Interfacial Soil Chemistry of Radionuclides in the Unsaturated Zone

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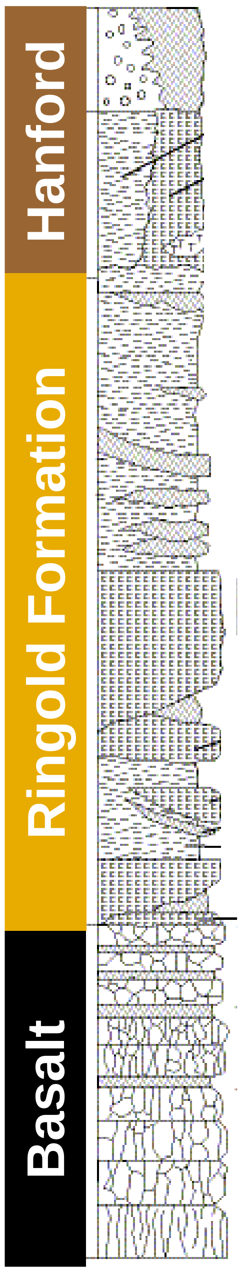
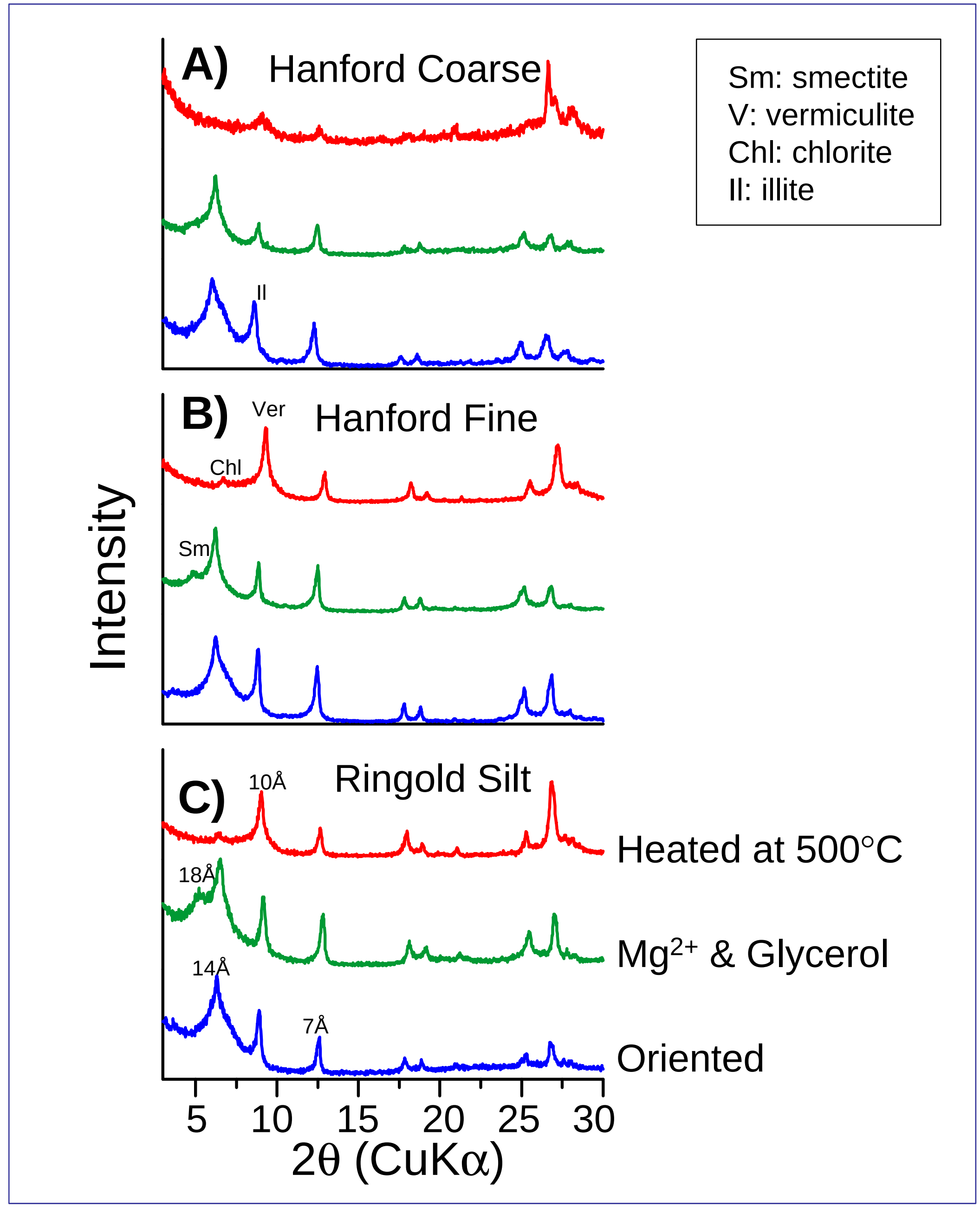


Primary Minerals

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

Secondary clays

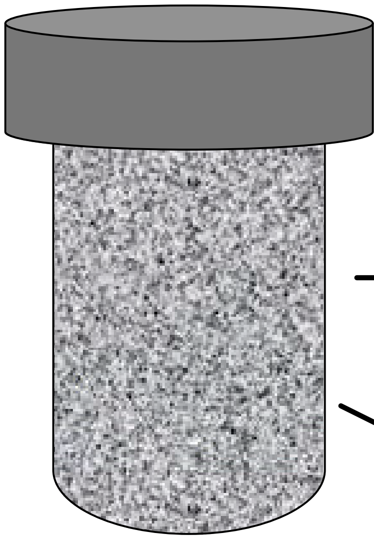
Smectite, vermiculite, illite, chlorite, kaolinite



Objectives

- Investigate dynamics of Cs and Sr uptake over time during reaction of synthetic tank waste leachate (STWL) with specimen clays and Hanford sediments.
- Determine the weathering behavior of clays and sediments under the STWL conditions imposed near-field by the waste leachate.
- Establish relations among mineral weathering processes and sorption behavior of Cs/Sr.

Kinetic studies: Coupled mineral transformation and contaminant sorption



Dissolved (<0.02 mm)

Colloidal (0.02-2.0 mm)

Solid Particulate

$Mg(NO_3)_2$ exchange

NH_4^+-oxalate (pH 3) extraction

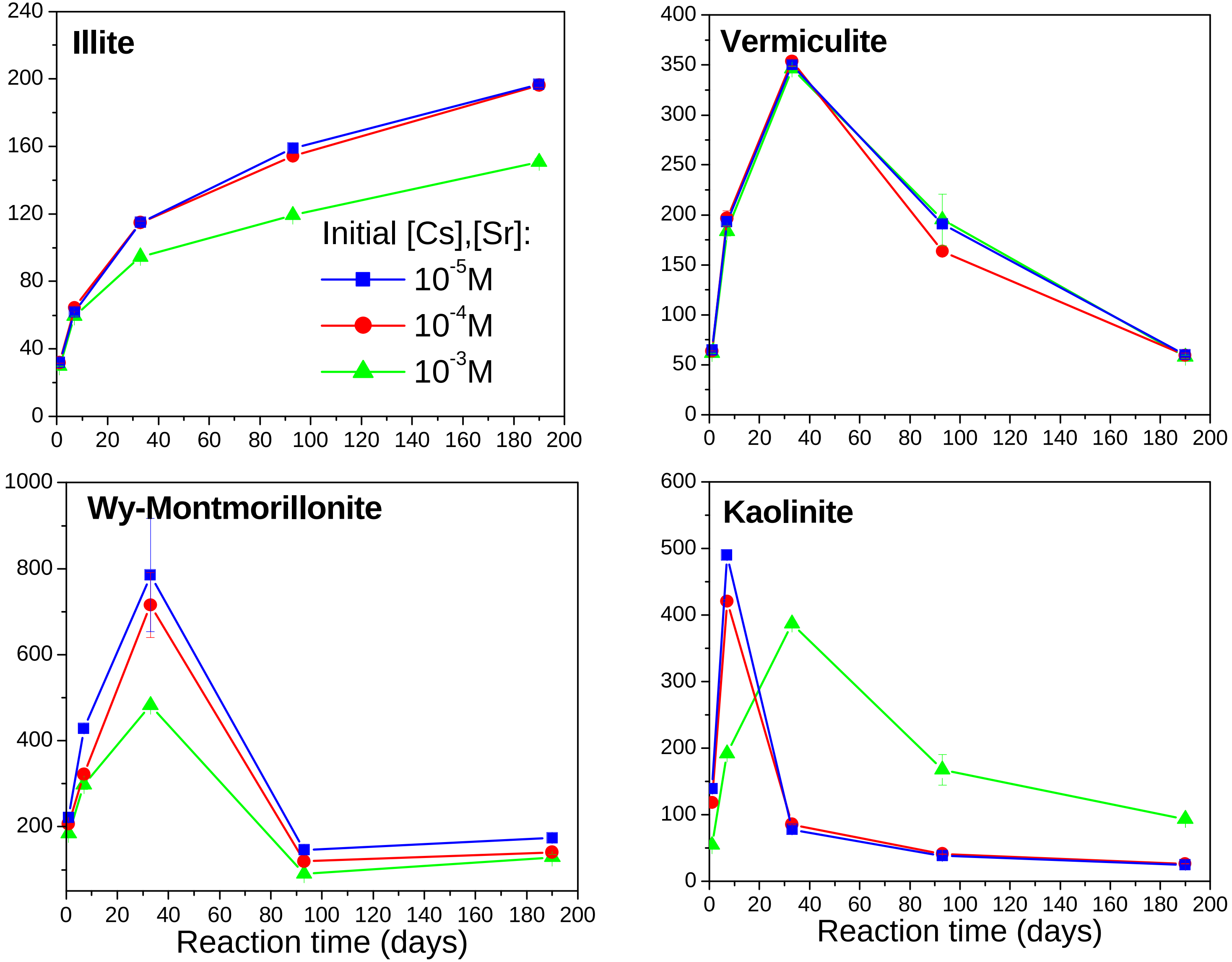
React clay and sediments with STWL in suspension from 0 to 180 d

2 M $NaNO_3$,
0.05 M $Al(OH)_4^-$,
pH 13.5,
Cs & Sr = 10^{-5} to 10^{-3}

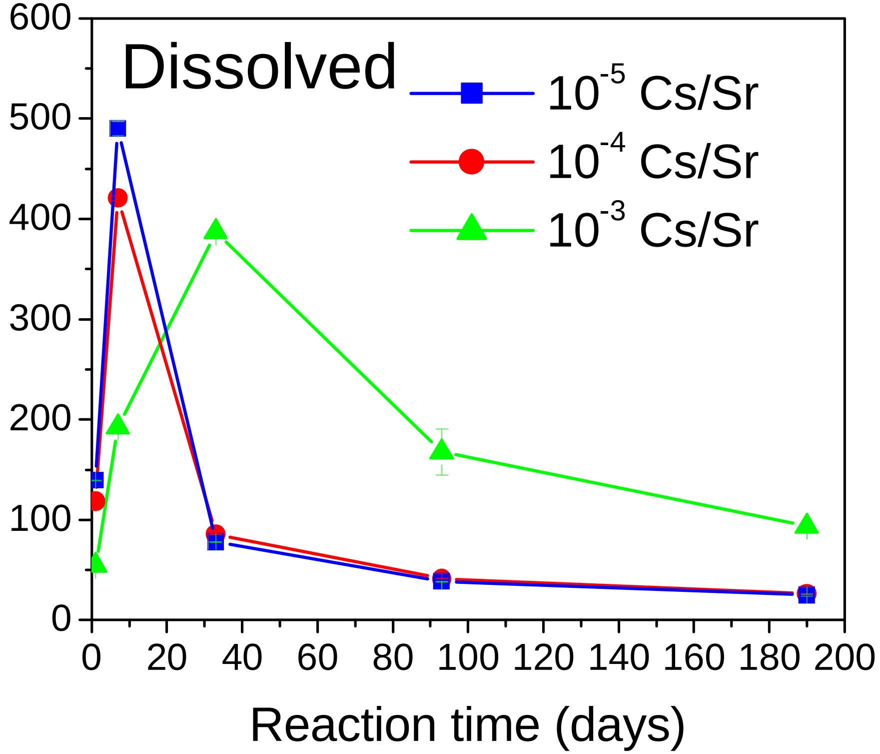
Solution Phase Analysis
Cs, Sr, Al, Si, Fe, pH

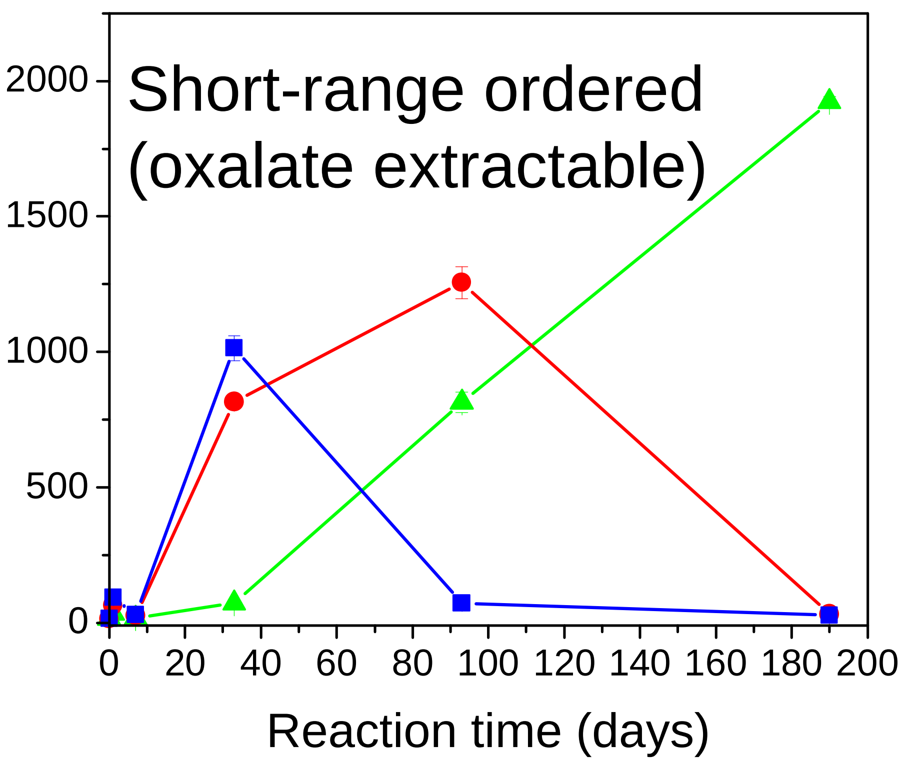
Solid Phase Analysis
XRD
SEM/EDX
TEM
FTIR
NMR
XAFS

Time series' of Si release from specimen clays (mmol kg^{-1})



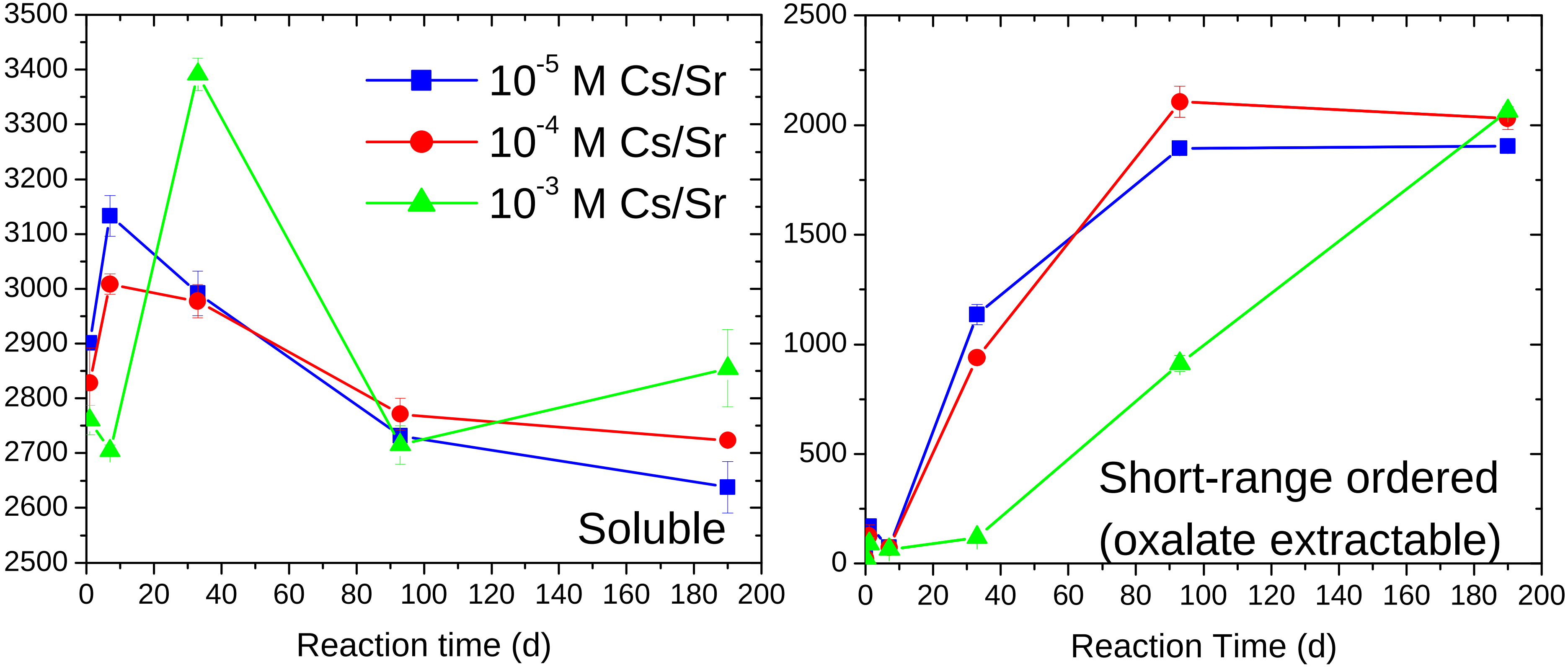
Kaolinite: Dissolution and precipitation of Si ($mmol\ kg^{-1}$ clay)

