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

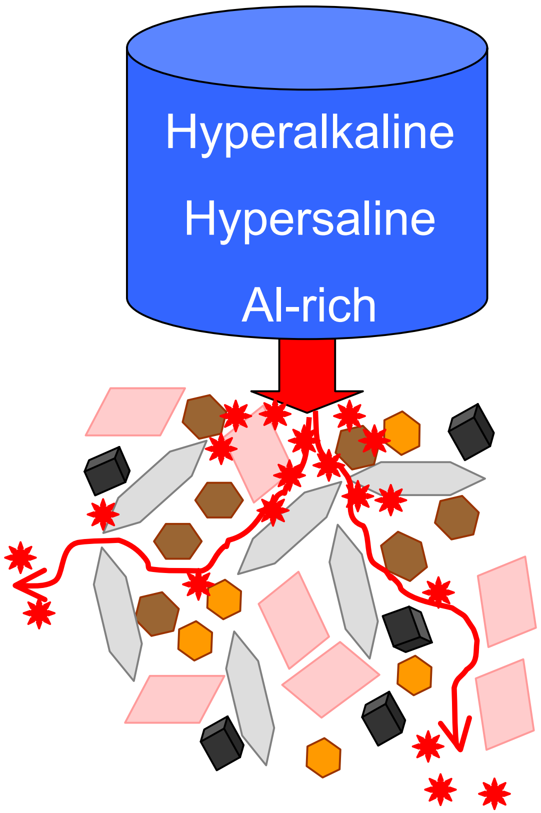
(May 2003)

Kathryn Nagy
Neil Sturchio

Department of Earth and Environmental Sciences
University of Illinois at Chicago

With acknowledgement to:
Sherry Samson - PNNL
Barry Bickmore - Brigham Young University

How did tank fluids react with sediment minerals?



Primary minerals dissolved;
secondary minerals formed
as colloids
and surface overgrowths.

How much radioactivity is immobilized in secondary minerals?

How has secondary mineralization affected radionuclide distribution?

Background & Problem

SX-tank farm cores

- Pervasive aluminosilicate ‘amorphous’ precipitates (Zachara et al., 2001)
- Cs plumes controlled by sorption/desorption
  (McKinley et al., 2001; Zachara et al., 2002; Steefel et al.)
- Cr immobilization controlled by Fe(II) release from primary minerals
  (Zachara et al., 2003)

BX-tank farm cores

- U(VI) uranophane family secondary precipitates (Catalano et al., *2002)*

Numerous experiments simulating tank/sediment interaction

- formation of zeolite phases both as colloids and overgrowths
  (e.g., Bickmore et al., 2001; Wan; Chorover and others; Harsh, Flury and others)

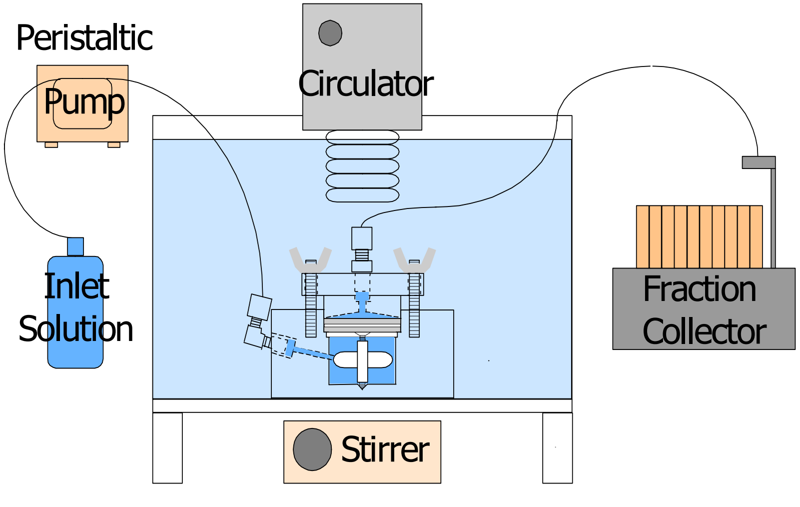
Chemical components of the precipitates are derived from the sediments.

How, when, and where are the new phases nucleating?

How stable are the new phases?

Approach

- Quantify reactions between tank fluids and Hanford sediment minerals.
- Investigate role of bulk fluid compositions and radionuclide uptake.
  - obtain kinetic data from monomineralic substrate experiments
  - identify new surface precipitates
  - determine thermodynamic data from same or similar experiments
  - quantify radionuclide uptake in new surface precipitates



Brief Review of Previous Results

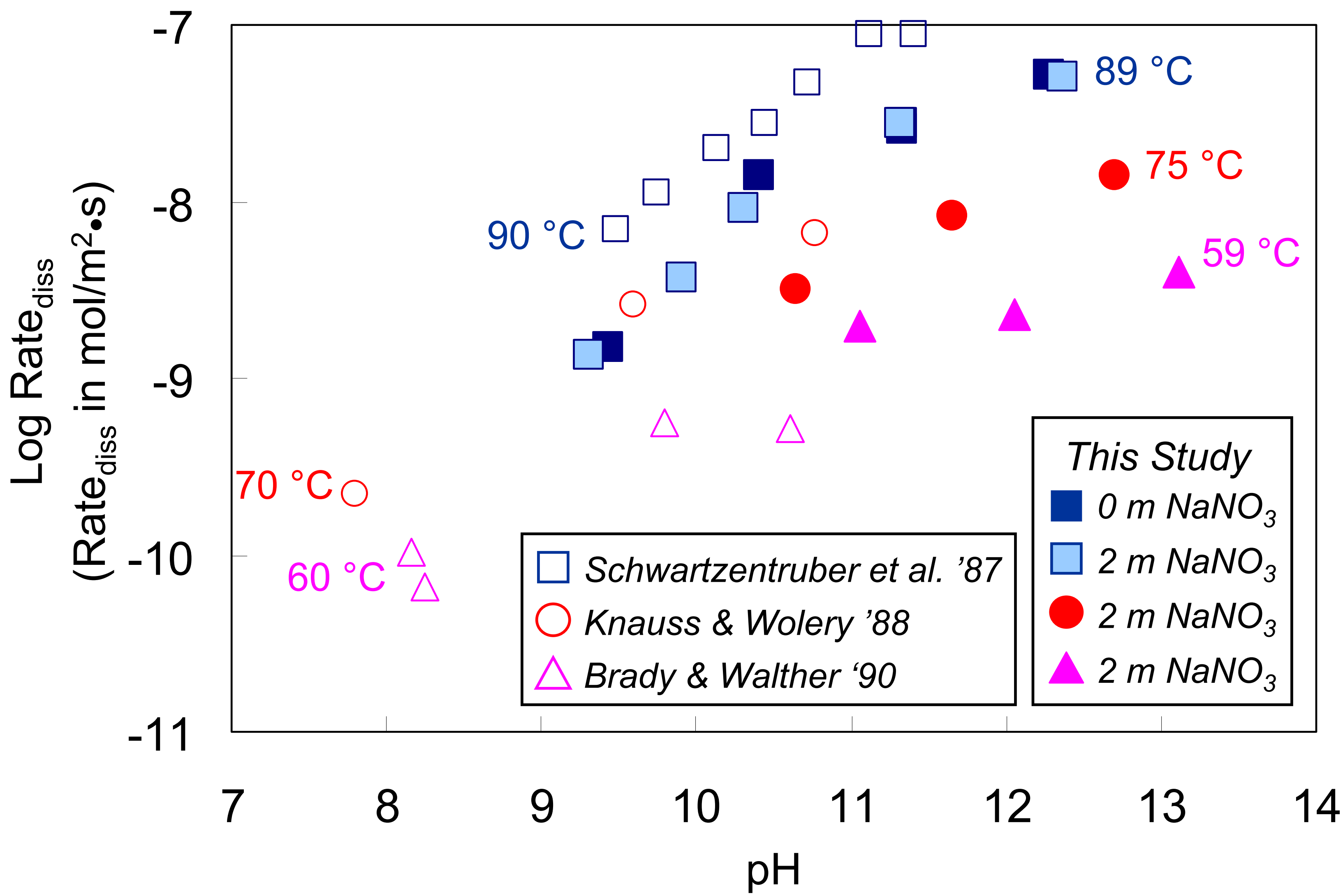
Quartz dissolution – aluminosilicate precipitates

