Reactivity of Primary Soil Minerals and Secondary Precipitates Beneath Leaking Hanford Waste Tanks

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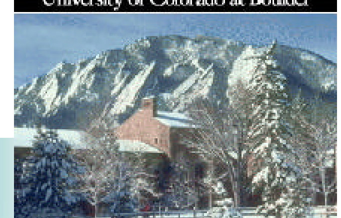
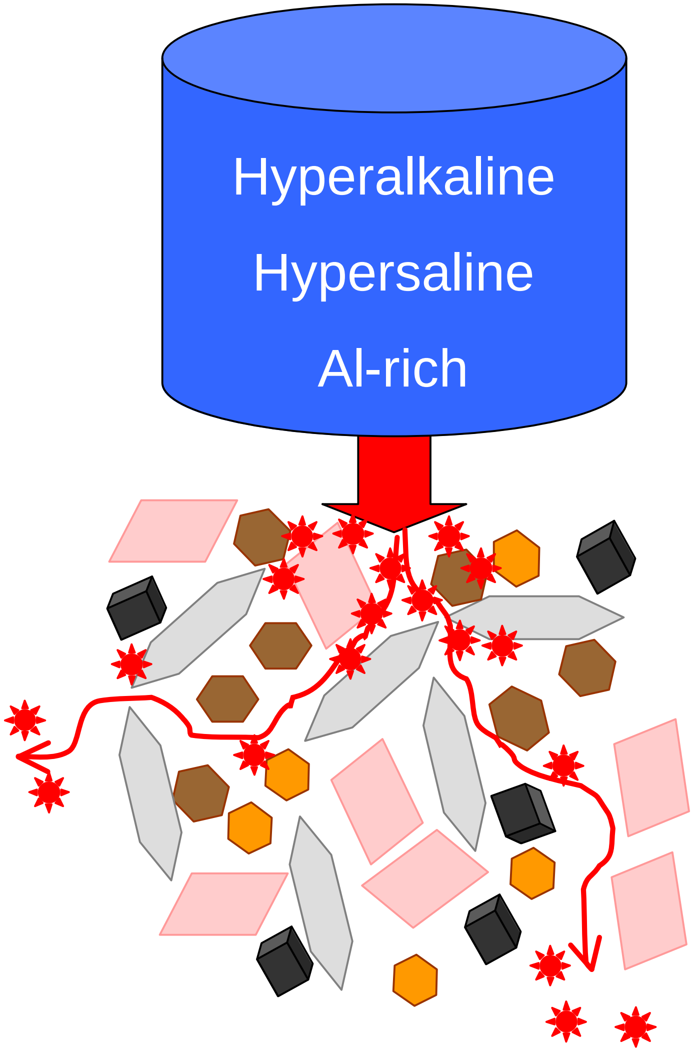




How have leaking tank fluids reacted with sediments?

Altered flowpaths?

Created colloids?

Radionuclide sorption?

Radionuclide coprecipitation?

Future distribution of contaminants?

Effects of remediation?

Approach

- Focus on reactions involving bulk composition of tank fluids (not only trace contaminants)
  - determine changes in mineral assemblage
  - quantify effect on fluid flow properties
  - quantify effect on reactive surfaces for sorption

- Develop quantitative mechanistic “model”
  - use kinetic data from monomineralic experiments
  - test with reactive/transport model on complex experimental data
  - finalize on unsaturated flow column experiments using tank fluid simulants and Hanford sediments

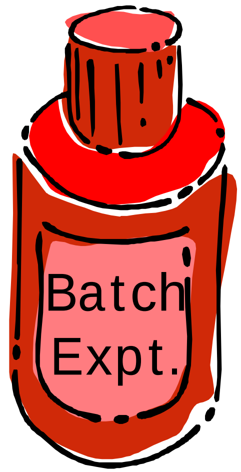
Results

- Kinetic data on mineral dissolution and growth
  - Quartz dissolution (Bickmore and Nagy, GCA, in prep.)
  - Cancrinite precipitation (Bickmore et al. (2001) ES&T)
  - Biotite dissolution (in progress)
  - Magnetite dissolution (in progress)

- Phyllosilicate surface area determination by AFM

  (Bickmore et al., Amer. Min., in review)

Quartz Dissolution Rates



Quartz: (Aldrich) pretreated
(magnetic separation/sulfuric acid wash)

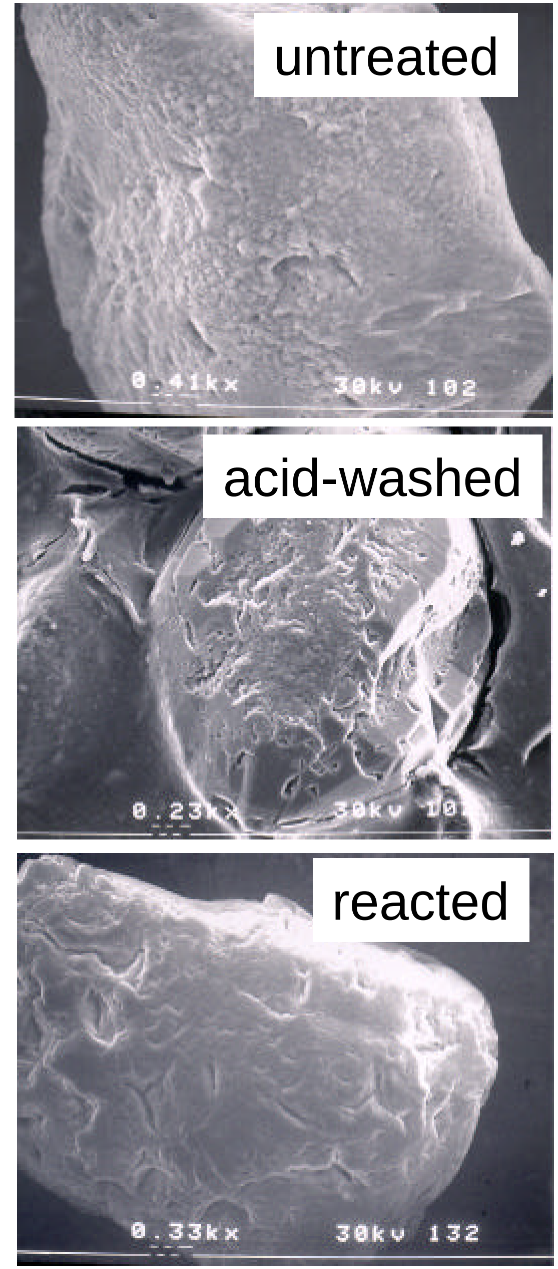
Solutions: ($NaNO_3$, $Al(NO_3)_3$, NaOH, CO_2-purged)

Experiments: 2 g quartz, 65 g solution
Time series: 8 bottles/experiment
59, 75, and 89 °C

Analyses: Al & Si (UV-Vis; ICP-AES);
pH (solid-state electrode)

