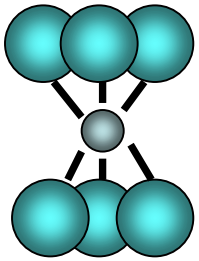
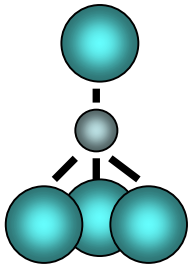
Caustic Waste-Soil Weathering Reactions and their Impacts on Trace Contaminant Migration and Sequestration





Principal Investigators:

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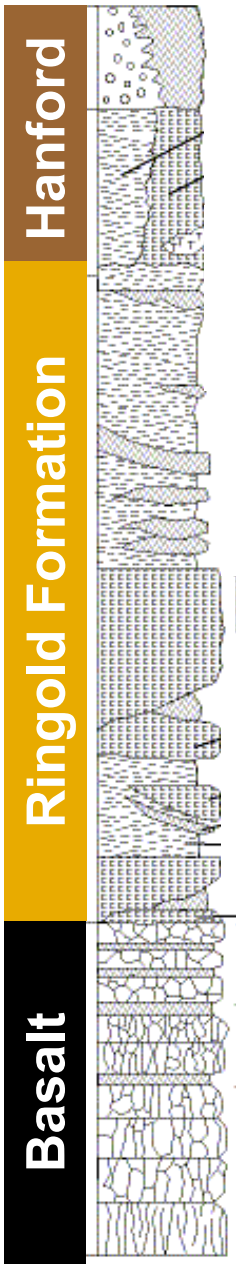
Karl T. Mueller (Penn State University)

Peggy A. O'Day (Arizona State University)

R. Jeff Serne (Pacific Northwest National Laboratory).

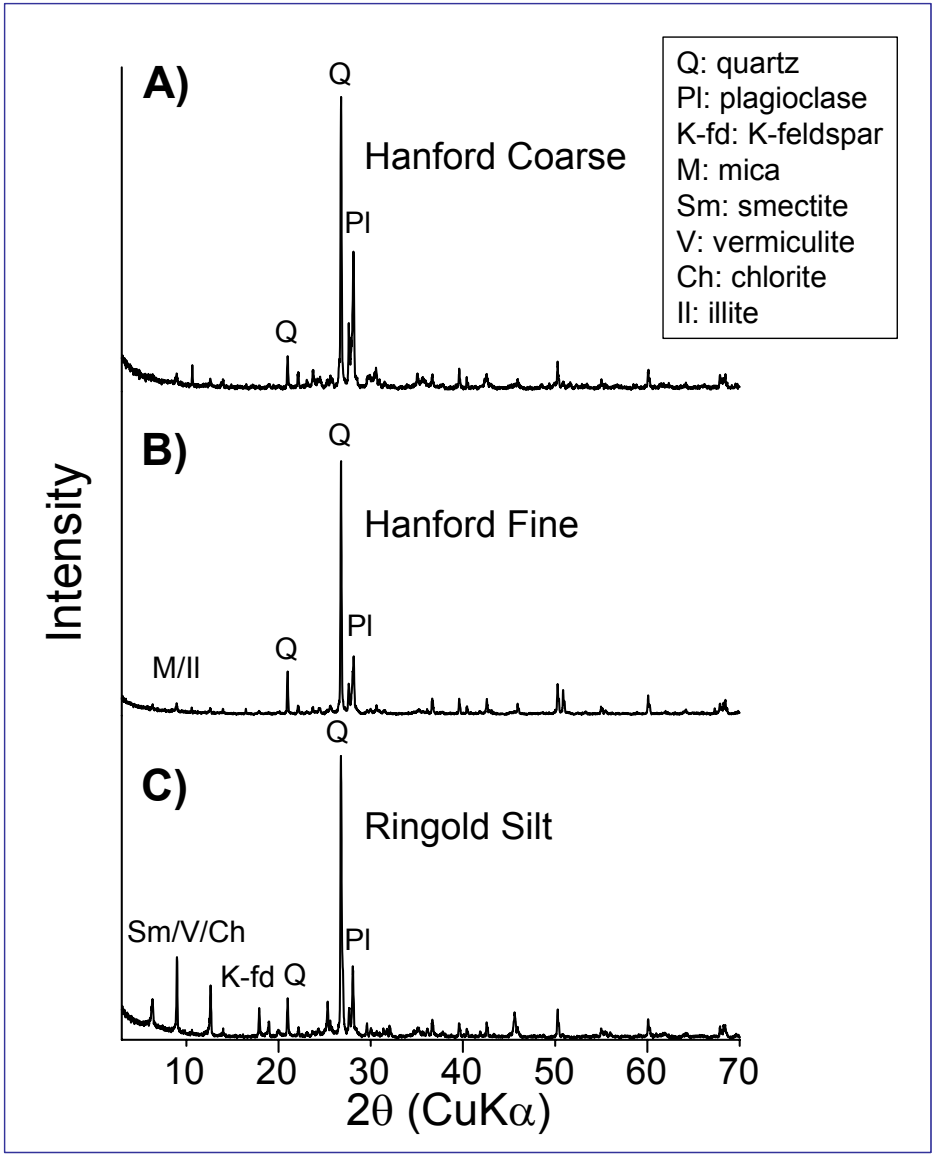


Primary Minerals

Quartz, plagioclase, mica, K-feldspar, basaltic fragments

Secondary clays

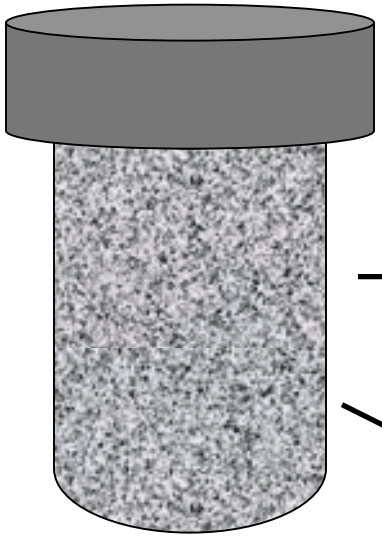
Smectite, vermiculite, illite, chlorite, kaolinite



Objectives

- Determine the **weathering behavior of clays and Hanford Sediments** under the intense geochemical conditions imposed near-field by the waste leachate, including **neoformation of secondary solids**.
- Investigate **long-term kinetics of Cs, Sr and I uptake** during reaction and establish the extent to which they are **coupled to solid phase dissolution and precipitation**.
- Determine changes in the **lability/siting of contaminants** in the weathering systems over time.

Kinetic Studies: Coupled Mineral Transformation and Contaminant Sorption



Dissolved (<0.02 μm)

Colloidal (0.02-2.0 μm)

Solid Particulate

React clay and sediments with STWL in suspension from 0 to 2 yr

2 M ($NaNO_3$), 0.05 M $Al(OH)_4^-$, pH 13.8 (NaOH), Cs & Sr = 10^{-5} to 10^{-3}

$Mg(NO_3)_2$ exchange

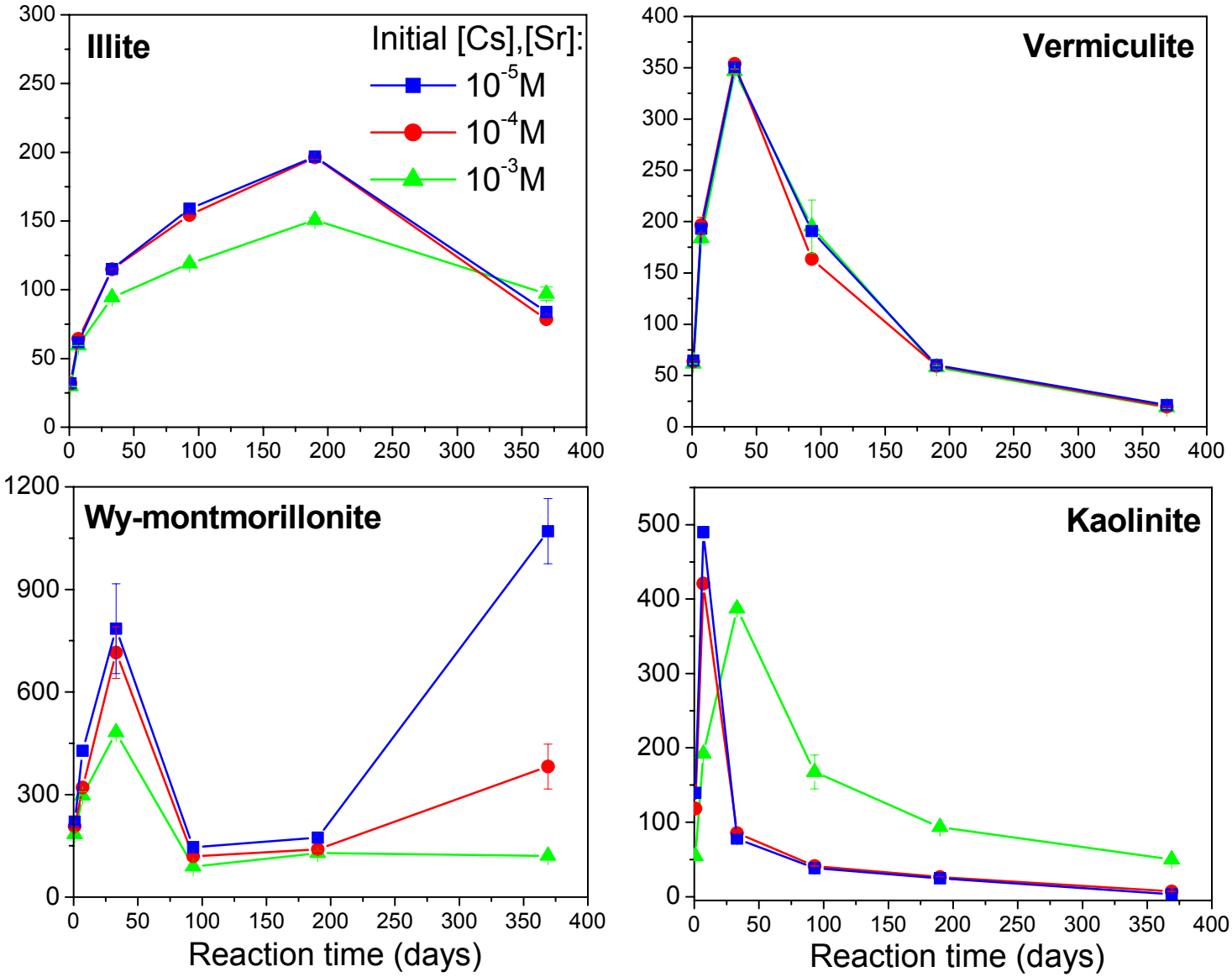
NH_4^+-oxalate (pH 3) extraction

Dissolution kinetics

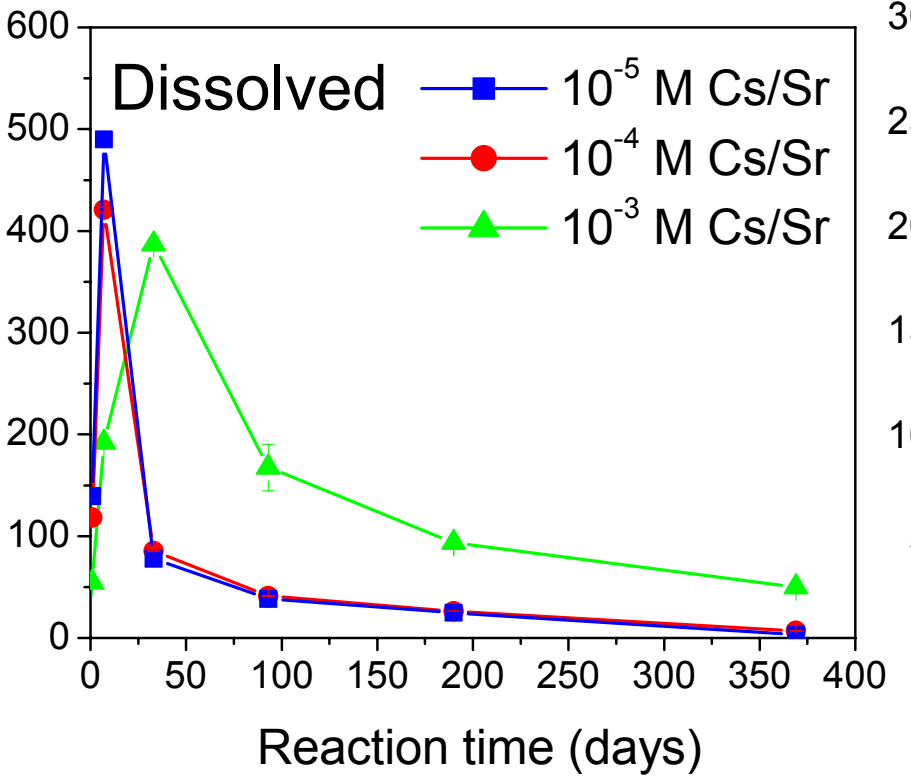
Solution Phase Analysis
Cs, Sr, Al, Si, Fe, pH