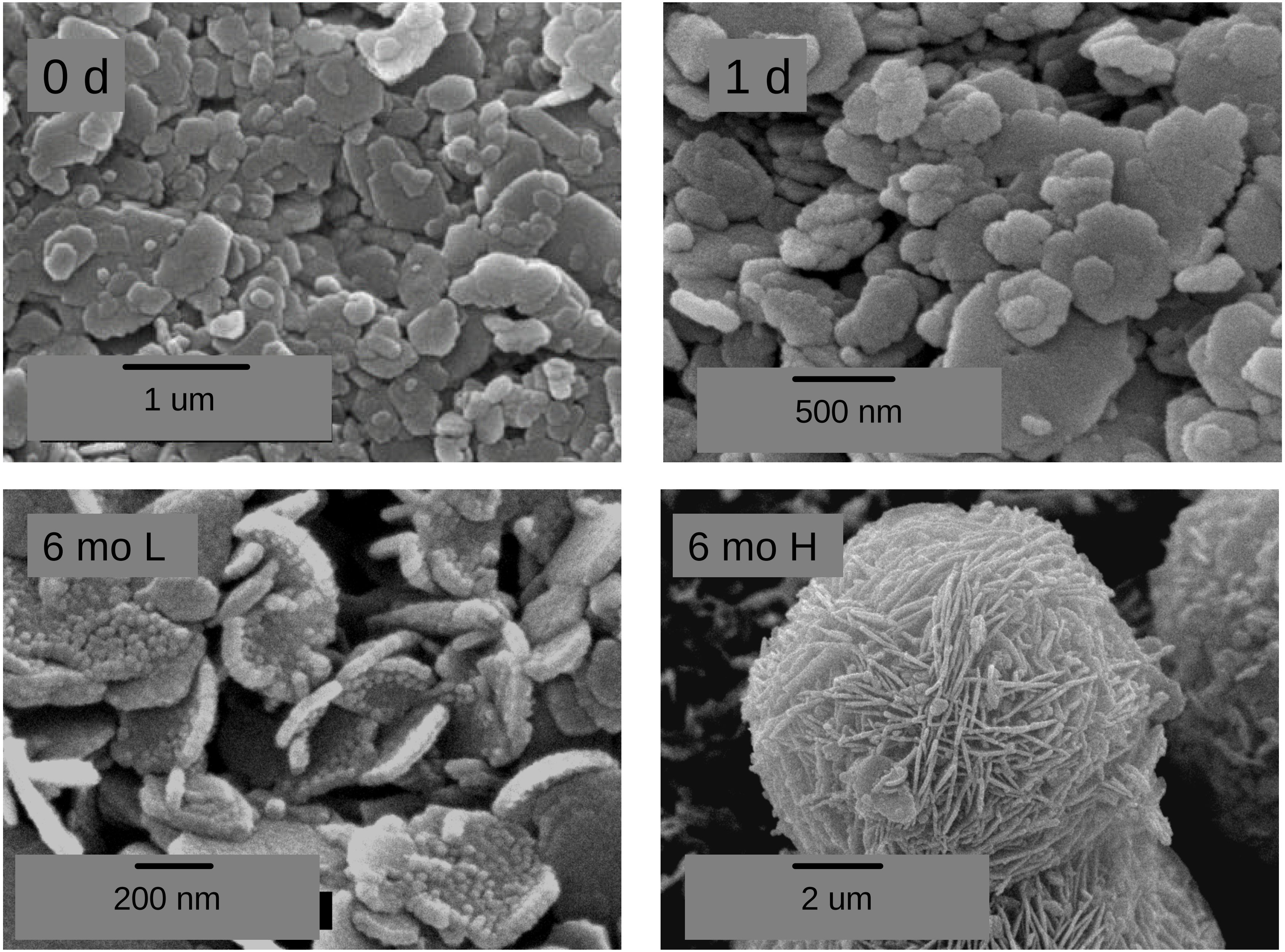




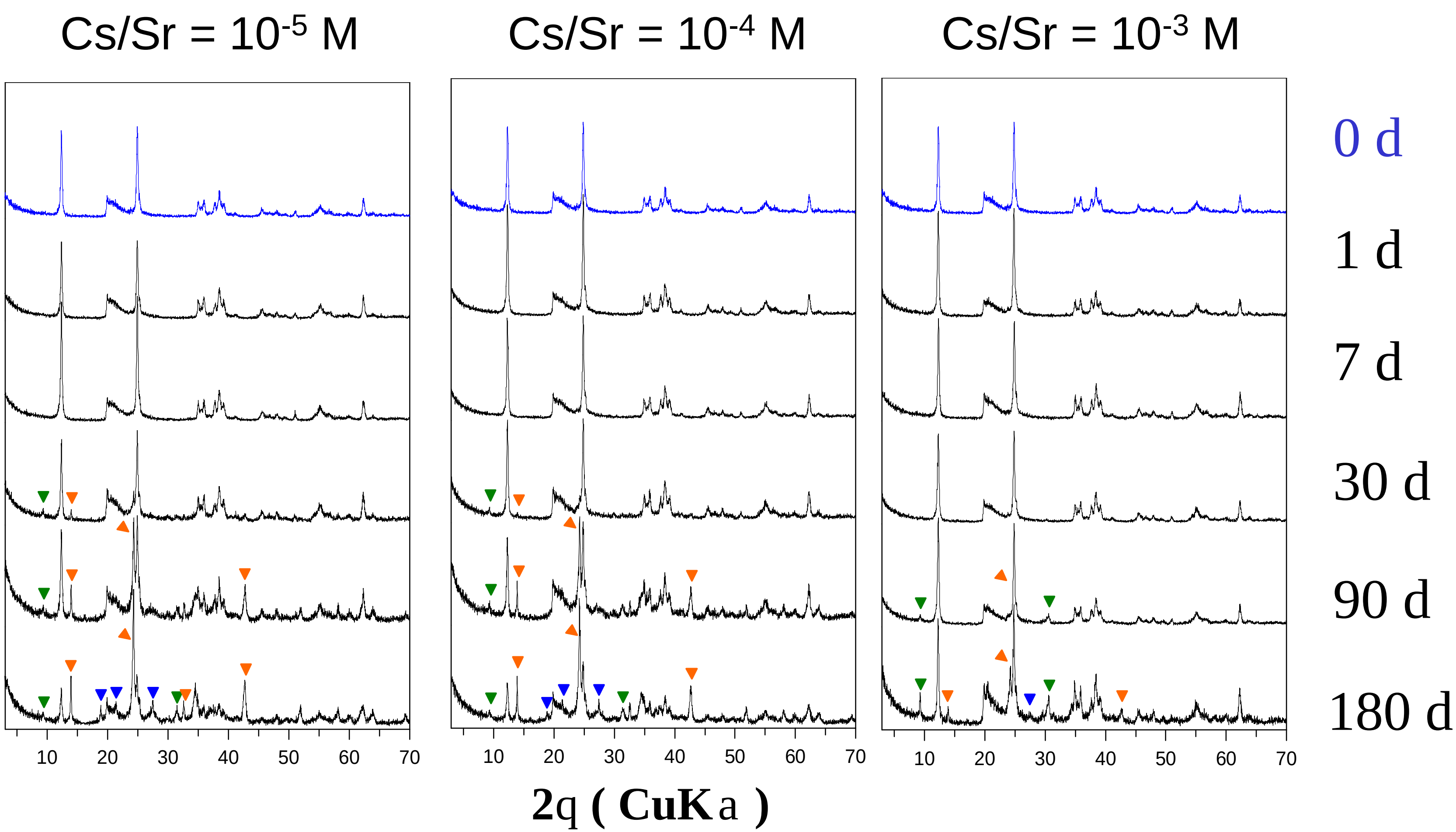
Chemical Formula: $[Si_4]Al_{3.66}Fe(III)_{.07}\ Ti_{0.16}O_{10}(OH)_8$

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




0 d
1 um
1 d
500 nm
6 mo L
200 nm
6 mo H
2 um

XRD patterns of kaolinite as a function of reaction time

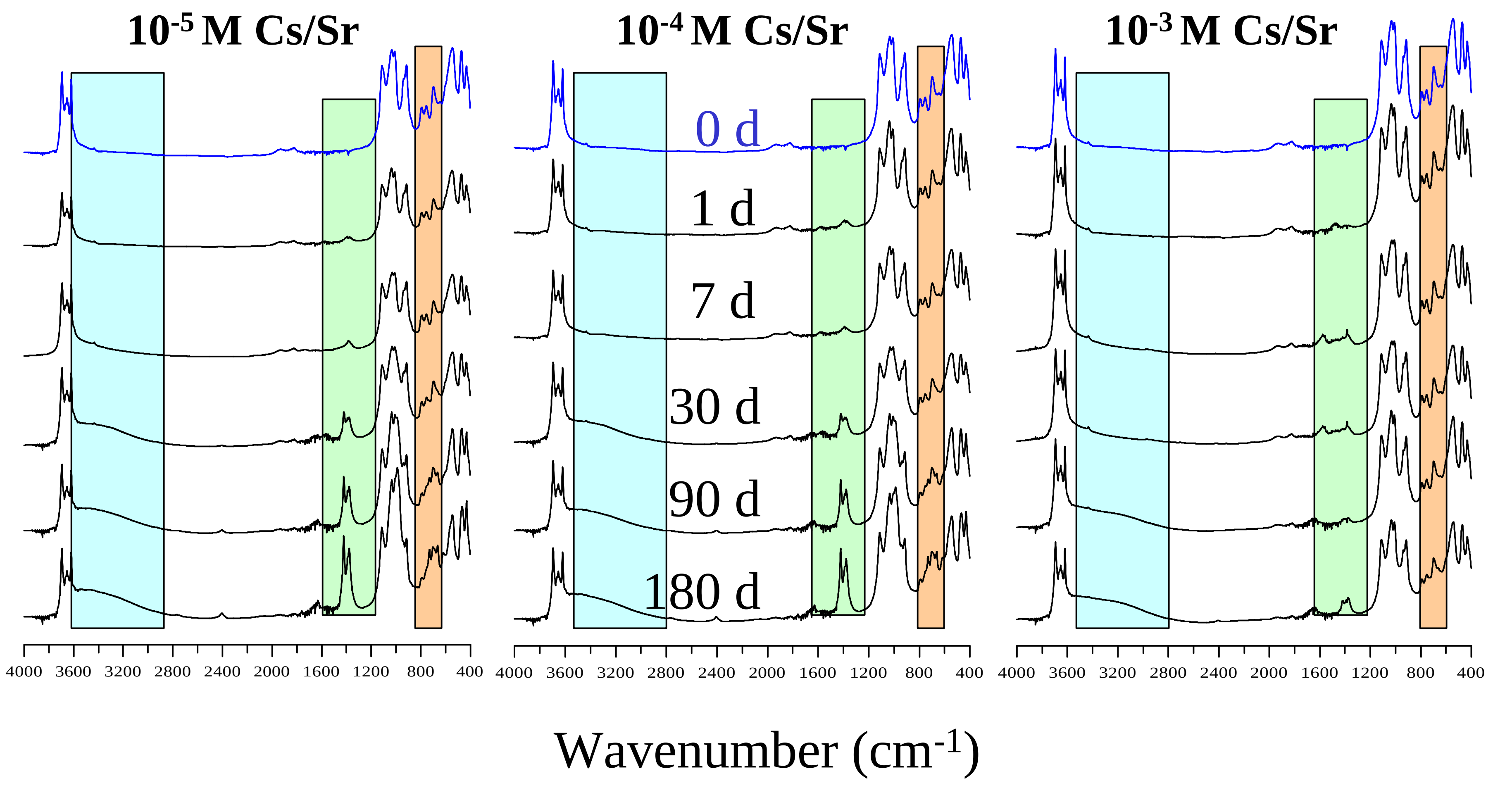


▼ $Na_{4-2x}Sr_xAl_4Si_8O_{24}$•$12H_2O$ (Sr-containing chabazite, "*strontian*")

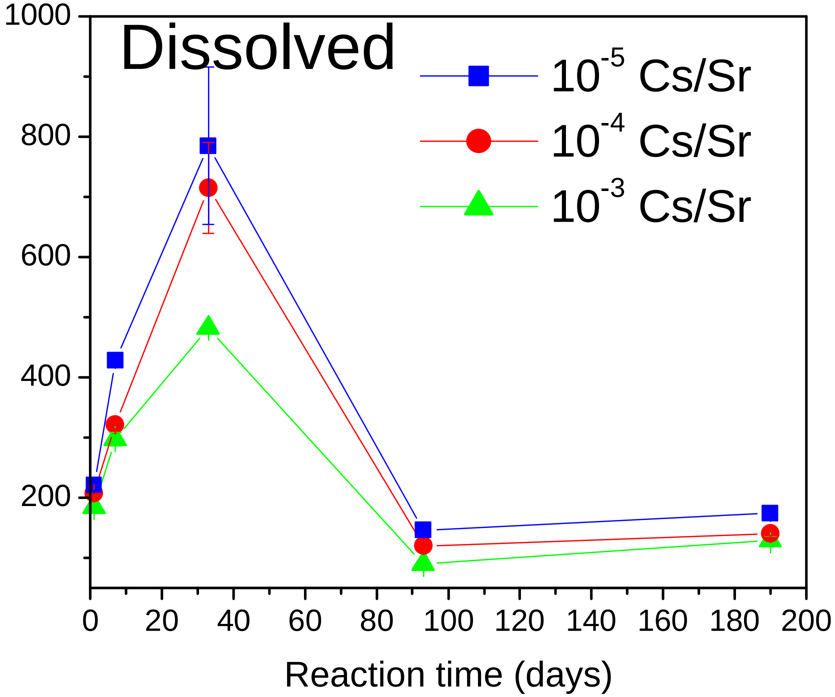
▼ $1.08Na_2O$ • Al_2O_3 • $1.68SiO_2$•$1.8H_2O$ (Sodalite)

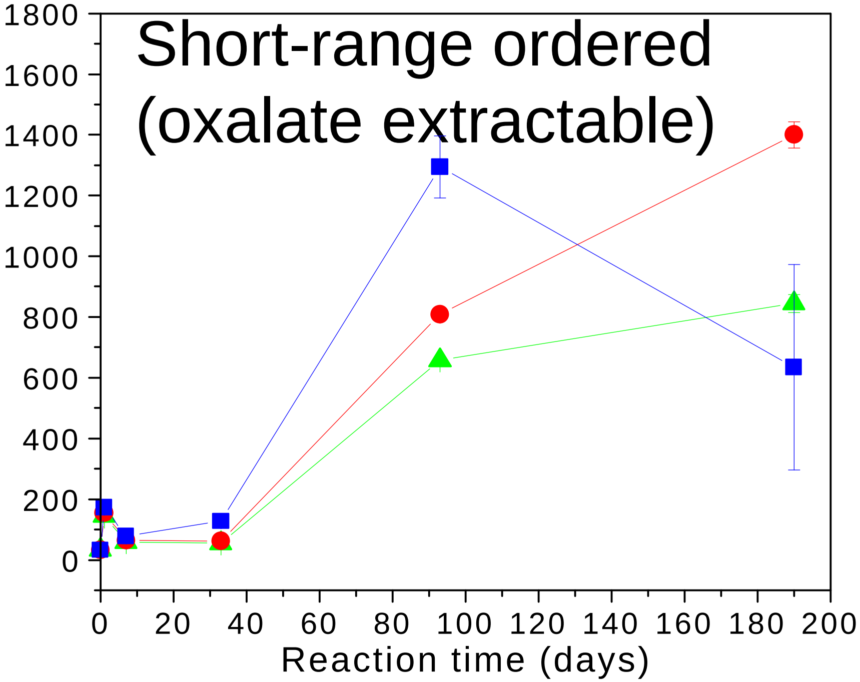
▼ $Na_8(Al_6Si_6O_{24})(NO_3)_2$•$4H_2O$ (Cancrinite)