Biotite dissolution – Fe(II) release
secondary precipitates

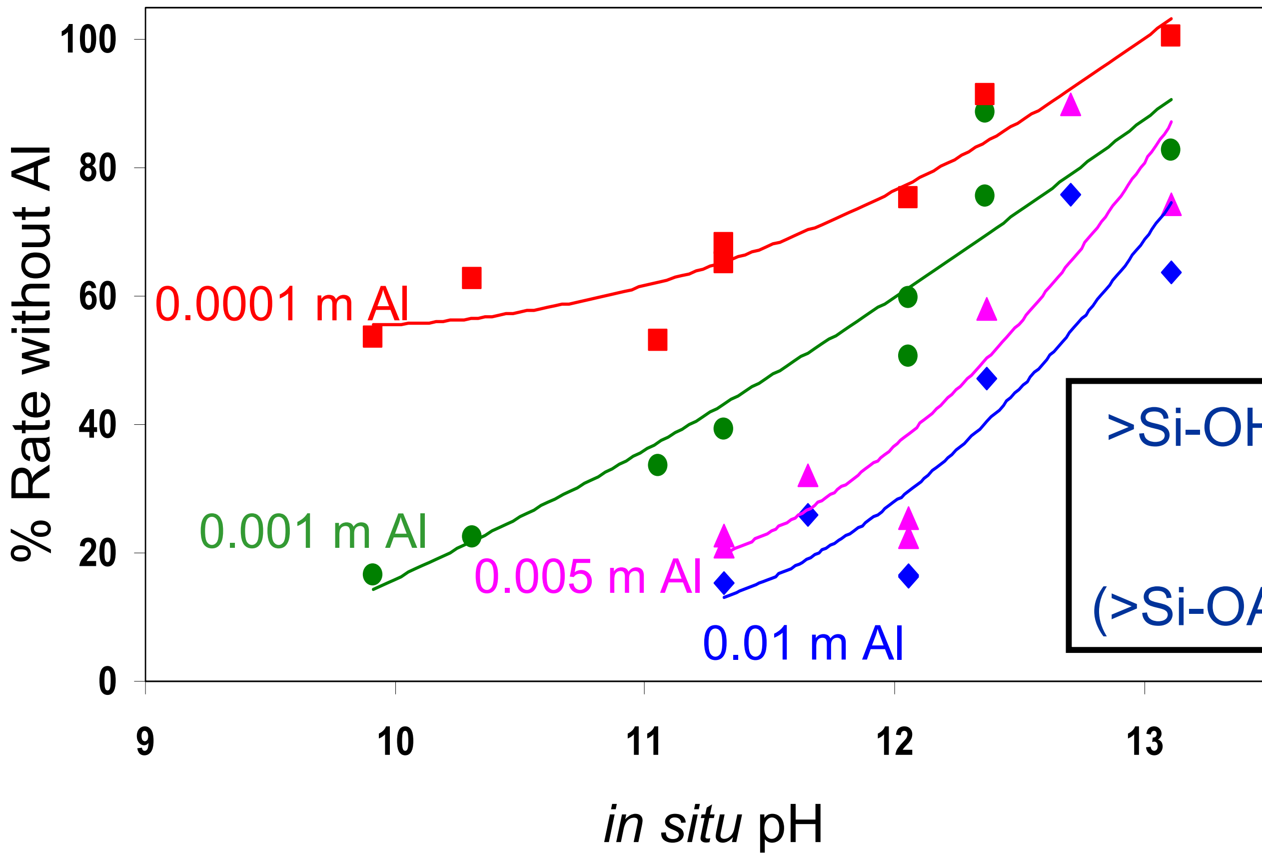
Brief Preview of Initial New Research

Quartz dissolution – aluminosilicate precipitates
with U(VI)-bearing BX tank simulants
with Cs-bearing SX tank simulants
role of surface roughness in nucleation kinetics

pH Dependence of Initial Dissolution Rates of Quartz



Al Reduces Quartz Dissolution Rate



$$>Si\text{-}OH^{o} + (Al(OH)_4^{-} – Na^{+})$$

$$\Downarrow$$

$$(>Si\text{-}OAl(OH)_3^{-} – Na^{+}) + H_2O$$

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)

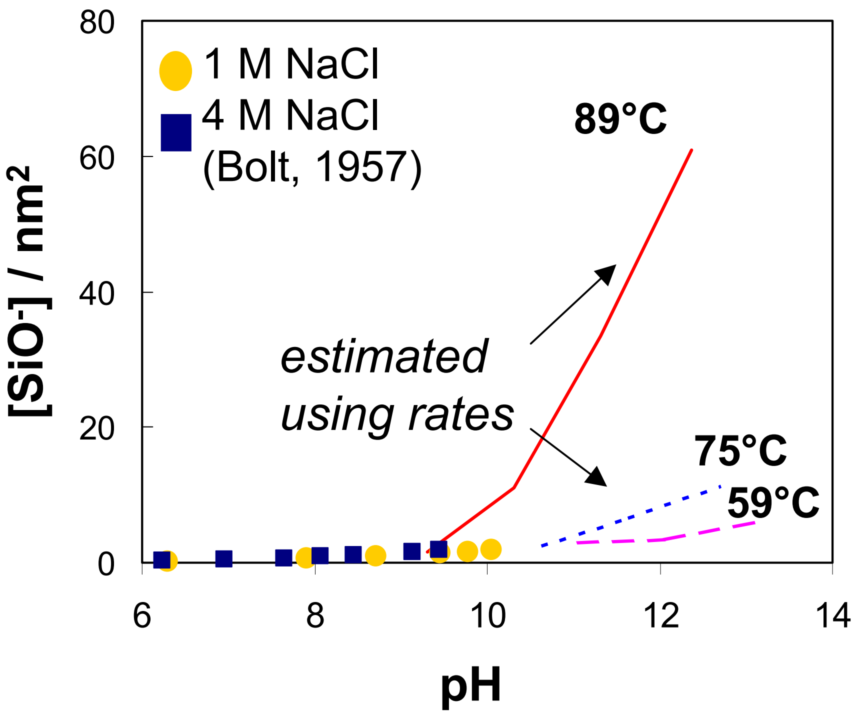
Inhibition of Quartz Dissolution by Sorbed Aluminum

$$\text{Rate} = \text{Rate}_{\text{Al-free}}\,(1 - \theta)$$

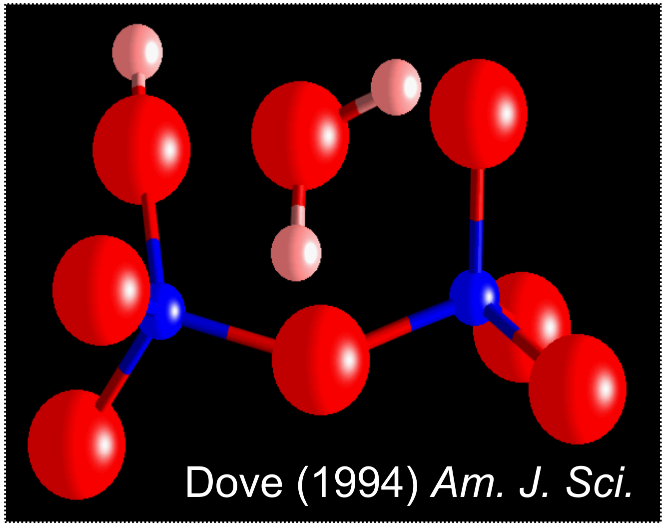
$$\frac{1}{\theta} = \frac{1}{bC\theta_{max}} + \frac{1}{\theta_{max}}$$