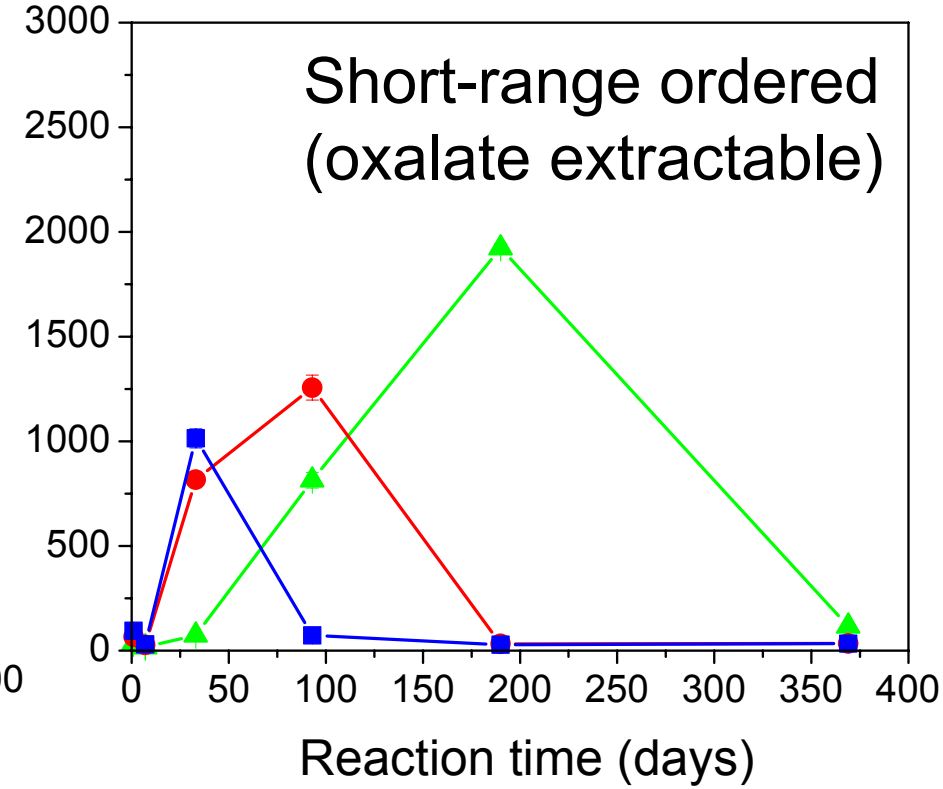
Solid Phase Analysis
XRD
SEM/EDX
TEM
FTIR
NMR
EXAFS

Time Series of Si Release from Specimen Clays (mmol kg^{-1})



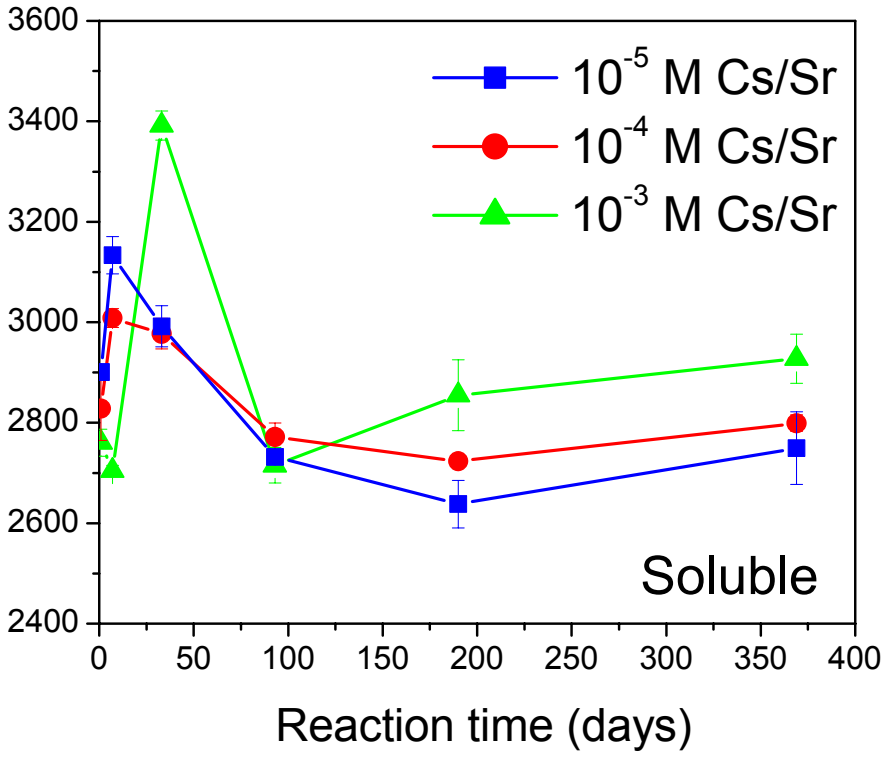
Kaolinite: Dissolution and Precipitation of Si (mmol kg^{-1} clay)

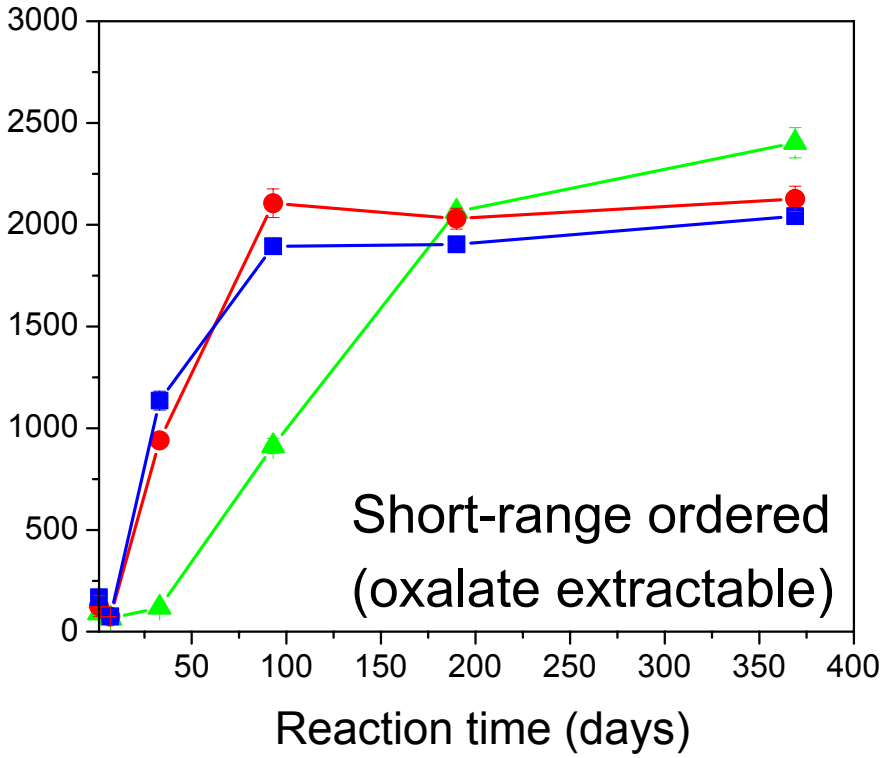




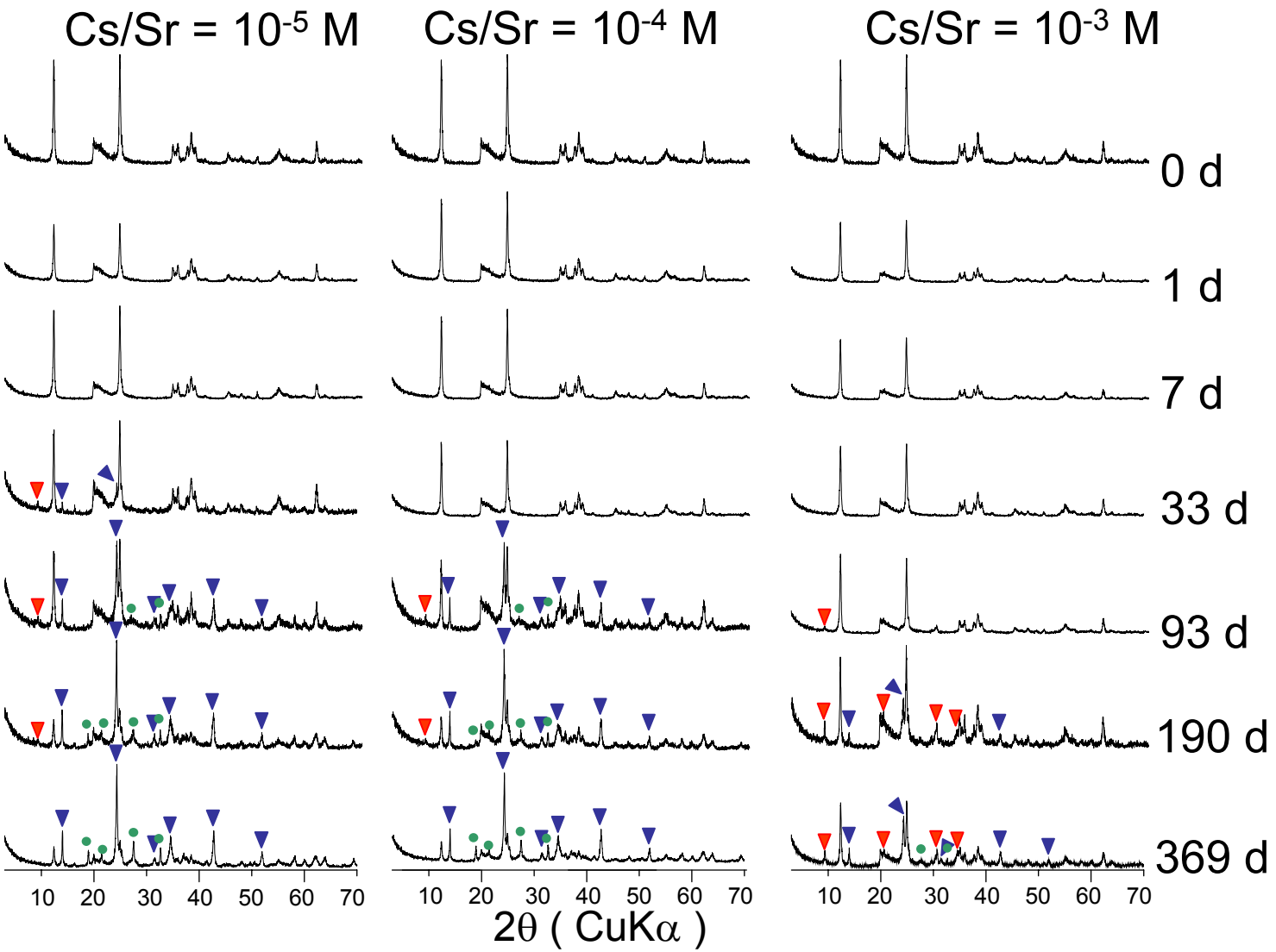
Chemical Formula: $[Si_4]Al_{3.66}Fe(III)_{.07}\ Ti_{0.16}O_{10}(OH)_8$

Kaolinite: Dissolution and Precipitation of Al (mmol kg^{-1} clay)



