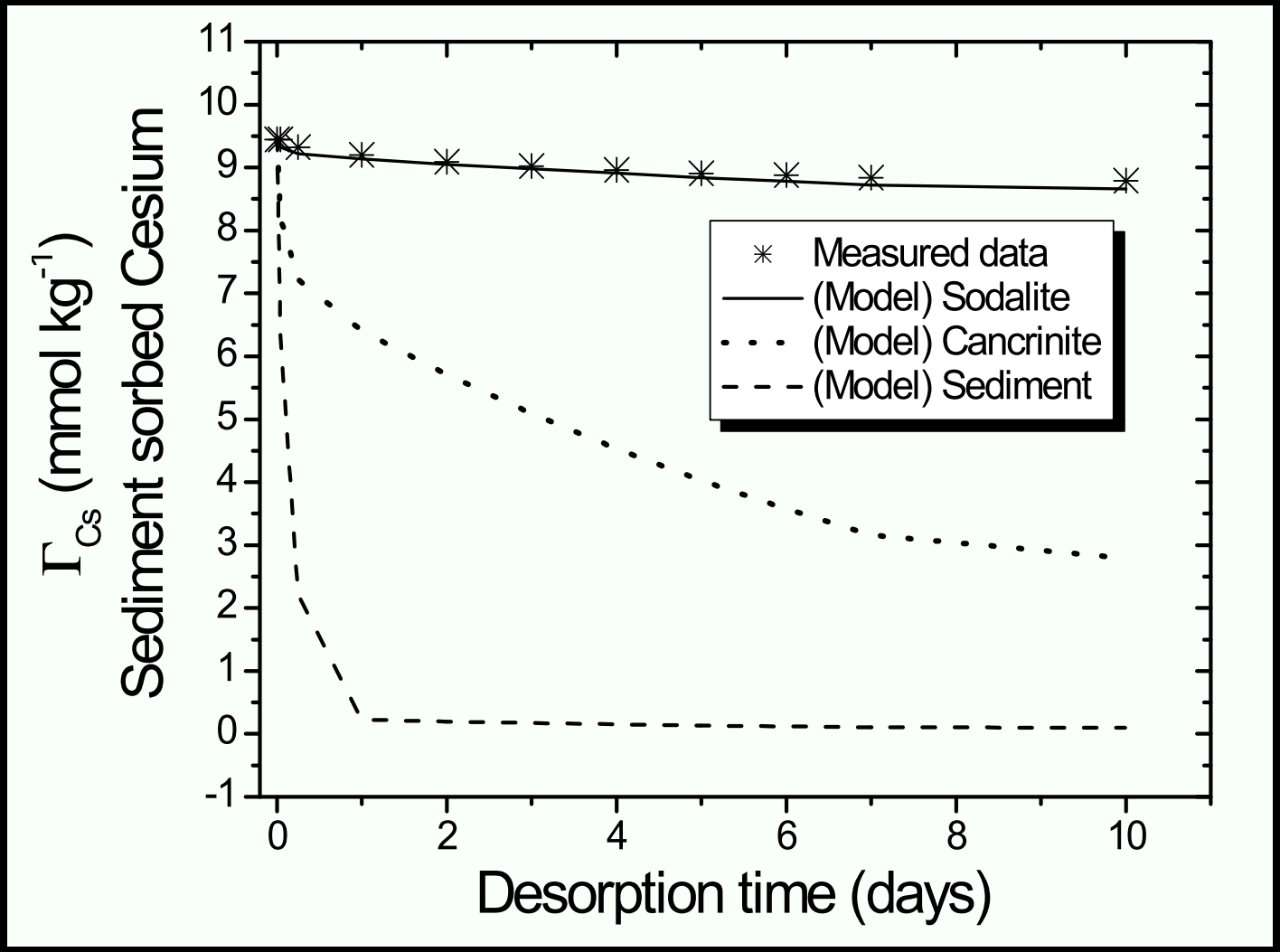
12 month aging

Reactive Transport Modeling : Reversibility of Cs exchange



Steefel et al. (2003) *J. Contam. Hydrol.*

Desorption: Preliminary experiments and transport modeling (after aging 10 months)