DRIFT spectra of kaolinite reaction products



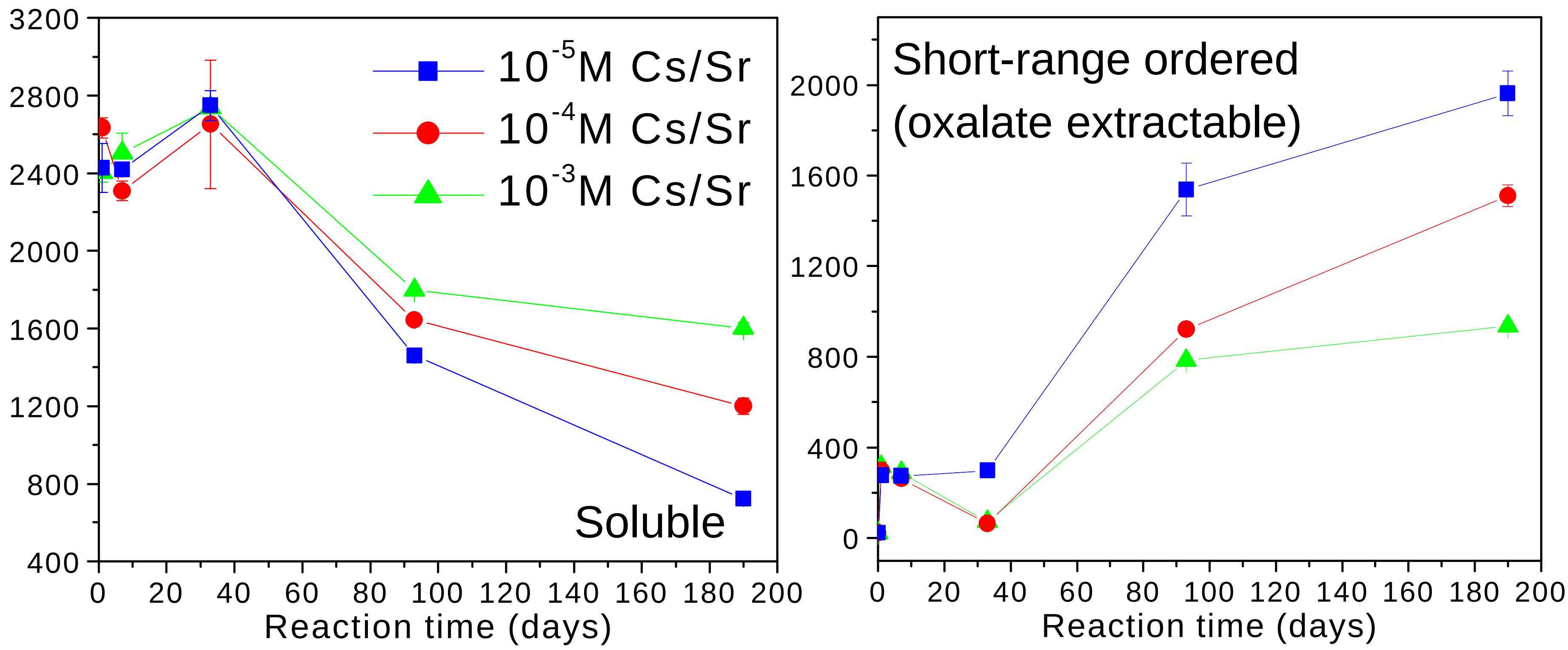
Montmorillonite: Dissolution and precipitation of Si ($mmol\ kg^{-1}$ clay)

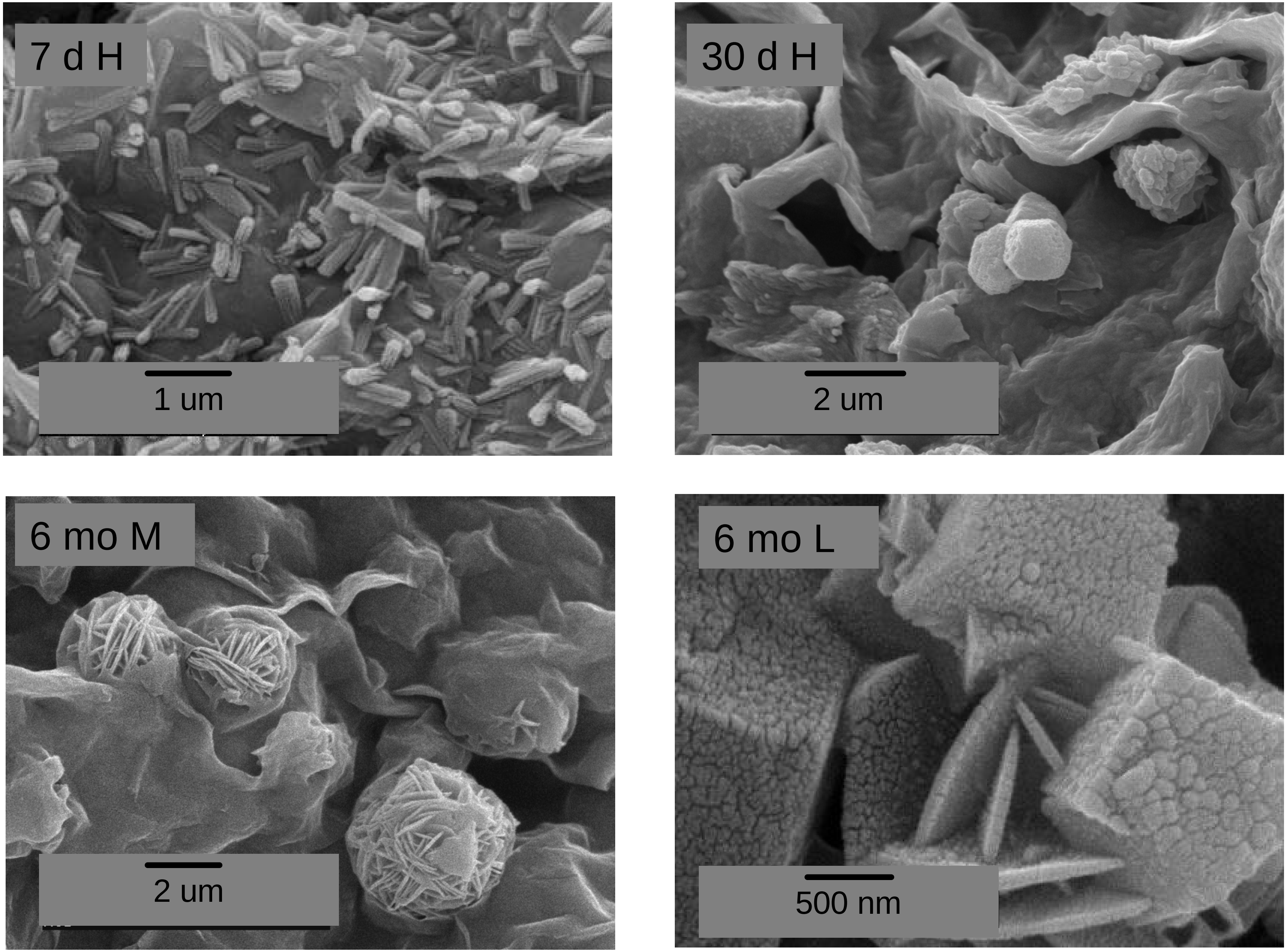




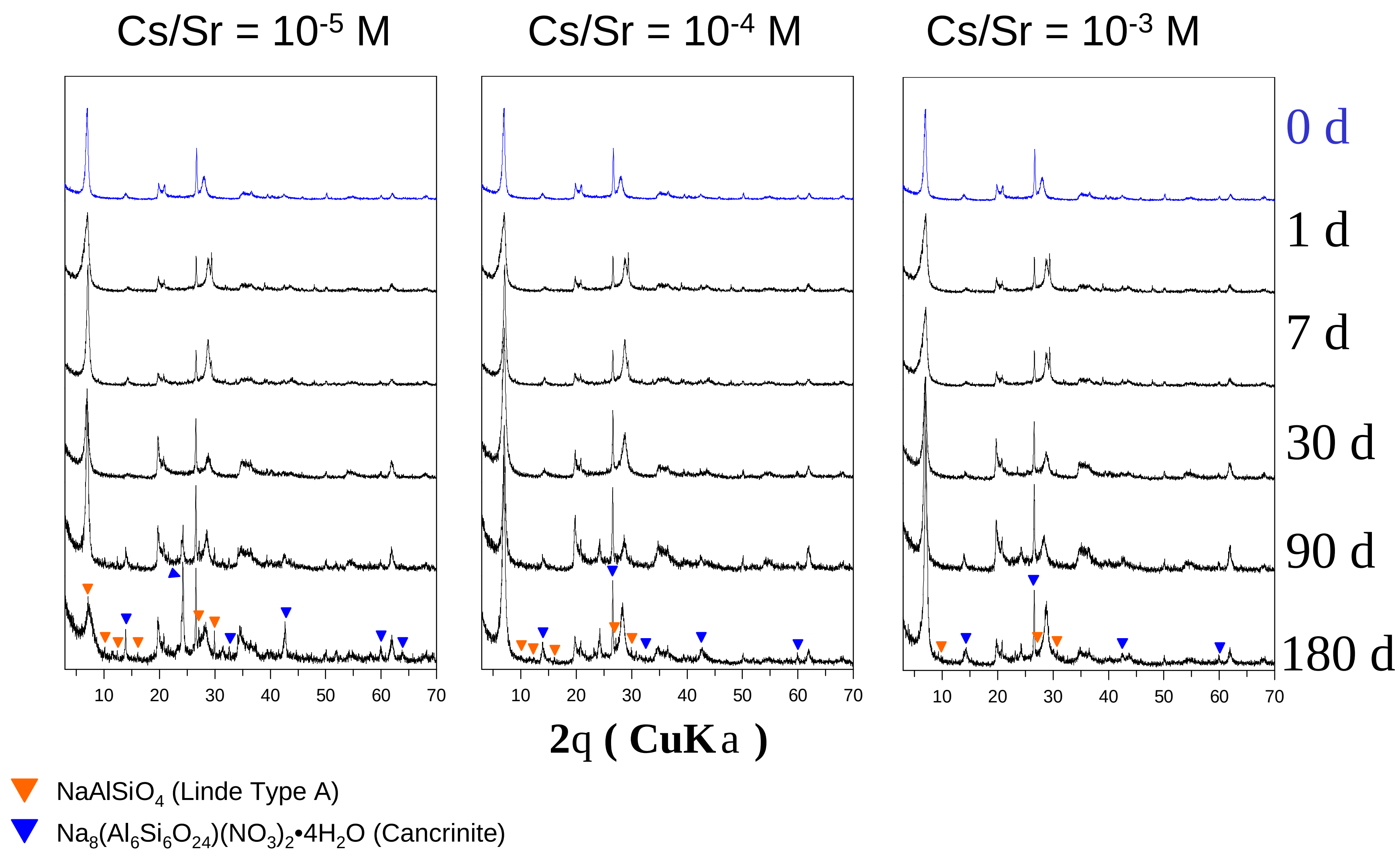
Chemical Formula: $Na_{0.56}[Si_{7.98}Al_{0.02}]Al_{3.01}Fe_{0.41}\ Mg_{0.54}Ti_{0.02}O_{20}(OH)_4$

Montmorillonite: Dissolution and precipitation of Al ($mmol\ kg^{-1}$ clay)




7 d H
1 um
30 d H
2 um
6 mo M
2 um
6 mo L
500 nm

XRD patterns of montmorillonite as a function of reaction time



Solid phase reaction products

1. Strontium aluminum silicate hydrate (▼)
   Zeolite: chabazite (Sr); $Na_{4-2x}Sr_xAl_4Si_8O_{24} \cdot 12H_2O$
   Zeolite structure Type Name-Code : Chabazite -CHA
   Crystal system : Rhombohedral

2. Sodium aluminum silicate hydrate (▼)
   Zeolite: unnamed zeolite; $1.08Na_{2-2x}Sr_xO \cdot Al_2O_3 \cdot 1.68SiO_2 \cdot 1.8H_2O$
   Zeolite structure Type Name-Code : Sodalite-SOD
   Crystal system : Cubic

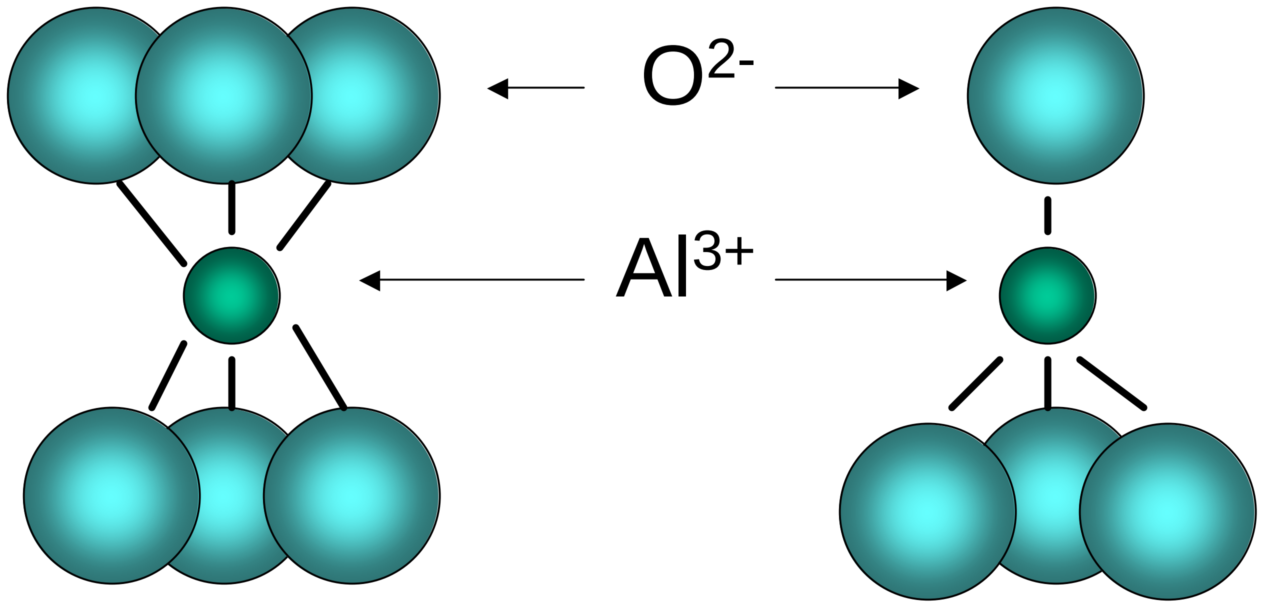
3. Sodium aluminum nitrate silicate hydrate (▼)
   Zeolite: unnamed zeolite; $Na_{8-2x}Sr_x(Al_6Si_6O_{24})(NO_3)_2 \cdot 4H_2O$
   Zeolite structure Type Name-Code : Cancrinite-CAN
   Crystal system : Hexagonal

4. Sodium aluminum silicate (▼)
   Zeolite: Zeolite A (Na); $NaAlSiO_4$
   Zeolite structure Type Name-Code : Linde Type A-LTA
   Crystal system : Cubic

Aluminum coordination in kaolinite and zeolite structures

Kaolinite Al^{VI}

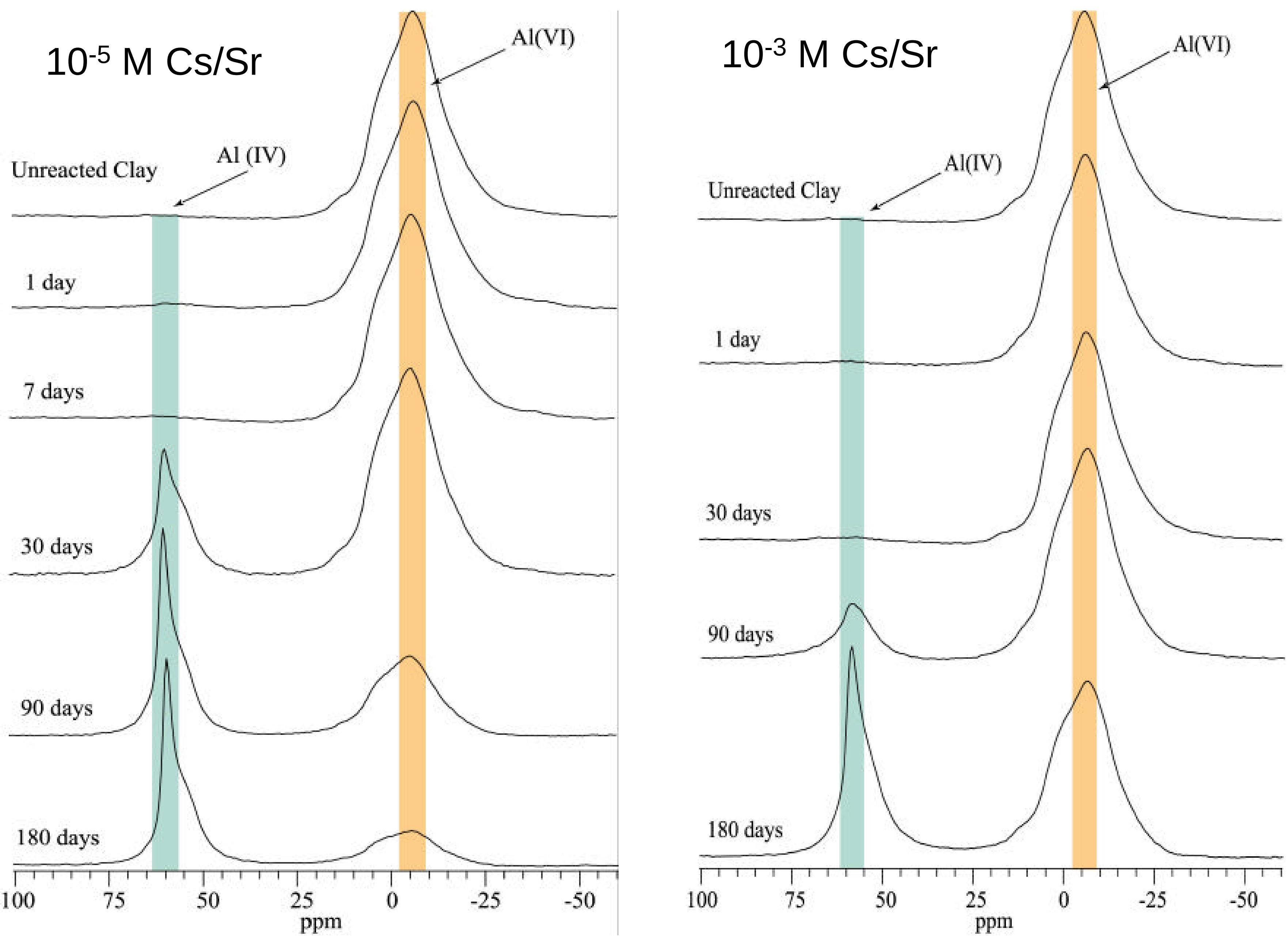
Zeolite Al^{IV}
(e.g., strontian/sodalite)