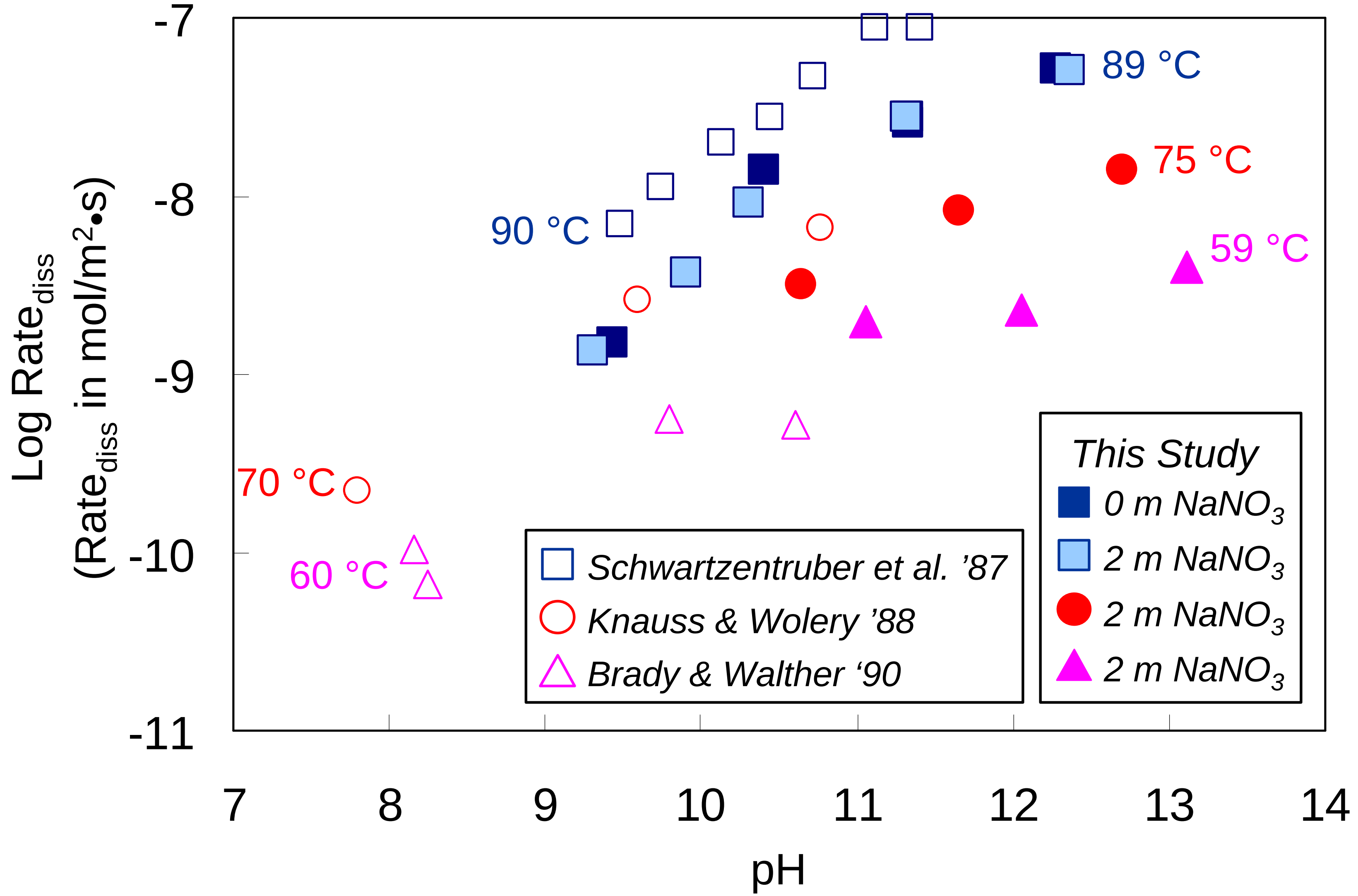
Speciation: Pitzer model (no polysilicate species)

Rates: Initial rates - linear with time

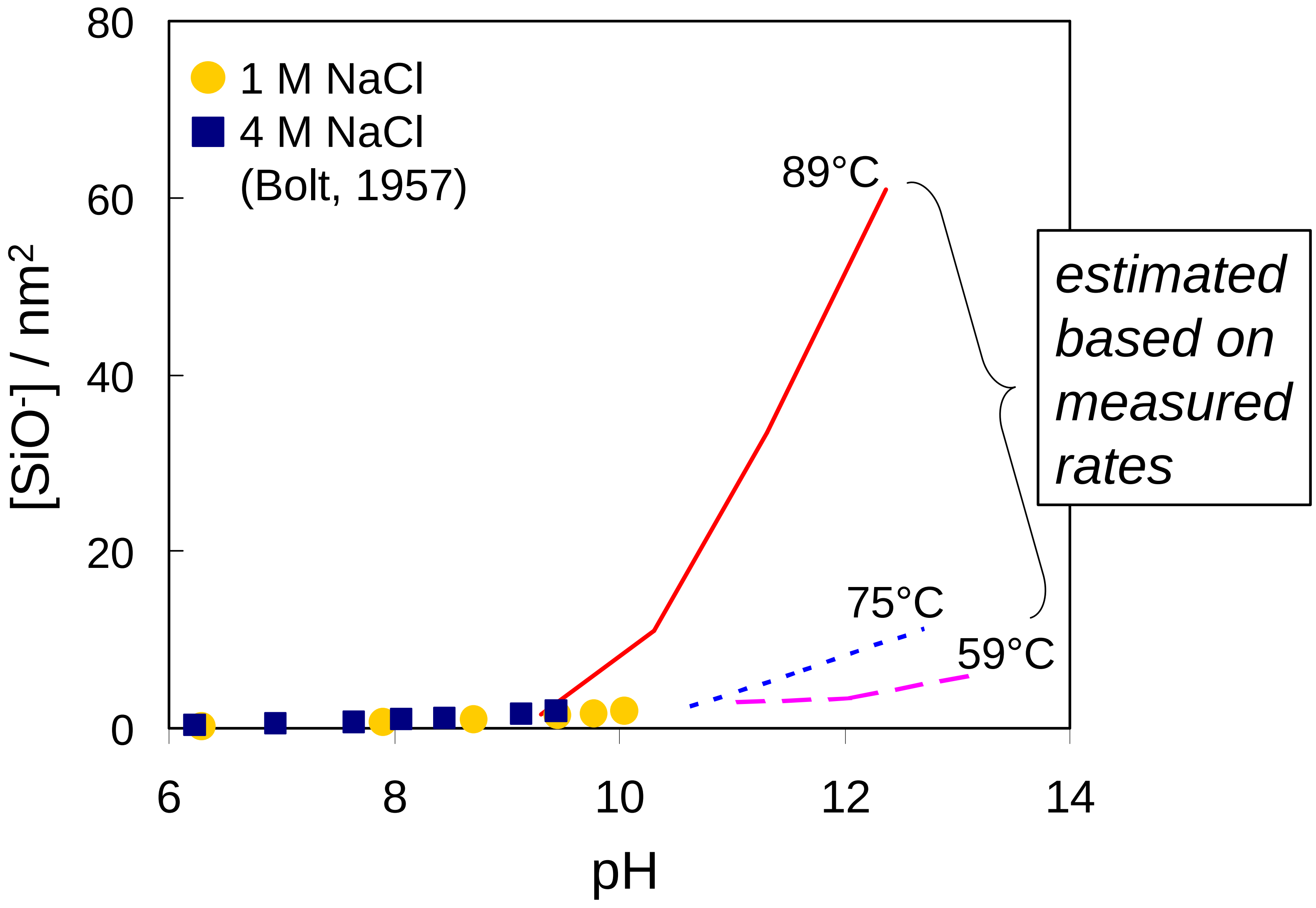


Quartz dissolution in the presence of $Al(OH)_4^-$(aq) B. R. Bickmore and K. L. Nagy, ms. in preparation