$b = -2996\ \text{pH} + 3967$

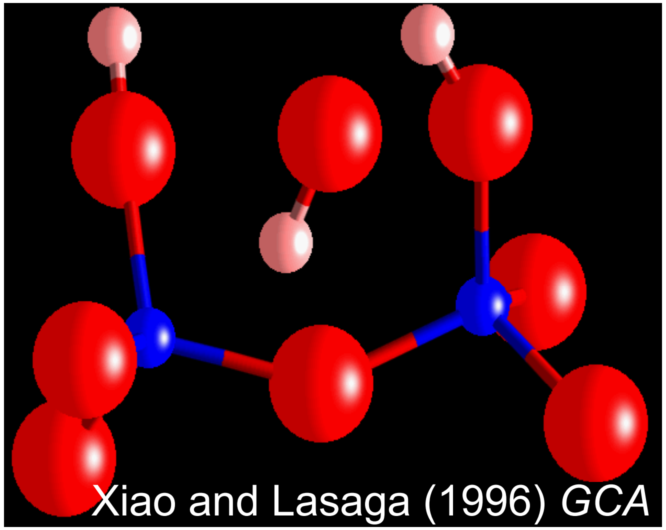
$\theta_{max} = -0.01958\ \text{pH} + 2.940$



low pH
low T



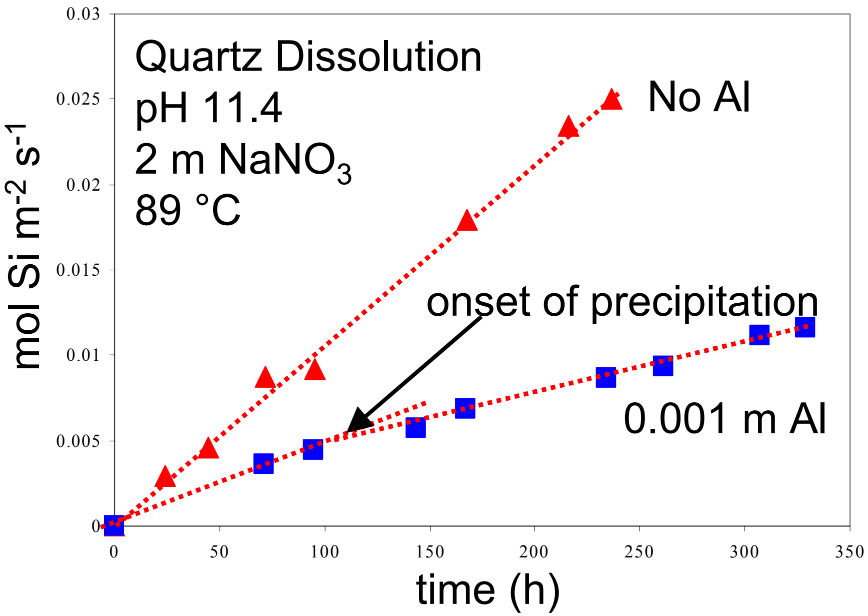
high pH
higher T



"Nitrate" Cancrinite

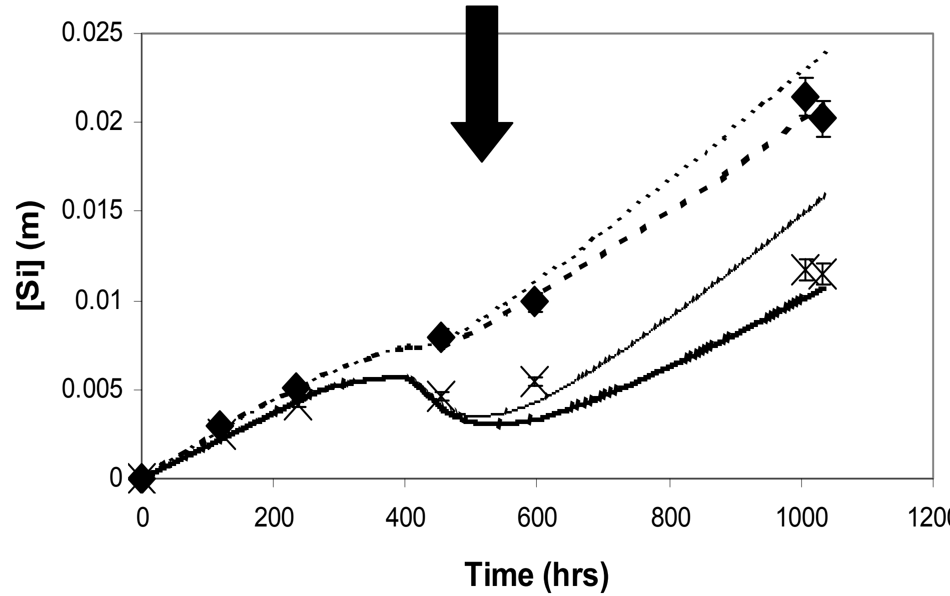
$Na_8(Al_6Si_6O_{24})(NO_3)_2 \bullet 4H_2O$

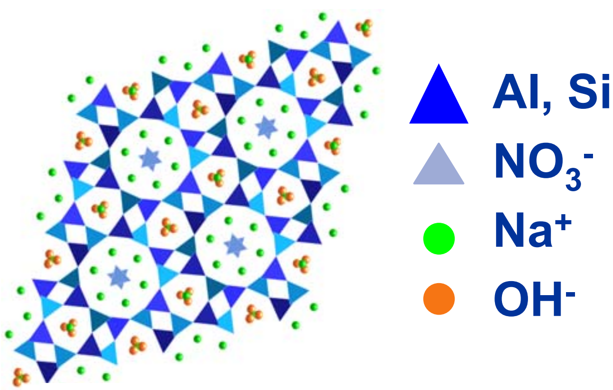
$$Rate_{ppt} = 1.03 \pm 0.05 \times 10^{-6} [Al]^{1.22} [Si]^{0.23}$$



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

\+ Stoichiometric removal of Si and Al as cancrinite



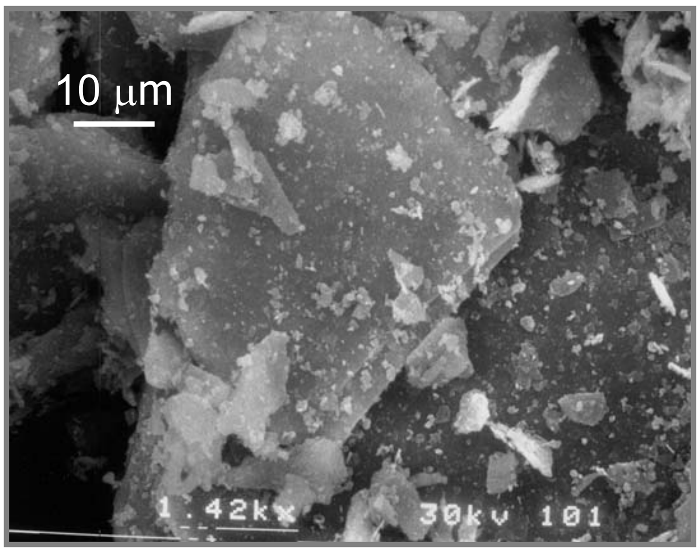


structure from Hund (1984) Z. Anorg. Atlg. Chem. 509, 153.