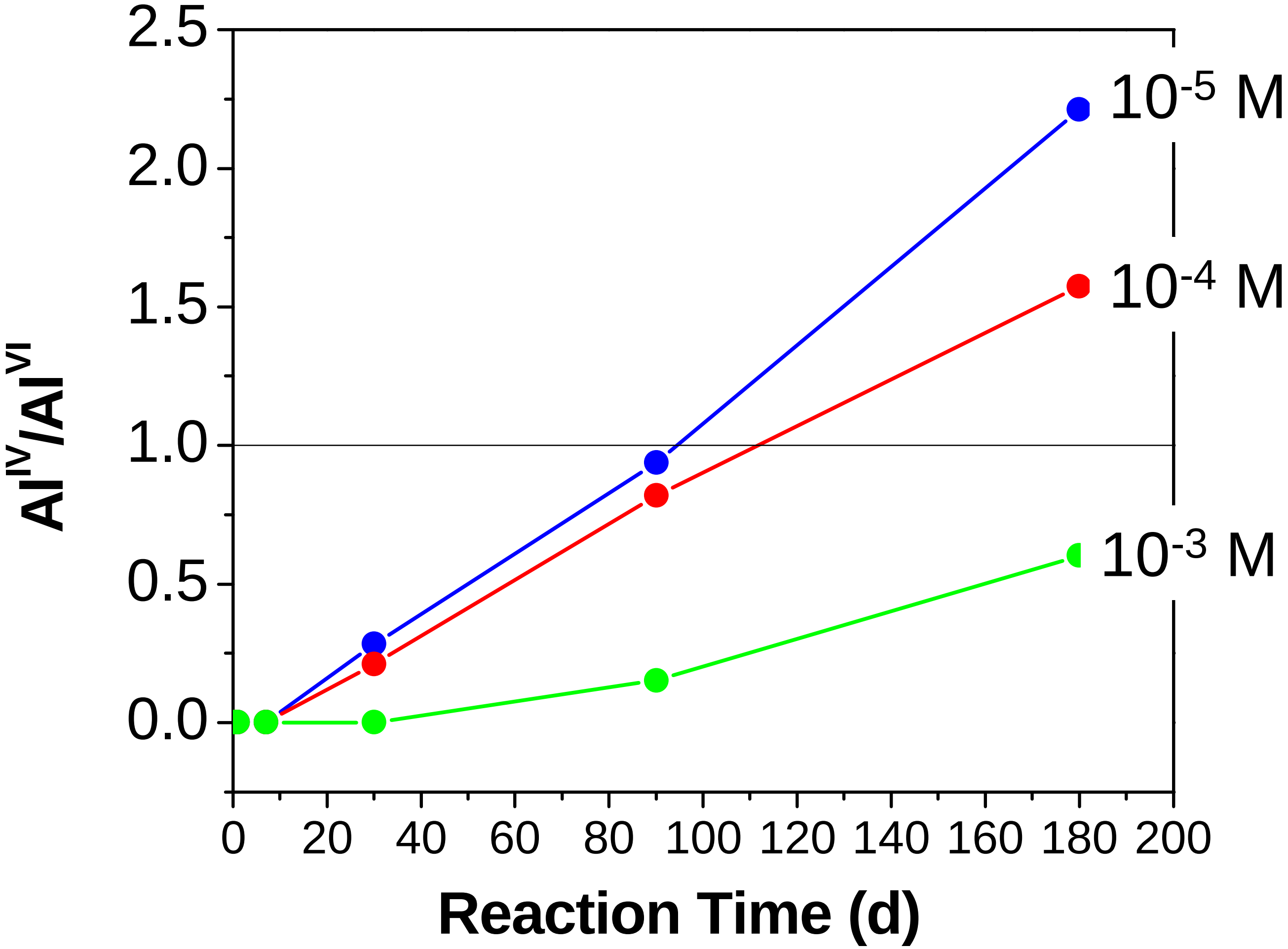
Octahedral sites

Tetrahedral sites

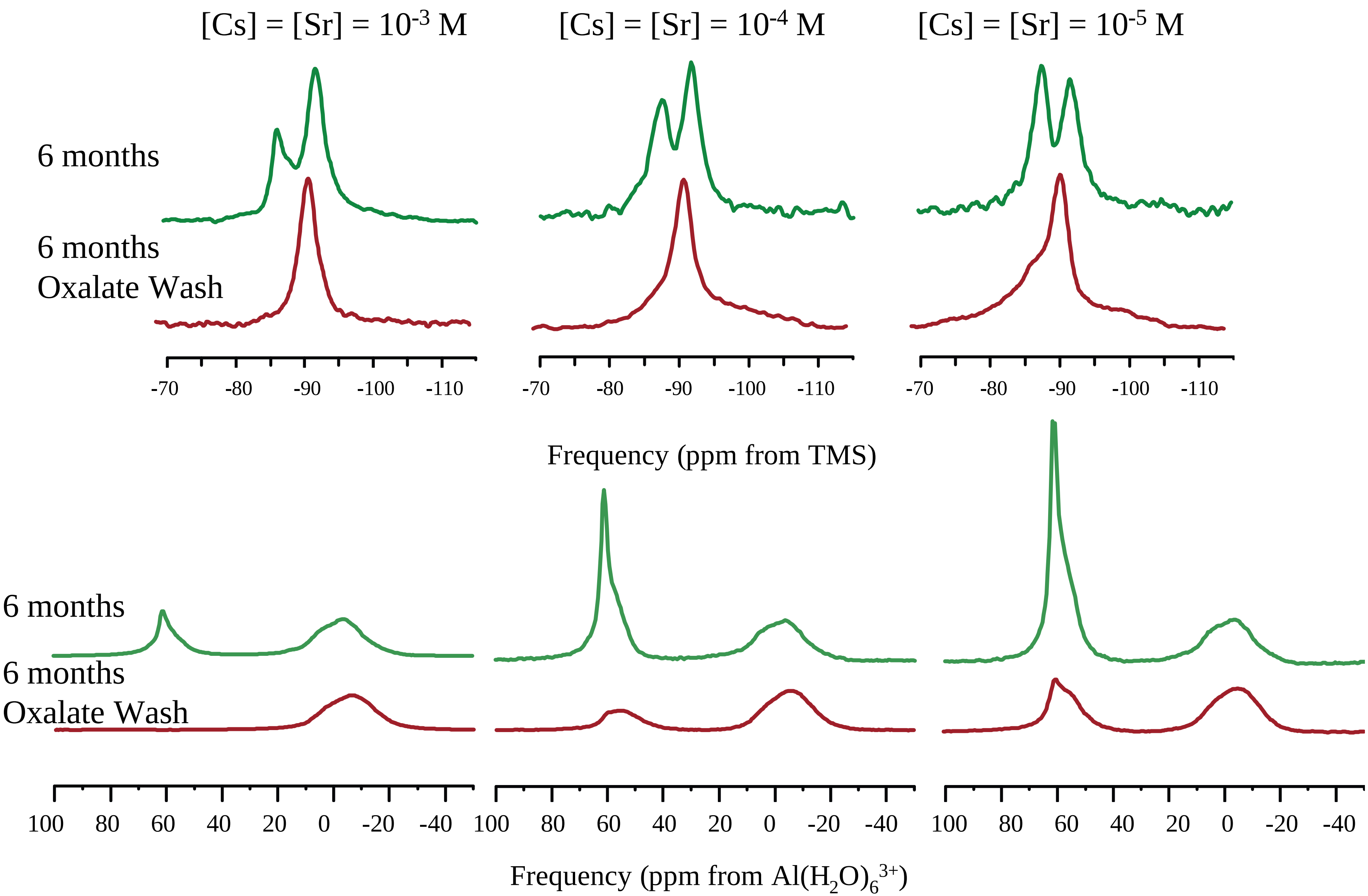
^{27}Al MAS NMR spectra of kaolinite transformation



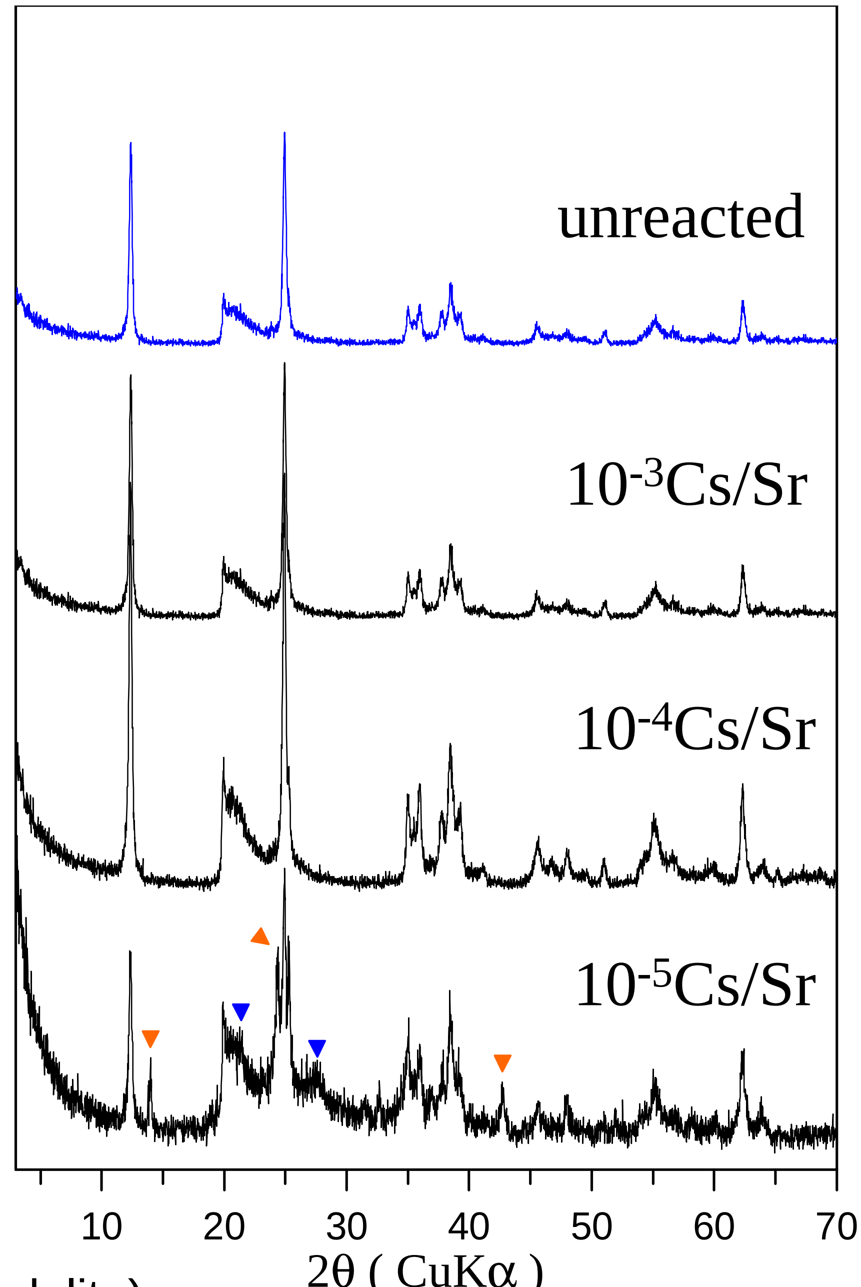
Al^{IV}/Al^{VI} ratio measured by NMR



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



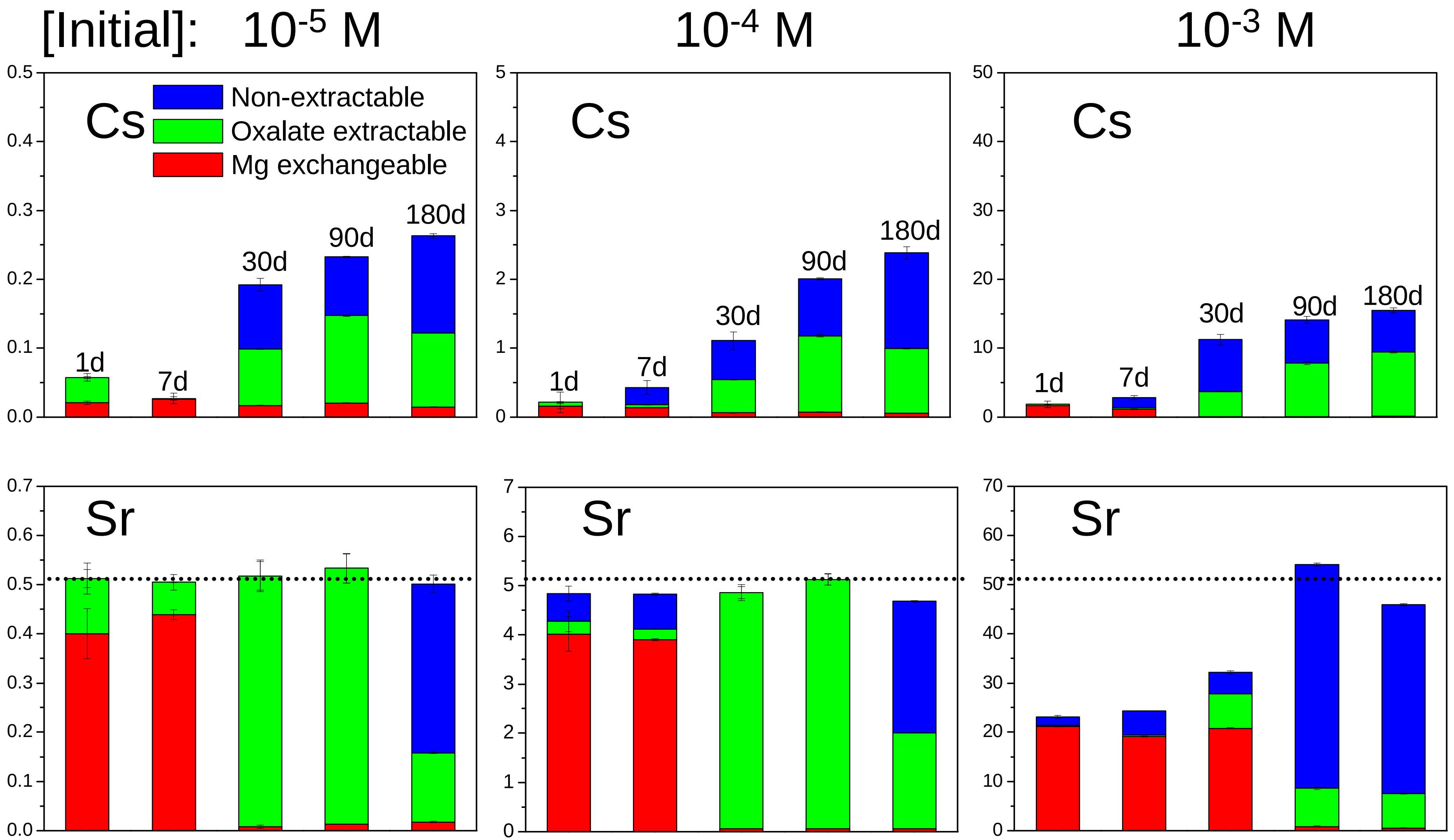
X-ray diffraction: acid oxalate extracted kaolinite after 6 month reaction time with STWL