Unsaturated Column Experiments

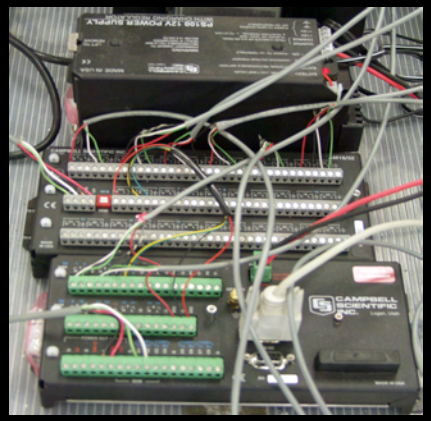
Hanging Water Columns

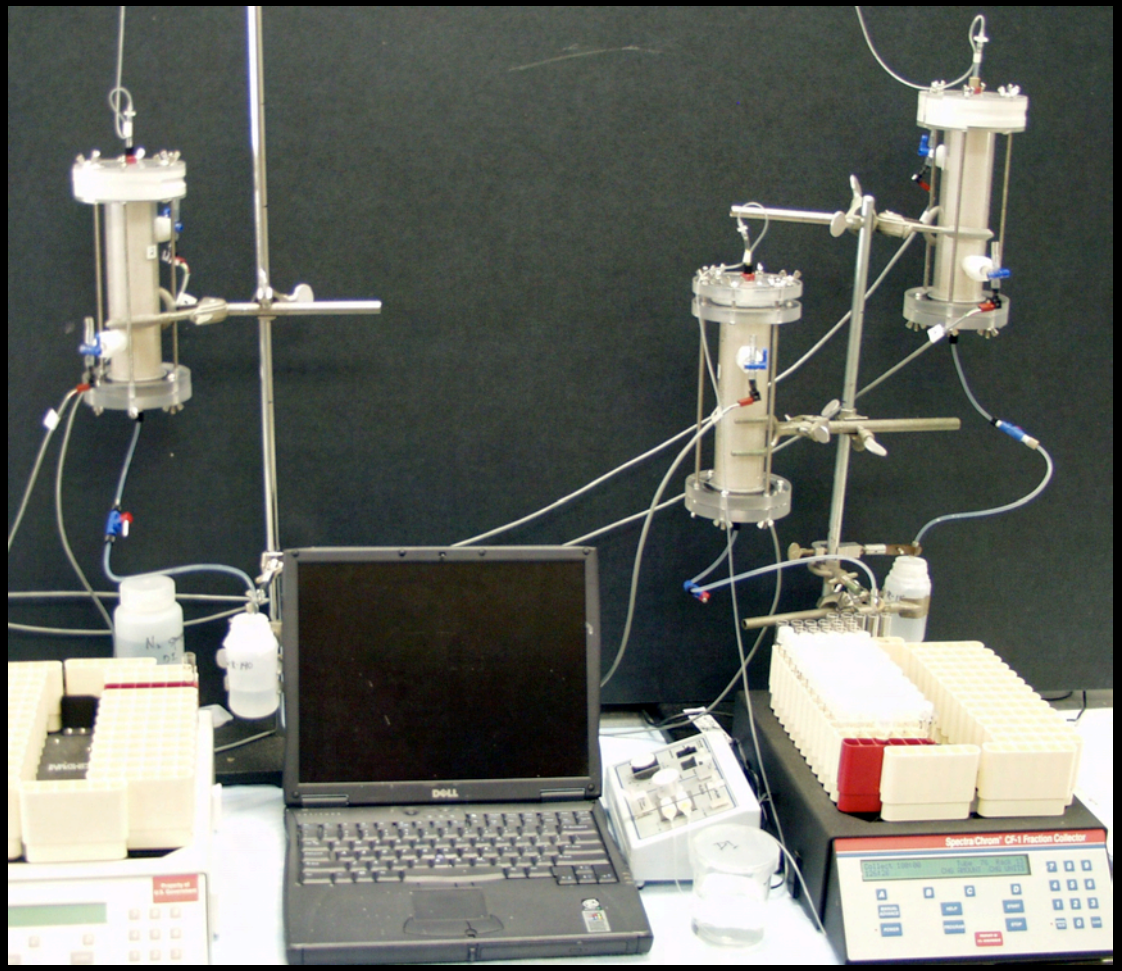
-- Column Length (20.32 cm) Diameter (3.81 cm)