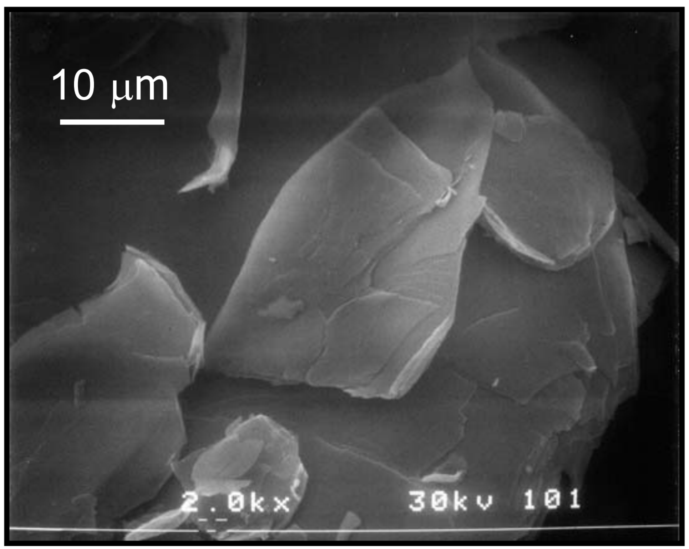
Biotite

$(K_{0.939}Ca_{0.001}Na_{0.055})(Mg_{1.574}Mn_{0.031}\,\mathbf{Fe^{2+}_{1.058}}\,Fe^{3+}_{0.058}\,Ti_{0.183})(Al_{0.989}Si_{2.966}O_{10})[(OH)_{1.709}F_{0.283}Cl_{0.008}]$