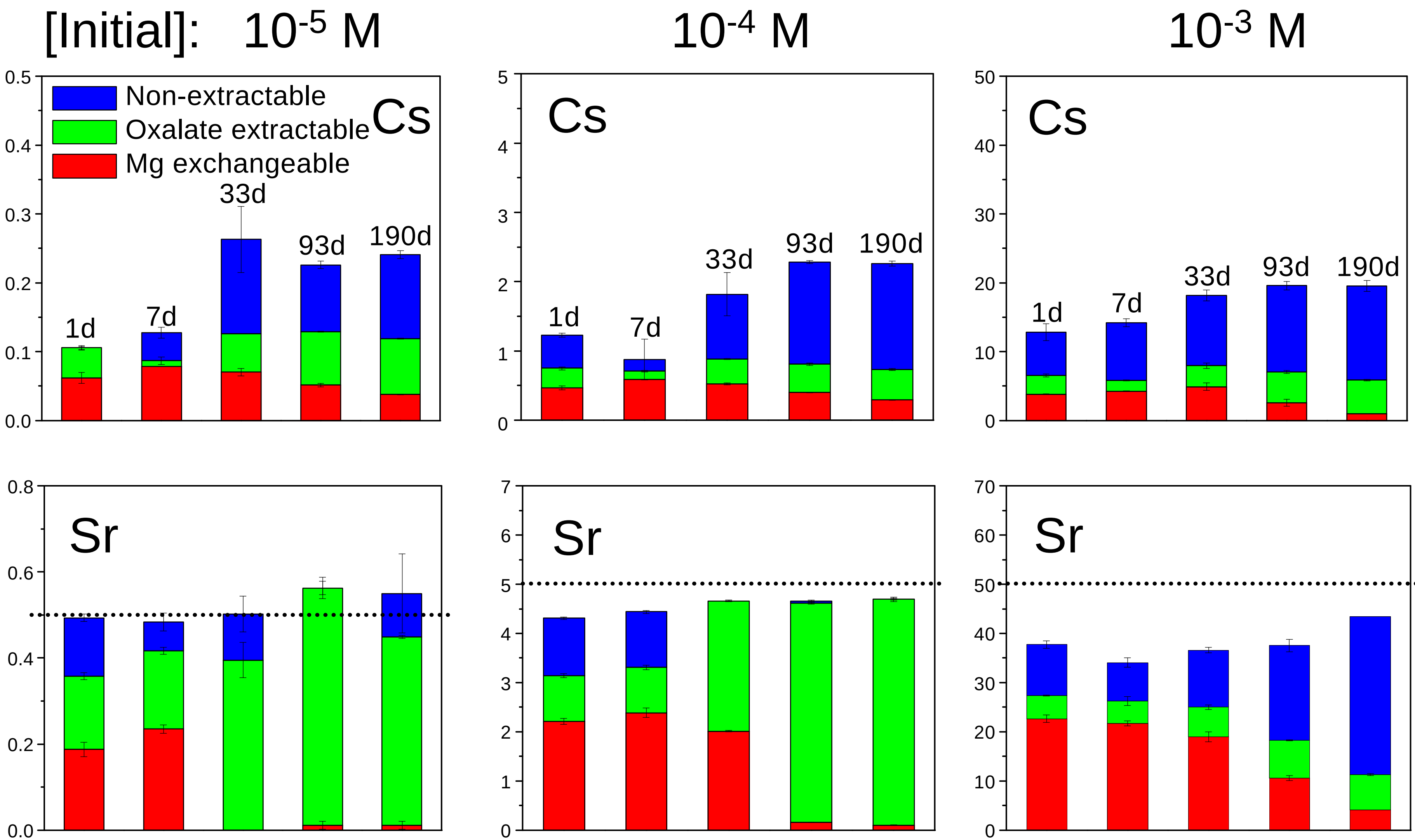
▼ $Na_8(Al_6Si_6O_{24})(NO_3)_2 \cdot 4H_2O$ (Cancrinite)

▼ $1.08Na_2O \cdot Al_2O_3 \cdot 1.68SiO_2 \cdot 1.8H_2O$ (Sodalite)

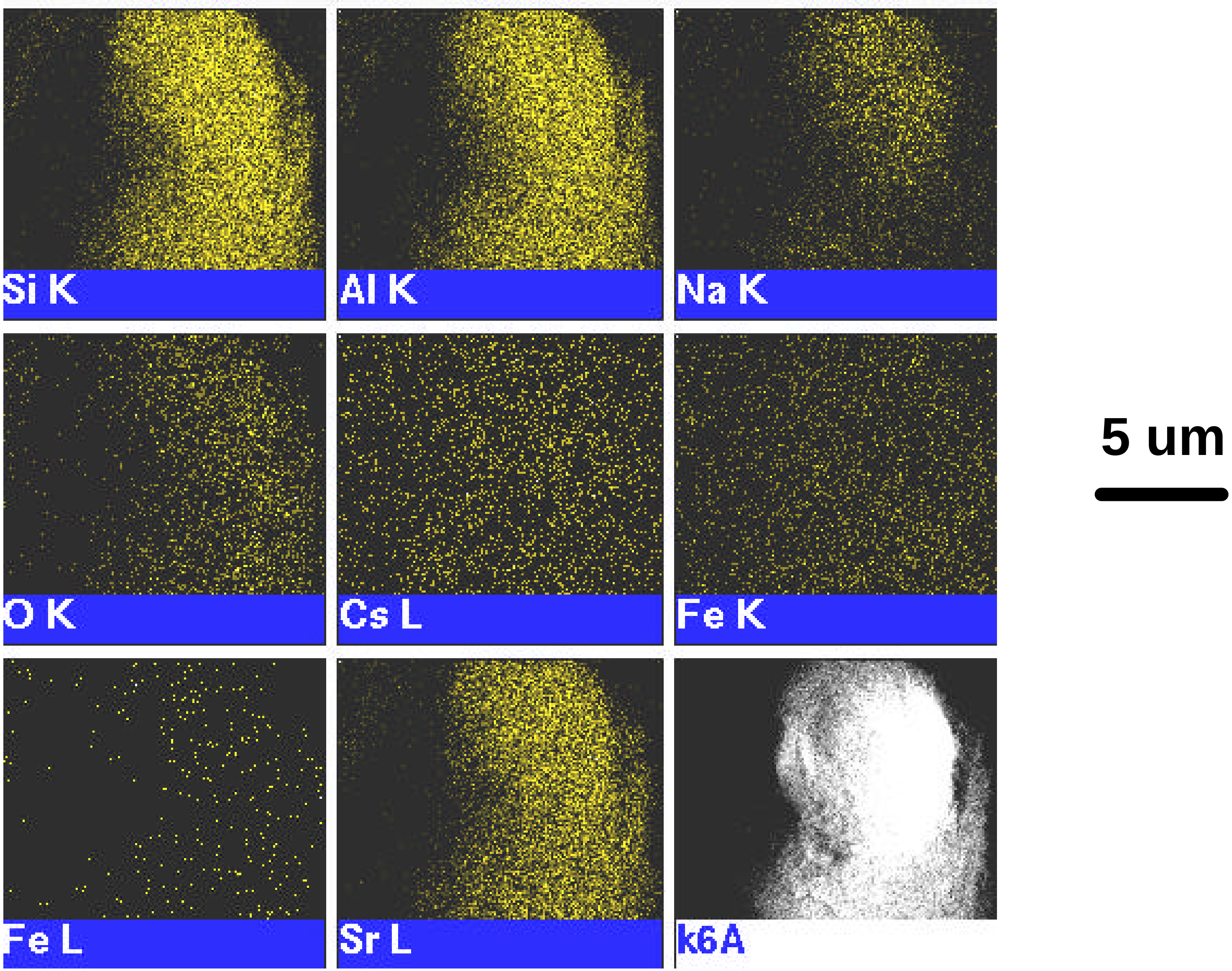
Uptake of Cs and Sr during mineral transformation *KGa-2* (mmol kg^{-1} clay)



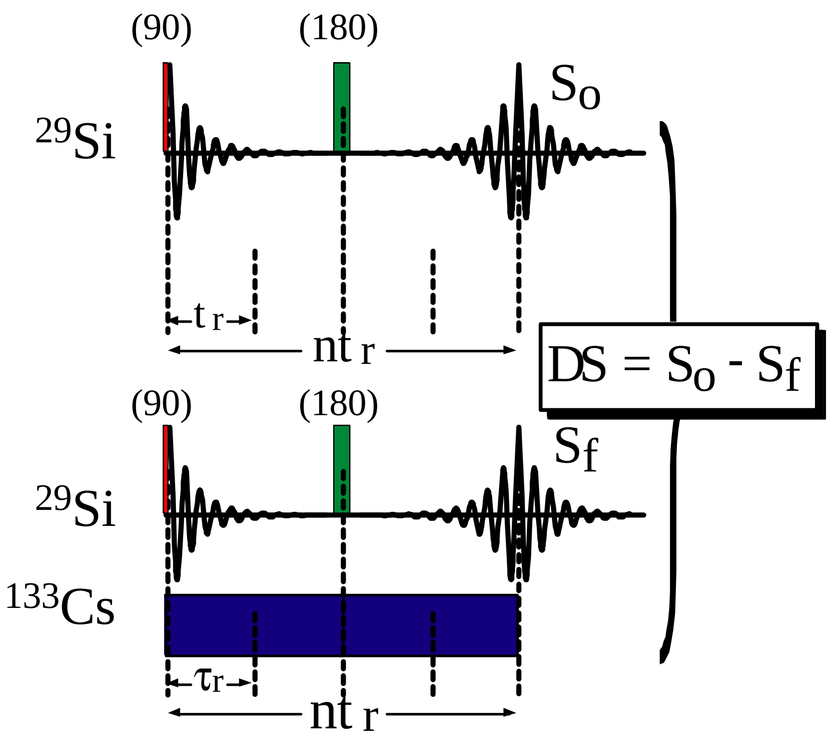
Uptake of Cs and Sr during mineral transformation *SWy-2* (mmol kg^{-1} clay)

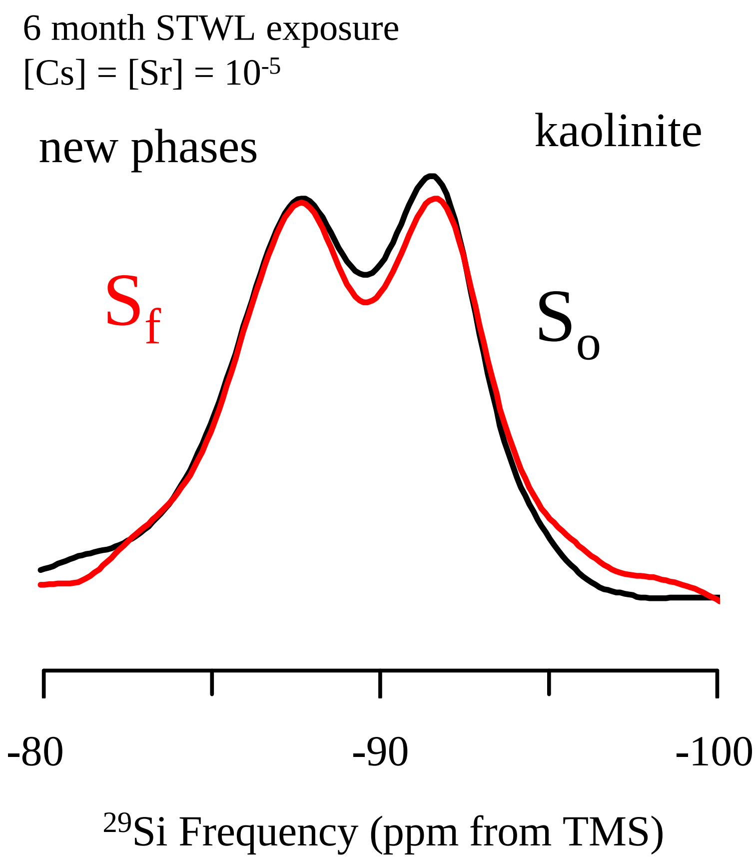


EDX of solid products



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





Non-mobile Cs at room temperature is associated with the kaolinite phase.

Mobility in a zeolite phase may be an issue.

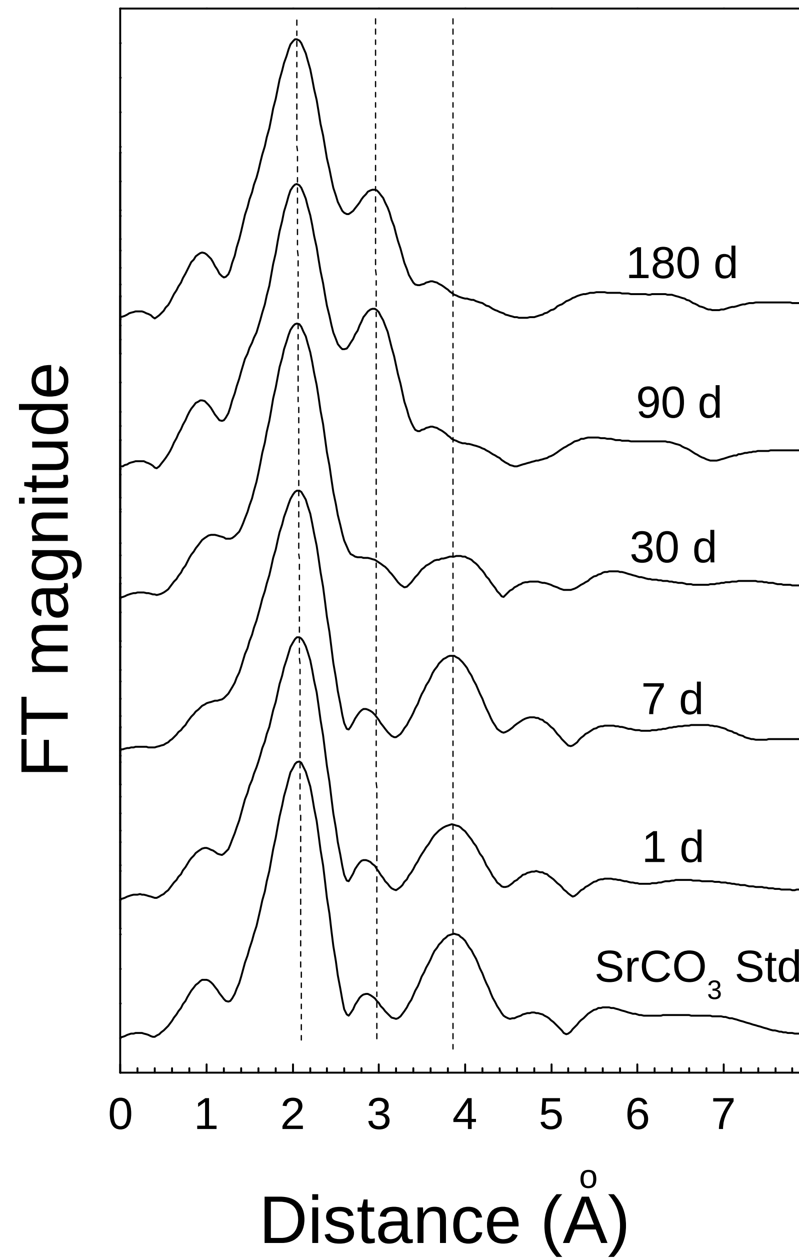
Sr-K edge EXAFS spectra of kaolinite reacted with

Cs/Sr = 10^{-3} M

Early times consistent with $SrCO_3$ solid.

At long times, second shell appears to be Al or Si.

Distances uncorrected for phase shift.



Summary and Implications: Lability of radionuclides is coupled to mineral transformations

- Kaolinite and montmorillonite are transformed to chabazite, sodalite or Linde type A and then cancrinite over 190 d in STWL.
- Mineral transformation rates depend on contaminant concentrations: rates decrease as Cs and Sr concentrations are increased from 10^{-5} to 10^{-3} M.
- Cs and Sr are incorporated into increasingly recalcitrant (less available) forms with increased aging time.

Summary (cont'd)

- Intense weathering, coupled to Ostwald ripening processes increase mineral crystallinity and decreasing mobility of these radionuclide contaminants in the near field STWL environment.
- Radionuclide fate after removal of STWL source is not clear.

