Interfacial Soil Chemistry of Radionuclides in the Unsaturated Zone

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Cs and Sr in TankWaste Leachate

solvent extraction
chemical separation
waste

$Na\text{-}NO_3\text{-}NO_2\text{-}Al(OH)_4^-\text{-}OH^-$

^{137}Cs and ^{90}Sr

Circumneutral Sediments

Smectite

Vermiculite

Illite

Feldspars, Micas

Neutralization of alkaline waste
- dissolution of soil minerals
- release/polymerization of Si
- co-precipitation with Al

e.g.,

$$Al(OH)_4^- + 0.5\ SiO(OH)_3^- + 1.5\ H^+ \Leftrightarrow 0.5(HO)_3Al_2O_3SiOH\ (s) + 2.5\ H_2O$$

Precipitation of Al hydroxides, carbonates, and metastable SRO Al/Si phases

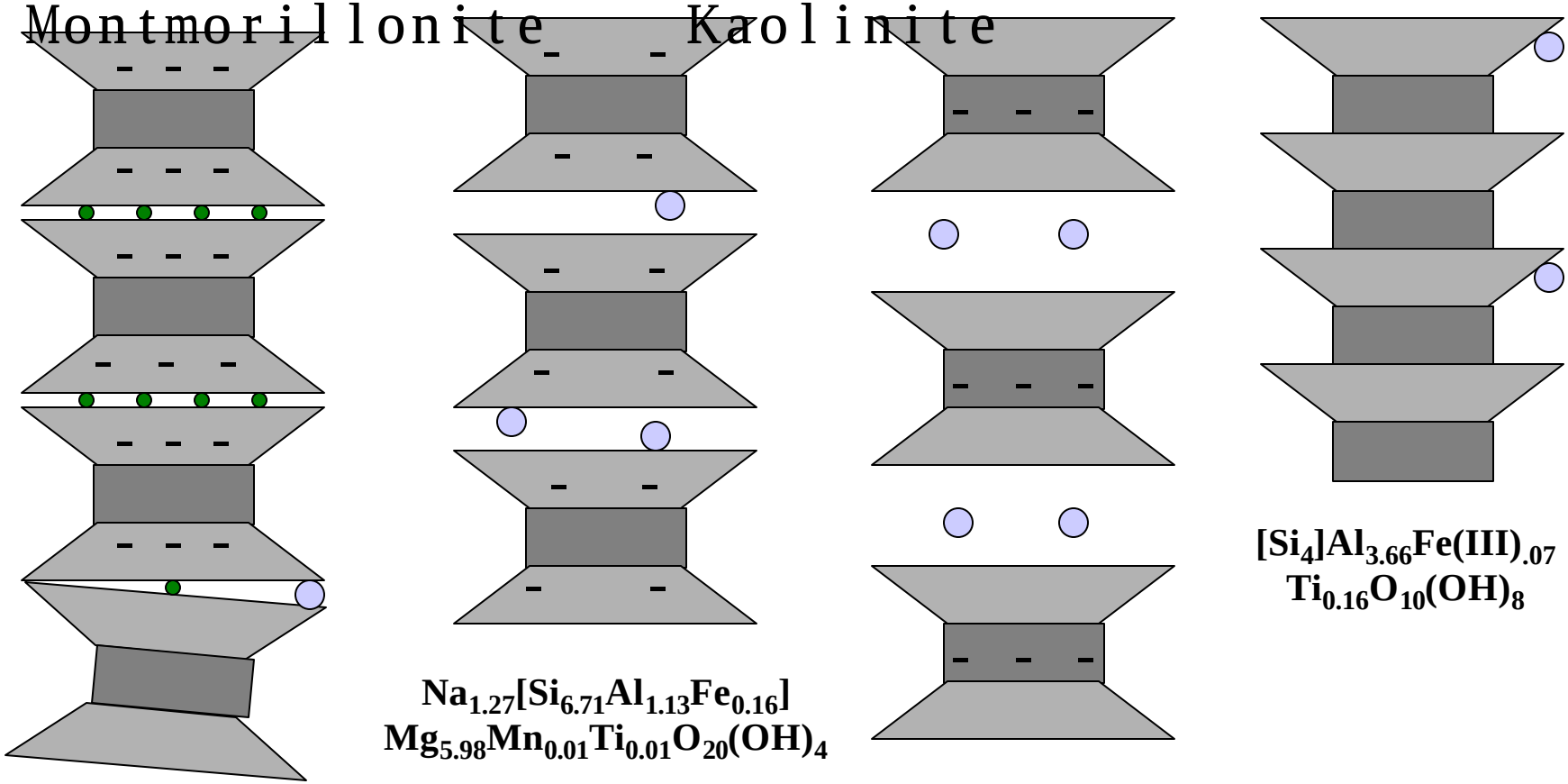
Specimen clays used in the study

Illite

Vermiculite

Montmorillonite

Kaolinite



$Na_{0.3}K_{1.37}$
$[Si_{6.77}Al_{1.23}]Al_{2.69}Fe_{0.76/0.06}$
$Mg_{0.43}Ti_{0.06}O_{20}(OH)_4$

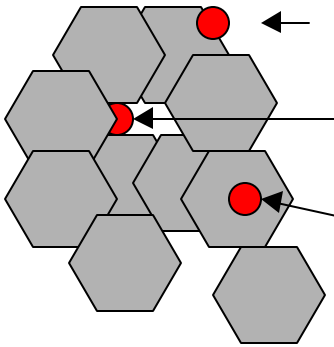
$Na_{1.27}[Si_{6.71}Al_{1.13}Fe_{0.16}]$
$Mg_{5.98}Mn_{0.01}Ti_{0.01}O_{20}(OH)_4$

$Na_{0.56}[Si_{7.98}Al_{0.02}]Al_{3.01}Fe_{0.41}$
$Mg_{0.54}Ti_{0.02}O_{20}(OH)_4$