Reduces $Cr(VI)O_4^{2-}$

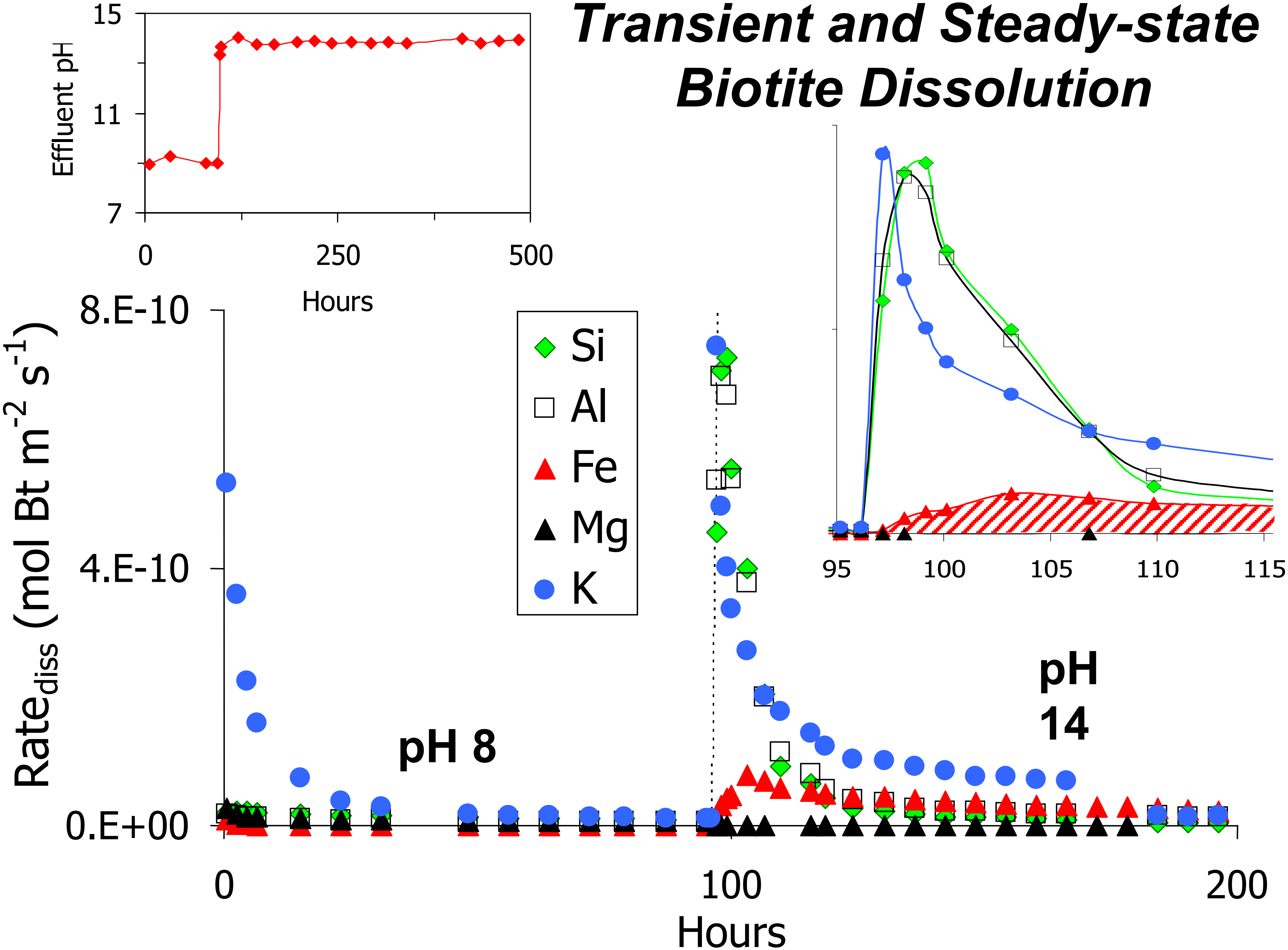


Unreacted Biotite
50 to 100 μm

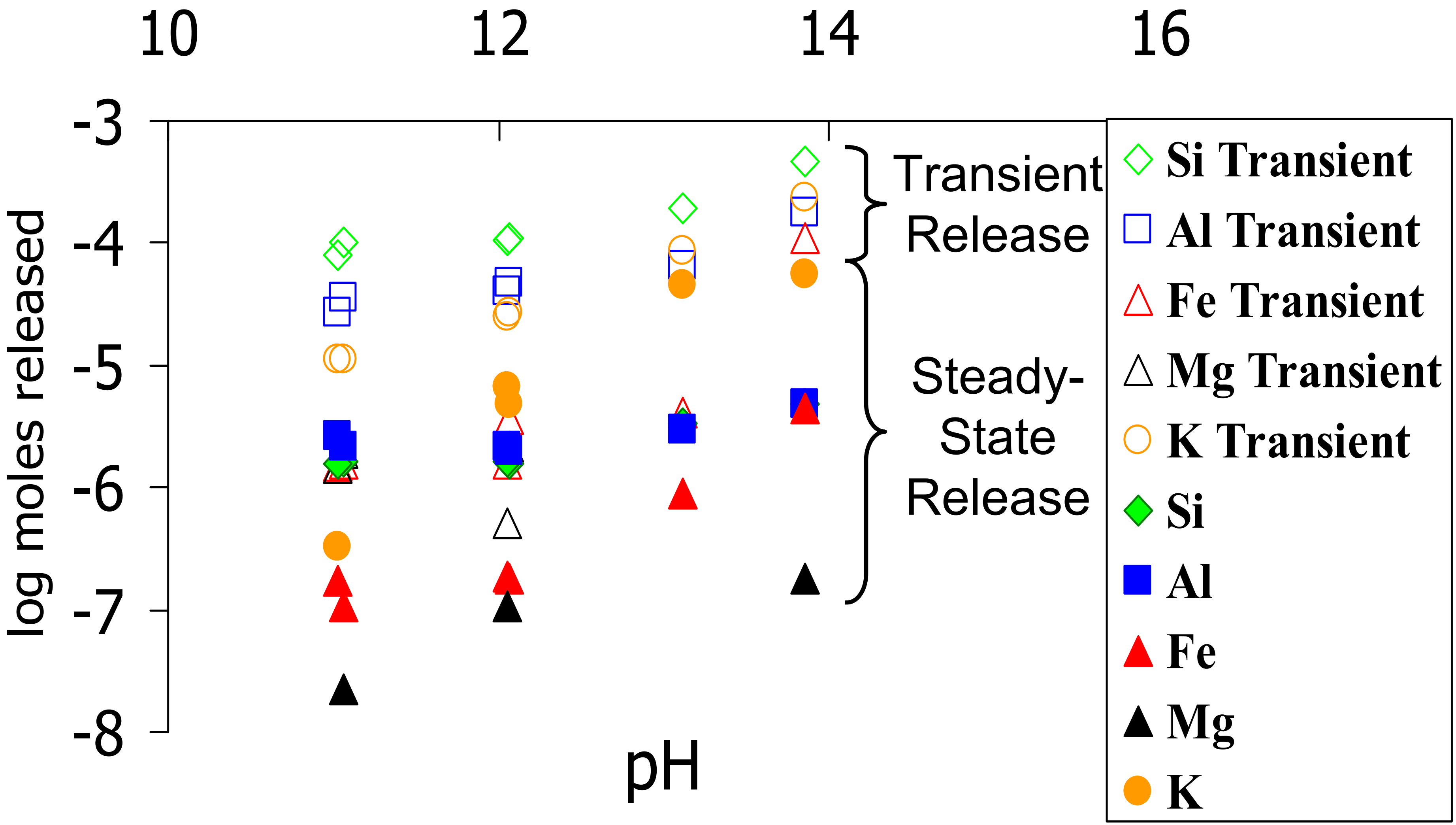


Pre-conditioned Biotite
pH 8, 340 h

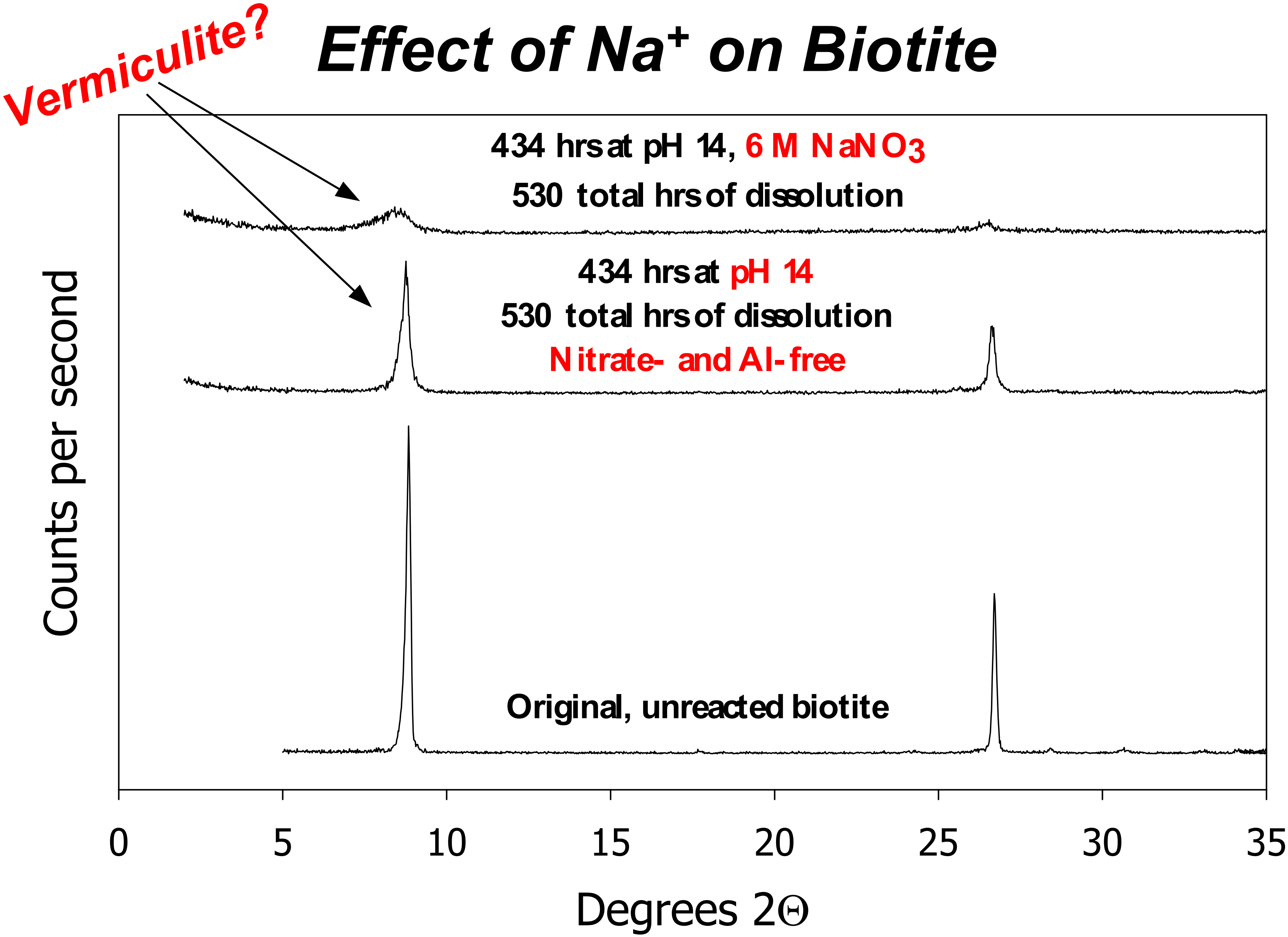
Transient and Steady-state Biotite Dissolution