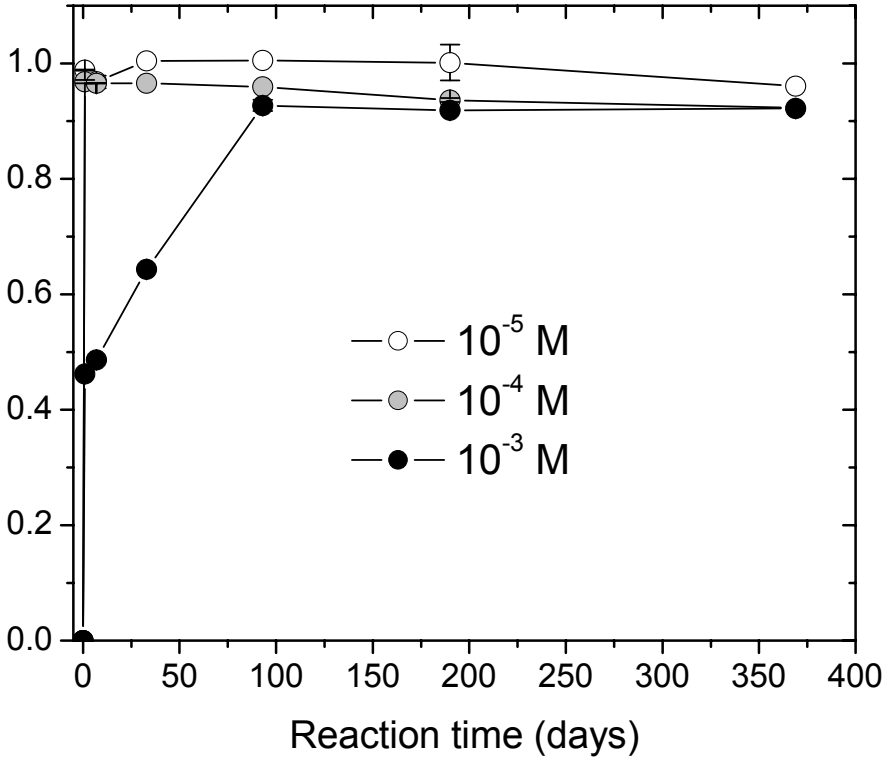


XRD Patterns of Kaolinite as a Function of Reaction Time

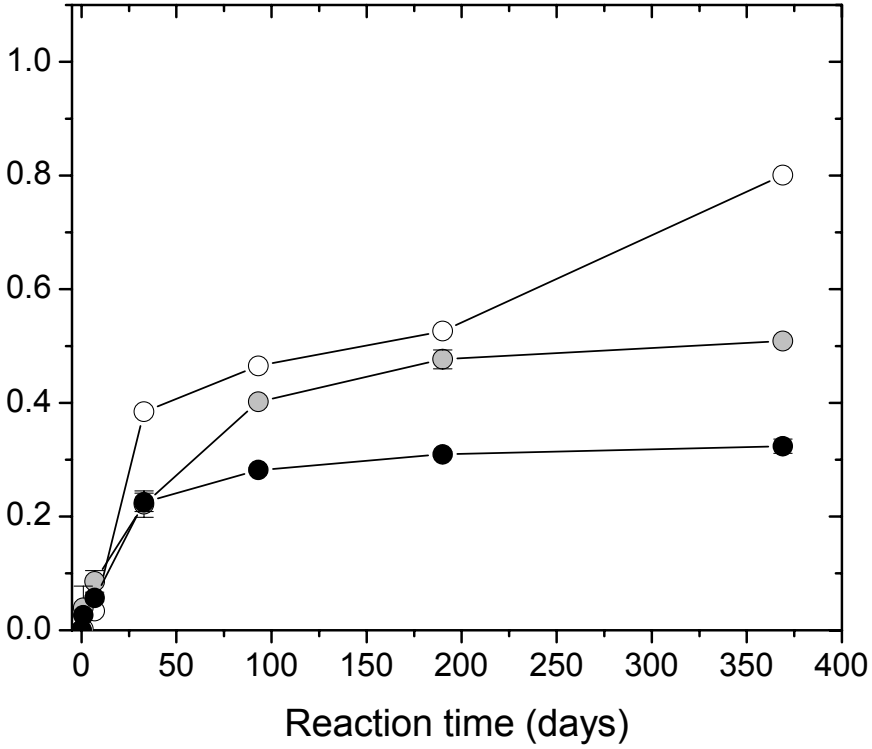


Radionuclide Sorption Kinetics (KGa-2)
Fraction Removed from Solution

Strontium

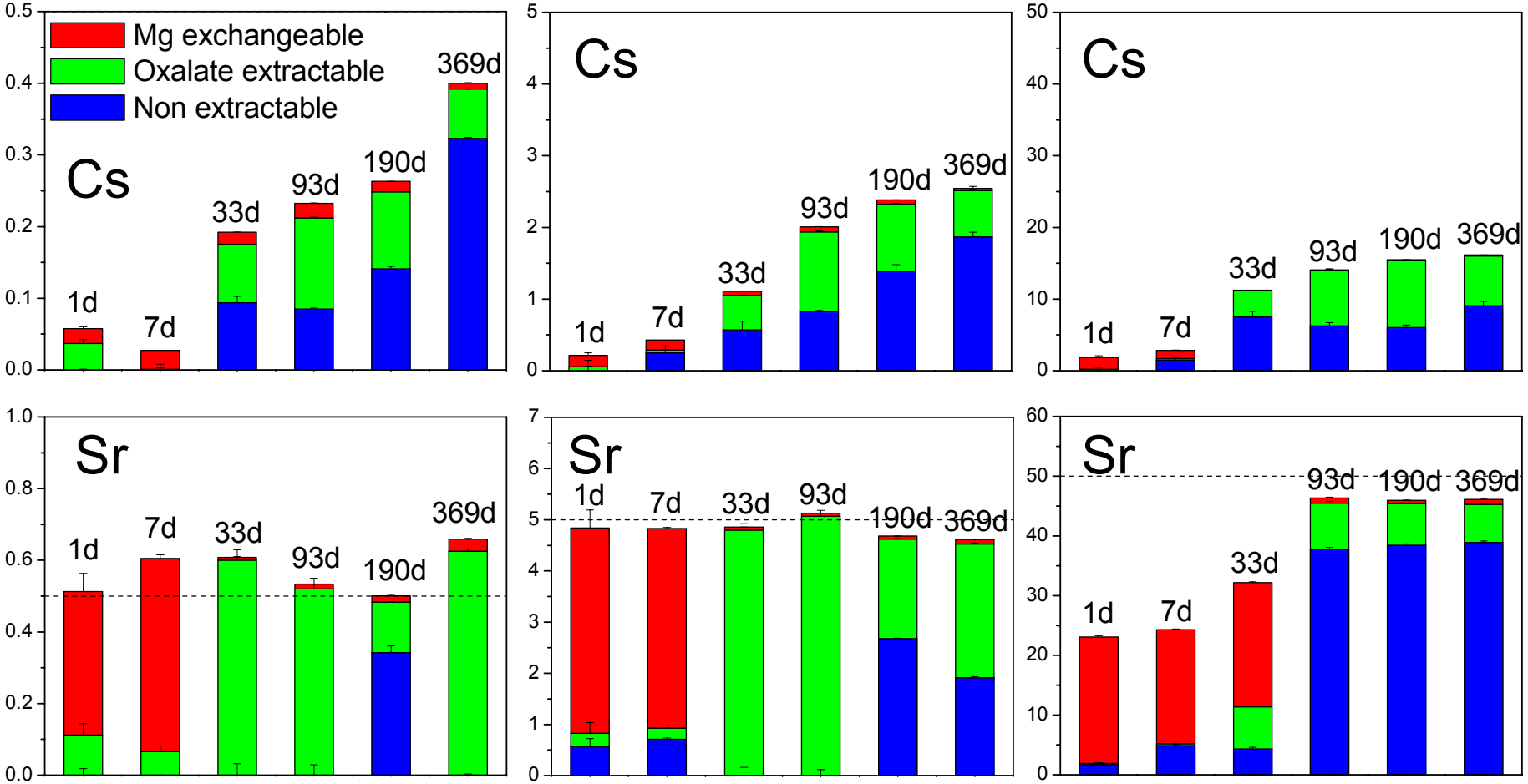


Cesium

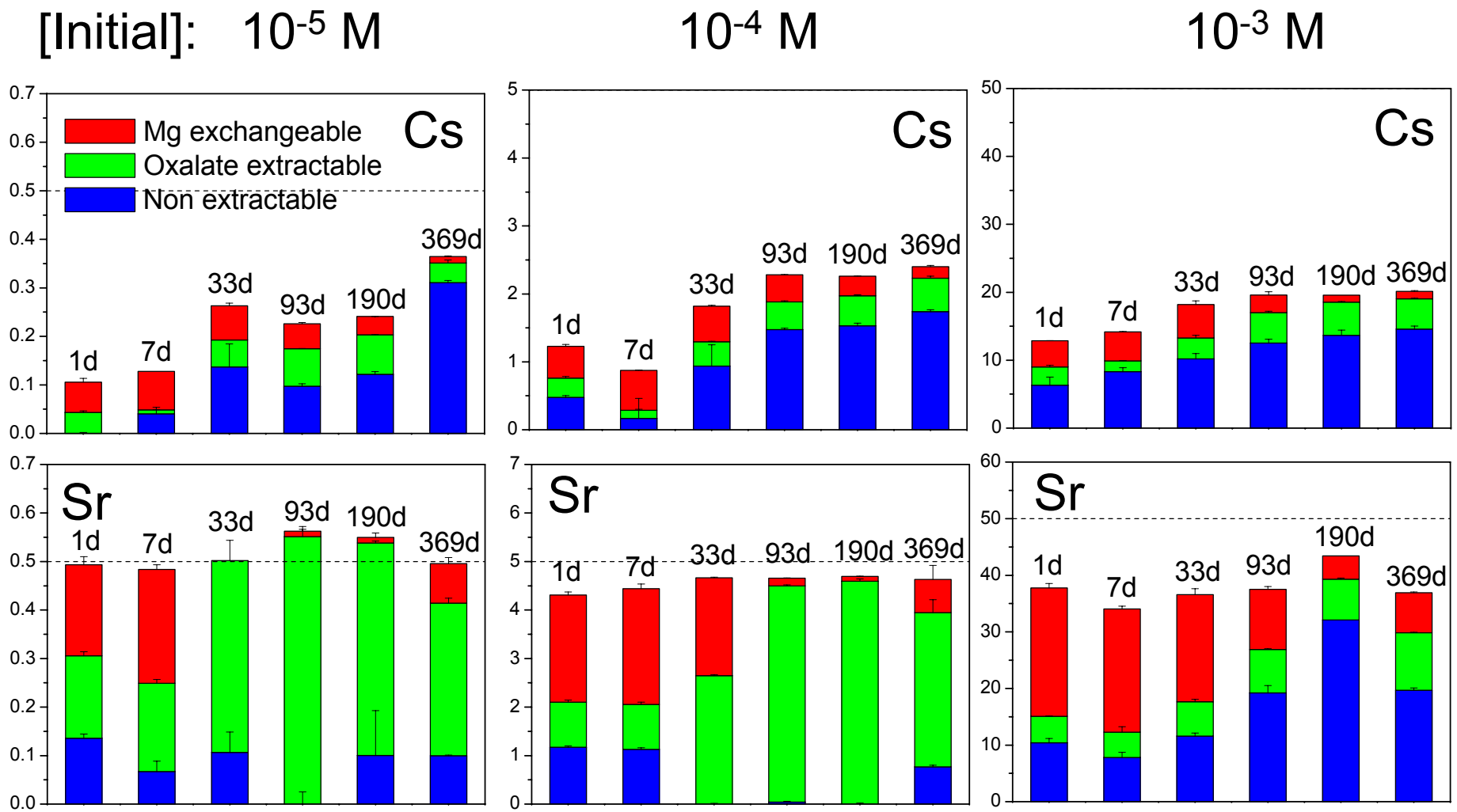


Uptake of Cs and Sr During Mineral Transformation *KGa-2* (mmol kg^{-1} clay)

[Initial]: 10^{-5} M 10^{-4} M 10^{-3} M



Uptake of Cs and Sr During Mineral Transformation *SWy-2* (mmol kg^{-1} clay)



Environmental Science and Technology
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Linking Cesium and Strontium Uptake to Kaolinite Weathering in Simulated Tank Waste Leachate

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GARRY CROSSON,§ AND
KARL T. MUELLER§

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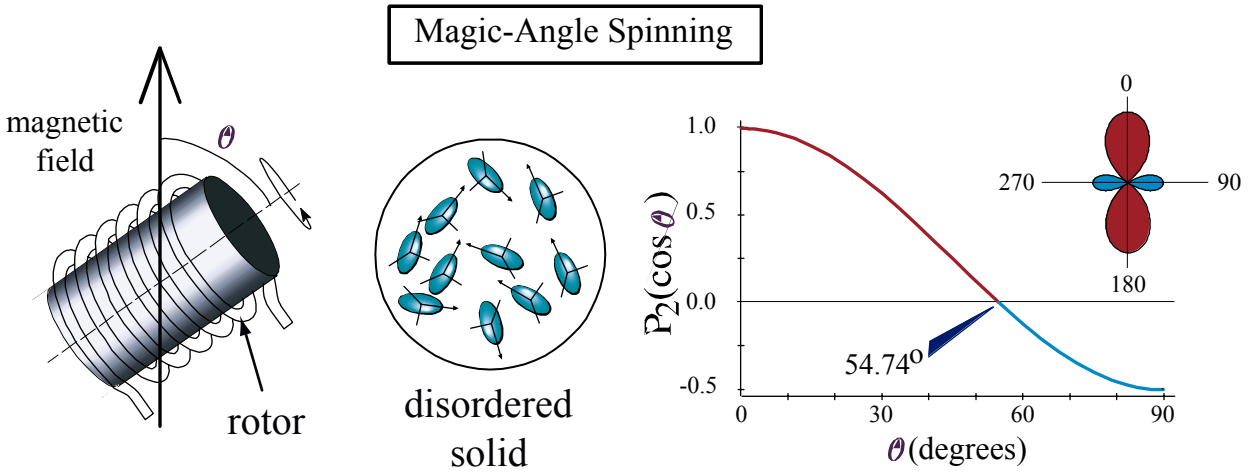
Weathering behavior of kaolinite was studied in batch systems under geochemical conditions characteristic of tank waste released to the vadose zone at the Hanford Site, WA (0.05 M Al_T, 2 M Na^+, 1 M NO_3^-, pH ~14, Cs^+ and Sr^{2+} present as co-contaminants). Time series experiments were conducted from 0 to 369 d, with initial Cs^+ and Sr^{2+} concentrations ranging from 10^{-5} to 10^{-3} M. Dissolution of kaolinite increased soluble Si and Al to maximum levels at 7 d (Cs and Sr concentrations of 10^{-5} and 10^{-4}

important U.S. Department of Energy sites (e.g., Hanford, WA; Savannah River, GA; Oak Ridge, TN) is composed of solutions that are unique in having extremely high pH and ionic strength (*7*). Contaminant sorption (defined here as uptake to the solid phase) under these conditions is likely to be affected by mineral transformation reactions that are not well-known.