$[Si_4]Al_{3.66}Fe(III)_{.07}$
$Ti_{0.16}O_{10}(OH)_8$

Effects of secondary precipitates on ^{137}Cs and ^{90}Sr

Precipitation from solution

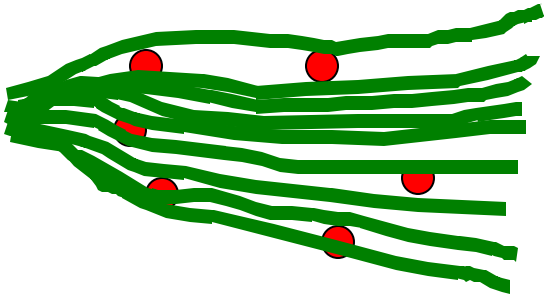


High specific surface
(300-1000 $m^2\ g^{-1}$)

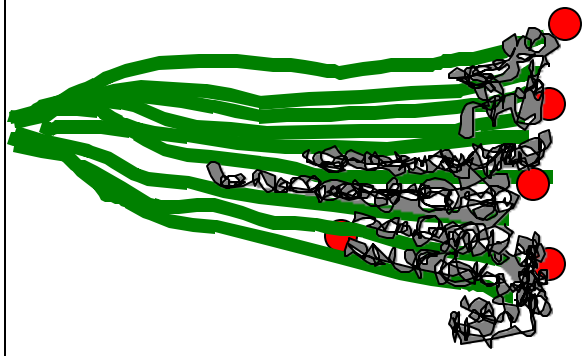
Colloidal (5-500 nm)

Mobile in the vadose zone?

Precipitation on 2:1 layer silicates



high Cs affinity
slow kinetics
low reversibility
high K_d, K_{ex}



low Cs affinity
fast kinetics
high reversibility
low K_d, K_{ex}

Objectives

- Investigate dynamics of Cs and Sr uptake over long times during reaction of STWL with specimen clays and Hanford sediments.
- Study the weathering behavior of clays and sediments under the intense geochemical conditions imposed by the waste leachate.
- Establish relations among mineral weathering processes and sorption/desorption behavior of Cs/Sr.

Experimental: Increasing complexity

homogeneous nucleation	heterogeneous (clays)	heterogeneous (soils)
Introduction of Cs/Sr Al-rich alkaline waste	Surface SRO precipitation on specimen clays	Surface SRO precipitation on Hanford soils
Reaction with $Si(OH)_4$	Effects on uptake of Cs/Sr, kinetics and reversibility	Effects on uptake of Cs/Sr, kinetics and reversibility
Neutralization	Changes in K_d, K_{ex}	Changes in K_d, K_{ex}
Precipitation of SRO aluminosilicates	Structure/mechanism	
Uptake/Release/Structure		

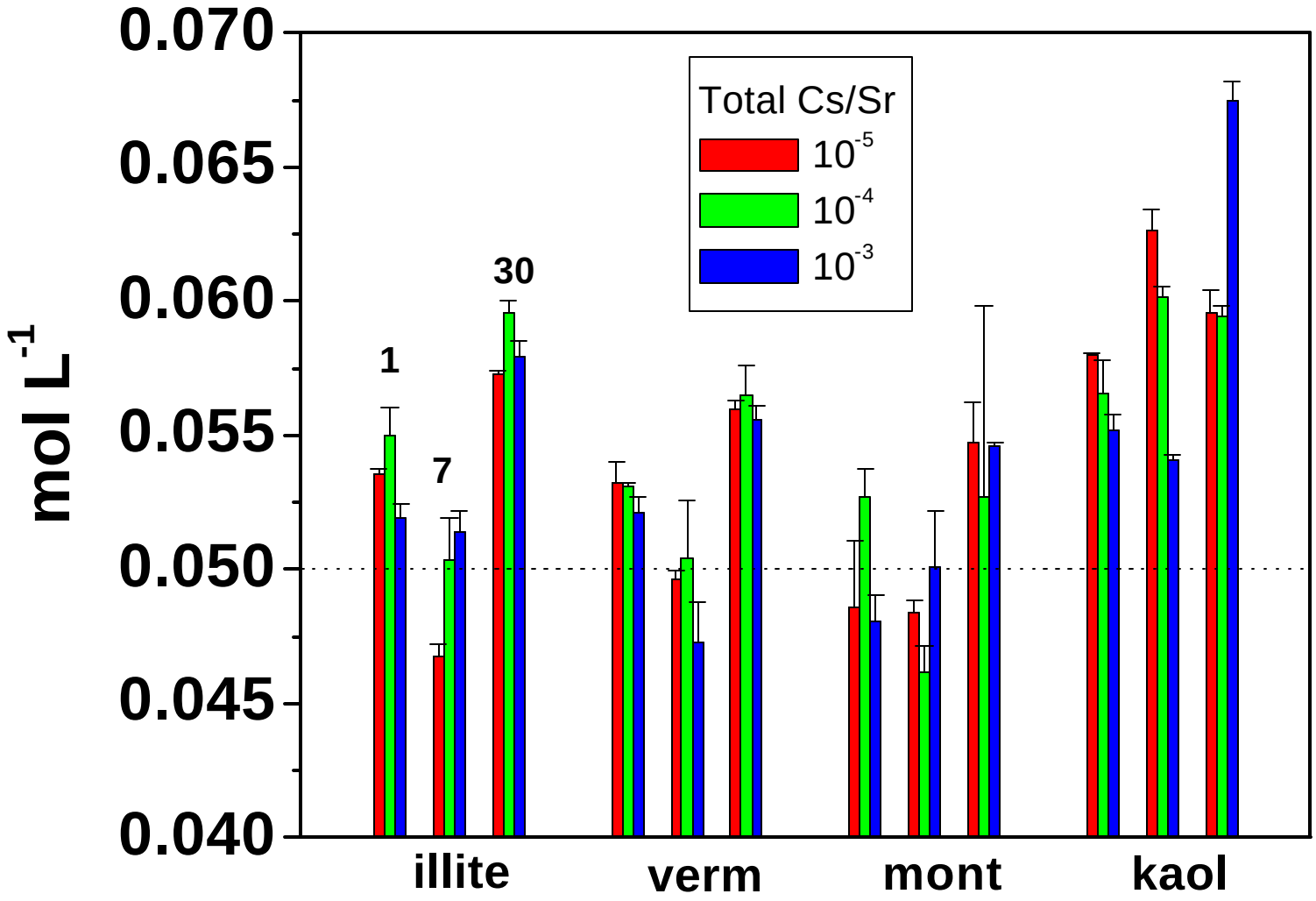
Batch uptake and release reaction

- STWL was prepared to simulate REDOX/PUREX waste streams:

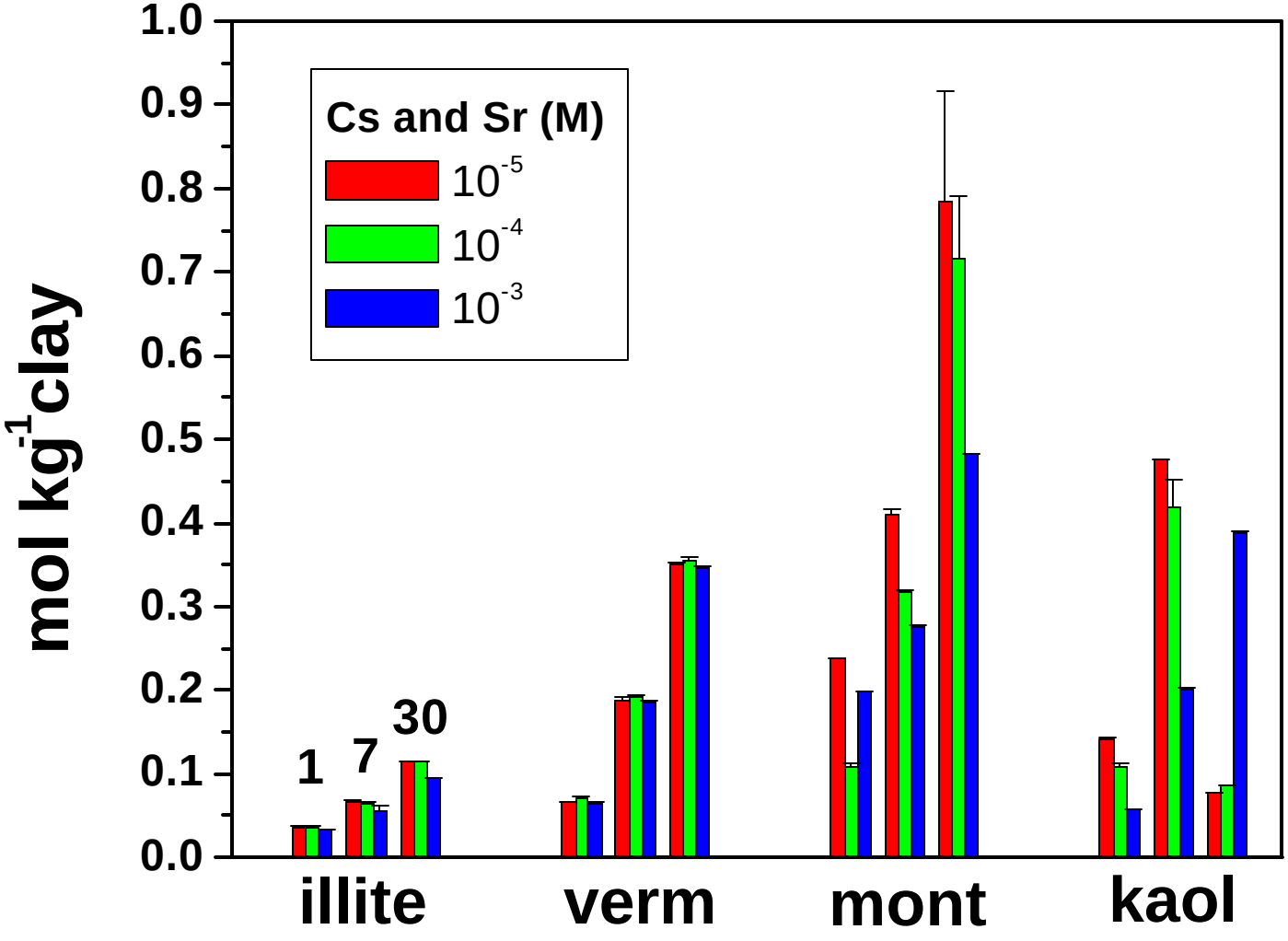
  Al_T = 0.05 M
  Na^+ = 2.05 M
  NO_3^- = 1.0 M
  OH^- = 1.0 M
  (pH 14)
  [Cs] and [Sr] = 10^{-5} to 10^{-3} M

- Solutions were prefiltered and purged with N_2(g) prior to sealing for reaction with specimen clays and Hanford sediments (Hanford coarse, Hanford fine, Ringold) for 24 hours to 30 days (continuing to 2 yr).
- End-over-end rotation at 1 rpm.