pH Dependence of Initial Dissolution Rates of Quartz



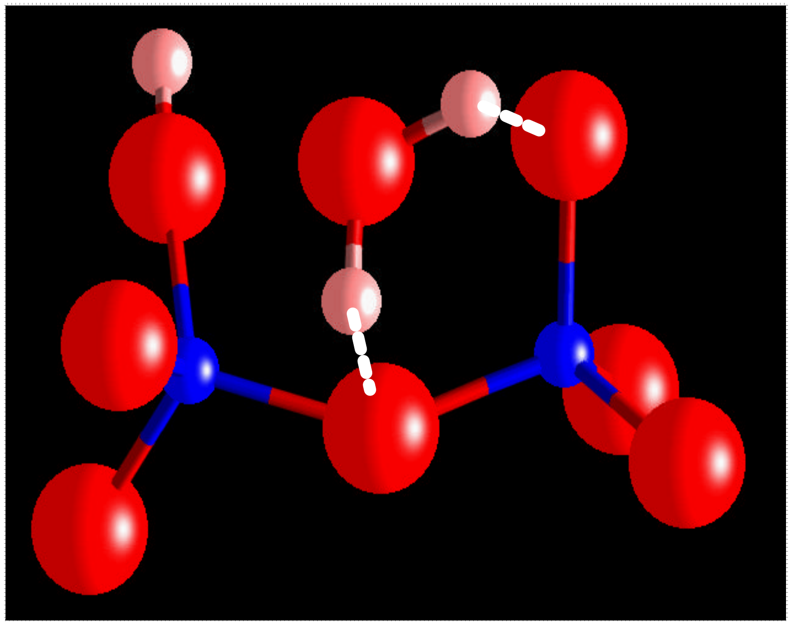
Surface Charge Modeling



Dependence of Quartz Dissolution Rate on pH

low pH, low temperature

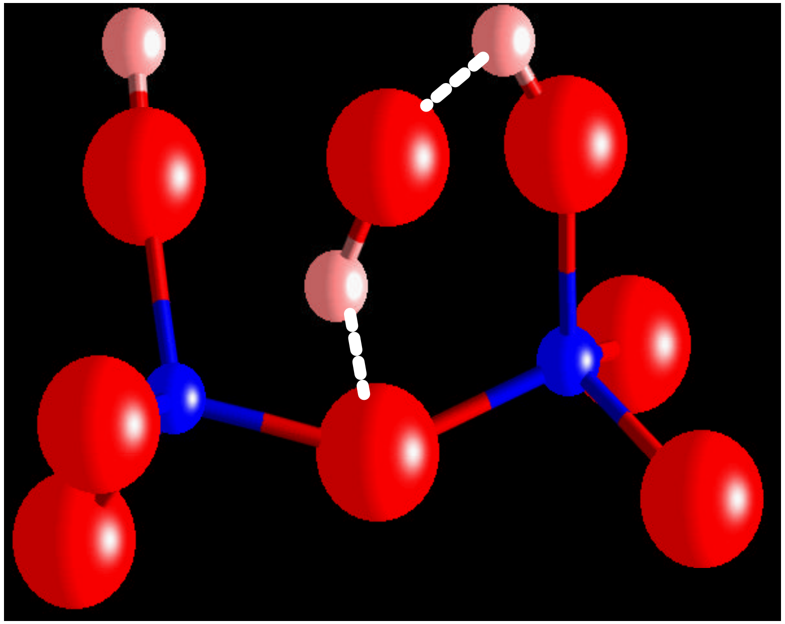
Mechanism #1



Dove (1994) *Am. J. Sci.*

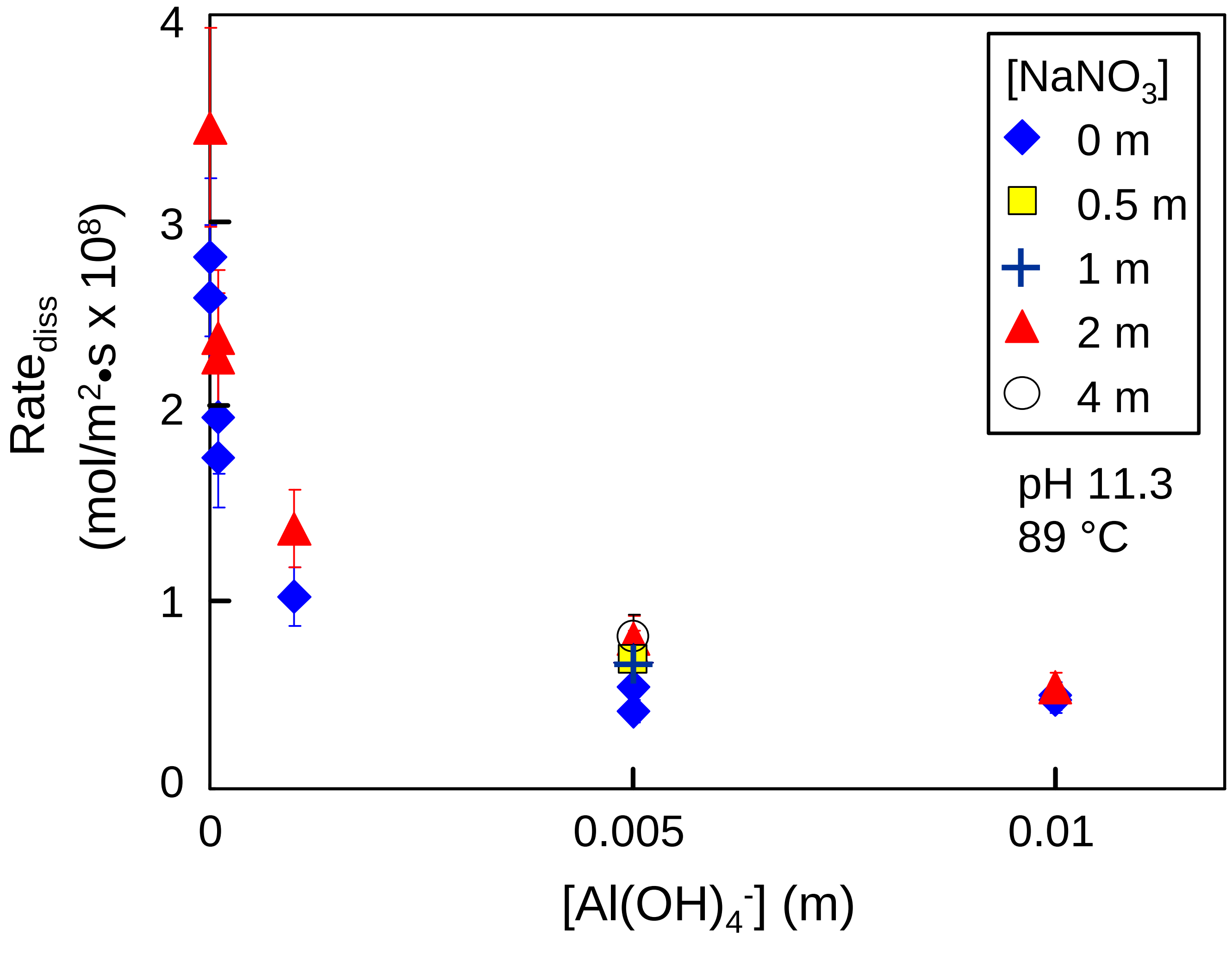
high pH, higher temperature

Mechanism #2

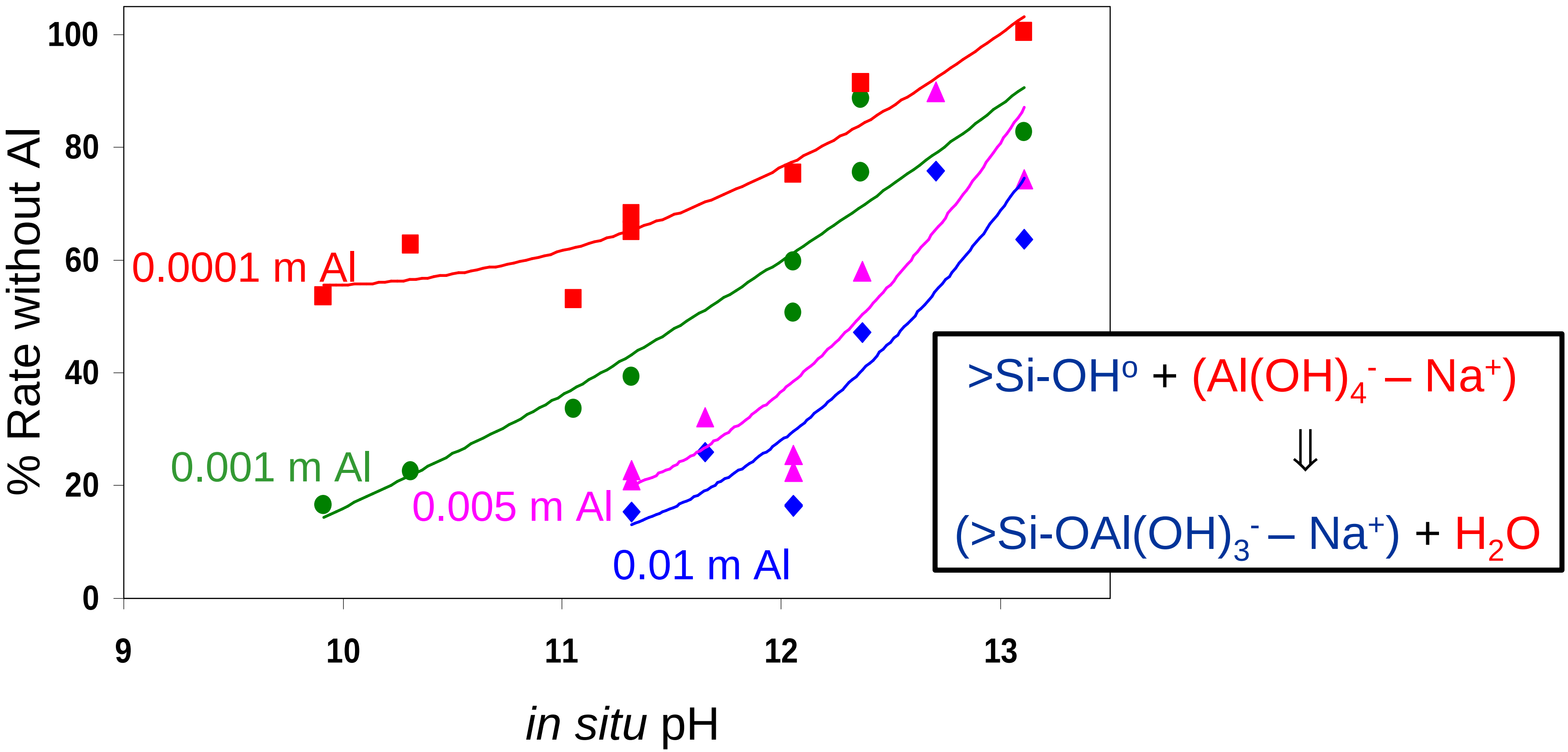


Xiao and Lasaga (1996) *GCA*