-- Low influent through a sprinkler at top

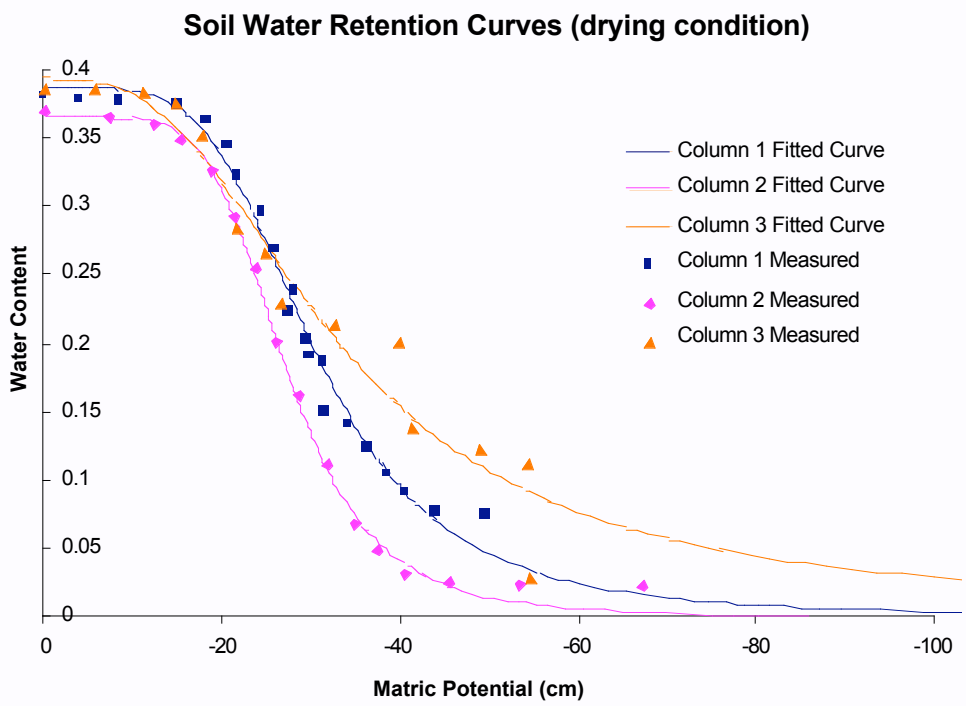
-- Suction pressure controlled at bottom by different height

-- Moisture monitored with tensiometers





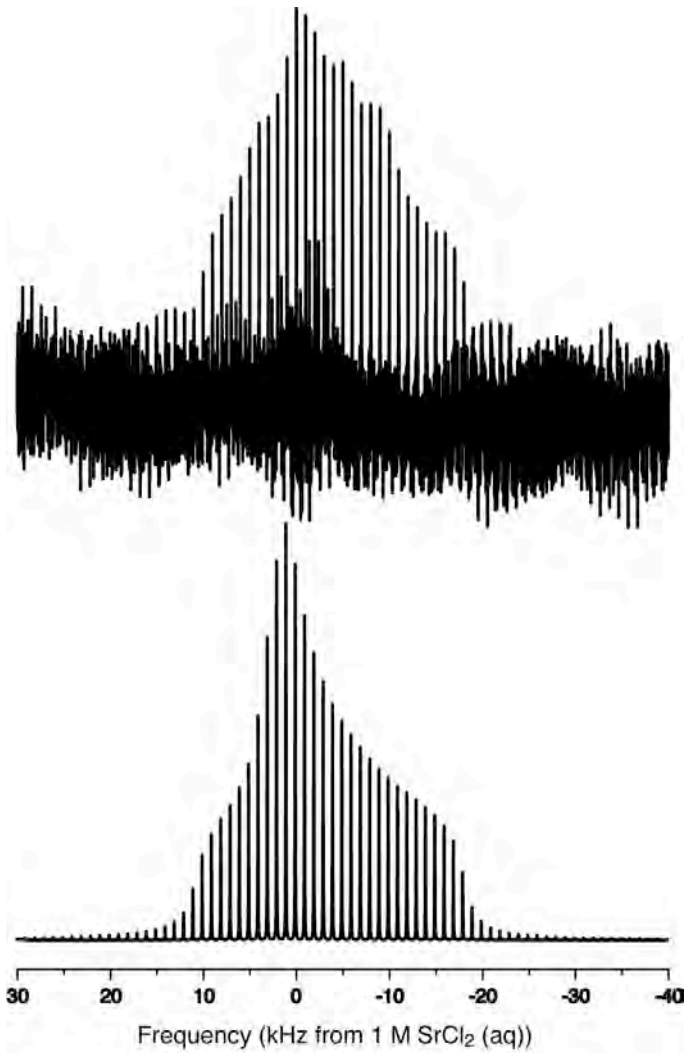
Moisture Contents of Unsaturated Columns