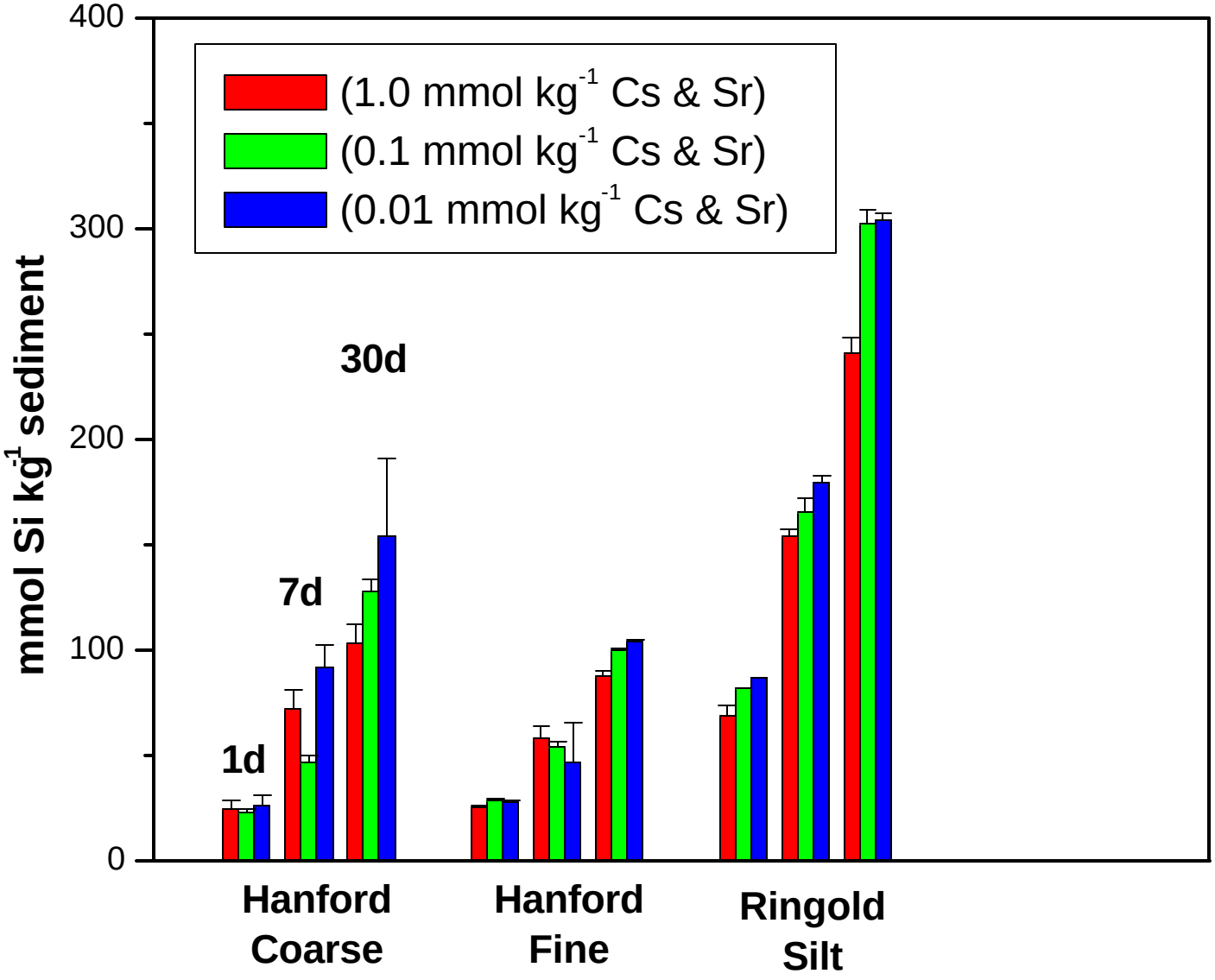
Dissolved Al



Dissolution of Si



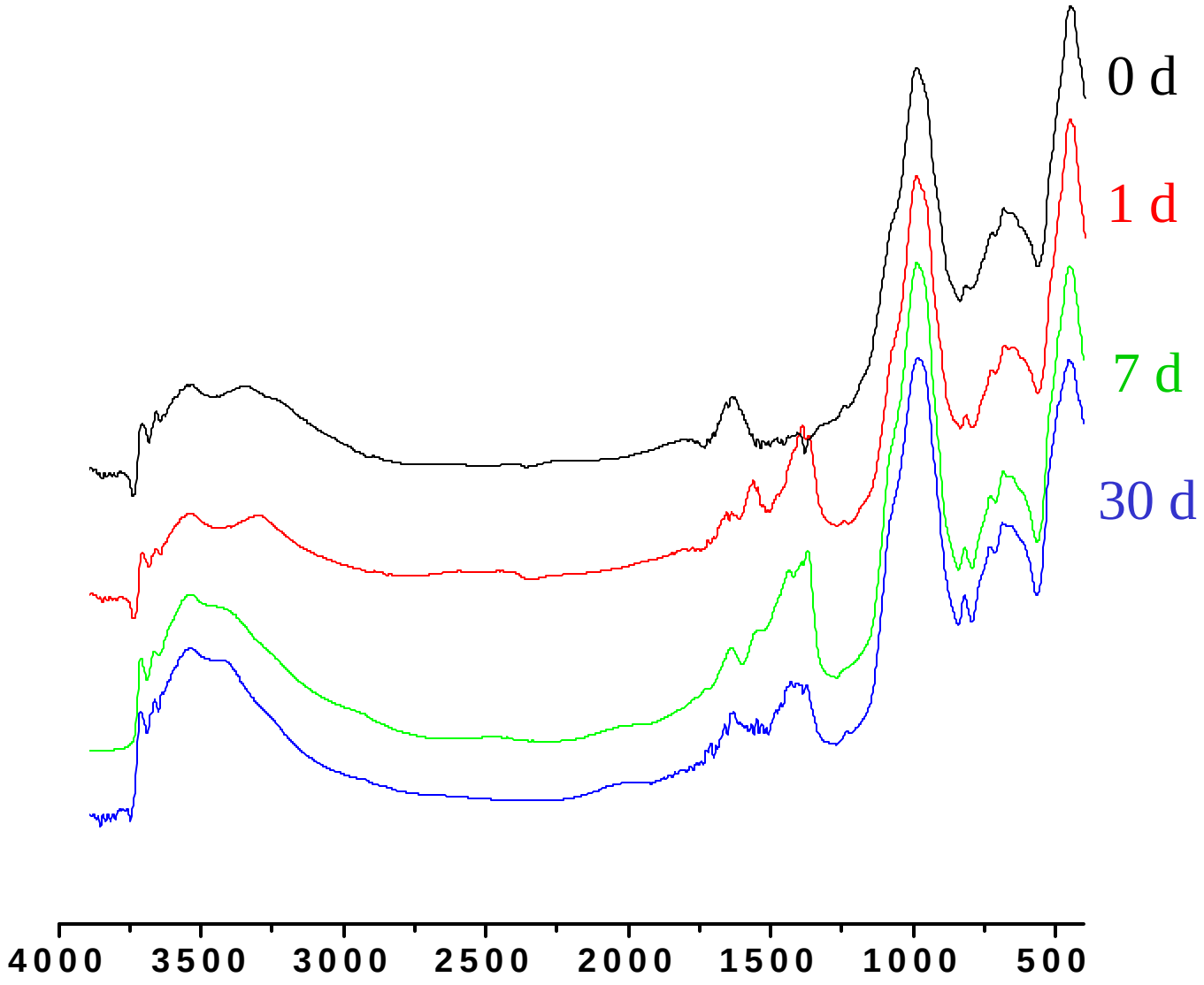
Dissolution of Si



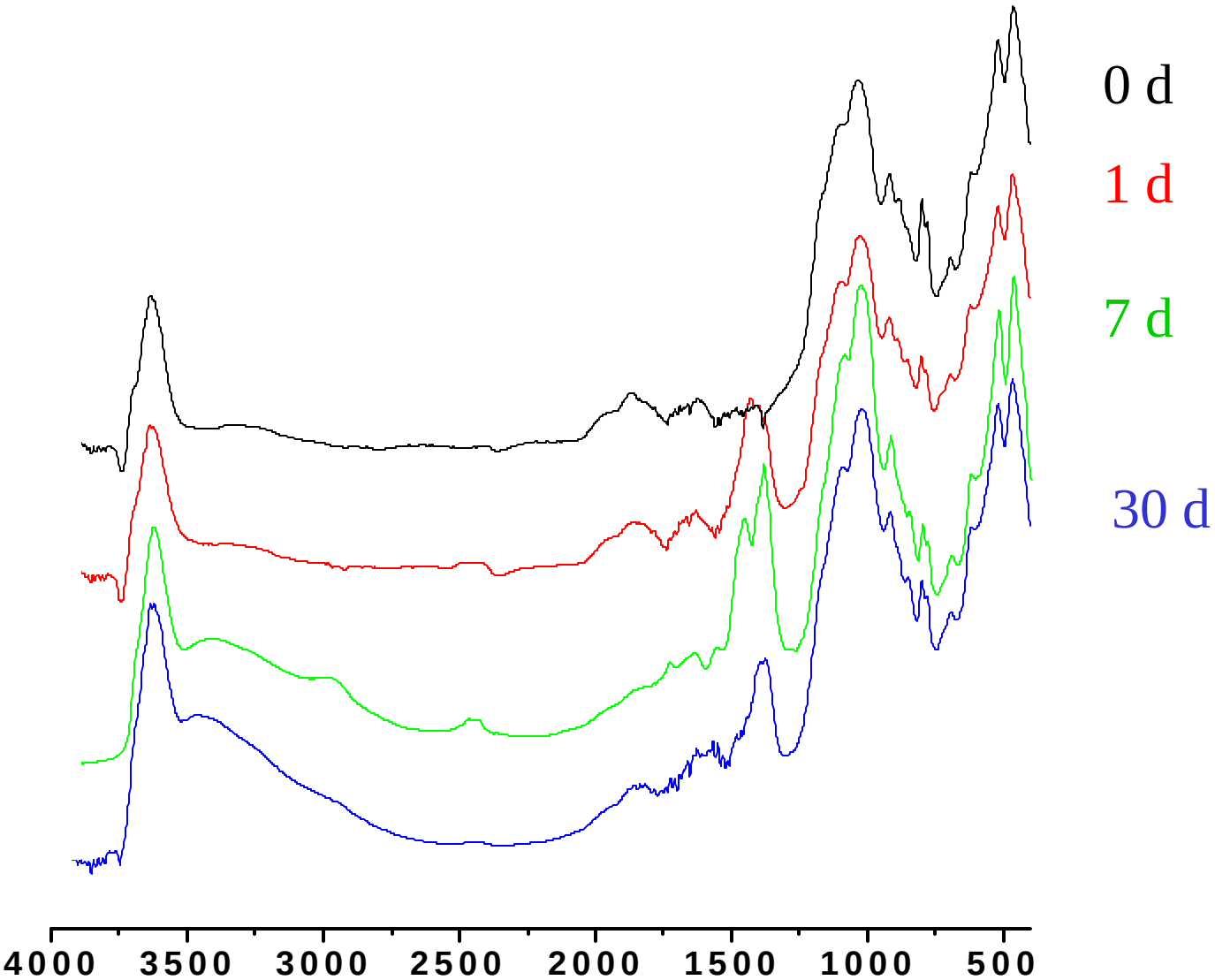
X-ray absorption studies

- Solid samples from selected uptake/release studies.