The effect of alkaline solutions on kaolinite transformation has been investigated previously (*8*–*12*). For example, Bauer et al. (*12*), examined kaolinite weathering over several months at 35 and 80 °C in 0.1–4 M KOH solutions and at solid–solution ratios ranging from 1:80 to 1:240. They reported the formation of illite, followed by KI-zeolite and phillipsite and then precipitation of the stable product K-feldspar. The aqueous chemistry of caustic tank waste leachate is dominated by Na^+, $Al(OH)_4^-$, and NO_3^- with variable quantities of the radionuclides ^{137}Cs and ^{90}Sr. The effects of these constituents on kaolinite transformation are unknown. Furthermore, most other studies of kaolinite dissolution have focused on initial dissolution rates at pH < 12 and conditions far from equilibrium with respect to solid-phase products (*13*–*20*). As a result, there is a lack of information on dissolution and precipitation reactions in aqueous systems representative of leaking tank waste that interacts with contaminated sediments at several U.S. DOE sites.

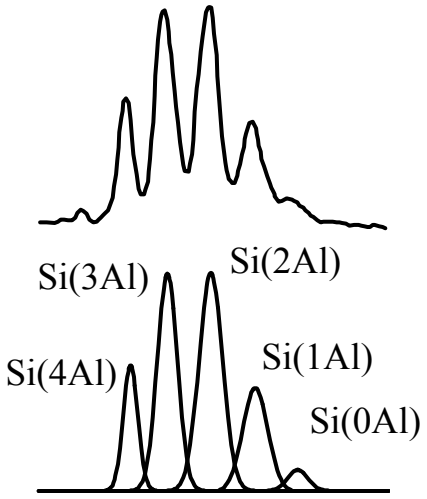
In this study, macroscopic and spectroscopic approaches were integrated to investigate kaolinite weathering and contaminant uptake under conditions representative of waste leachate at the Hanford Site, WA.

Solid-State NMR to Study Weathered Clay Samples



line broadening $P_2(\cos\theta) = 1/2\ (3\cos^2\theta - 1)$

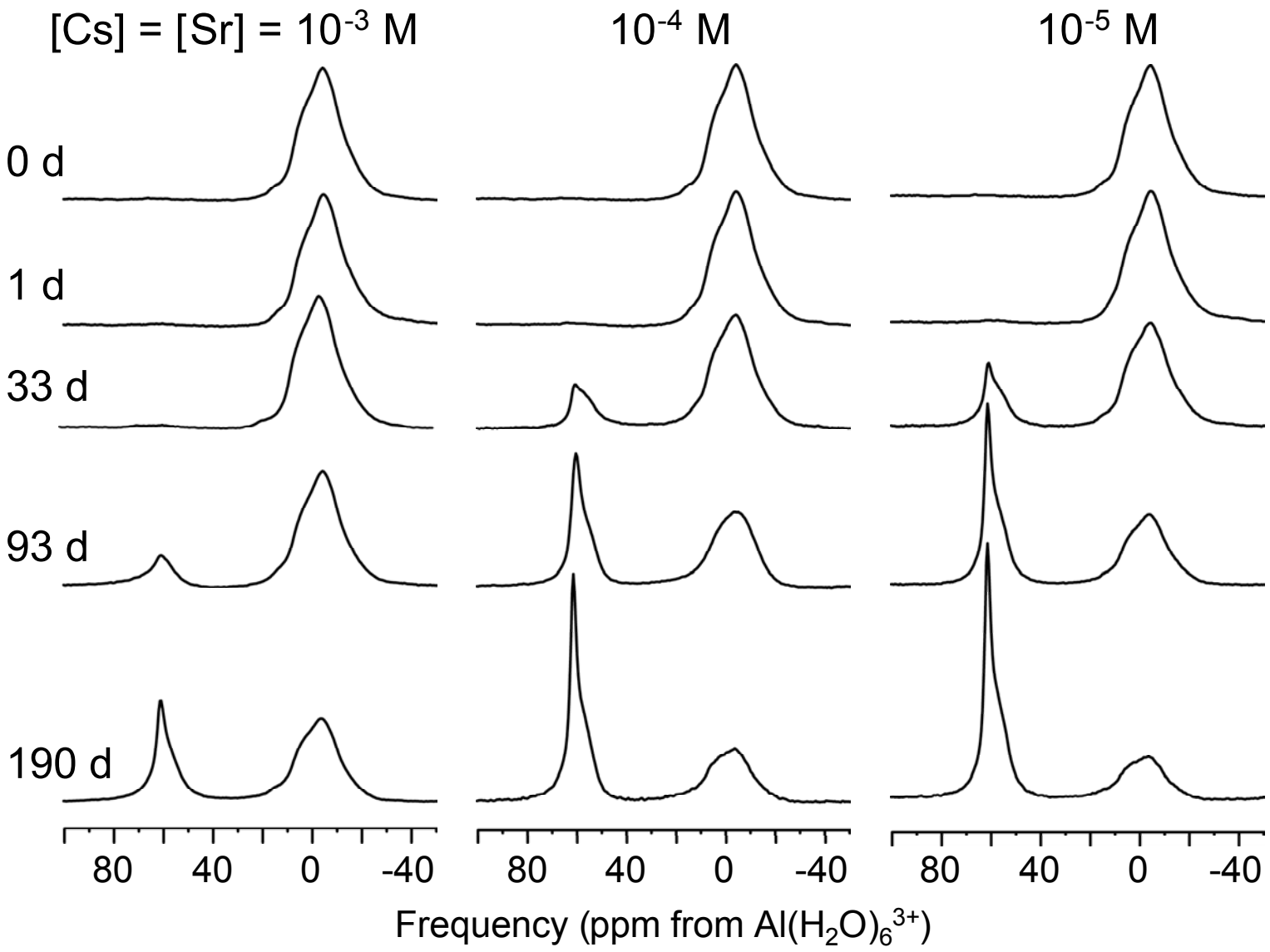
^{29}Si MAS of a Zeolite



NMR Parameters (9.4 T)

Nucleus	Freq./MHz	Abund.
^{23}Na (I=3/2)	105.8	100%
^{27}Al (I=5/2)	104.2	100%
^{29}Si (I=1/2)	79.19	4.7%
^{87}Sr (I=9/2)	17.3	7.0%
^{133}Cs (I=7/2)	52.4	100%

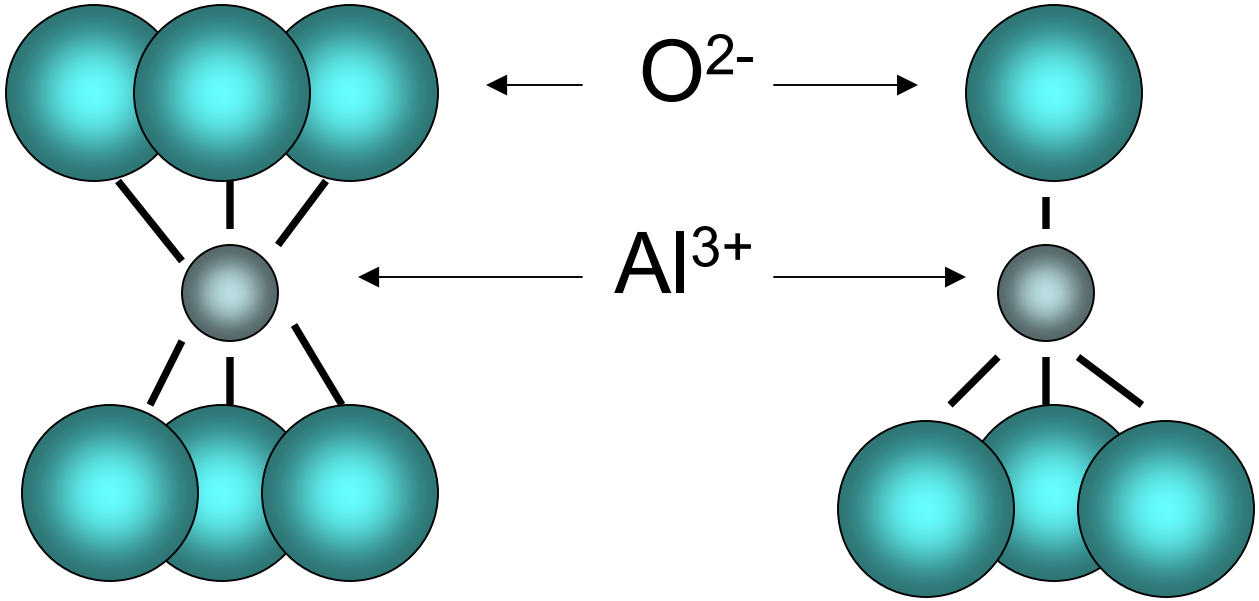
^{27}Al MAS NMR Spectra of Kaolinite Transformation



Aluminum Coordination in Kaolinite and Zeolite Structures

Kaolinite Al^{VI}

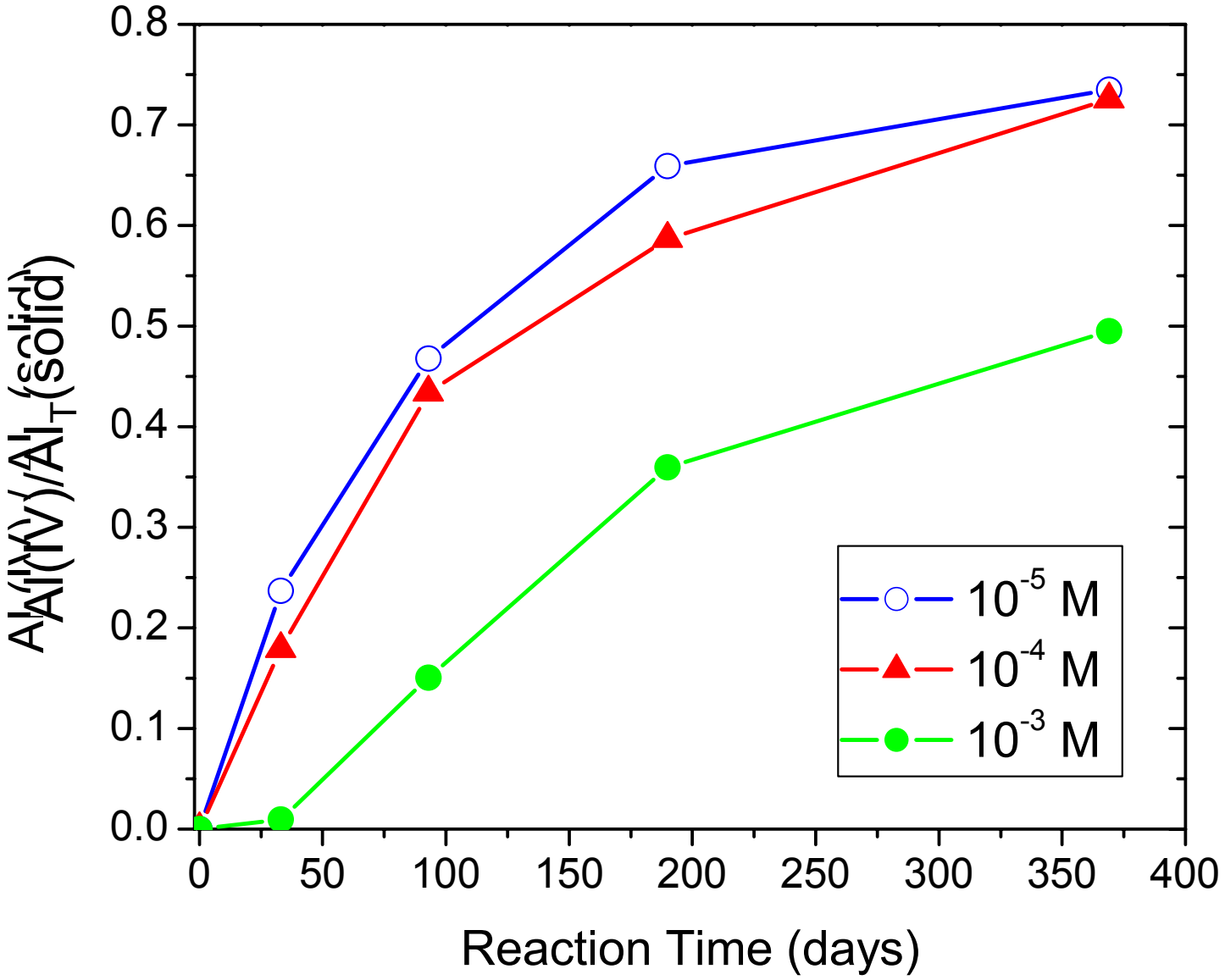
Zeolite Al^{IV}
(e.g., strontian/sodalite)