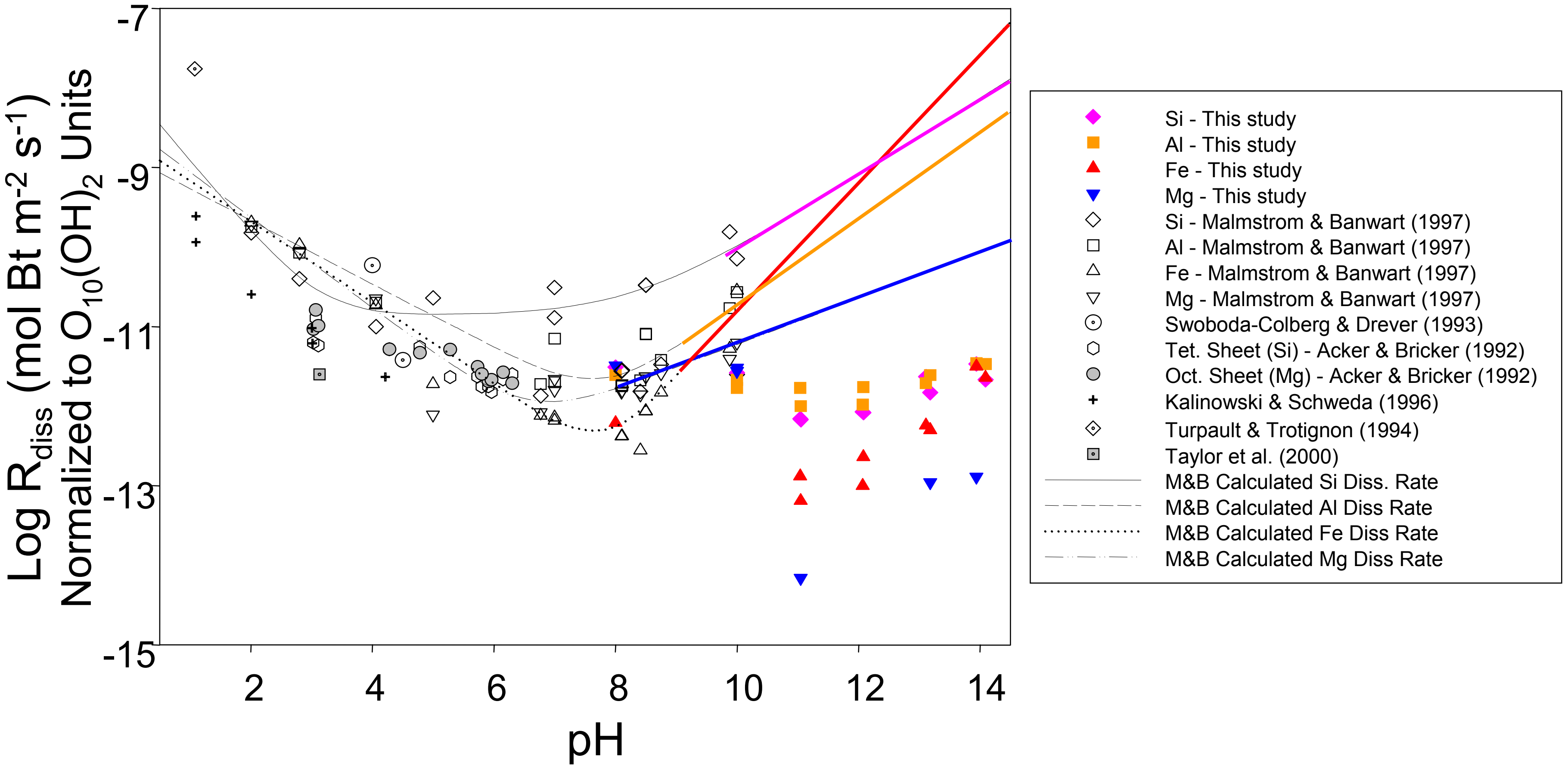
Transient release (~100 hours)
10-100X greater than steady-state release