Dependence of Quartz Dissolution Rate on [Al]

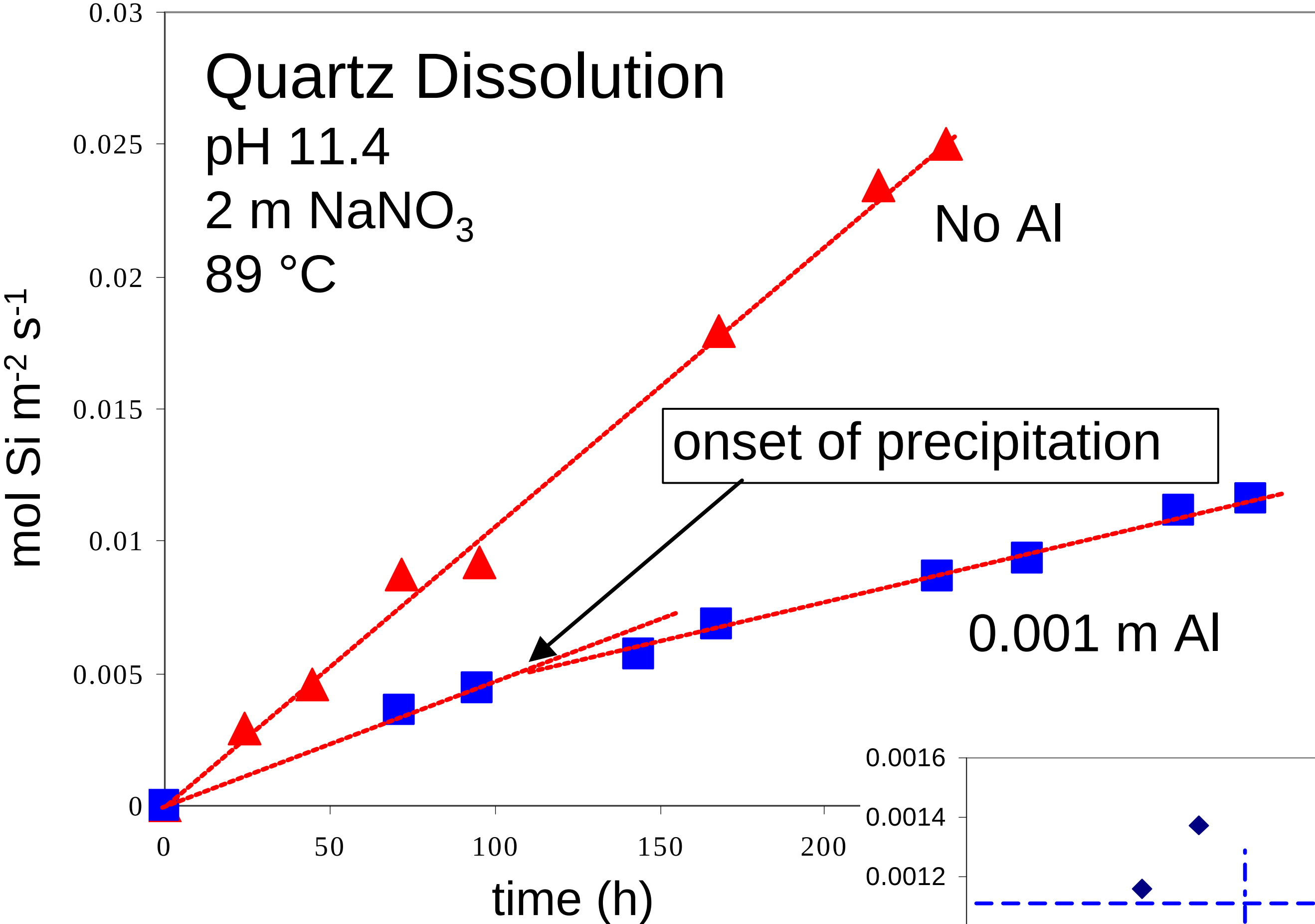


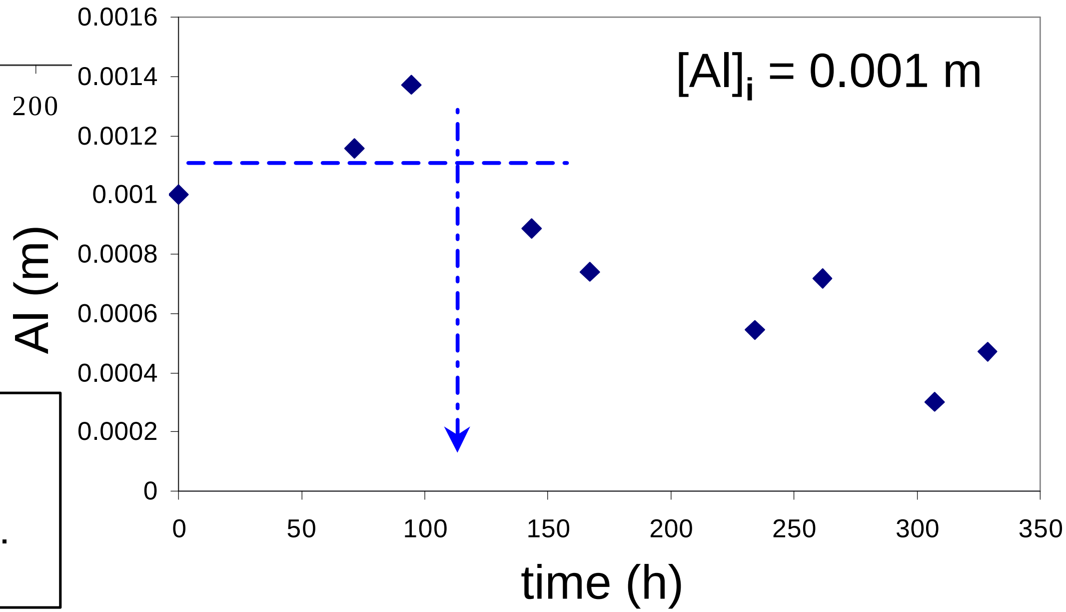
Al Reduces Quartz Dissolution Rate



model consistent with

- Slower rate at lower pH and higher $[Al(OH)_4^-]$
- Aluminosilicate species observed at high pH
  (enhanced by ion-pairing; McCormick et al., J. Phys. Chem., 1989)
- Precipitated aluminosilicate gels at pH 9 with Al:Na = 1:1
  (Milliken, Discuss. Faraday Soc., 1950)