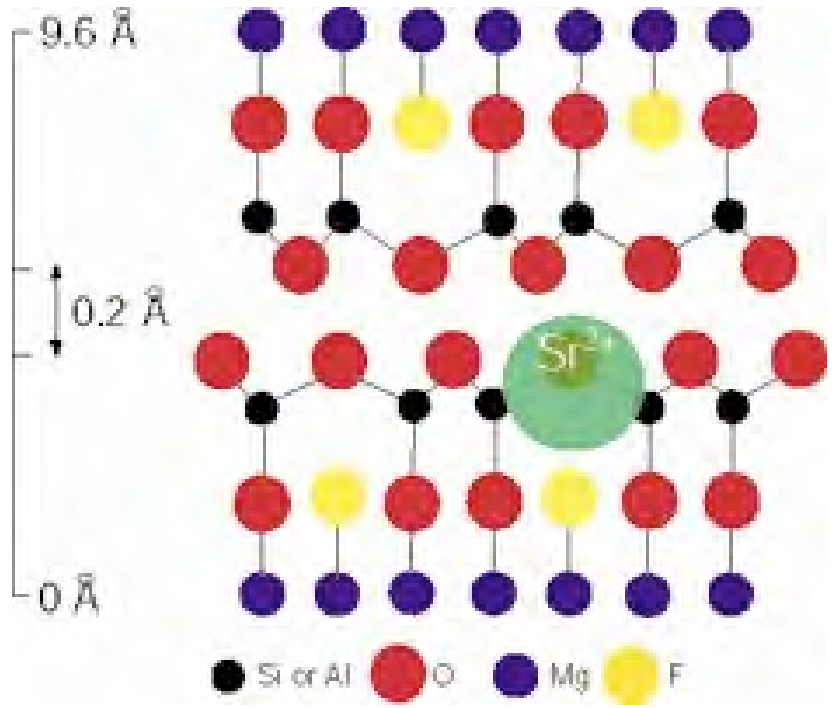


Curve Fit Results (RETC)

Column #	1	2	3
Saturation (Suction)	24% (-40 cm)	37% (-30 cm)	82% (-20 cm)
R^2	0.978	0.997	0.954
Θ_s	0.388	0.367	0.394
α	0.035	0.038	0.036
n	4.68	6.00	3.04

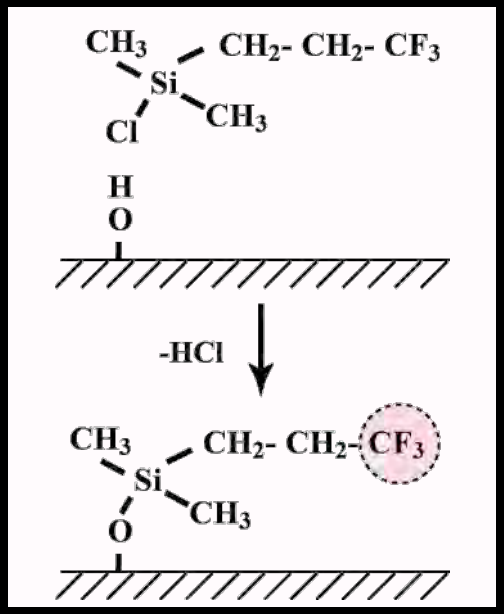
^{87}Sr NMR in the Environment: Sequestration in Mica