- Elucidate changes in Cs/Sr molecular environment as a function of [sorbate] and exchange.
- XAFS experiments on beamline X17B at BNL.
- Analysis of data using UWXAFS program and FEFF6 simulations.

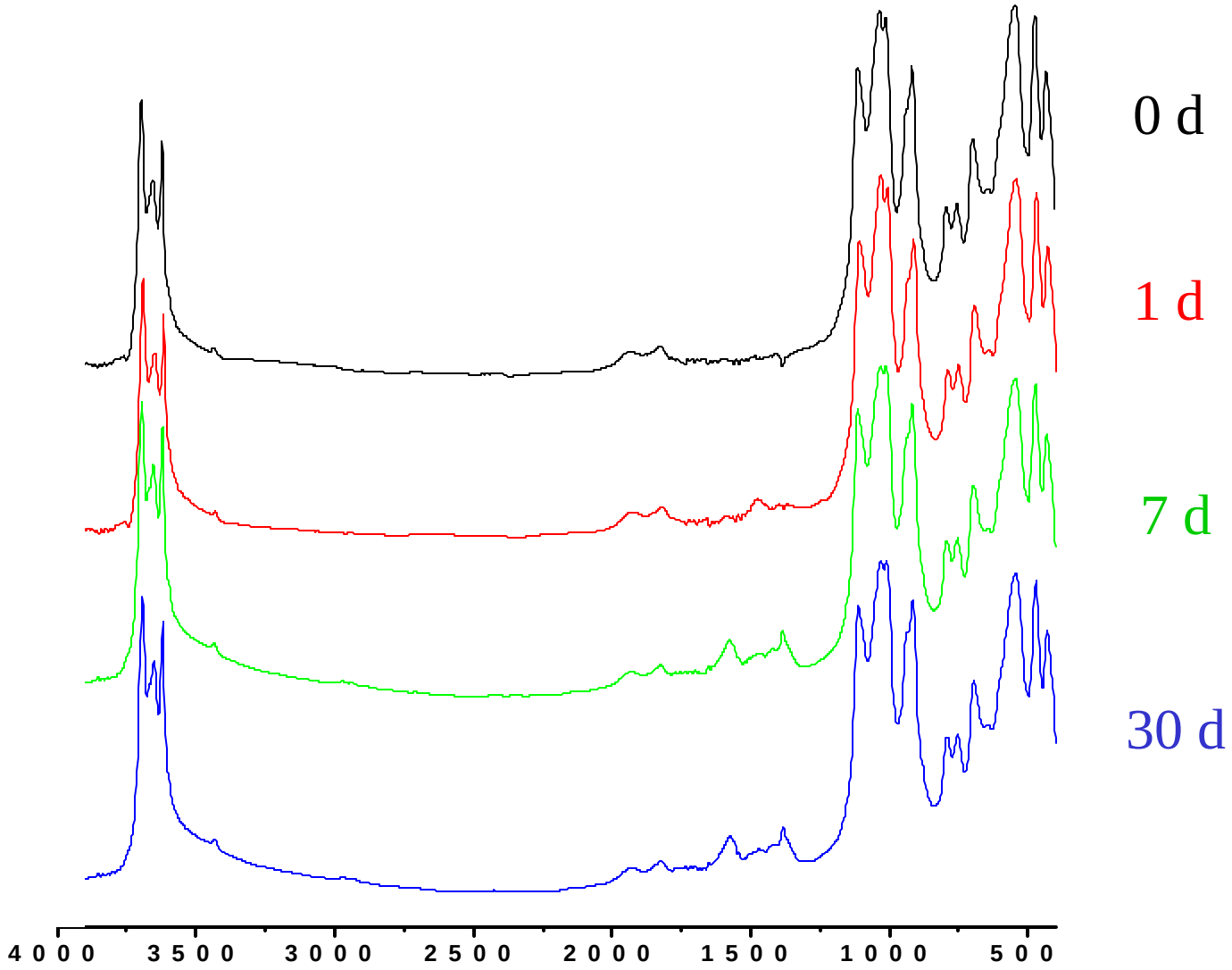
DRIFT spectra: Vermiculite C (10^{-5} Cs/Sr)