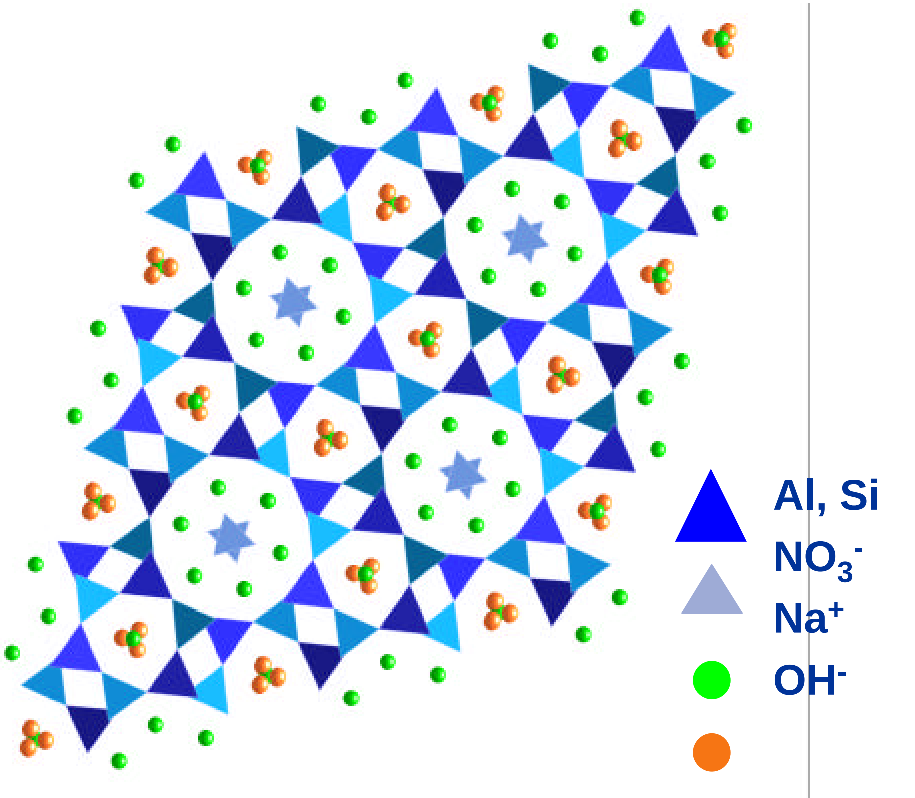


Cancrinite precipitates as quartz dissolves in Al-bearing Na-nitrate solutions

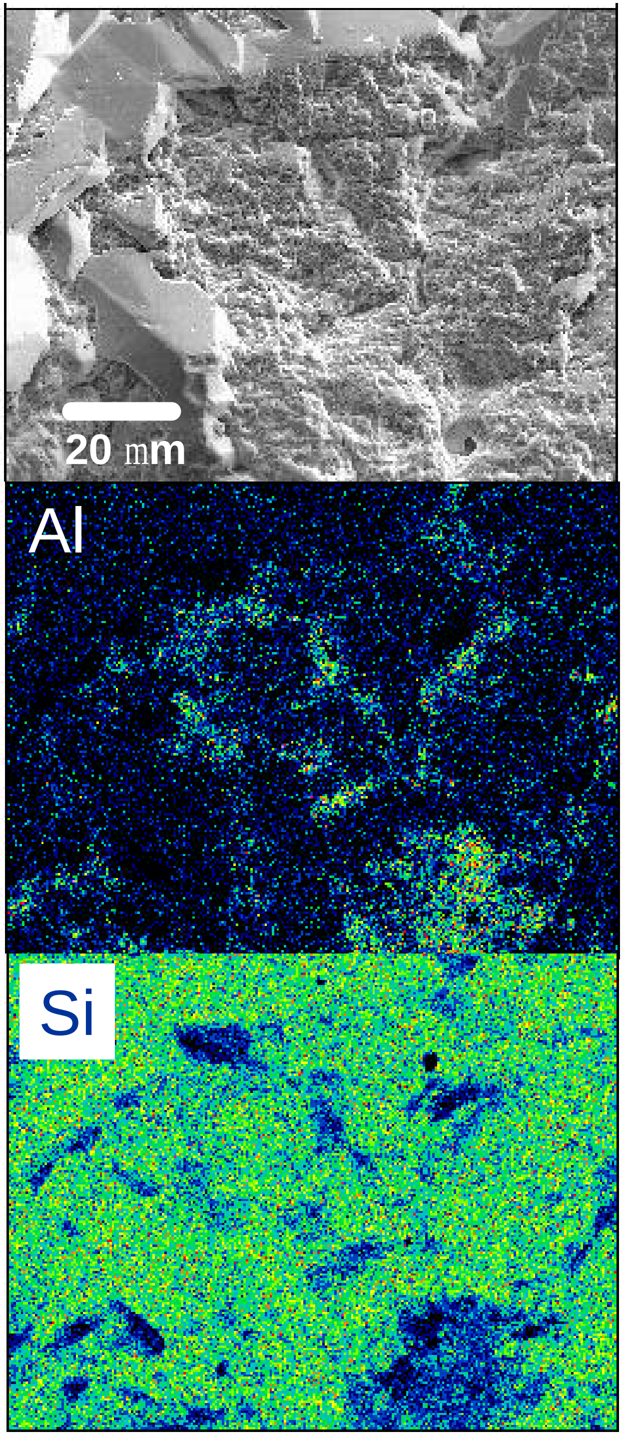
Nitrate-canrinite precipitation on quartz sand in simulated Hanford tank solutions
B. R. Bickmore, K. L. Nagy, J. S. Young, and J. W. Drexler, 2001, ES&T

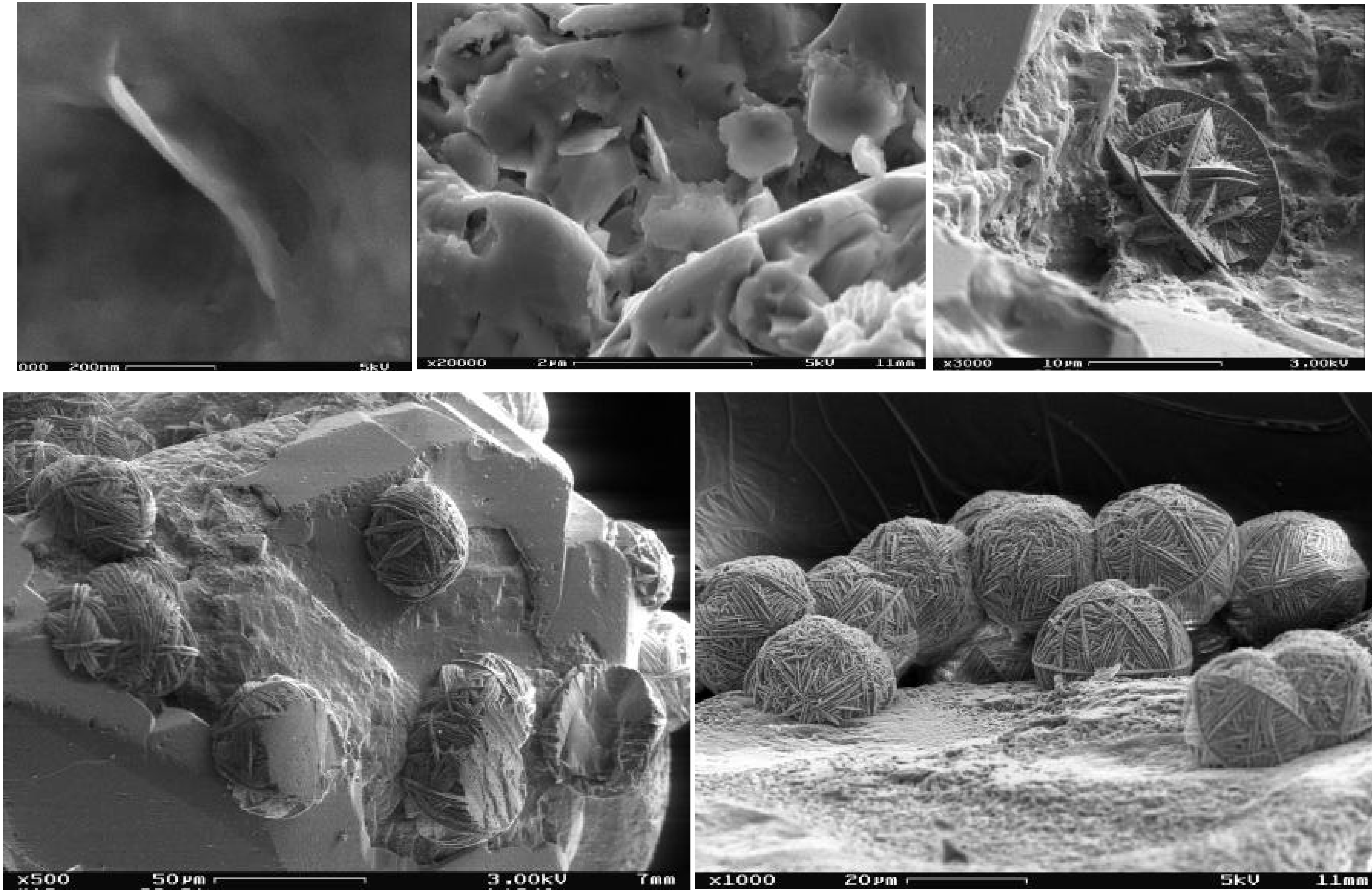
“Nitrate” Cancrinite

$Na_8(Al_6Si_6O_{24})(NO_3)_2 \bullet 4H_2O$



structure from Hund (1984) Z. Anorg. Atlg. Chem. 509, 153.