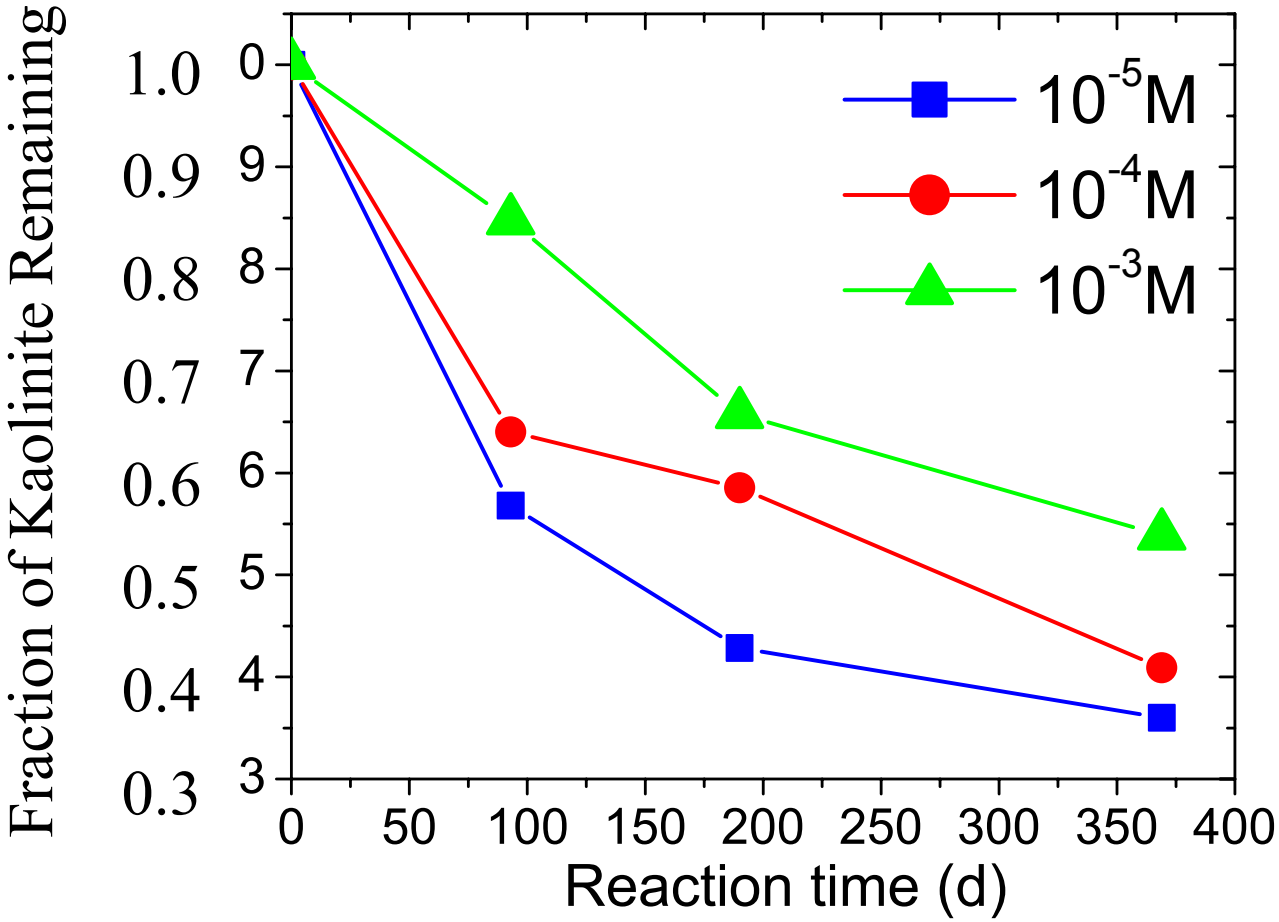
Octahedral sites

Tetrahedral sites

Al Coordination Ratio from ^{27}Al MAS NMR



Mass Loss of Kaolinite as Measured by TGA



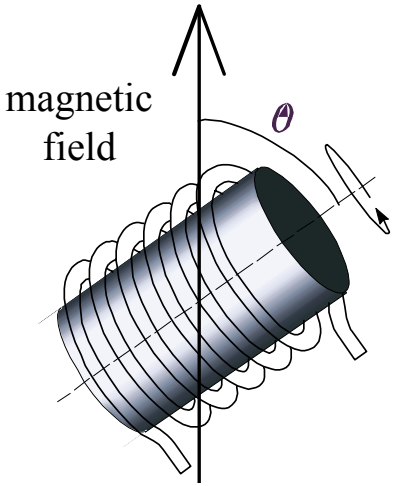
Quantitative Rate Calculations

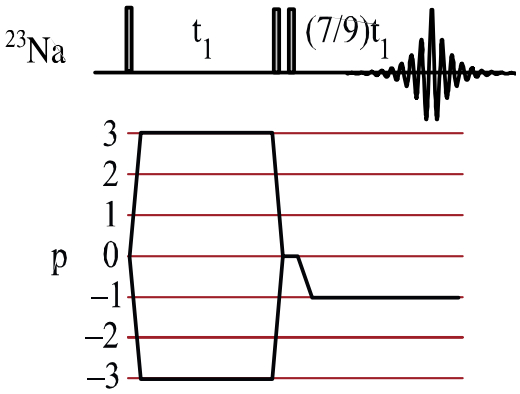
Tabulated below are first order rate constants (d^{-1}) and half-lives (d) for Cs sorption and for kaolinite weathering in STWL. Weathering rates were calculated from ratio of [Al^{IV}/(Al^{IV}+ Al^{VI})] MAS NMR peak intensities of reacted solids. All regressions resulted in $R^2 > 0.8$ and $p < 0.01$.

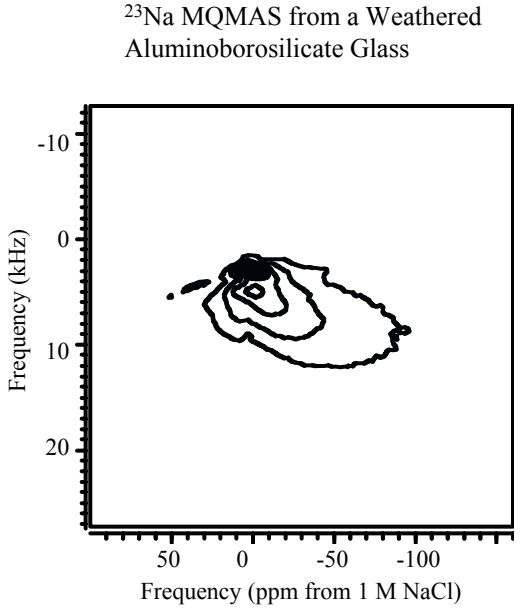
Cs_0 and Sr_0	Rate Constant, *k* (d^{-1})		Reaction half-life, $t_{1/2}$ (d)	
(mol kg^{-1})	*Cs sorption*	*^{27}Al NMR*	*Cs sorption*	*^{27}Al NMR*
10^{-5}	4.09×10^{-3}	3.51×10^{-3}	169	197
10^{-4}	1.93×10^{-3}	3.42×10^{-3}	359	203
10^{-3}	0.99×10^{-3}	1.97×10^{-3}	699	351

Advanced Solid-State NMR Approaches: MQMAS

L. Frydman and J. S. Harwood, J. Am. Chem. Soc. 117, 5367 (1995)
- correlation of isotropic dimension with MAS dimension
- spinning at 54.74°
- averages away second-order quadrupolar effects

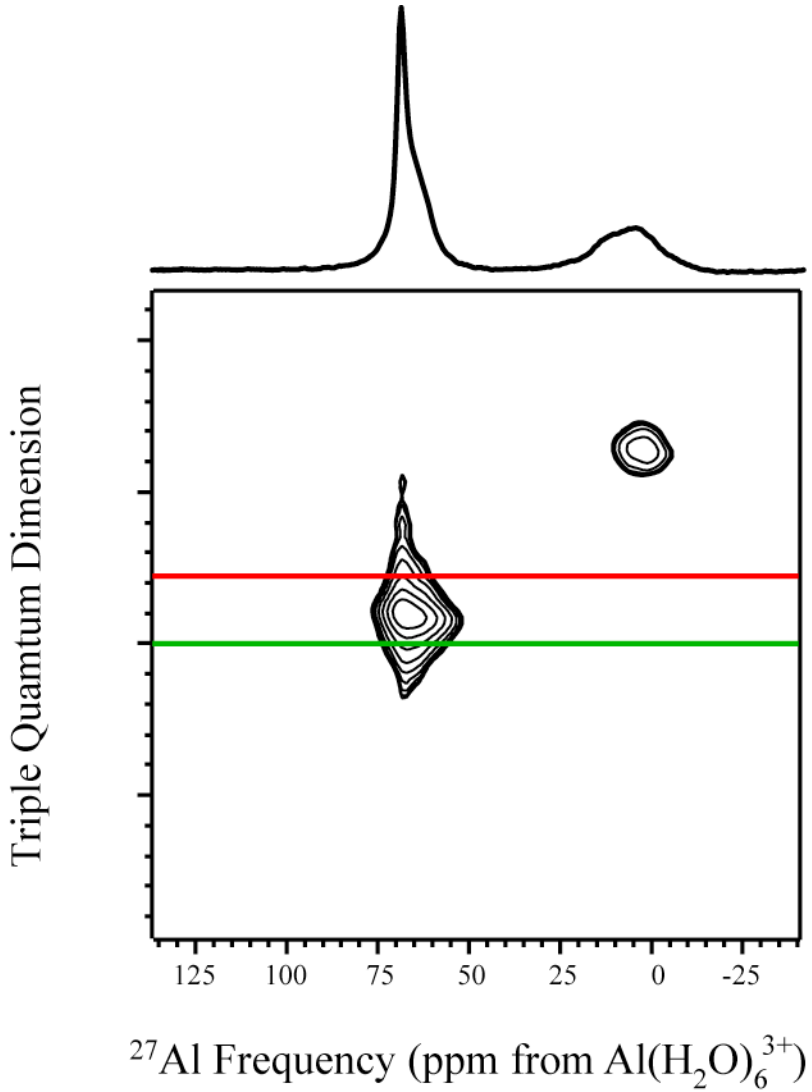


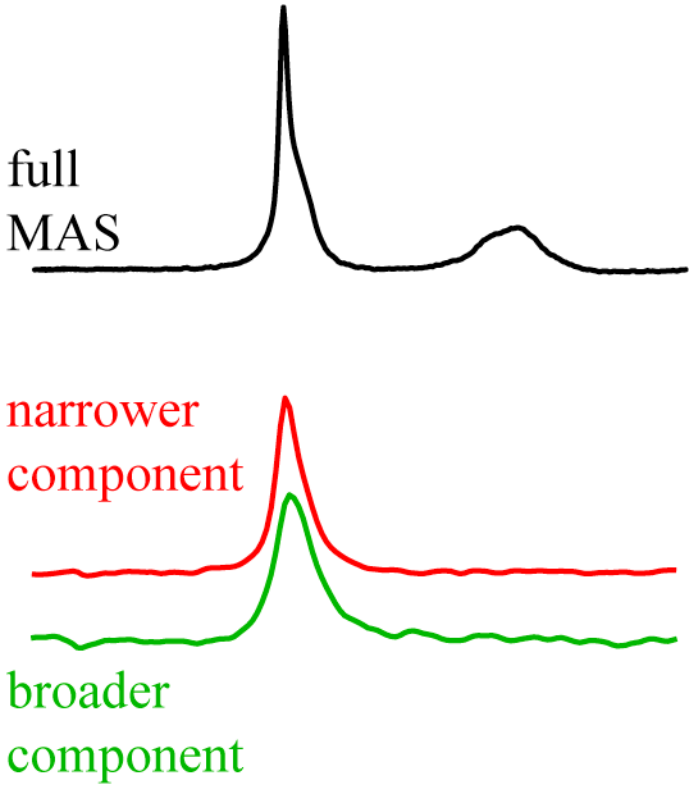




see J. M. Egan and K. T. Mueller, J. Phys. Chem. B 104, 9580 (2000)