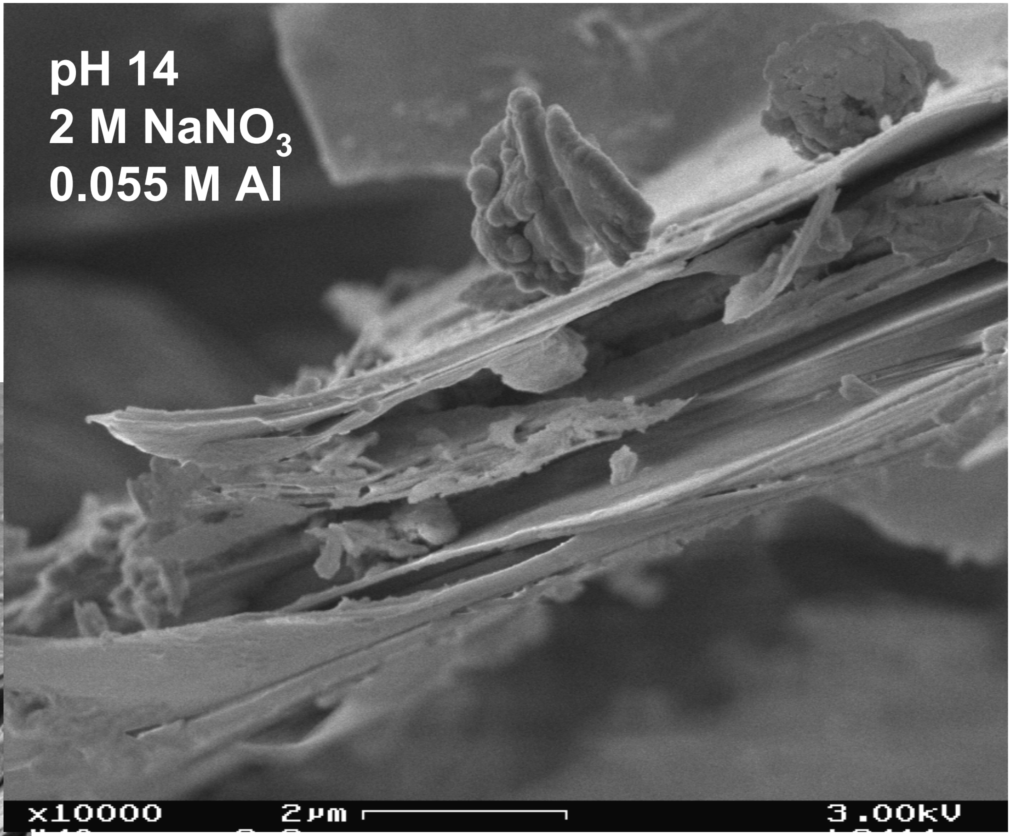
Effect of Na^+ on Biotite

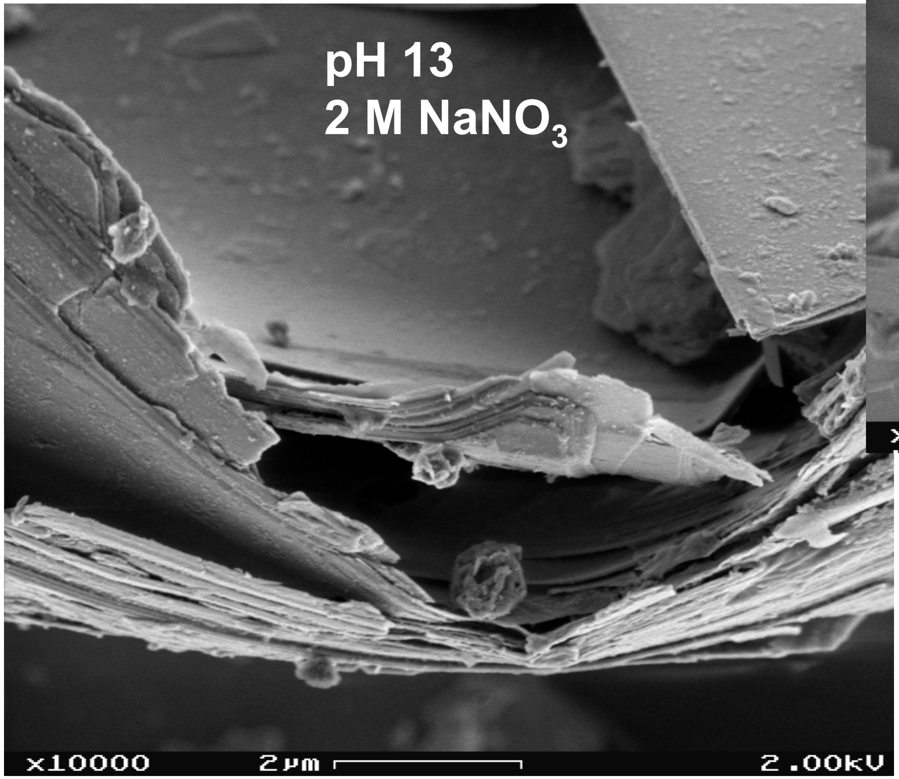


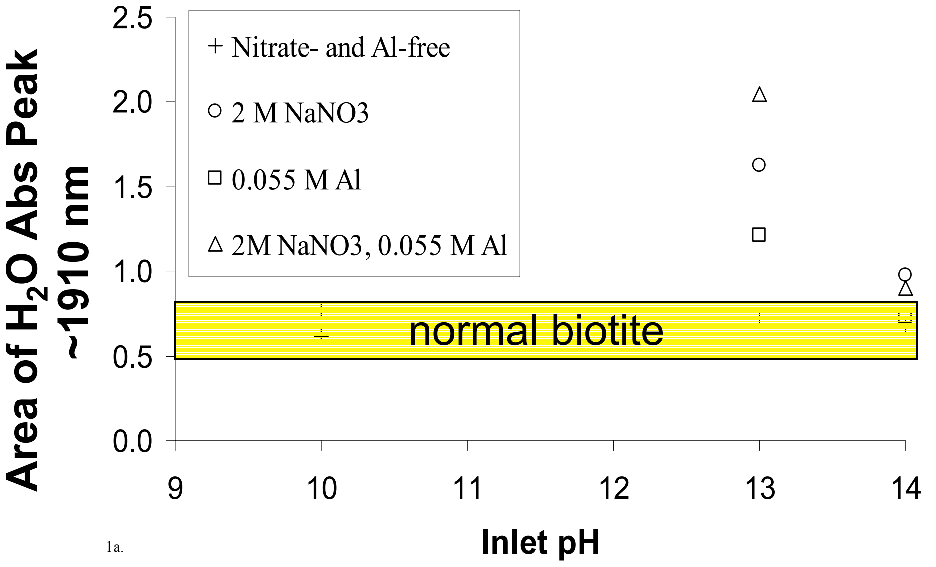
Biotite Dissolution Rates



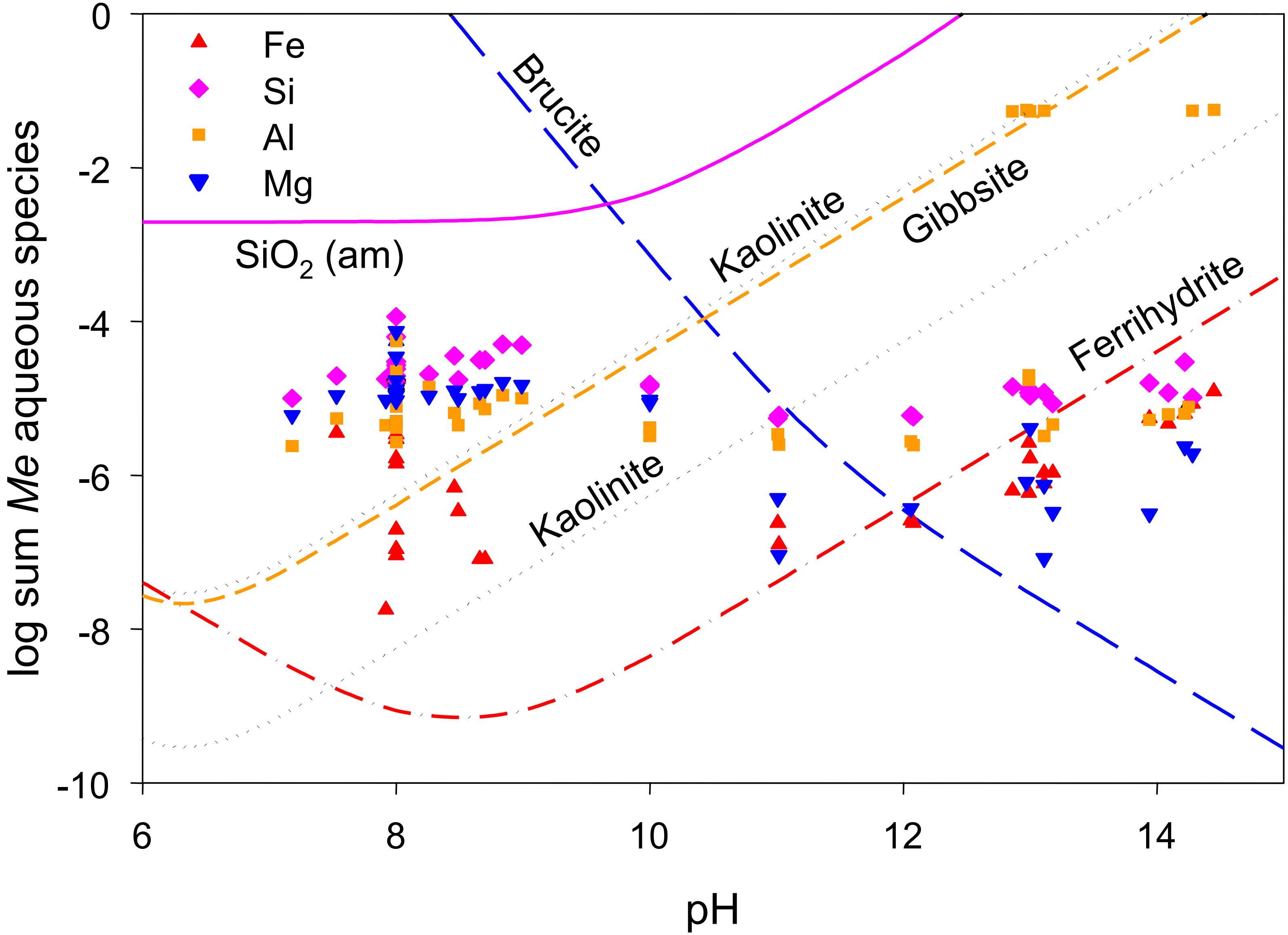
Secondary phase formation on reacted biotite