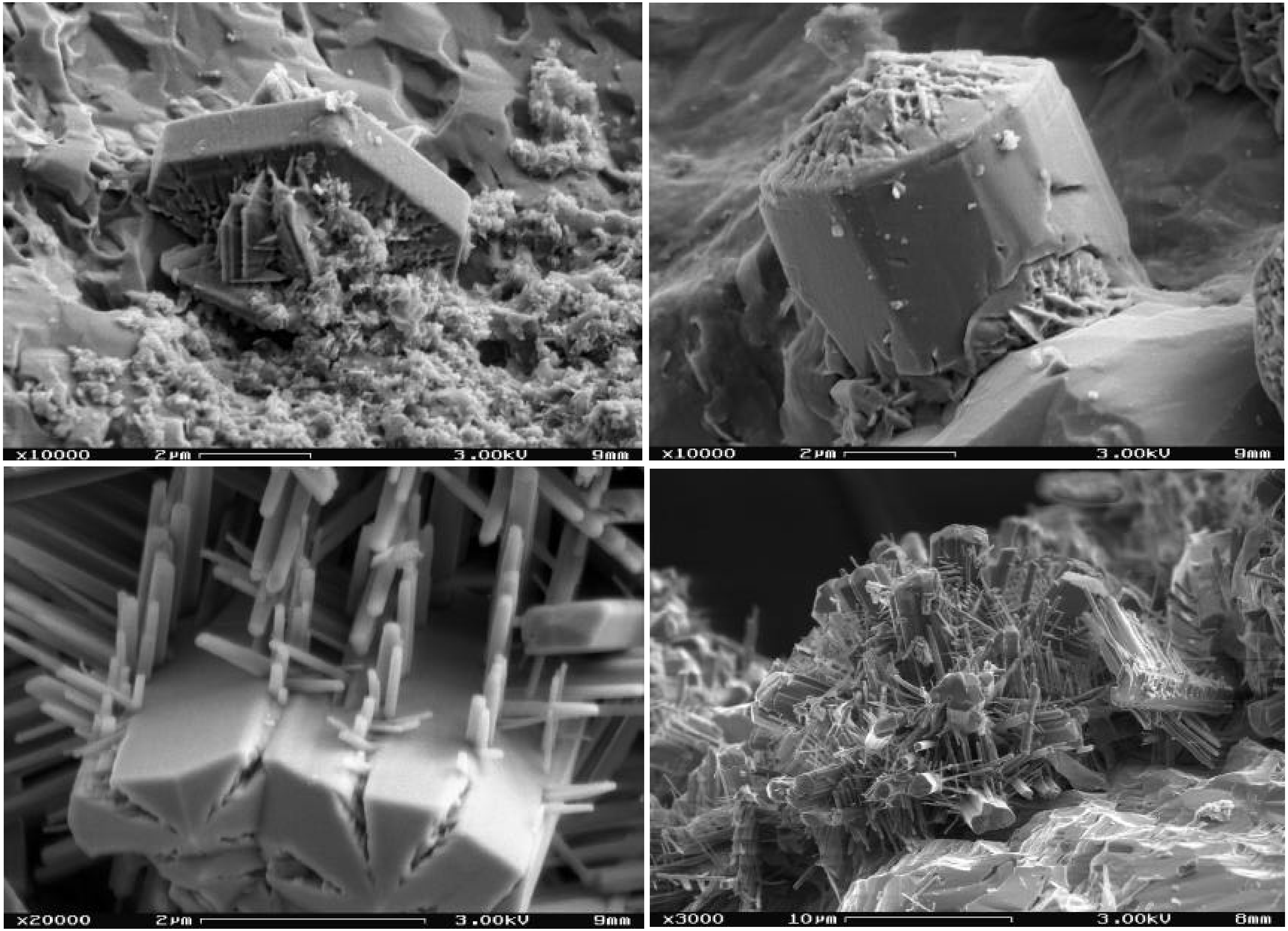




0.005 m $Al(OH)_4^-$ - 24 days

0.01 m $Al(OH)_4^-$ - 13 days

pH 11.3; 2 m Na^+; 2 m NO_3^-

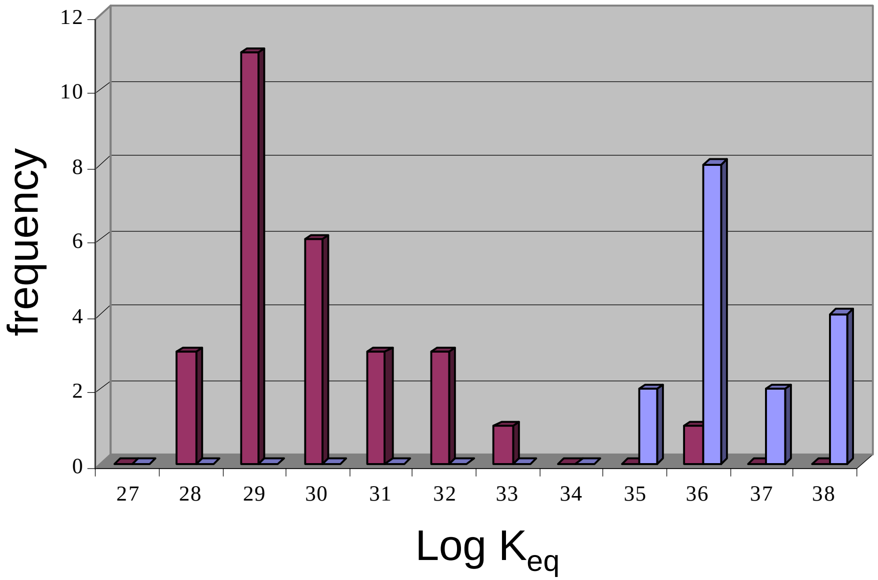


pH 12.4; 2 m Na^+; 2 m NO_3^-

Cancrinite Precipitation Reaction

$$8\ Na^+ + 6\ Al(OH)_4^- + 6\ H_2SiO_4^{2-} + 2\ NO_3^-$$
$$\Leftrightarrow$$
$$Na_8Si_6Al_6O_{24}(NO_3)_2 4H_2O(s) + 12\ OH^- + 8\ H_2O$$

$$K_{eq} = \frac{\{OH^-\}^{12}}{\{Na^+\}^8\{Al(OH)_4^-\}^6(H_2SiO_4^{2-}\}^6\{NO_3^-\}^2}$$



pH 12.4 (1.0 m OH^-)

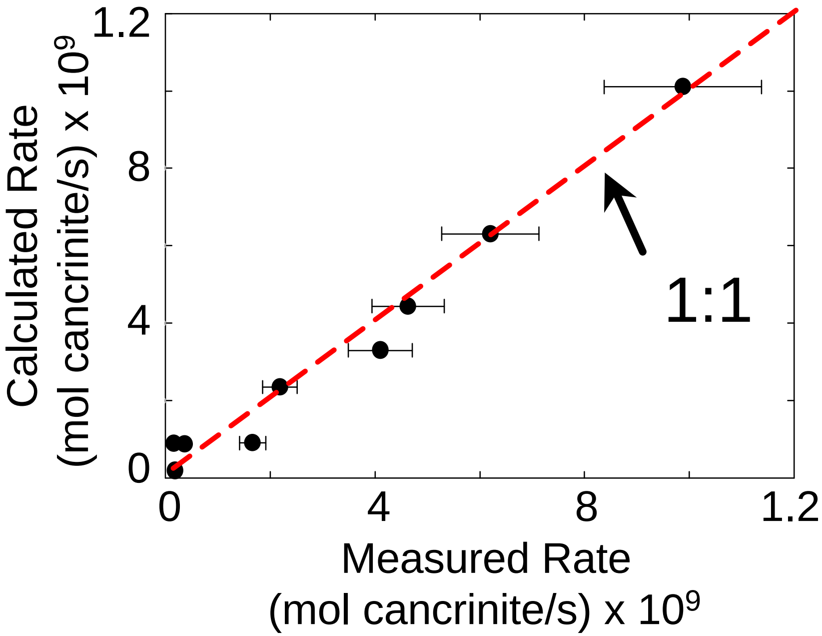
Log K_{eq} = 36.2 ± 0.6 (95% confidence)

pH 11.3 (0.1 m OH^-)