^{27}Al MQMAS of Weathered Kaolinite Sample



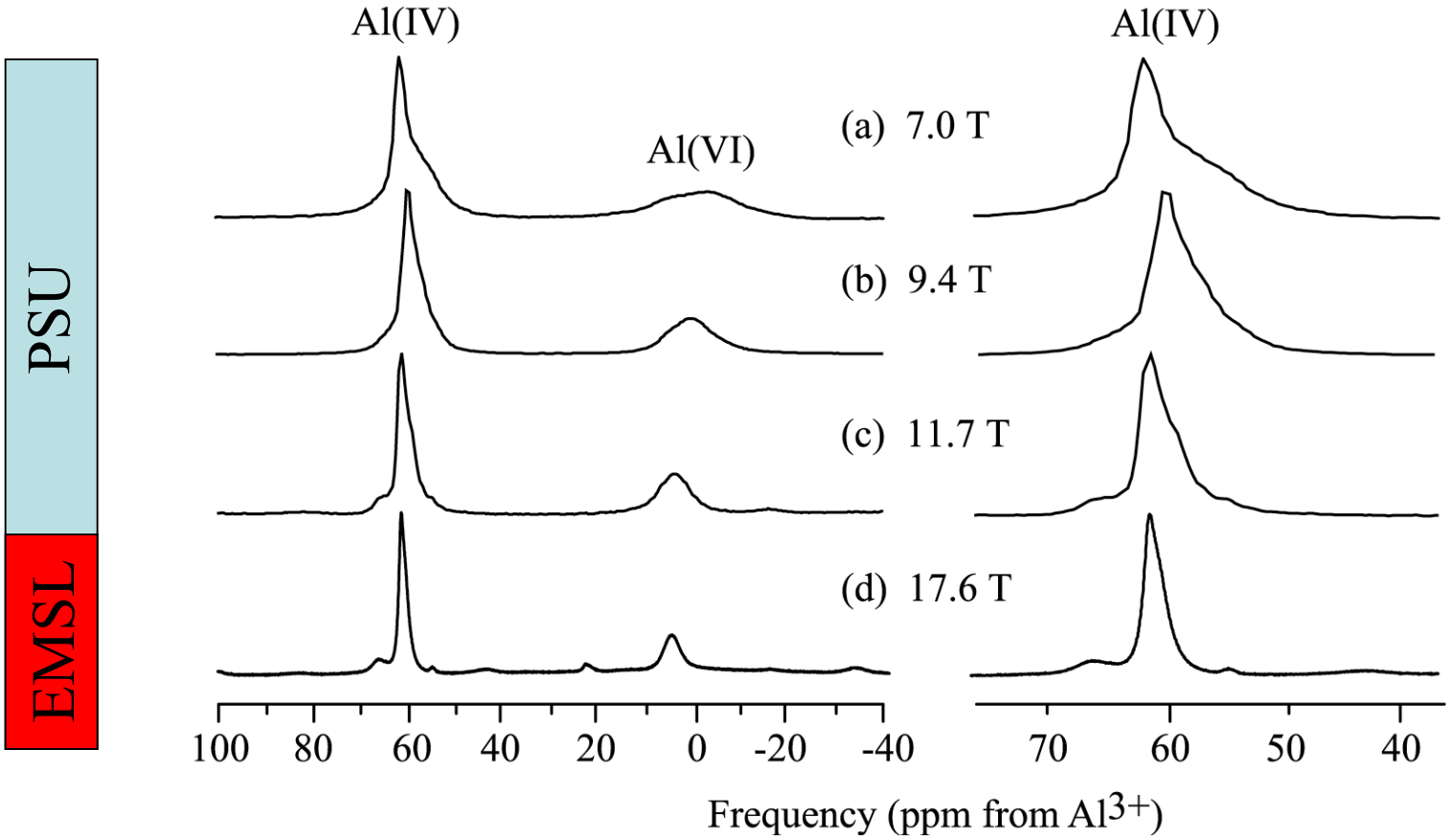


Indications via MAS intensity scaling and MQMAS that two octahedral Al environments are present.

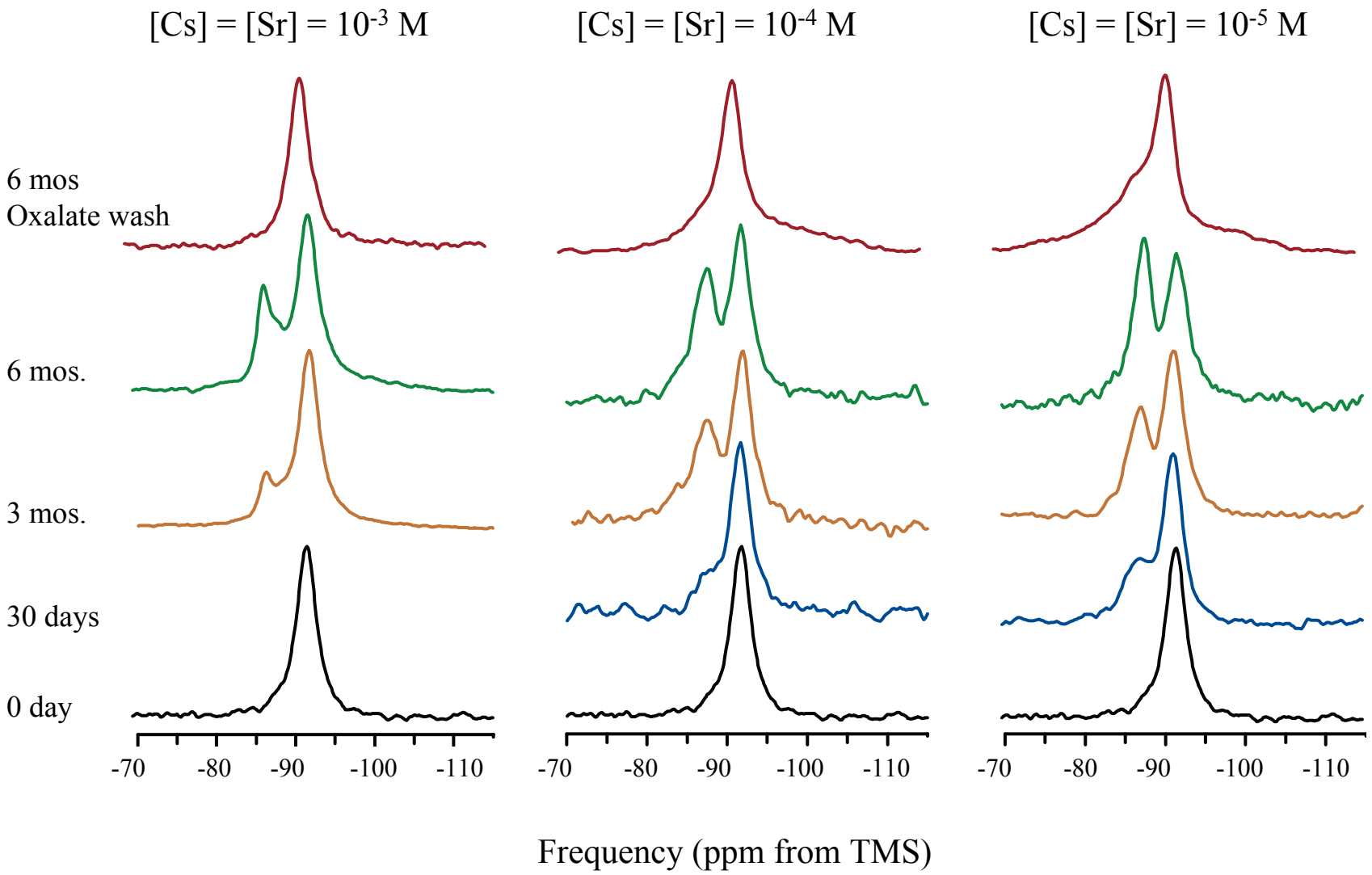
Variable-Field NMR of ^{27}Al: Resolution for Quantification

$$\delta_{tot} = \delta_{iso}^{(CS)} + \delta_{iso}^{(2Q)}$$

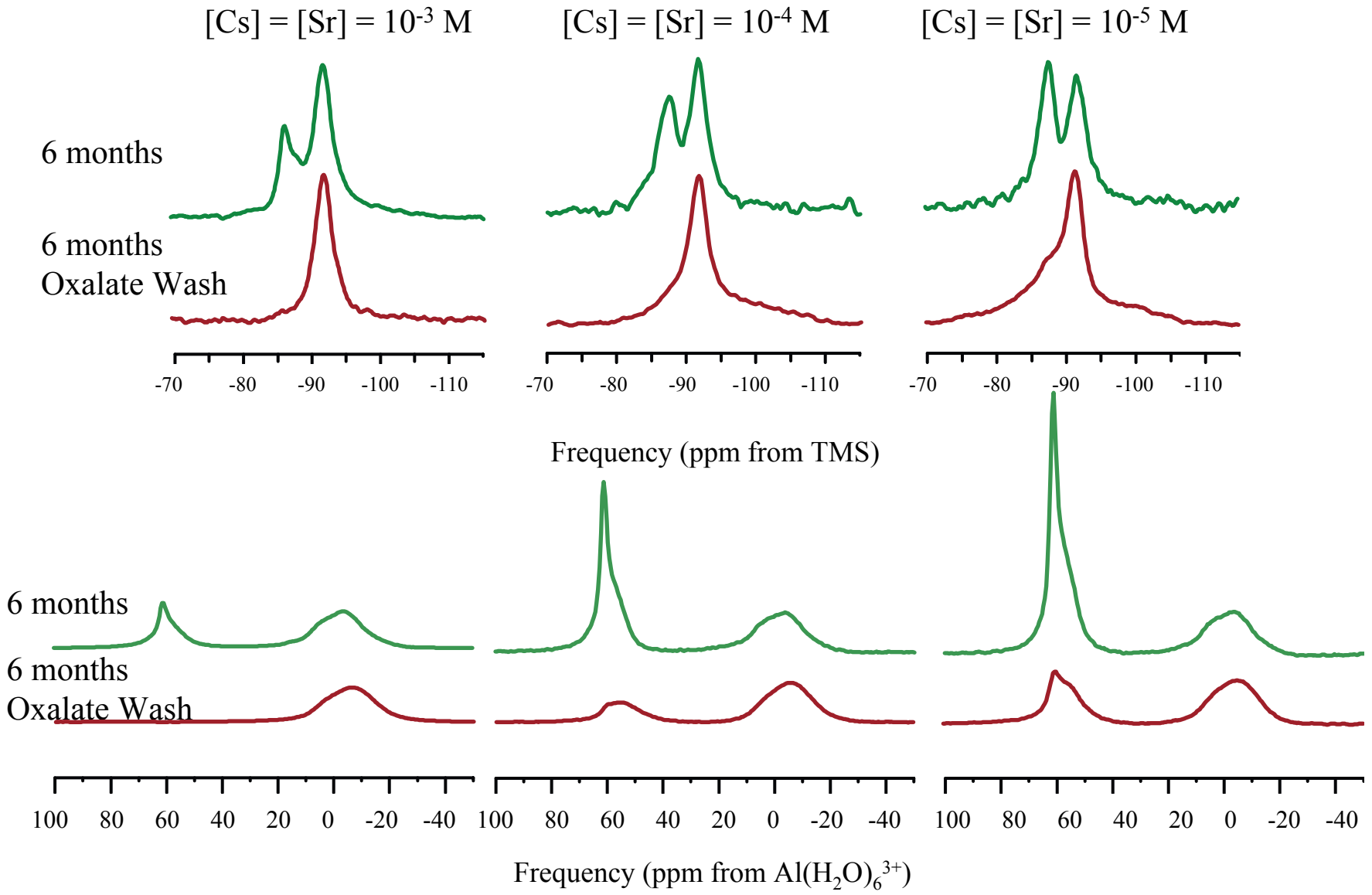
$$= \delta_{iso}^{(CS)} - \frac{3}{40}\left(\frac{C_Q}{\nu_L}\right)^2 \frac{I(I+1)-\frac{3}{4}}{(I(2I-1))^2}\left(1+\frac{\eta^2}{3}\right)\times 10^6$$



^{29}Si MAS NMR Studies of Kaolinite Transformation

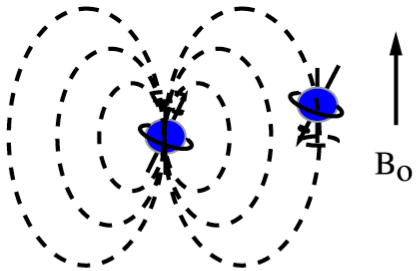


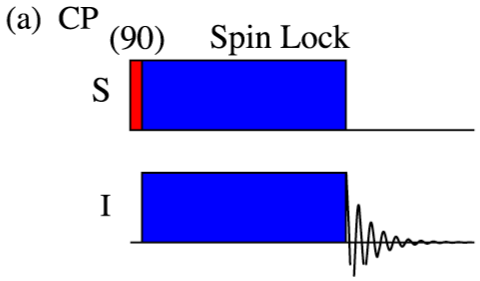
^{27}Al and ^{29}Si MAS NMR Studies of Kaolinite Transformation: Acidic Oxalate Wash



Advanced Solid-State NMR Approaches: One- and Two-Dimensional HETCOR

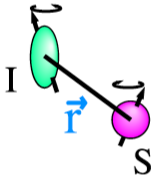
- Heteronuclear correlation experiments: use couplings between the nuclei to probe interatomic interactions





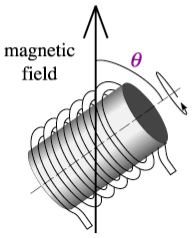
selectivity

(proximity or motion)