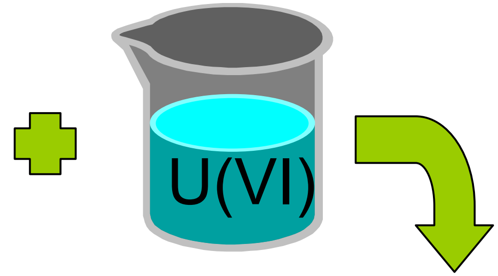


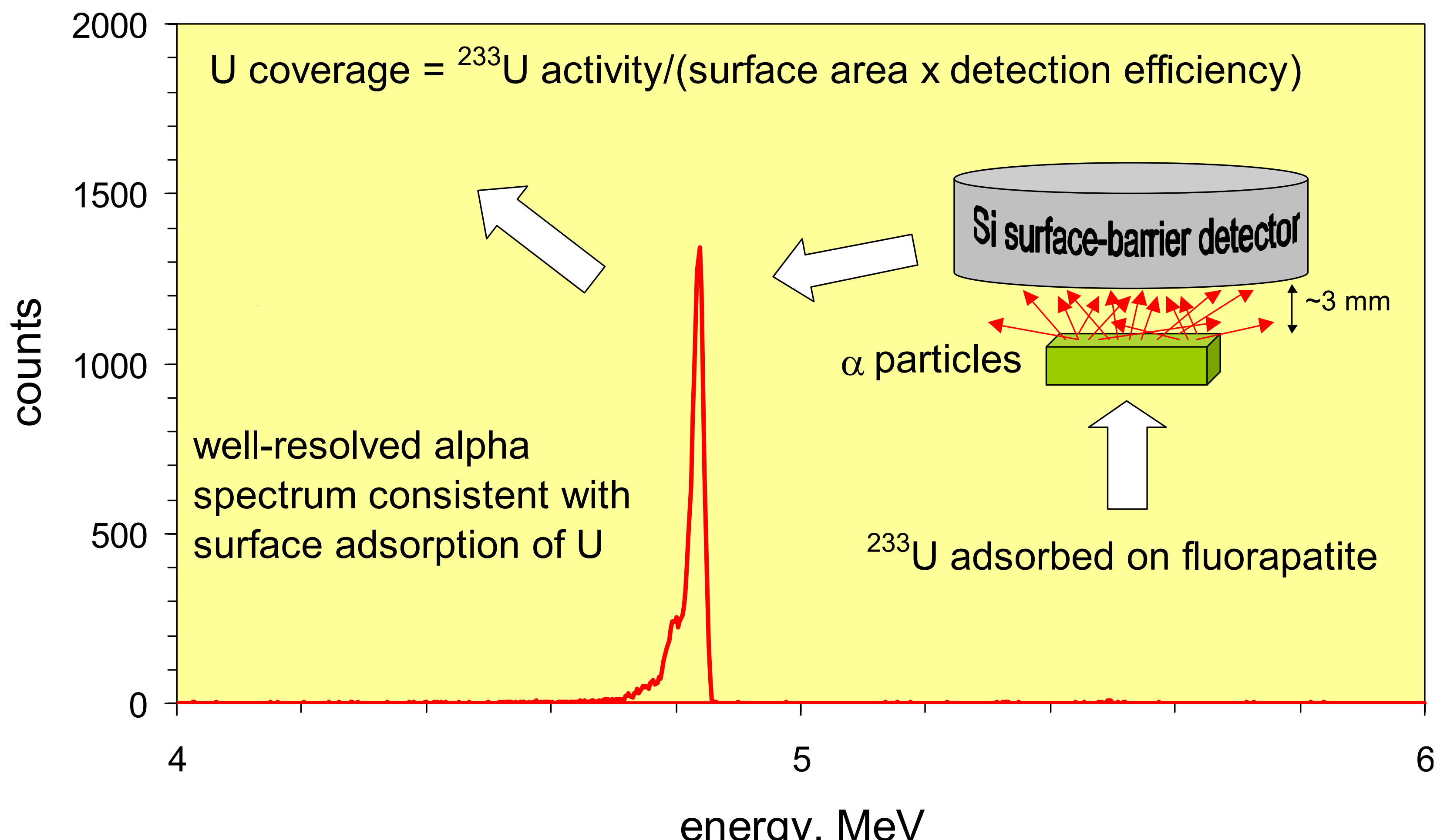


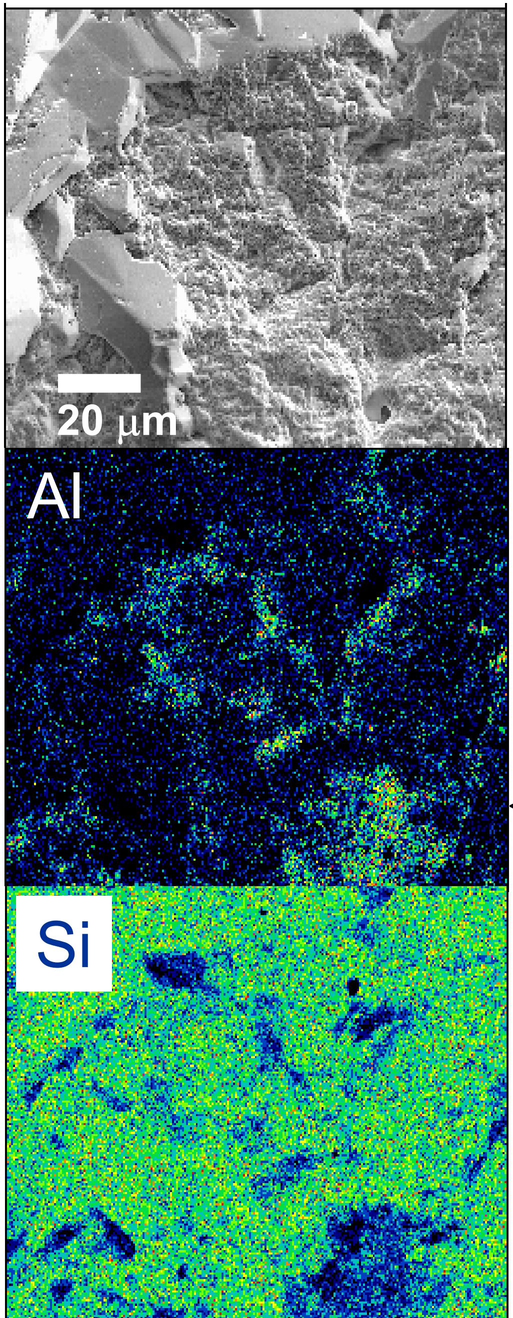
Possible Secondary Phase Solubilities



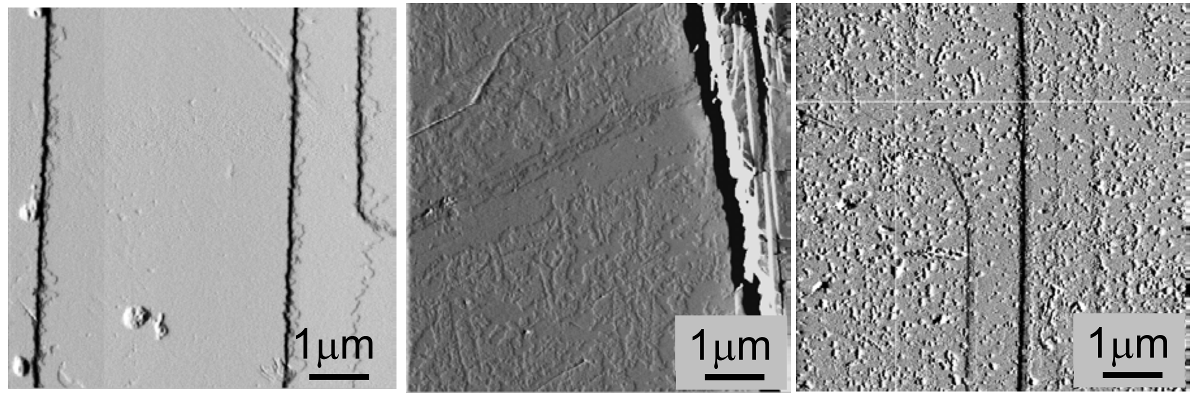
Radionuclide Incorporation
(ex: apatite)







Apatite (TMAFM)



Natural growth surface | Mechanically Scratched surface | Dissolved surface

Overgrowths on quartz initiated as Al-rich films on rough areas of particle surface.

Planned Experiments

Overgrowth kinetic experiments using single crystal quartz with characterized roughening
+ radionuclide (U(VI) and Cs) incorporation.