Log K_{eq} = 30.4 ± 0.8 (95% confidence)

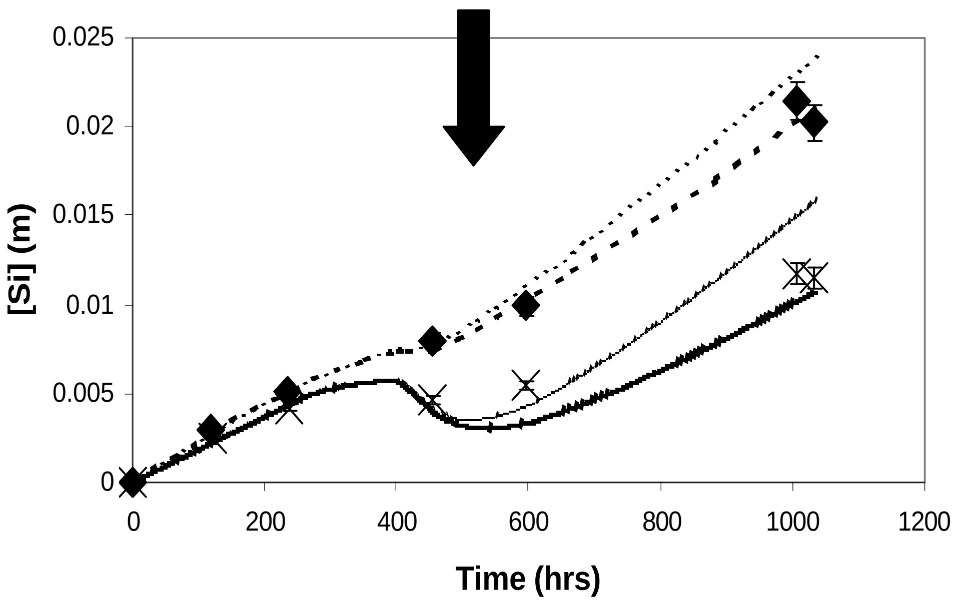
Initial Precipitation Rates

$$Rate_{ppt} \text{ (mol cancrinite/s)} = 1.03 \pm 0.05 \times 10^{-6} [Al]^{1.22} [Si]^{0.23}$$

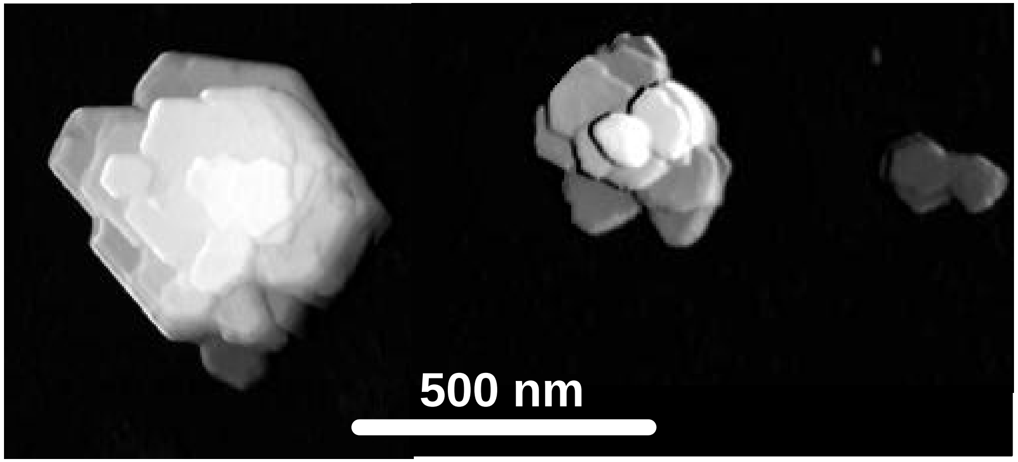


Quartz $Rate_{diss}$ in Al solutions + Reduced surface area from image analysis

+ Stoichiometric removal of Si and Al as cancrinite



Reactive surface area of phyllosilicates

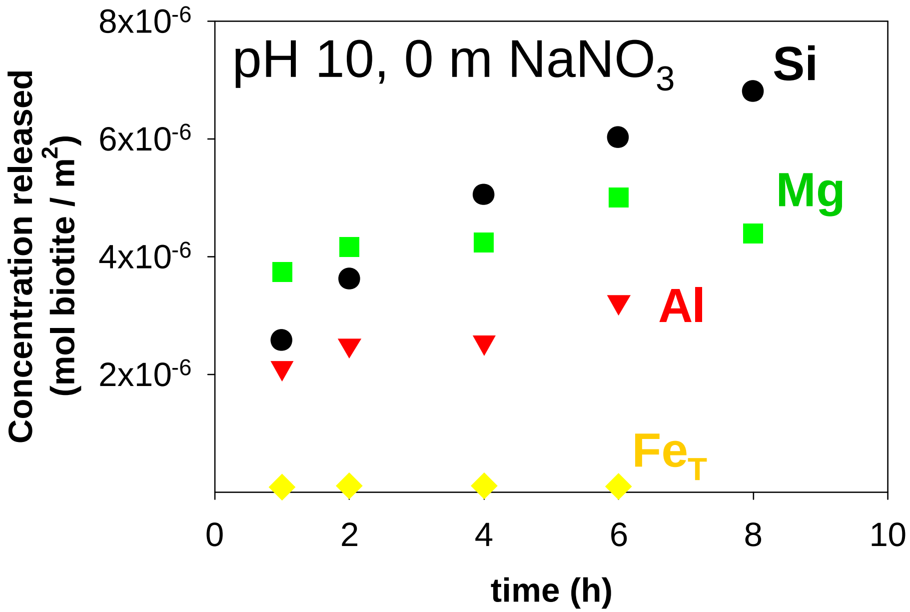


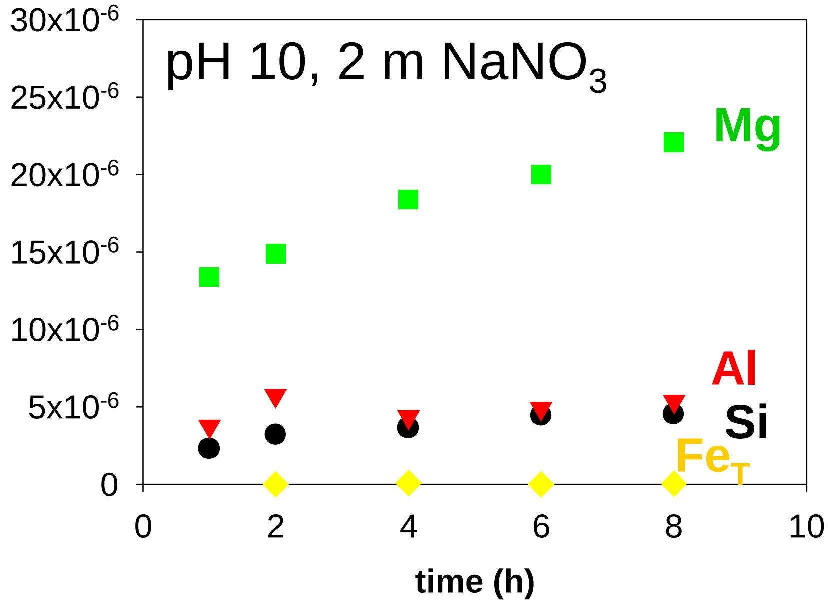
	KGa-1	KGa-1b	KGa-2
# particles	32	52	77
Mass (g)	5.19×10^{-12}	5.67×10^{-12}	2.35×10^{-12}
ESA/TSA (%)	27.3 ± 0.7	30.0 ± 0.8	18.2 ± 0.5
SSA (m^2/g)	10.1 ± 0.3	11.3 ± 0.3	24.1 ± 0.6
SSA (m^2/g, BET_{pub})	8.2-11.2 *(5)*	11.7-12.5 *(2)*	22.4-24 *(3)*