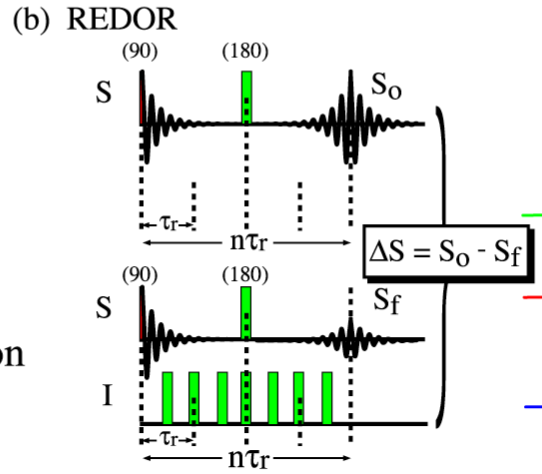


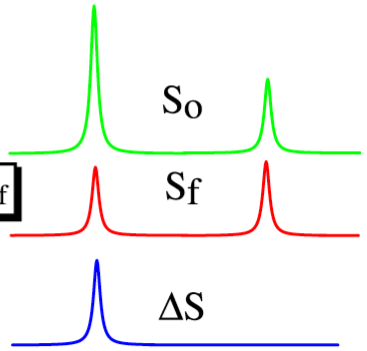
Dipolar Coupling Constant

$$D = \frac{\gamma_I \gamma_S \hbar}{2\pi r^3}$$



Use MAS to retain high resolution

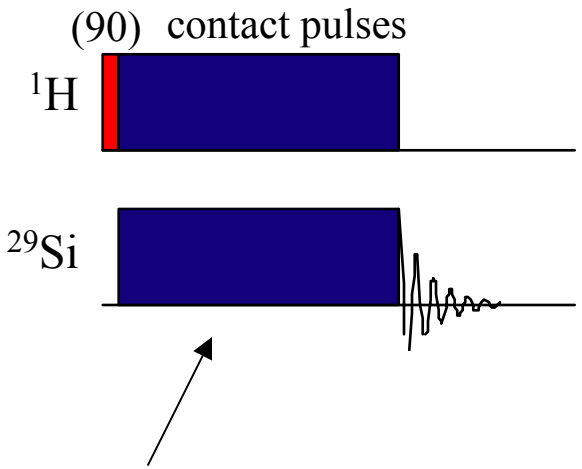




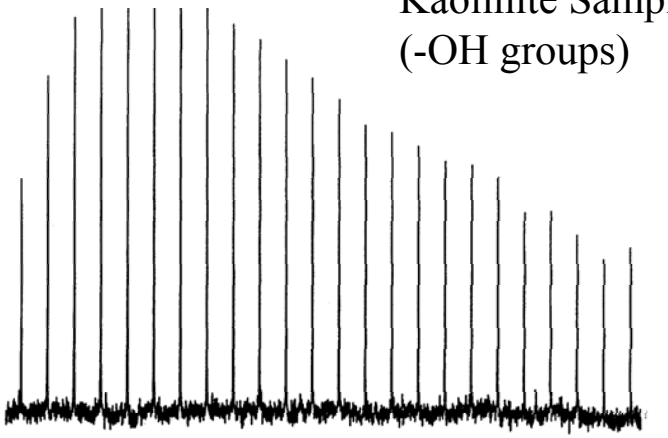
editing

Variable-Contact Cross-Polarization Experiments

Variation of contact time for long radiofrequency pulses provides discrimination of different sources of polarization transfer.

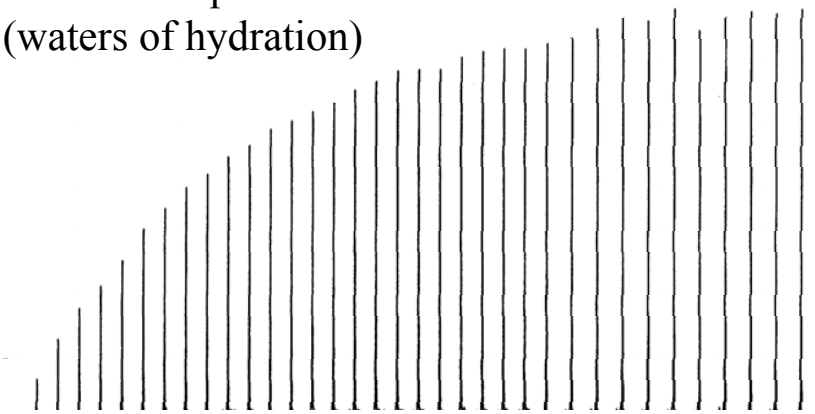


Kaolinite Sample
(-OH groups)



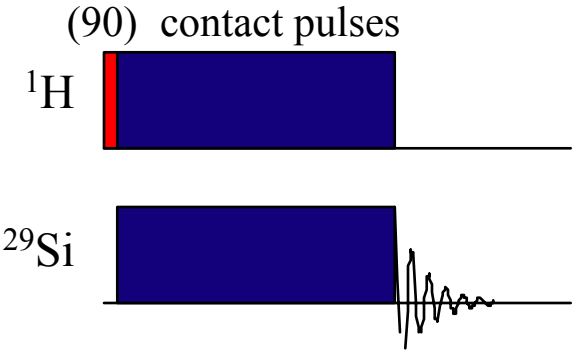
0.5 ms 12.0 ms

Zeolite Sample
(waters of hydration)



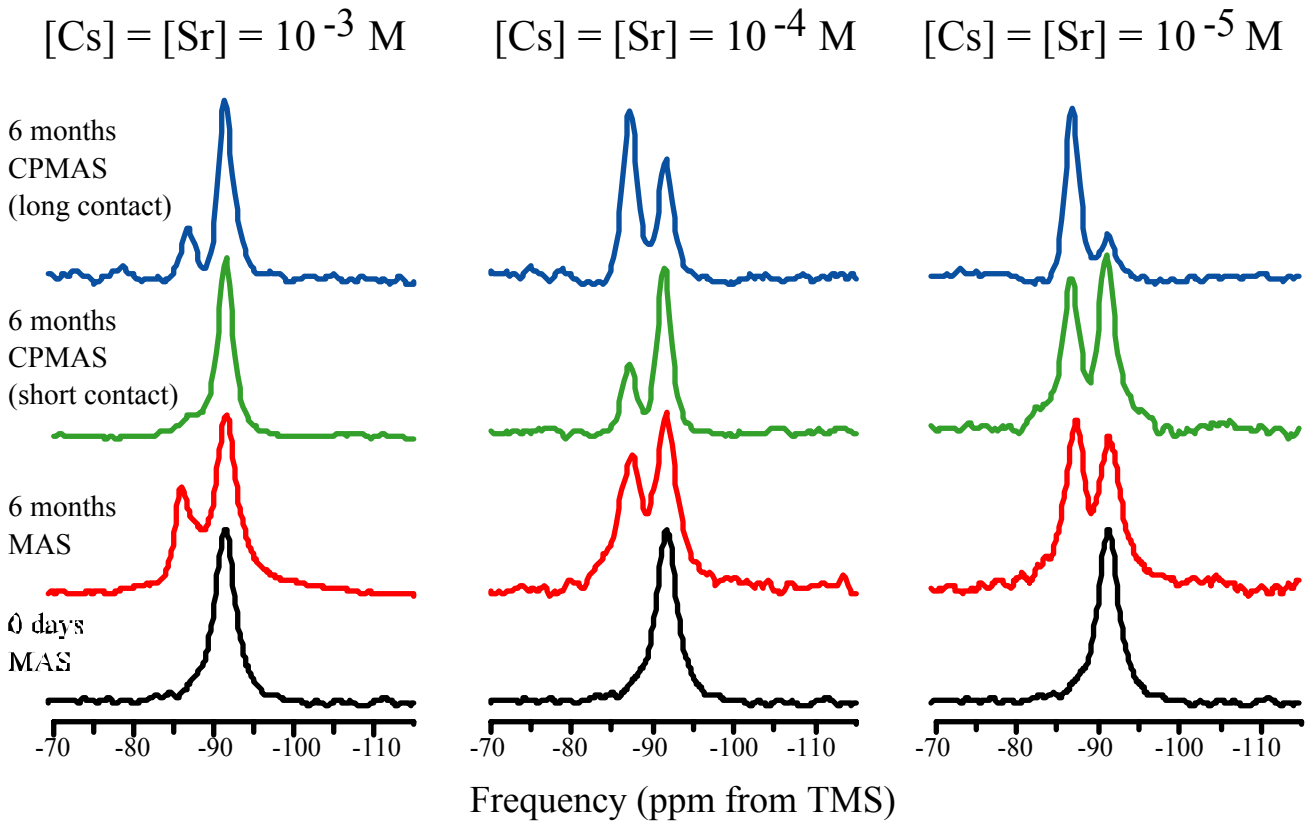
0.5 ms 17.5 ms

Variable-Contact Cross-Polarization Experiments

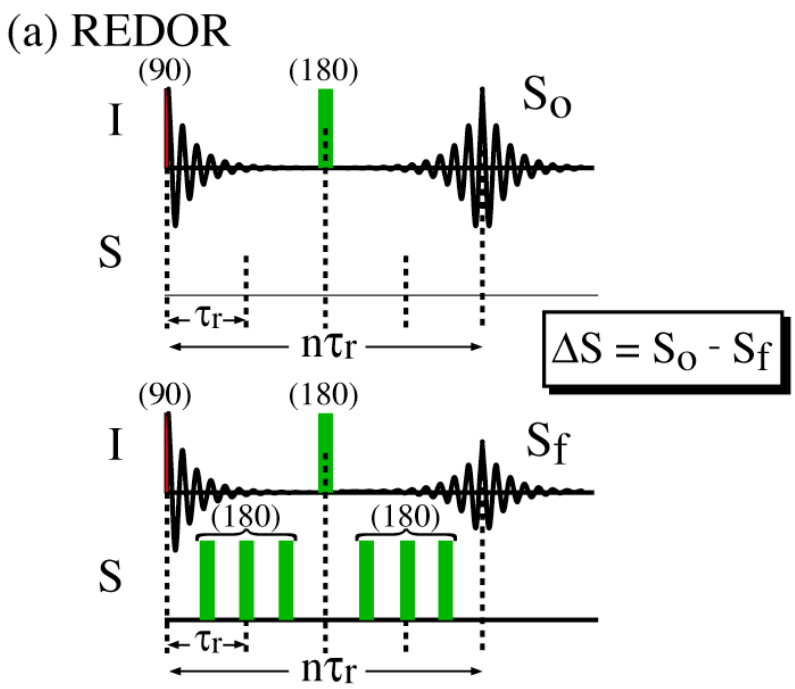


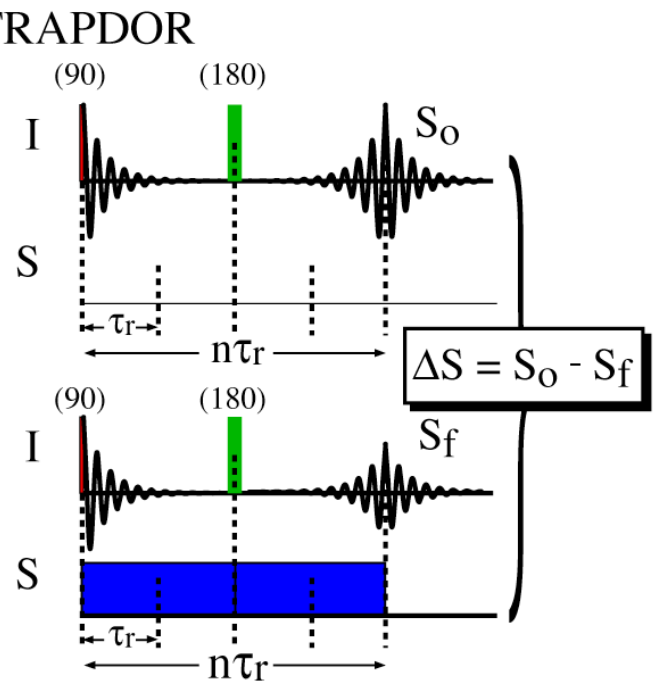
short contact time
(1-4 ms)
selects Si-OH

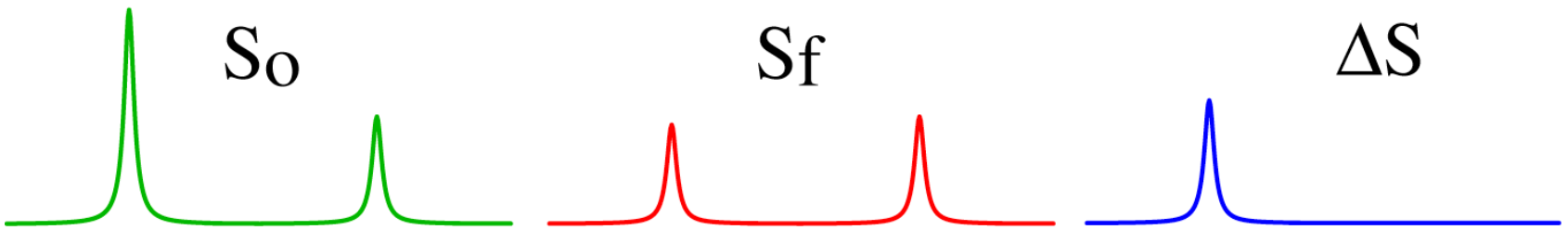
longer contact time
(15-20 ms)
favors hydrated phases