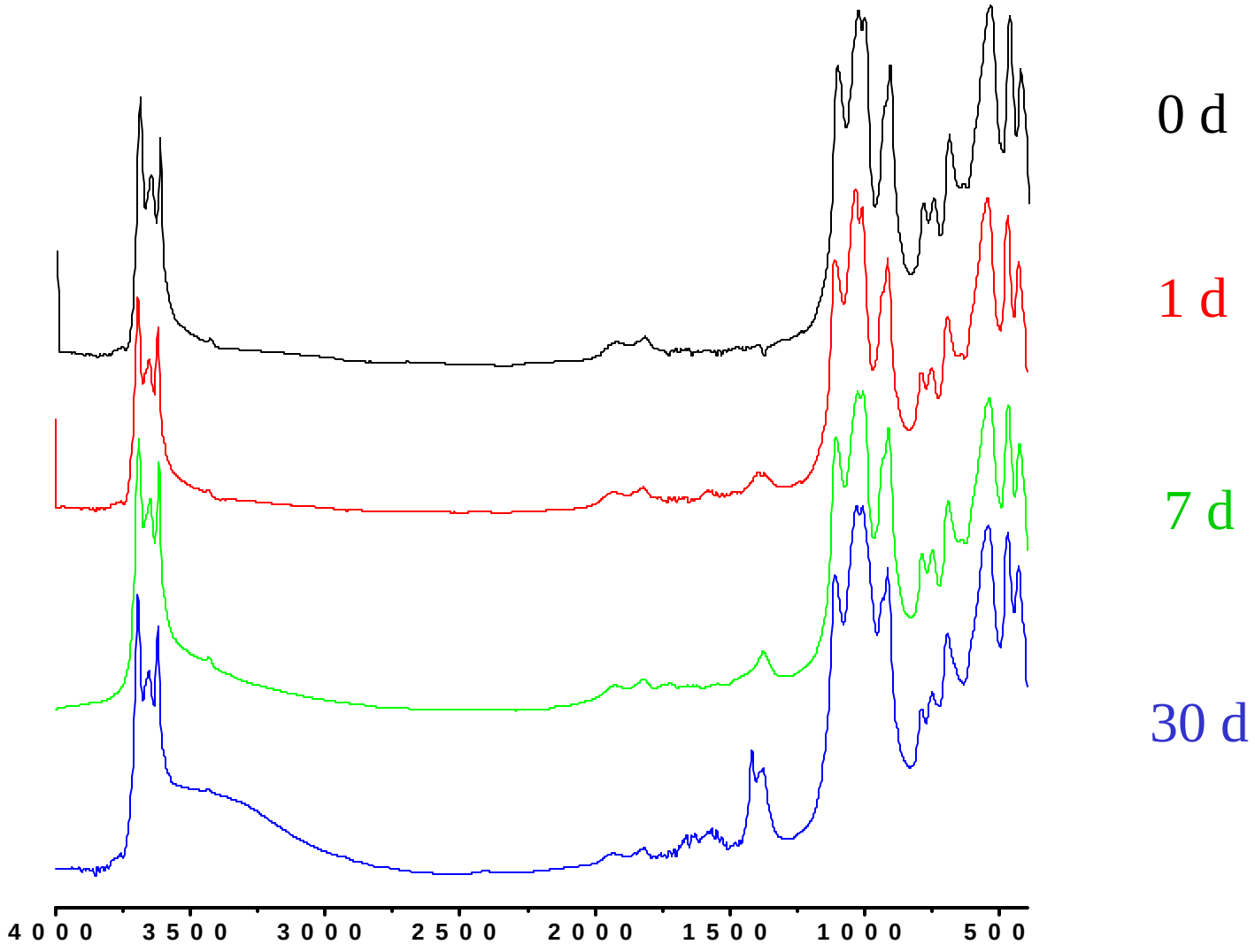
DRIFT spectra: Smectite C (10^{-5} Cs/Sr)