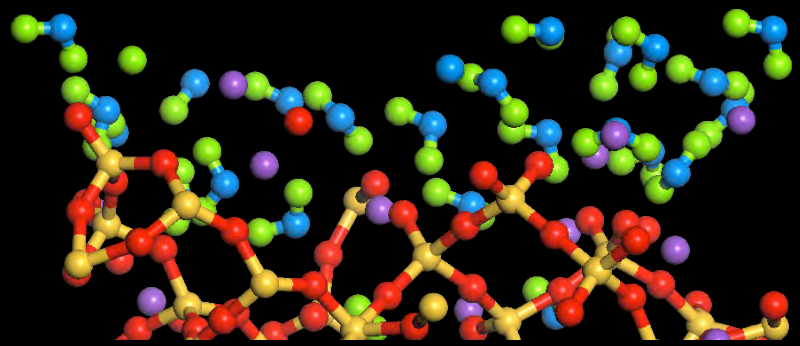


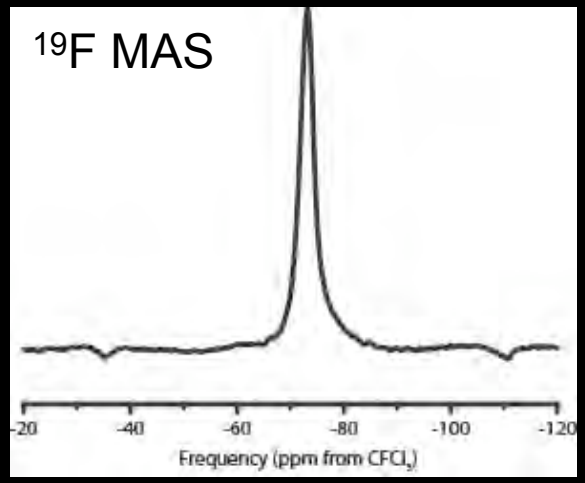


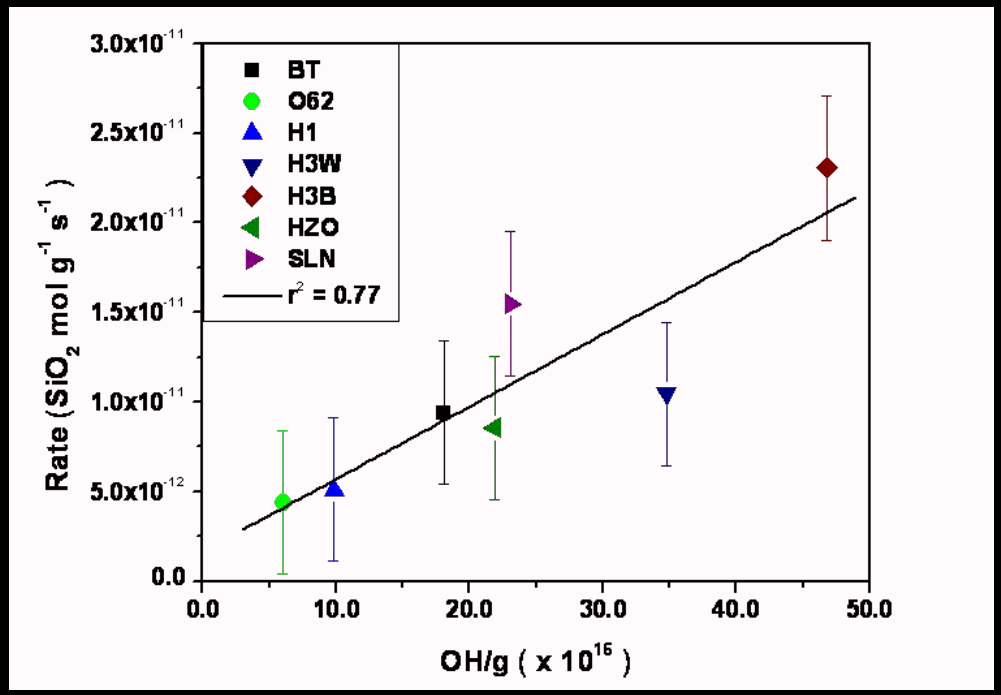
G. M. Bowers, R. Ravella, S. Komarneni, and K. T. Mueller, *Journal of Physical Chemistry B* **110**, 7159-7164 (2006).