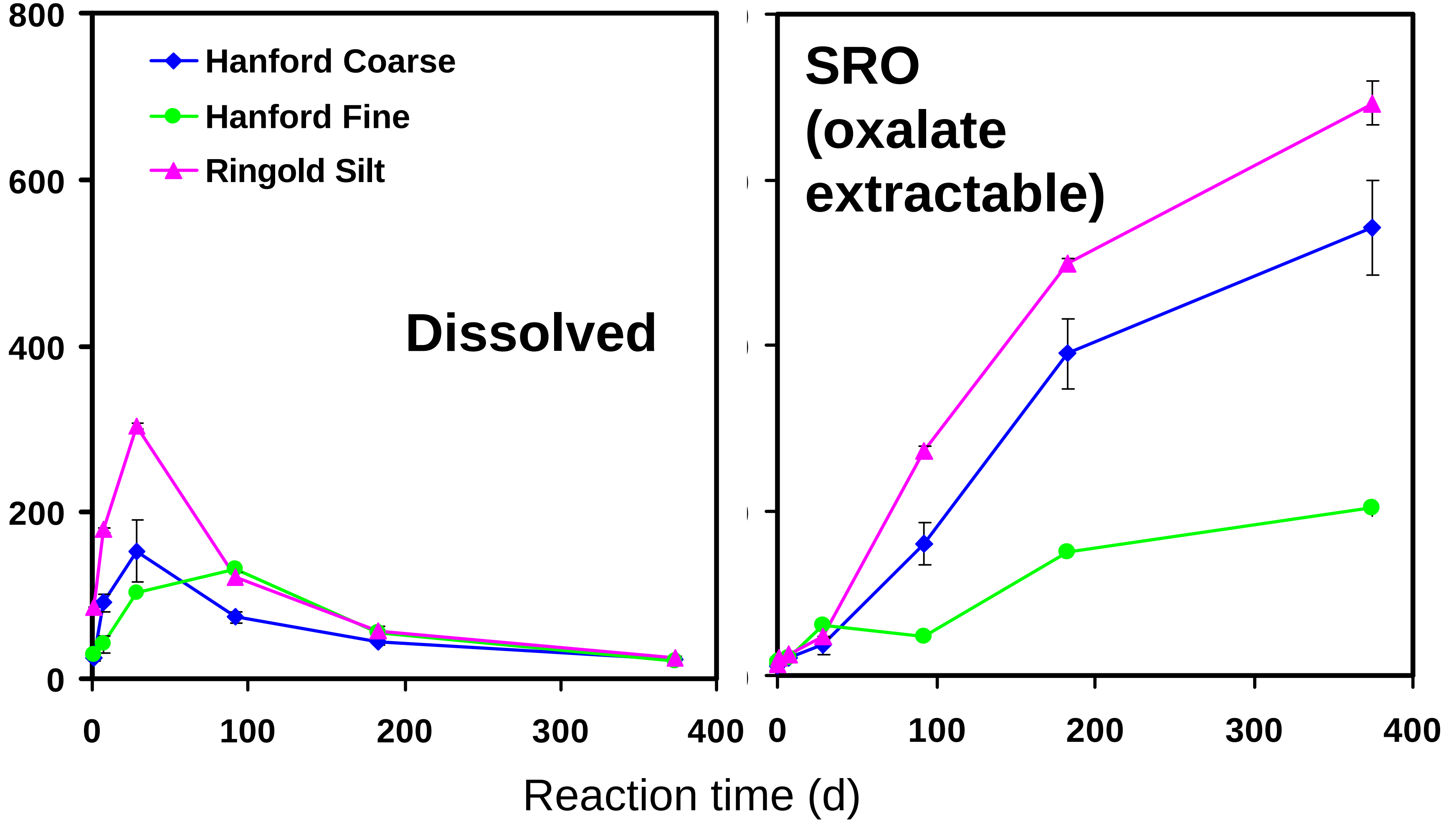
Current and FY02 work

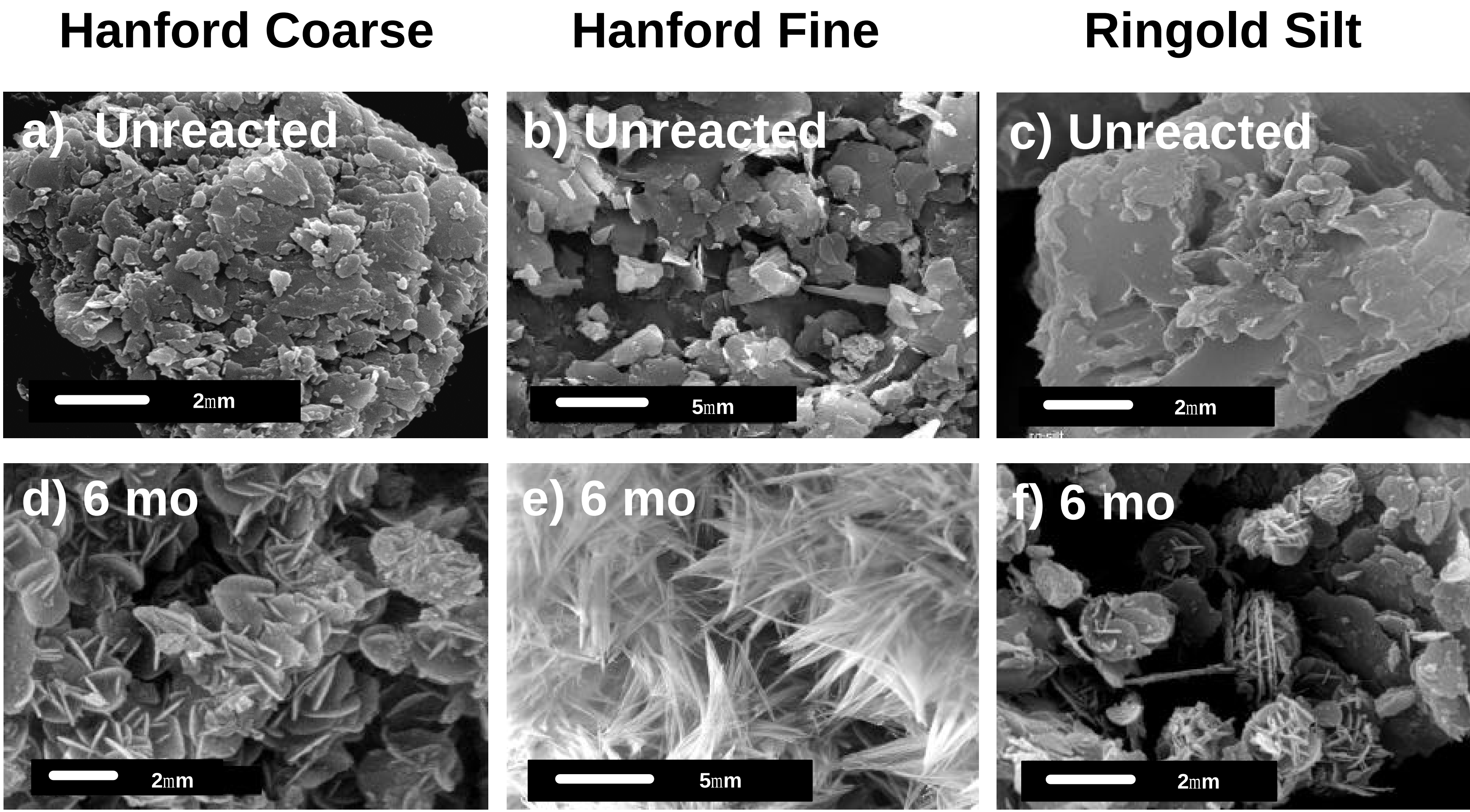
- Extending experiments to longer term (1yr and 2 yr).
- Desorption kinetics of Cs and Sr coupled to dissolution of metastable solid-phase products at neutral pH and moderate ionic strength.
- Sr K-edge EXAFS and HRXRD analysis of the specimen clay time series’, establish the siting of Sr in the secondary phases.
- Presentation of results at national meetings (ACS, AGU, SSSA) and preparation of manuscripts for journal publication.

Sediments: Dissolution and precipitation of Si

(mmol kg^{-1} sediment)

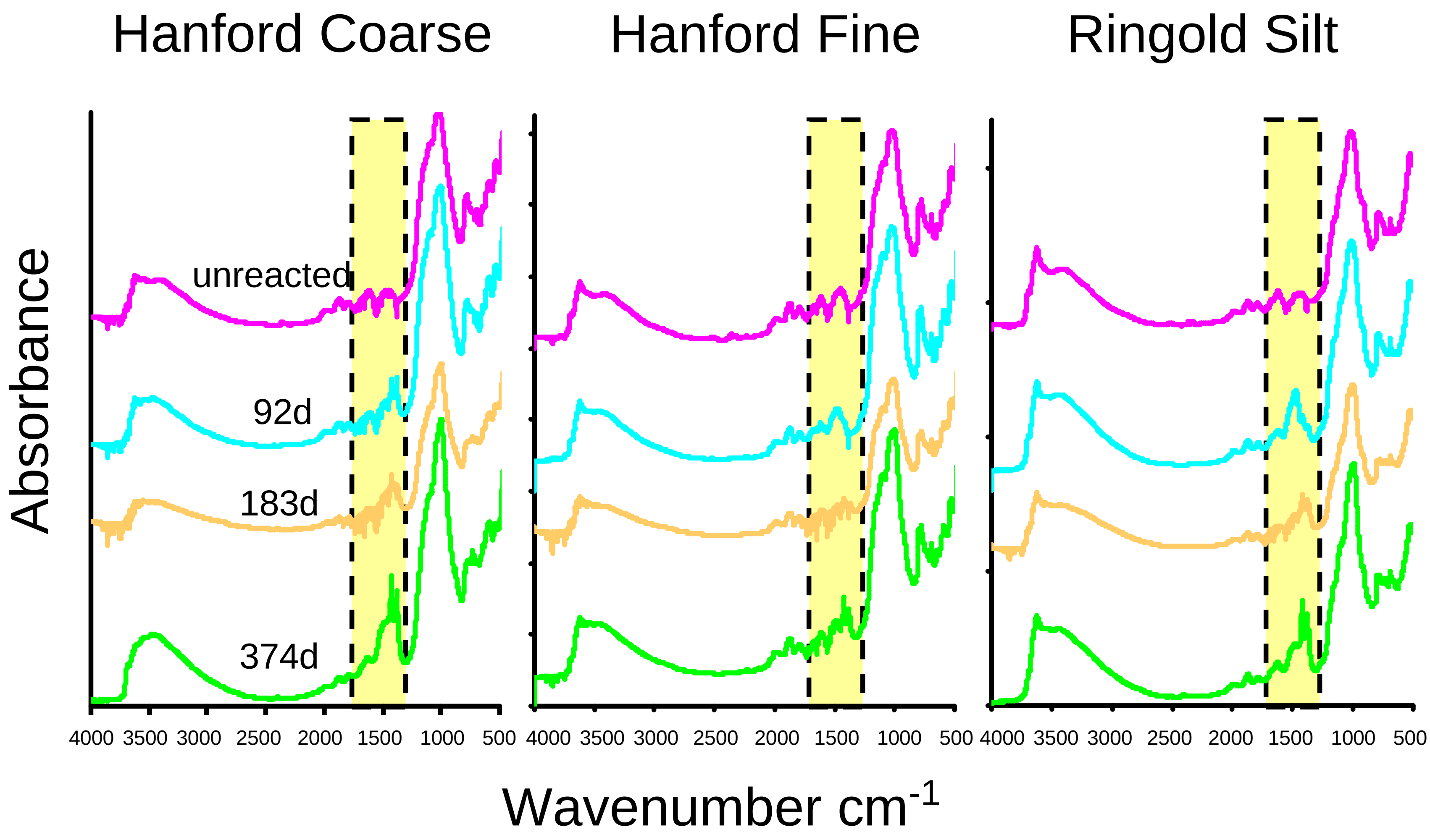
Initial Cs & Sr = 10^{-5} M



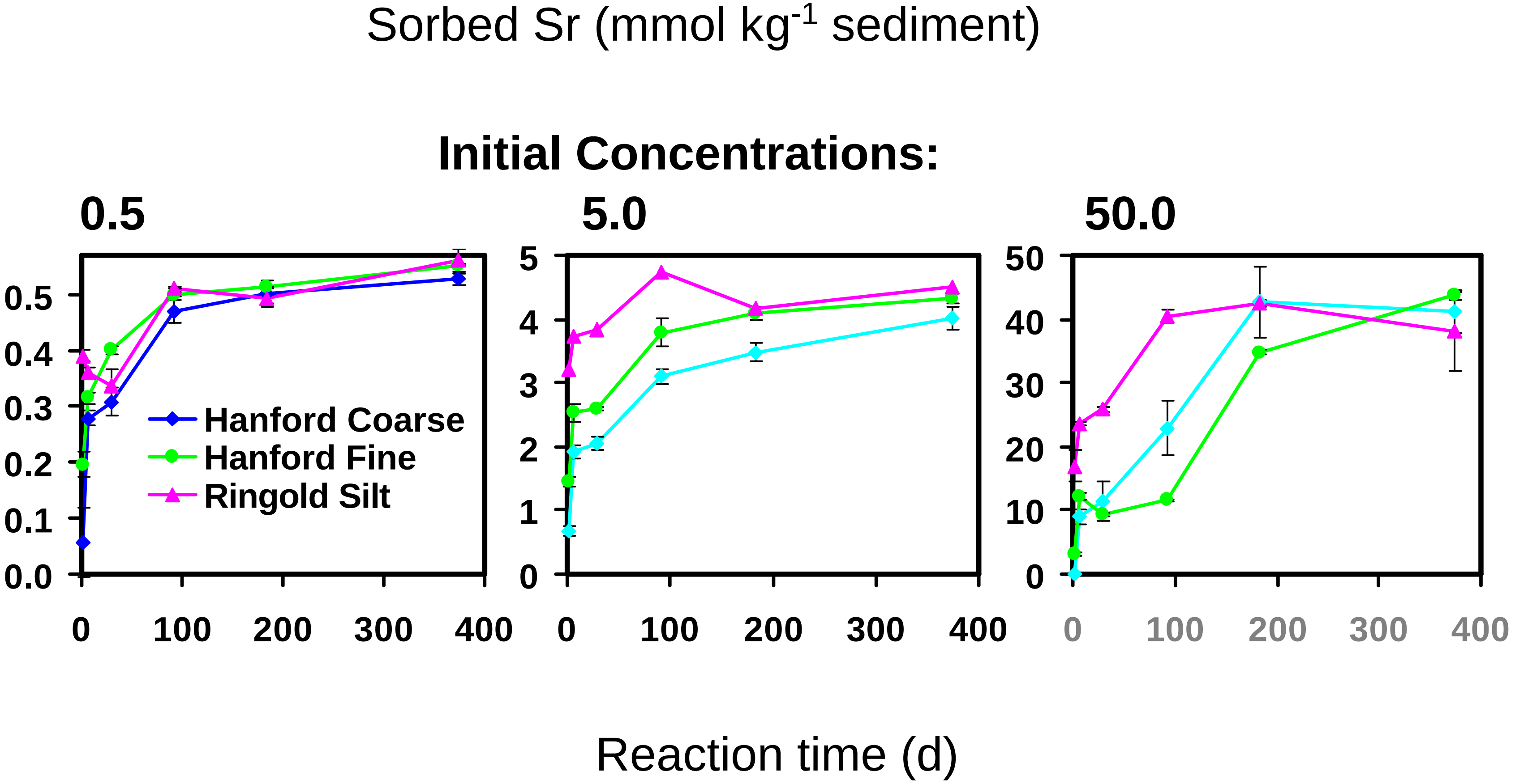


SEM images of (a-c) unreacted sediments (d-f) 6 mo weathering products. Initial Cs & Sr = 10^{-5} M.