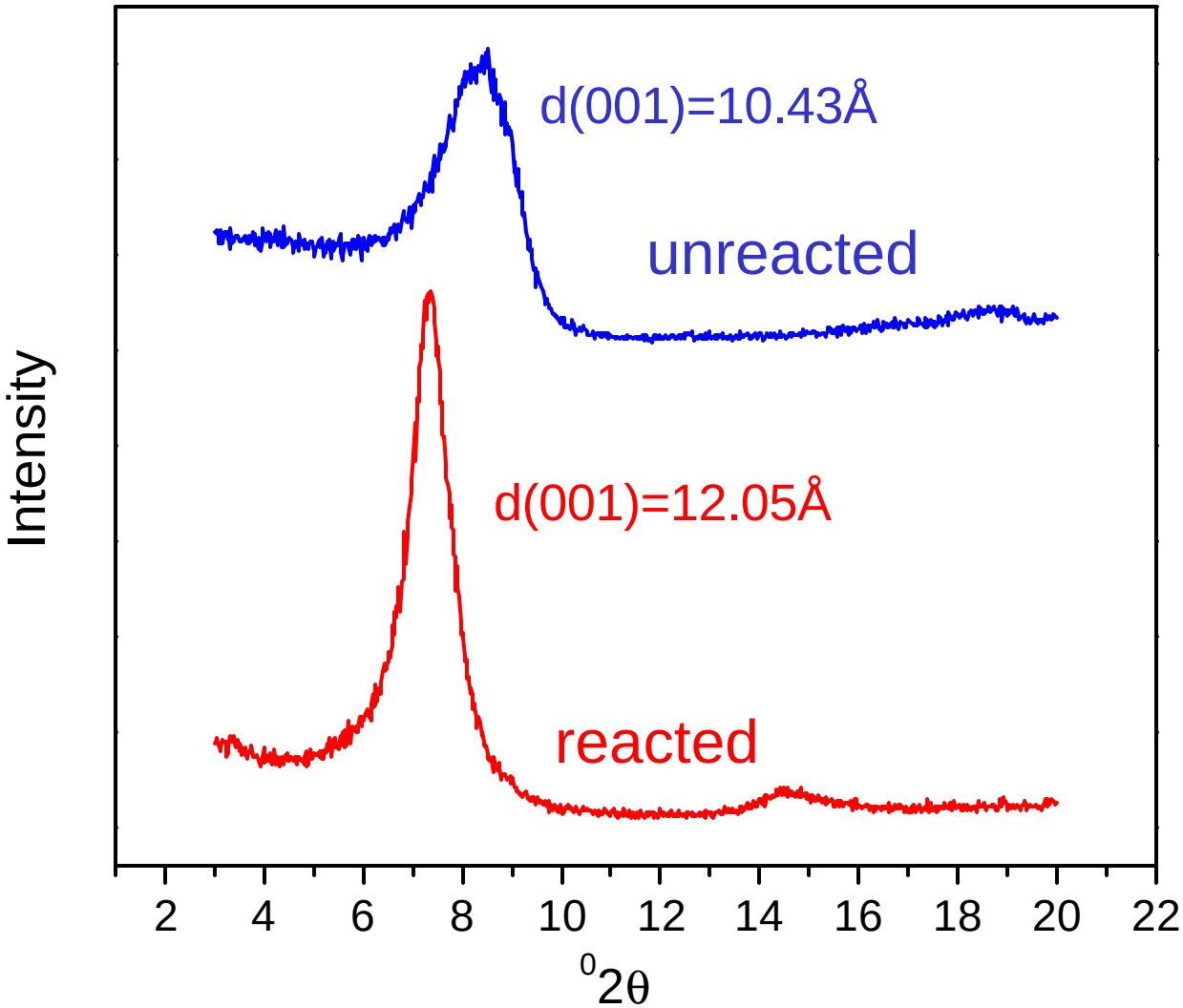


DRIFT spectra: Kaolinite (Cs/Sr = 10^{-3})

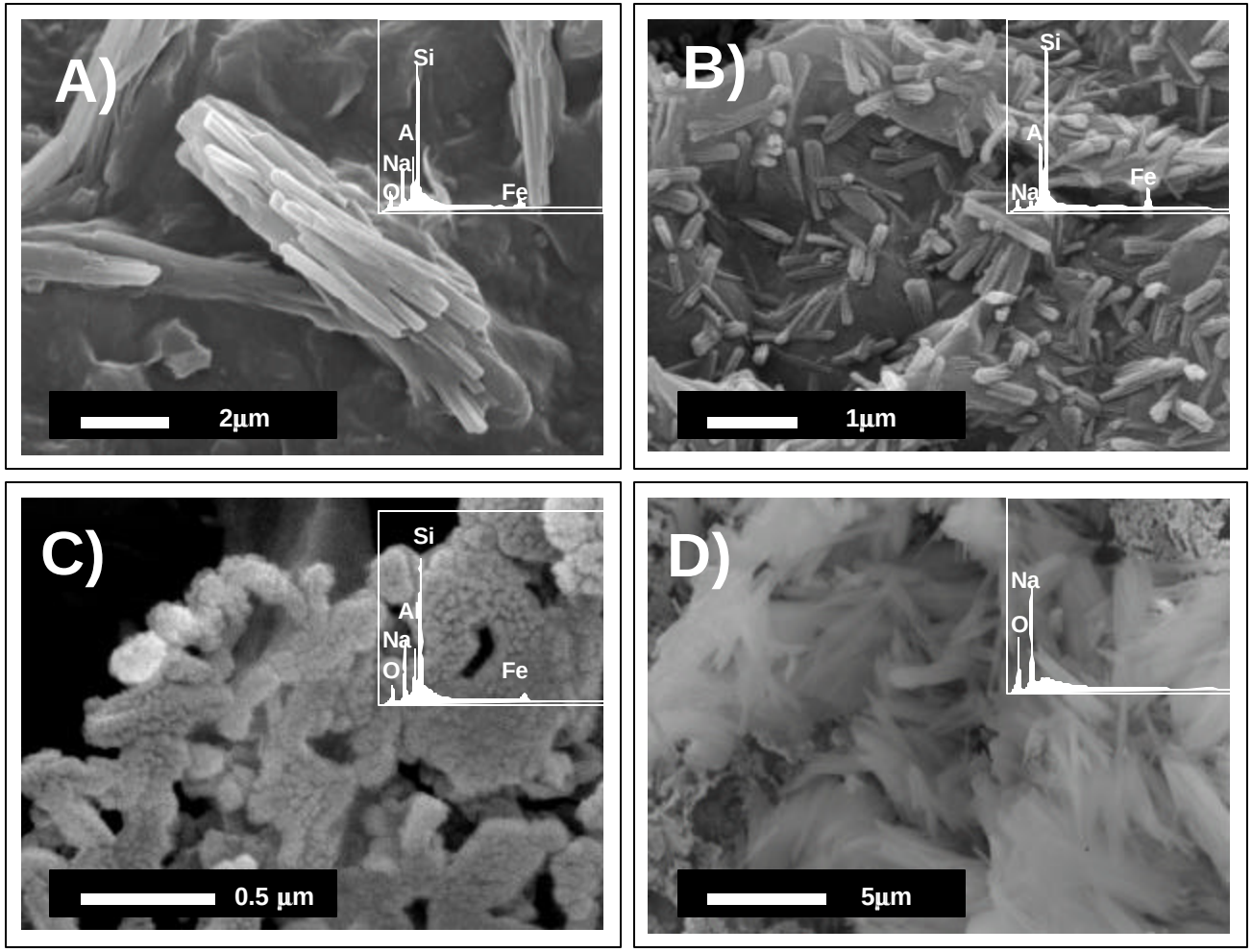


DRIFT spectra: Kaolinite (Cs/Sr = 10^{-5})