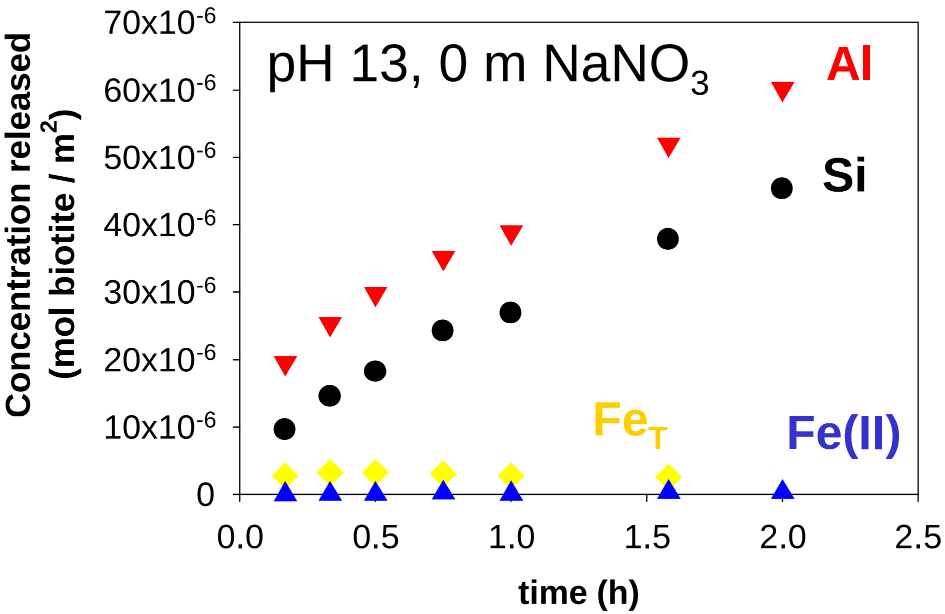
Approach could be used to assess reactive edge and basal surface areas of micas at Hanford site.

Quantifying surface areas of clays by atomic force microscopy
B. R. Bickmore, K. L. Nagy, P. E. Sandlin, and T. S. Crater, in review

Biotite Dissolution Kinetics @ 25°C

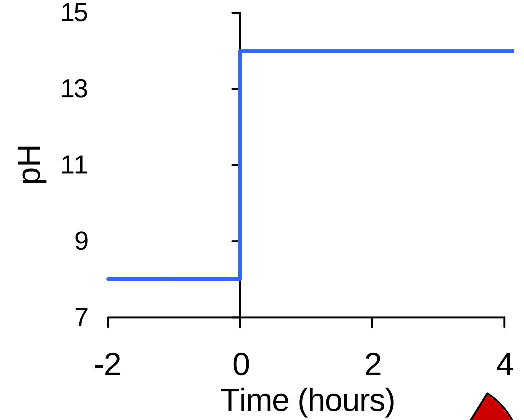


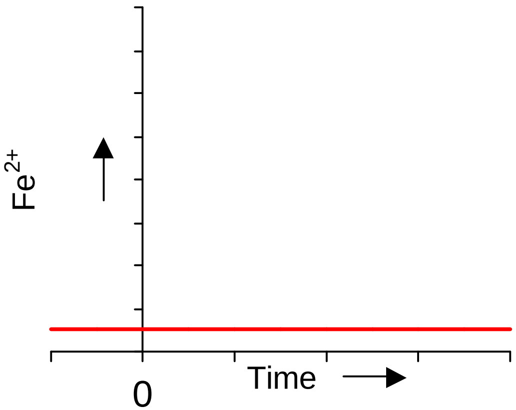


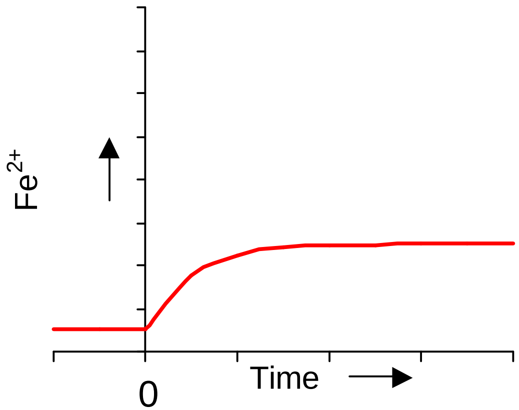


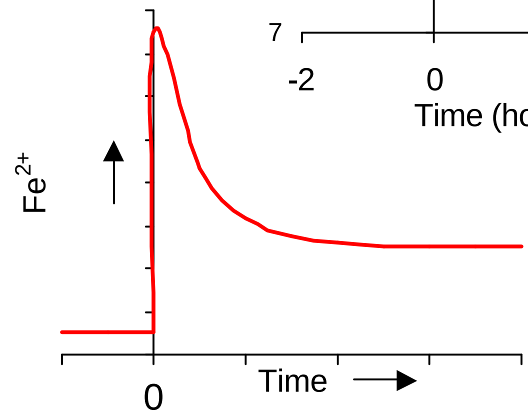
- Biotite dissolves incongruently
- Saturation with Mg-phase & Fe-oxide controls Mg and Fe release
- Fe(II) rapidly oxidizes to Fe(III)
- Fe(II) measured at high pH & short time

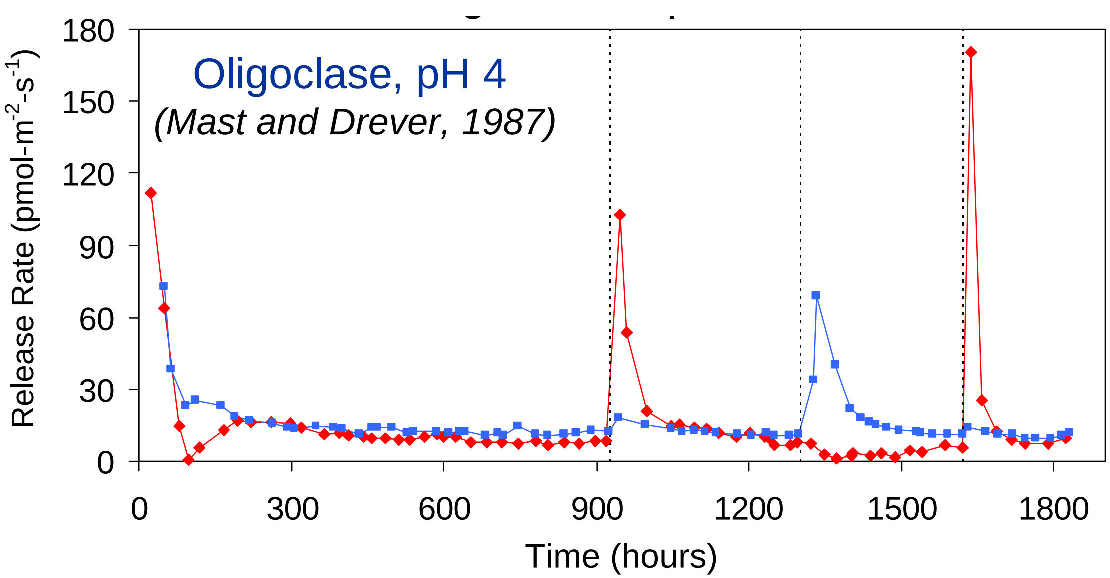
Fe(II) release from biotite and magnetite: Steady-State vs. Nonsteady-State Fate of CrO_4^{2-}, TcO_4^-, Cs^+ ?











Example of recurrent transients

Future Plans

- Continue kinetics experiments (CU)
- Conduct saturated and unsaturated flow column experiments (PNNL)
- Refine models with new data
- Use refined models for parameter-sensitivity feedback to experiments (PNNL, CU)
- Present and publish results