DRIFT Spectra



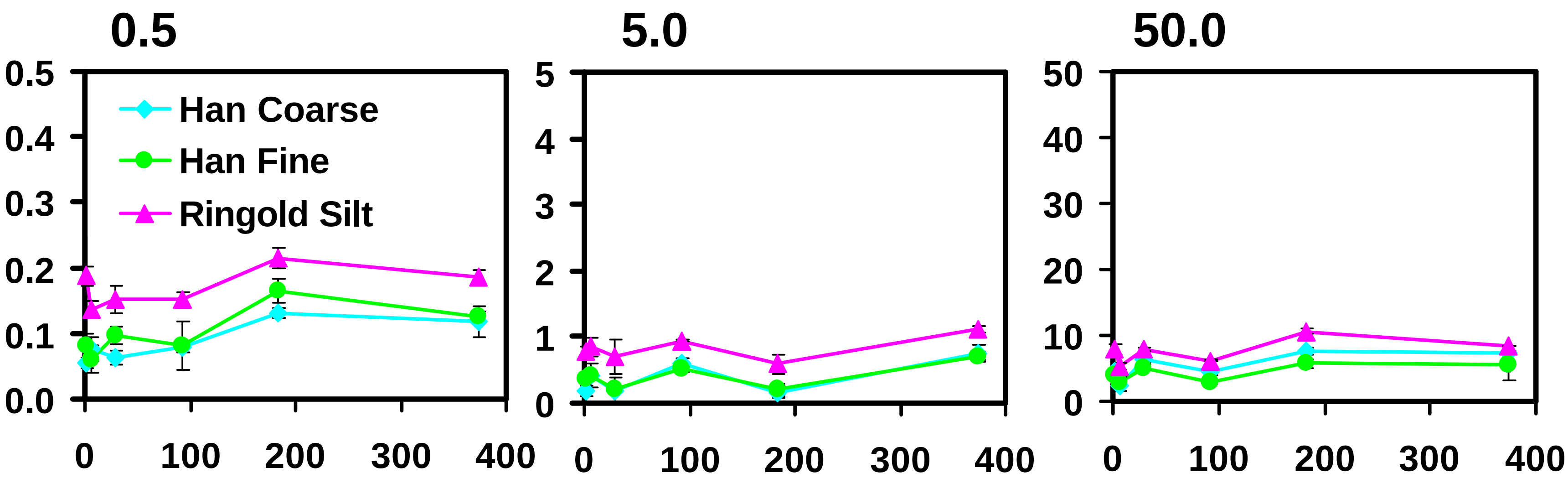
Sediments: Sr uptake kinetics



Sediments: Cs uptake kinetics

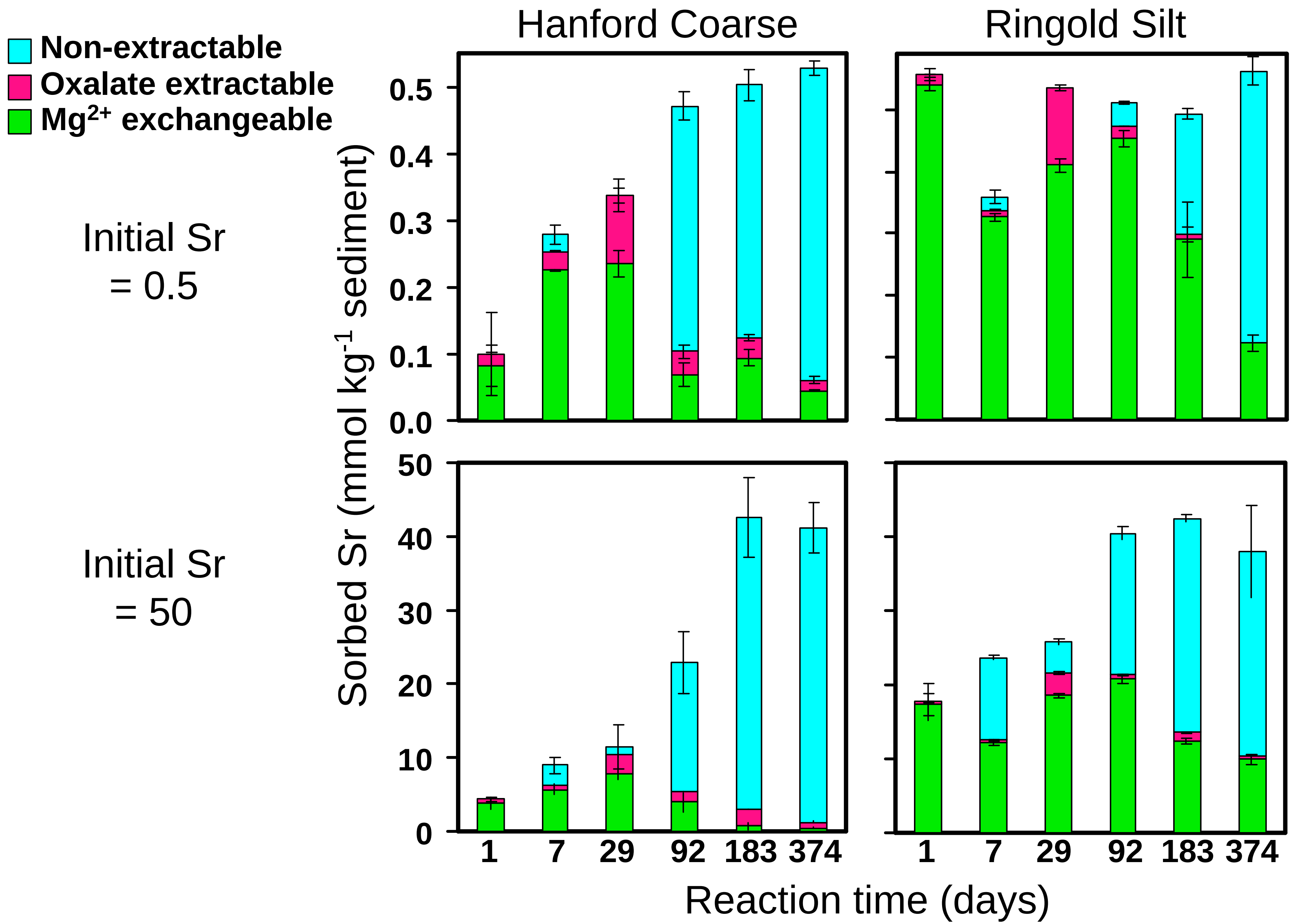
Sorbed Cs (mmol kg^{-1} sediment)

Initial Concentrations:

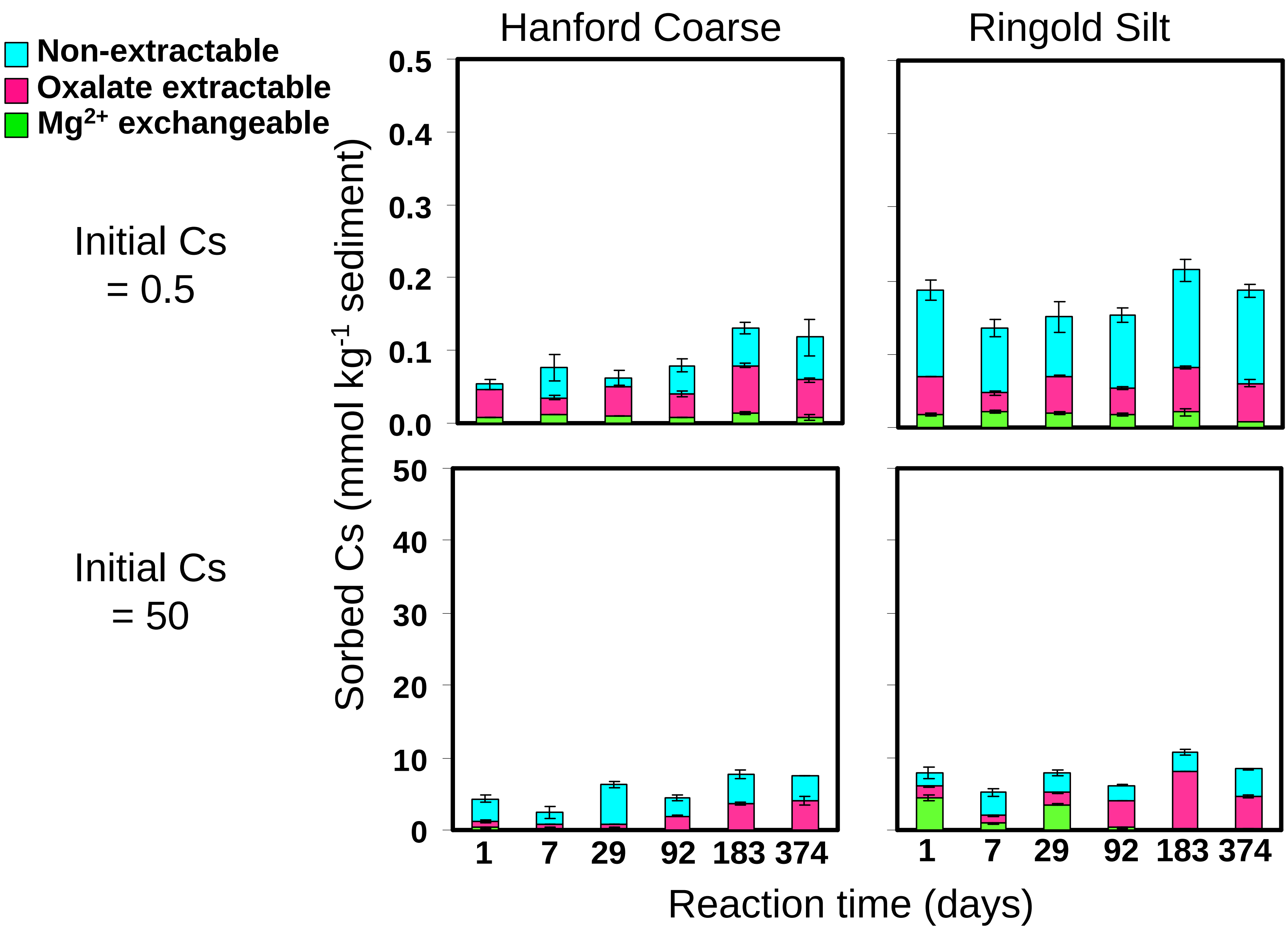


Reaction time (days)

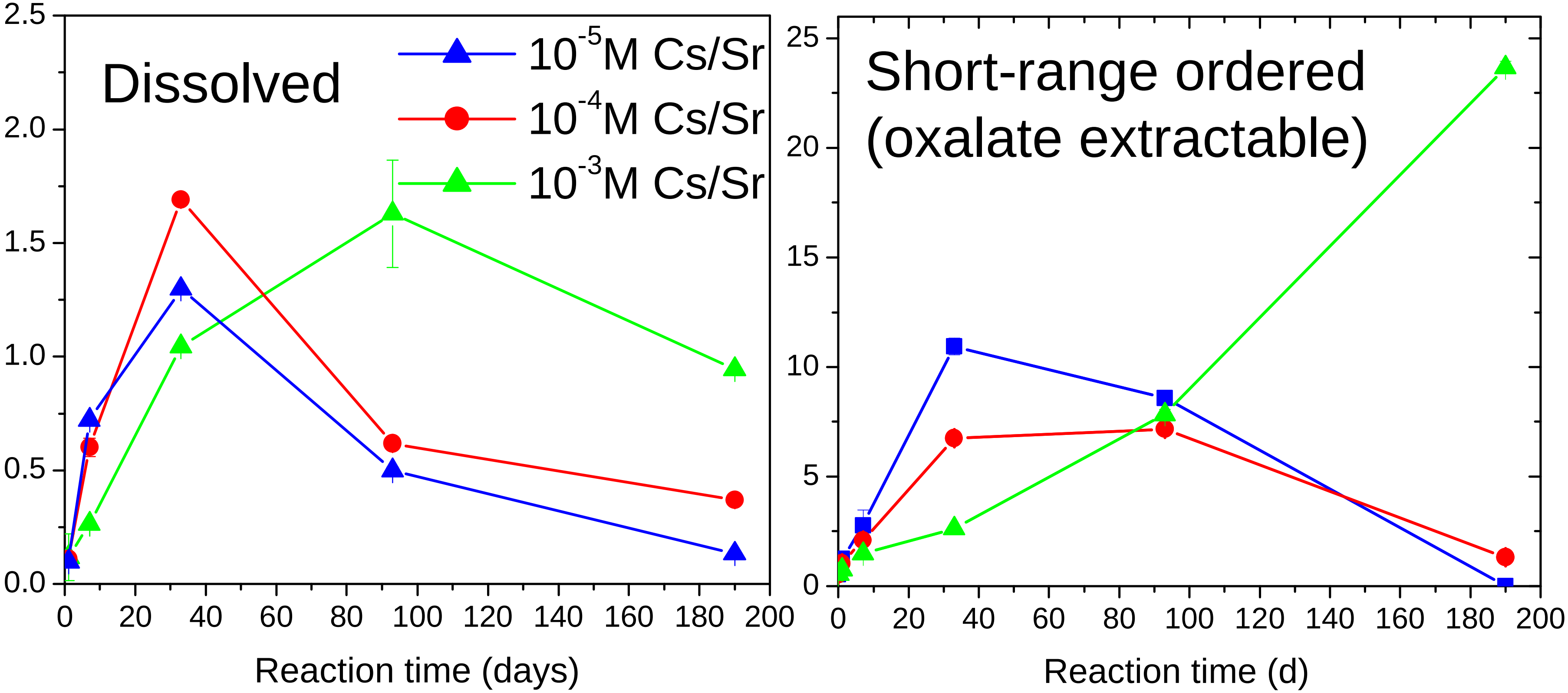
Sediments: Desorption of Sr



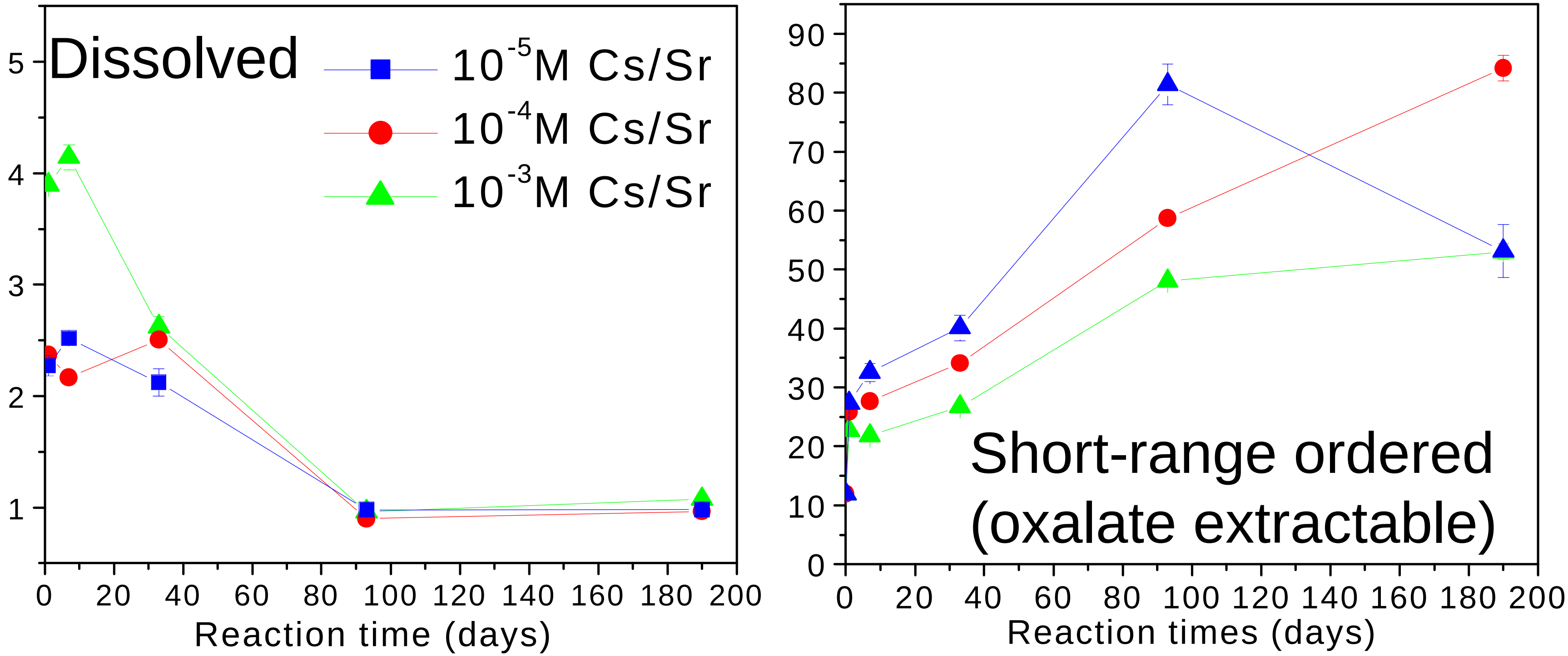
Sediments: Desorption of Cs



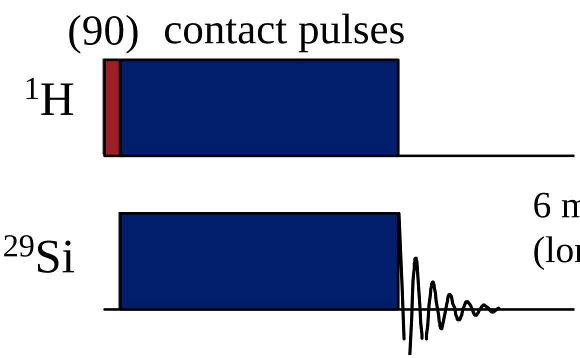
Kaolinite: Dissolution and precipitation of Fe ($mmol\ kg^{-1}$ clay)