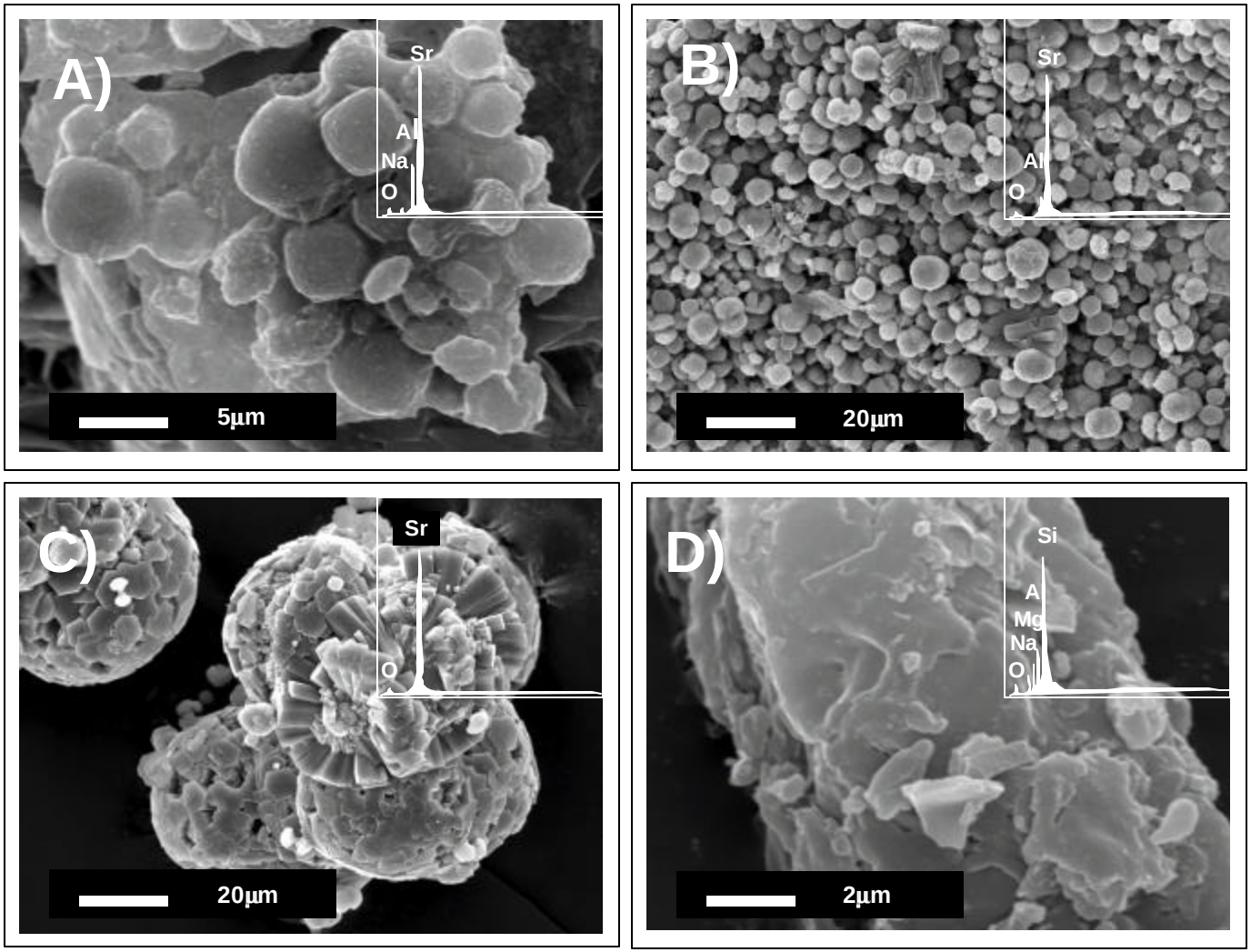




Basal spacings, d(001), obtained from XRD of oriented samples of unreacted and reacted (7 d, high Cs/Sr) montmorillonite after heat treatment at 110°C indicate a transition from interlayer Na^{+} to interlayer Sr^{2+} (increased basal spacing) despite the fact that initial $[Na^{+}] = 2000*[Sr^{2+}]$.



SEM images and EDX data of solid products formed in the presence of montmorillonite after 7 d reaction time (highest levels of Cs/Sr). Frame (d) is consistent with XRD data (not shown) that indicate the formation of nitratine. Other frames show secondary products contain Al and Si.



SEM images and EDX data of solid products formed in Al-bearing controls (STWL only, aged for 7 d in presence of 10^{-3} M (A through C) and 10^{-5} M (D) Cs/Sr). The formation of strontianite (frame C, $SrCO_3$), confirmed by XRD and DRIFT and an unidentified Na/Al/Sr bearing mineral (A and B) were observed. Strontianite formation was not observed directly (SEM or XRD) when layer silicates were present, nor at lower initial [Sr] (frame D). Thus, the nature of precipitates formed was strongly dependent on the presence and type of clays.

Summary: Results to date

- Batch sorption-weathering studies of specimen clays and sediments (0, 1, 7, and 30 d)
  - Sorption extent/dynamics
  - Extractability
  - Weathering induced changes in mineralogy (carbonate and zeolite production)
- NMR studies of ^{133}Cs sorbed to specimen clays (MAS and VT experiments).
- XAS studies of ^{133}Cs sorbed to specimen clays.

Plans for the next year

- STWL Homogeneous precipitation studies
  - variable Cs/Sr loading
  - PCO_2
  - pH
  - Si
- Continuation of STWL batch studies with clays and sediments (3, 6, 12, 24 months).
- Spectroscopic studies of Cs/Sr sorbed clays and weathered reaction products.