^{19}F MAS-NMR:
Reactive Surface Area on Oxide Surfaces



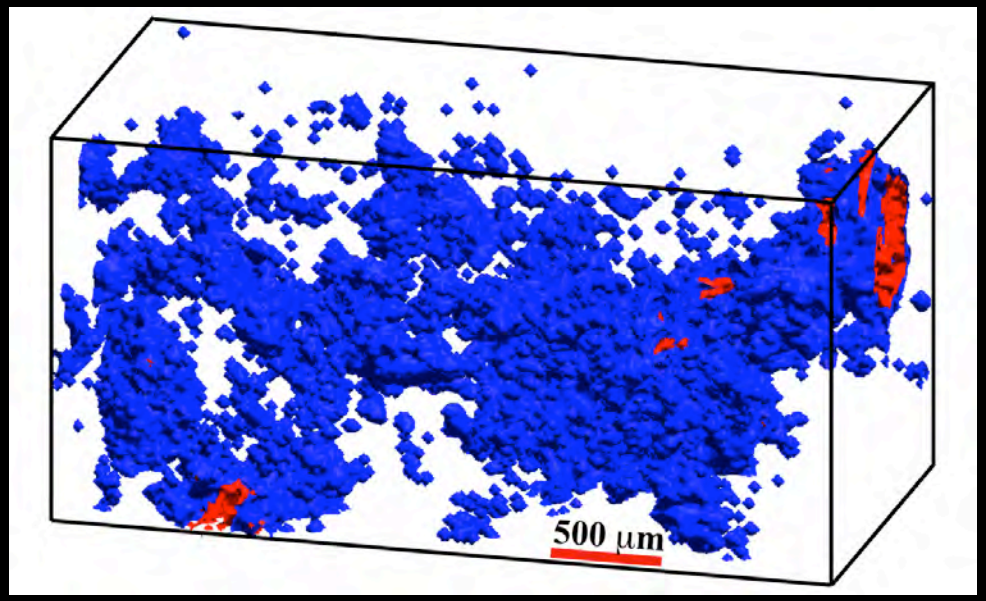


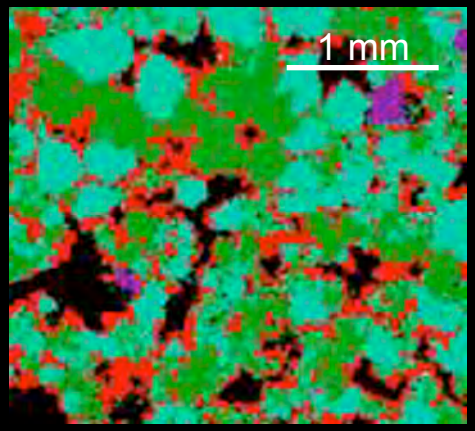


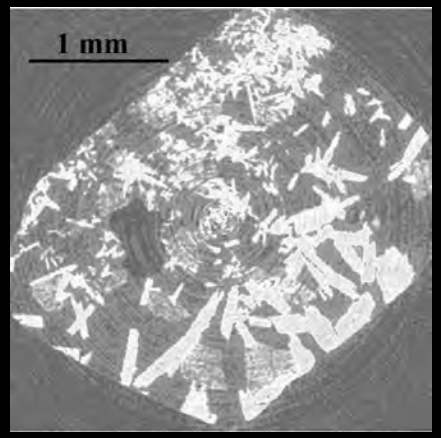


Planned column characterizations: X-ray microtomography

3-D imaging of pore structure







- *Quantify porosity, pore connectivity at different scales*
- *Link physical and chemical heterogeneity*

Summary & Expected Outcomes

- Current column Studies: Comparison of desorption rates and mechanisms for Sr, Cs, and I under saturated and unsaturated conditions, different field flush-out scenarios
- Novel applications of spectroscopies/imaging to constrain molecular-scale mechanisms: adsorption, recalcitrant sequestration in aluminosilicates, carbonate ppc/diss.
- Synthesis of processes (sediment alteration, aging, desorption), rates, and mass transfer using reactive transport modeling
- Transferable model parameters that can be applied at the field scale at different sites

THE UNIVERSITY OF ARIZONA
TUCSON ARIZONA
Arizona's First University.

UC MERCED

PENNSTATE 1855

BERKELEY LAB
ERNEST ORLANDO LAWRENCE BERKELEY NATIONAL LABORATORY

Pacific Northwest National Laboratory
Operated by Battelle for the U.S. Department of Energy