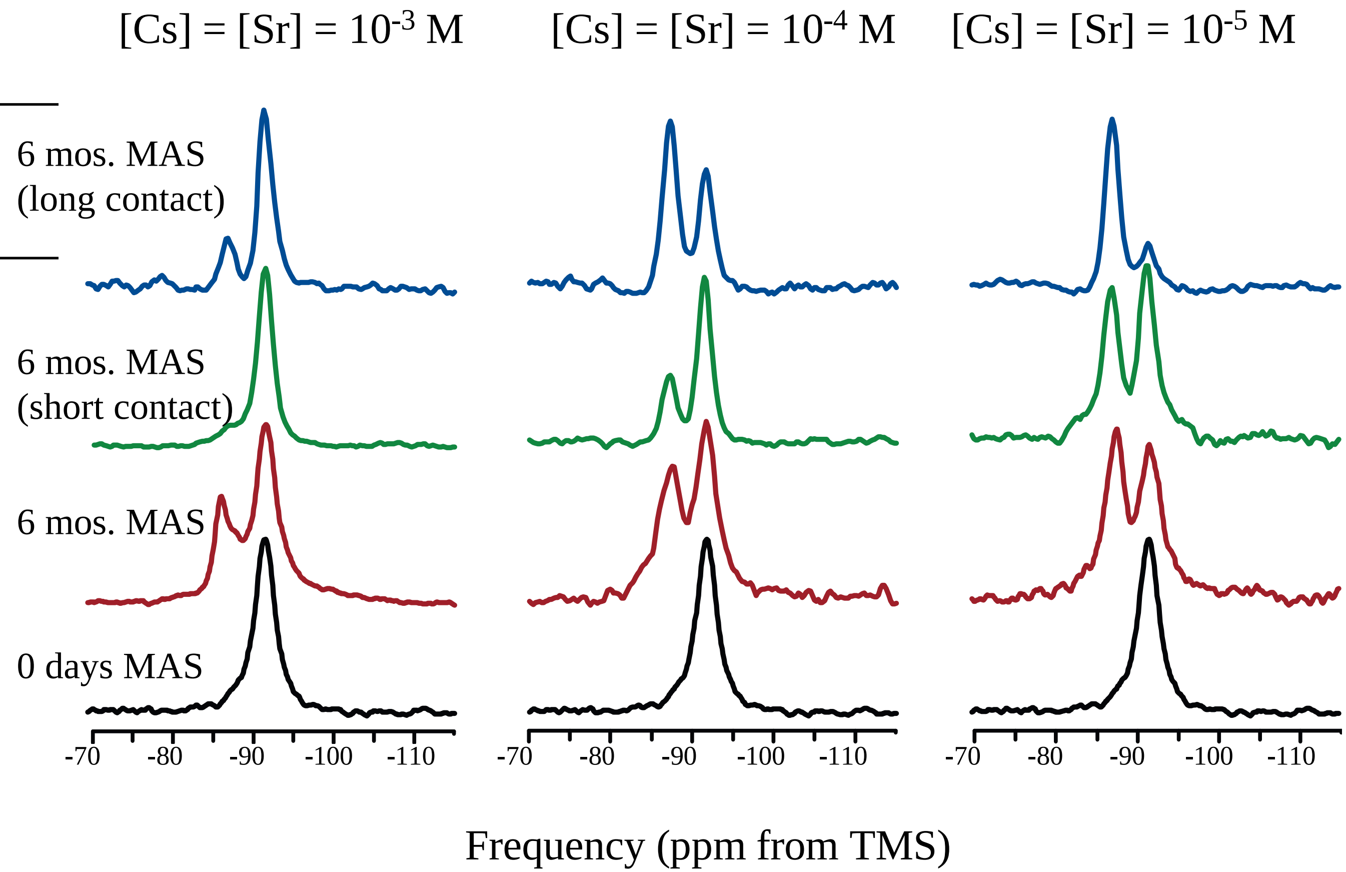


Montmorillonite: Dissolution and precipitation of Fe ($mmol\ kg^{-1}$ clay)



$^{1}H/^{29}Si$ CPMAS NMR Studies of Kaolinite Transformation

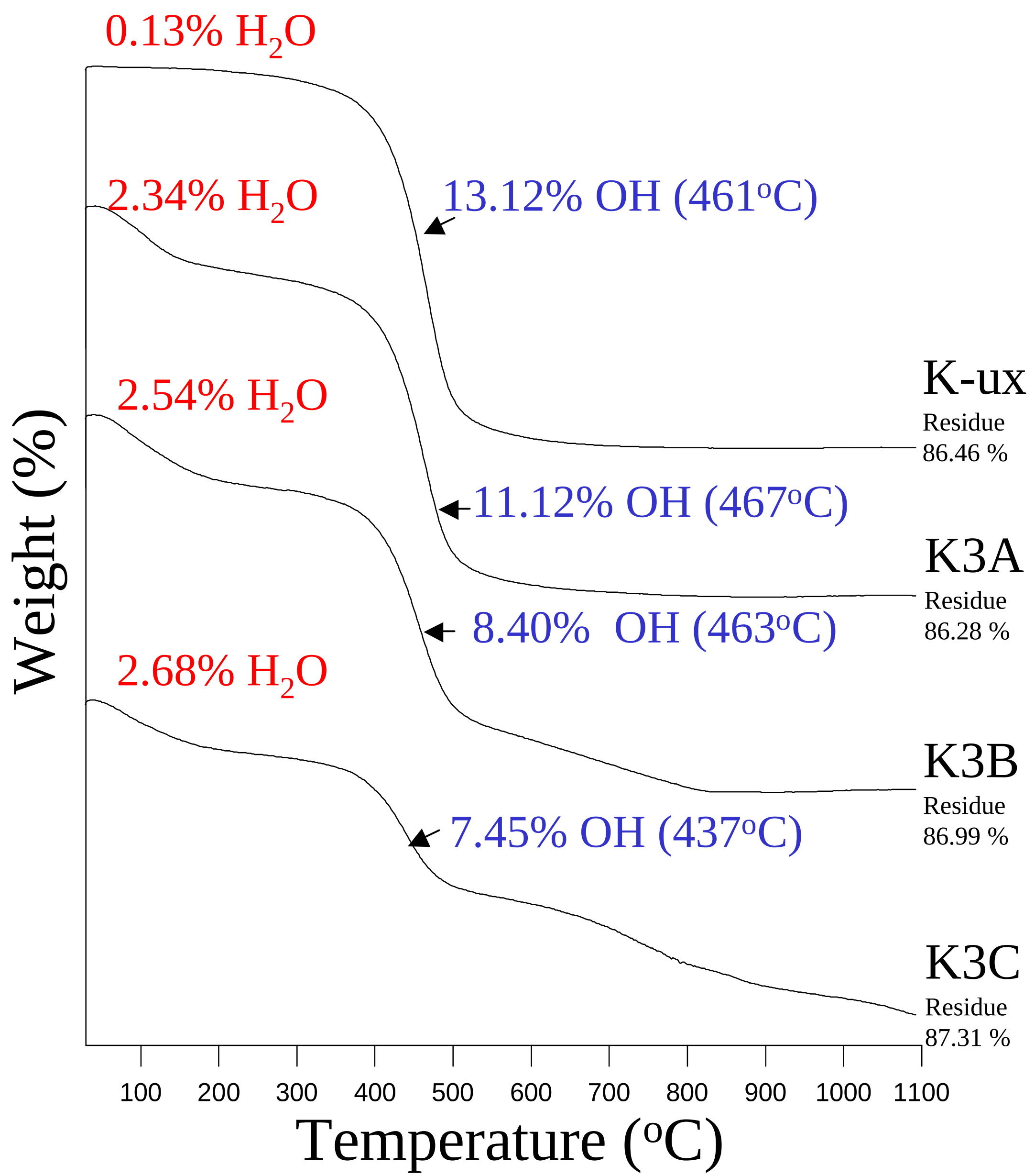




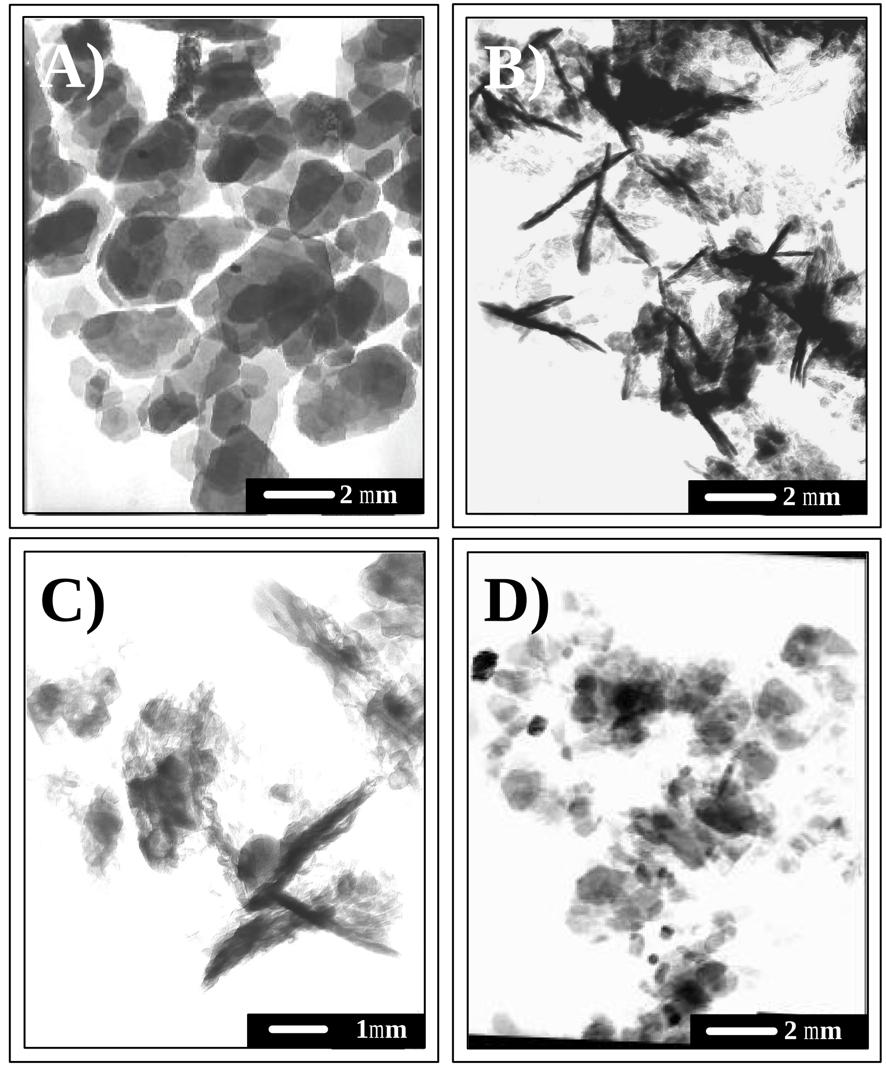
short contact time
(1-4 ms)
selects Si-OH

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

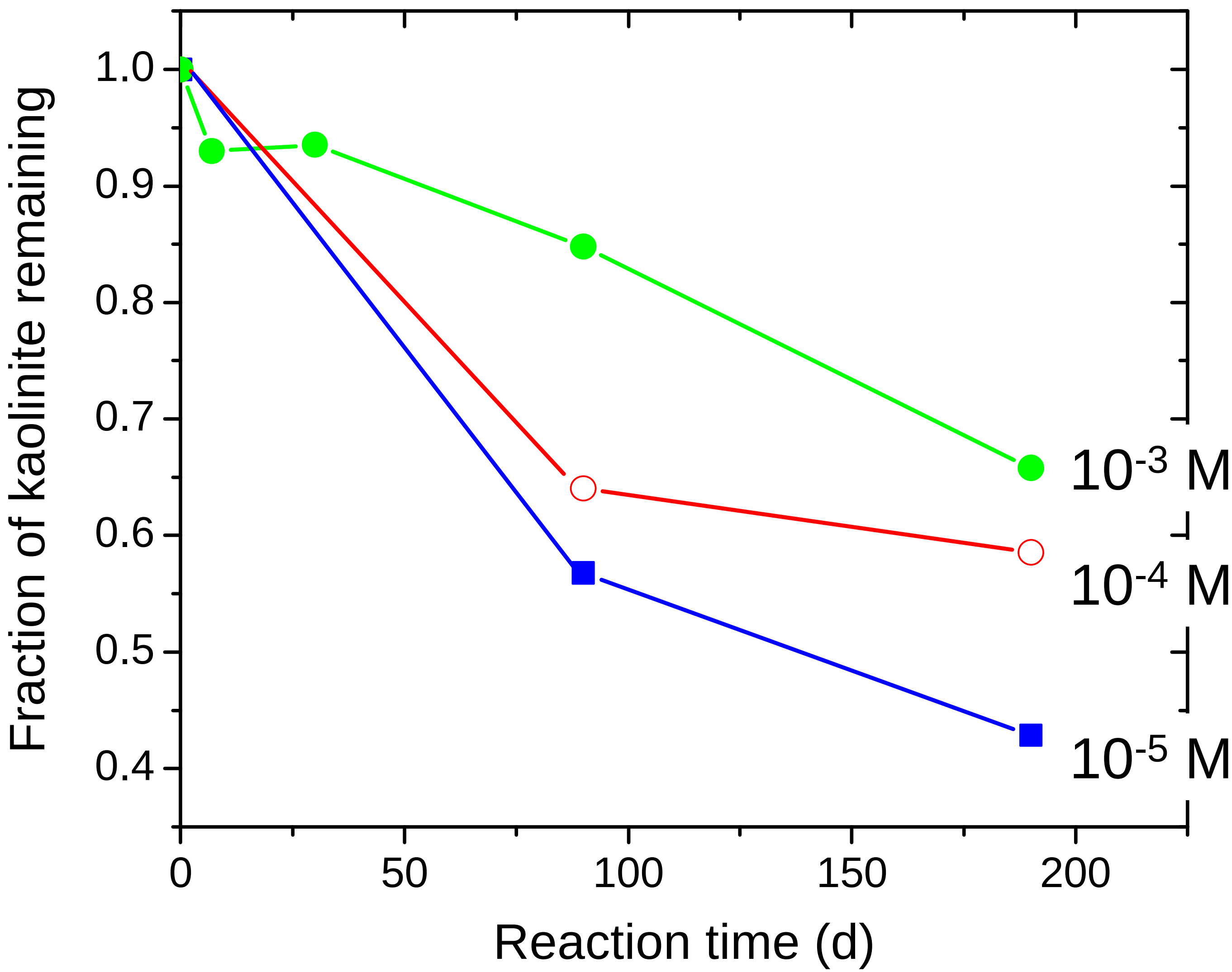
TGA of Kaolinite at 93 d



TEM images of
(A) unreacted kaolinite, and reacted kaolinite after 190 d with Cs/Sr at:
(B) 10^{-5} M,
(C) 10^{-4} M, and
(D) 10^{-3} M.



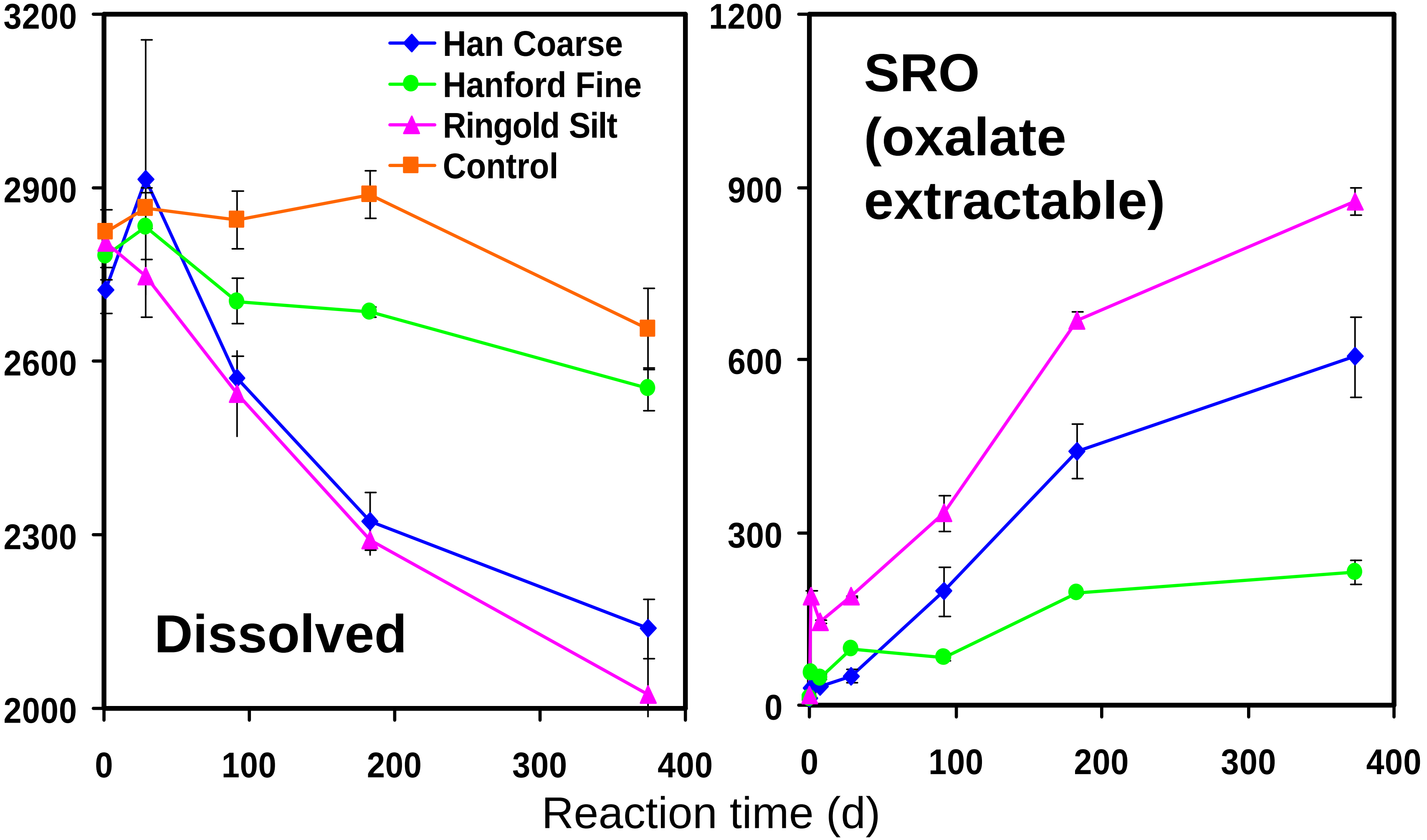
Mass loss of kaolinite as measured by TGA



Sediments: Dissolution and precipitation of Al

(mmol kg^{-1} sediment)

Initial Cs & Sr = 10^{-5} M



^{29}Si MAS NMR Studies of Kaolinite Transformation