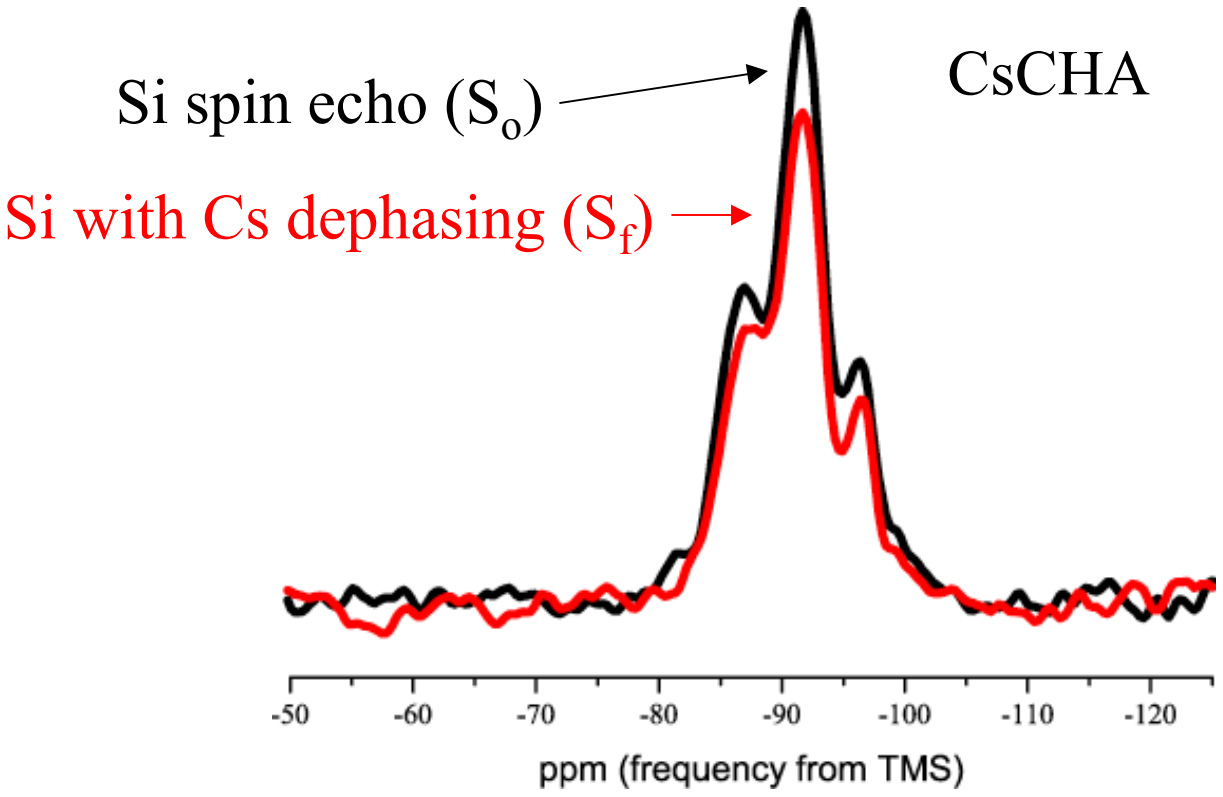
One-Dimensional Heteronuclear Correlation Experiments: Spectral Editing Based on Dipolar Interactions





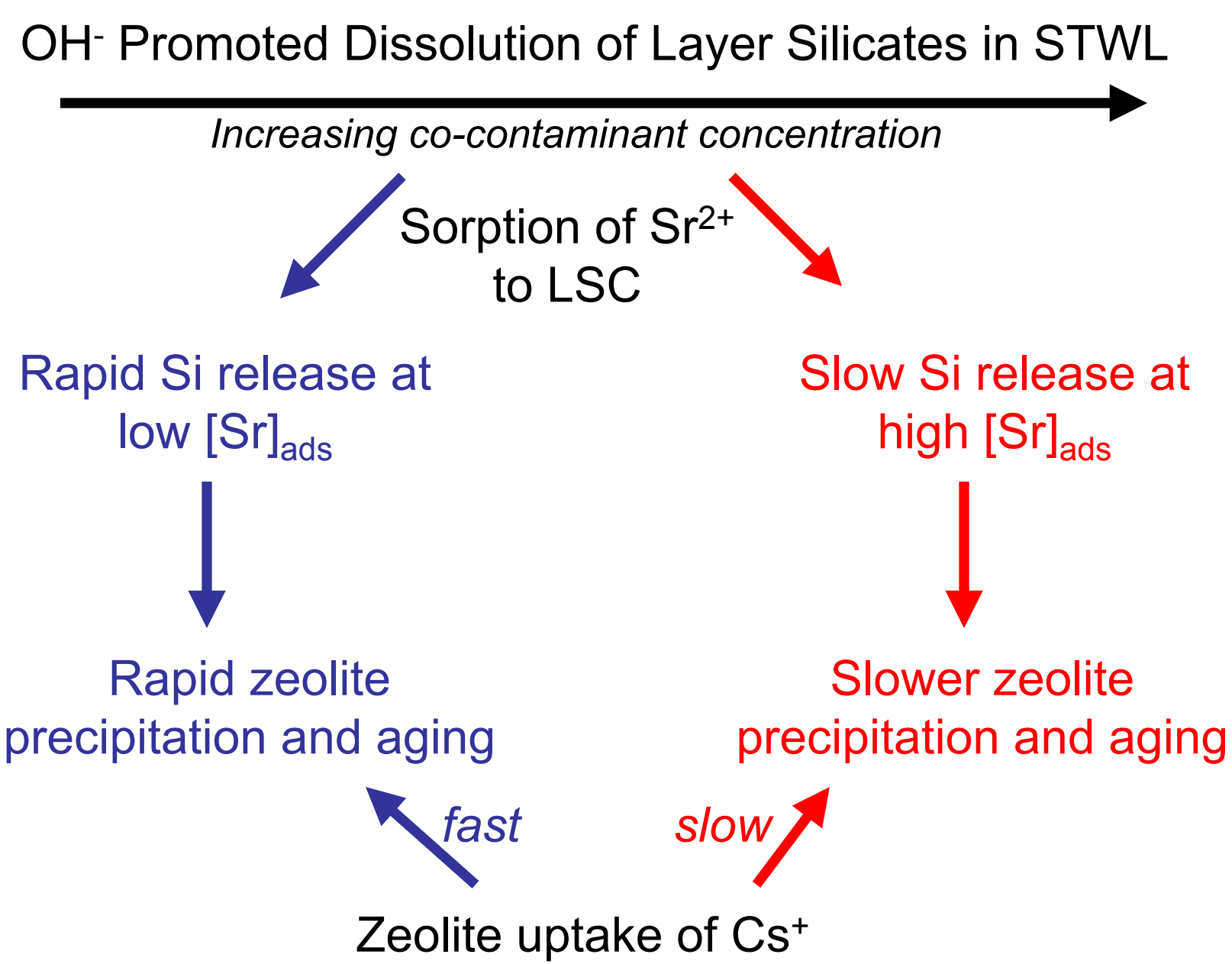


Heteronuclear Correlation NMR Studies: $^{29}Si/^{133}Cs$ REDOR Experiments

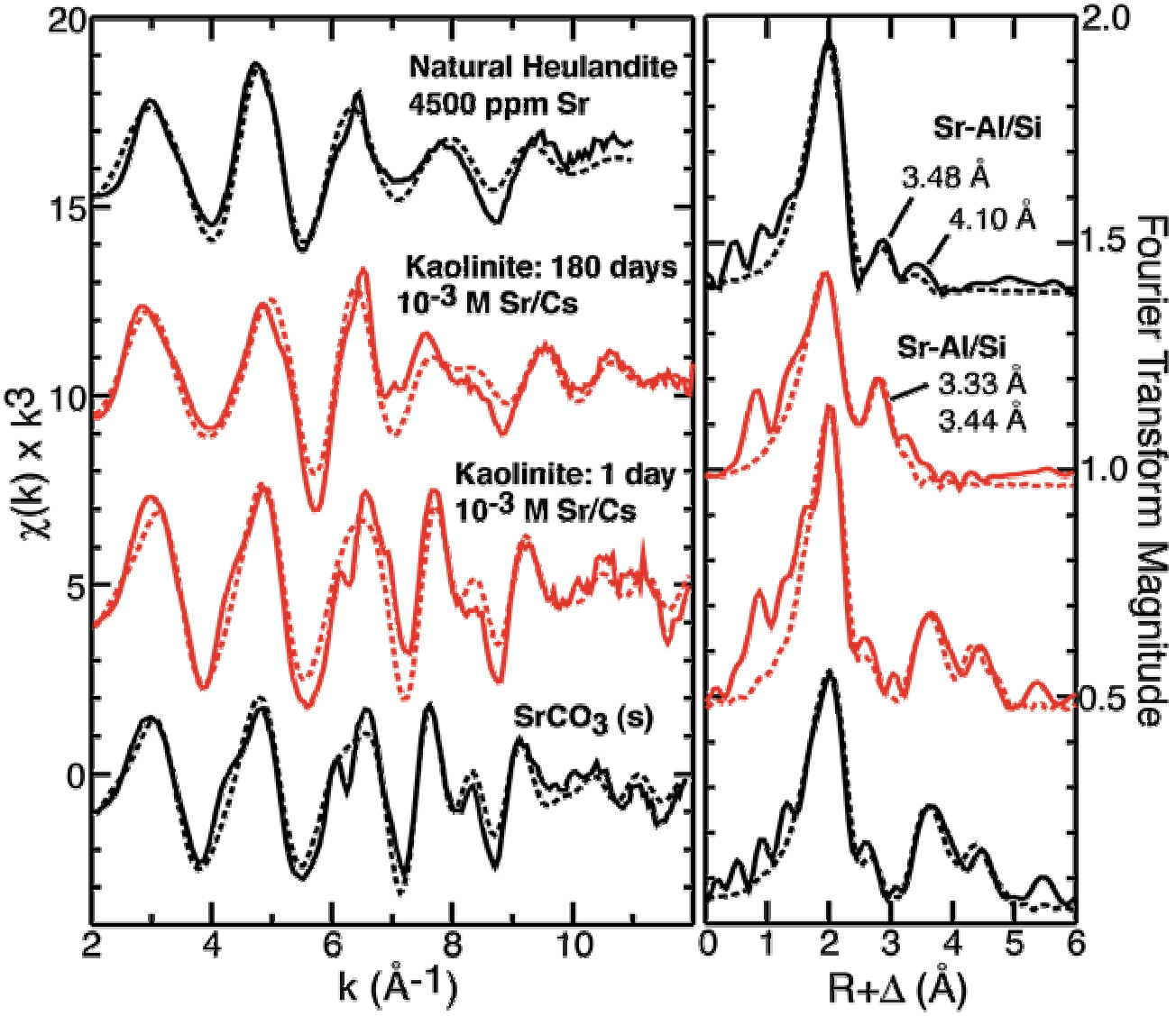


Principal Findings from 1999 EMSP Project

- Caustic waste-soil weathering reactions result in Si release and neoformation of "secondary" solids that sequester Cs and Sr into increasingly recalcitrant forms.
- The secondary solids comprise zeolites chabazite, nitrate sodalite and nitrate cancrinite, depending upon system composition and duration of reaction.
- Specimen clay systems differ in their dissolution kinetics and, therefore, the rate of secondary solid formation.
- Specimen clays provide a baseline for interpretation of weathering processes occurring in heterogeneous sediment samples.


OH- Promoted Dissolution of Layer Silicates in STWL
Increasing co-contaminant concentration
Sorption of Sr2+ to LSC
Rapid Si release at low [Sr]ads
Slow Si release at high [Sr]ads
Rapid zeolite precipitation and aging
Slower zeolite precipitation and aging
fast
slow
Zeolite uptake of Cs+

Sr EXAFS Data: Change in Sr-Containing Environments



Primary Objectives of the Renewal 2003 EMSP Project

- Measure the kinetics of coupled clay transformation reactions and radionuclide sorption along an expanded gradient in solution chemical conditions and soil saturation.
- Determine the molecular nature of contaminant binding sites in neo-formed precipitates and reacted clays/sediments by conjunctive use of microscopy and spectroscopy.
- Determine the rate and extent of contaminant release by desorption, dissolution and dispersion of weathered clays at circumneutral pH (i.e., establish the stability of sorbent-sorbate interactions after removal of the waste leachate source).

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- The EMSL NMR User Facility at PNNL: access to 750 and 800 MHz NMR spectrometers
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Solid-State NMR of Complex Materials