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

(work in progress: Nov. 2000)

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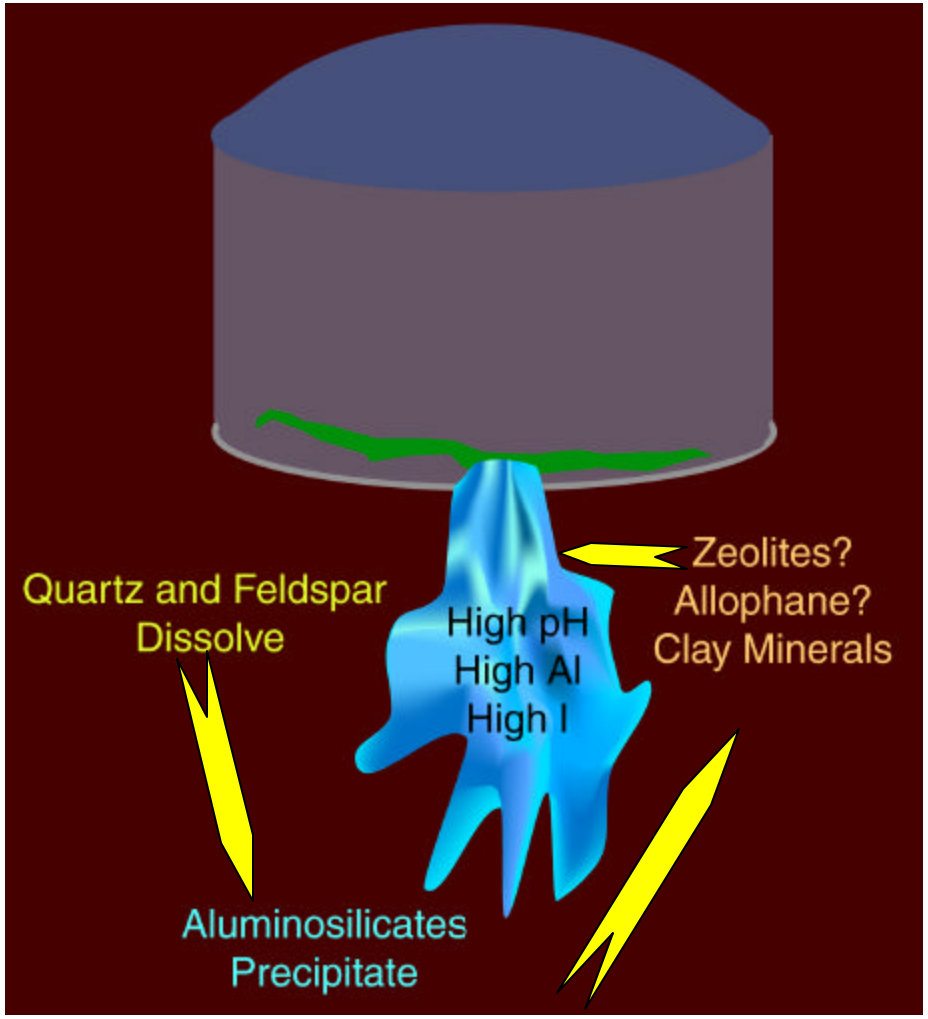
How have leaking tank fluids reacted with sediments?



Altered flowpaths?

Created colloids?

Radionuclide sorption?

Radionuclide coprecipitation?

Can we predict future distribution of contaminants?

How would remediation affect contaminant distribution?

Quartz: SiO_2
Feldspar: $NaAlSi_3O_8$, $CaAl_2Si_2O_8$
Allophane: $xAl_2O_3 \cdot ySiO_2 \cdot nH_2O$
Smectite: $M^+_{0.5}(Al_2)(Si_{3.5}Al_{0.5})O_{10}(OH)_2$
Zeolite: $Na_2(Al_2Si_3O_{10}) \cdot 2H_2O$
Gibbsite: $Al(OH)_3$

Approach

- Focus on reactions involving dominant 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 fundamental data from monomineralic experiments
  - test with reactive/transport model on progressively more complex experimental data
  - finalize on unsaturated flow column experiments using tank fluid simulants and Hanford sediments
- Connect to ongoing investigations
  - EMSP
  - Hanford VZ/GW Science and Technology
  - River Protection

Expected Results

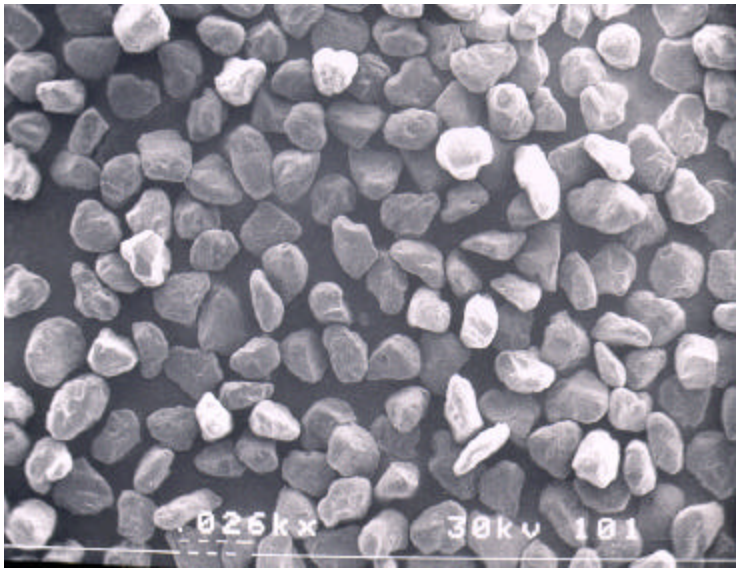
- Kinetic data on mineral dissolution and growth relevant to modeling the interaction of tank fluids with Hanford sediments
- Mechanistic model of these reactions in terms of reactive surface area for sorption
- Incorporation of such data into reactive/transport modeling of Hanford site
- Application to column experiment simulations
- Application to estimating future reactions and transport of radionuclides

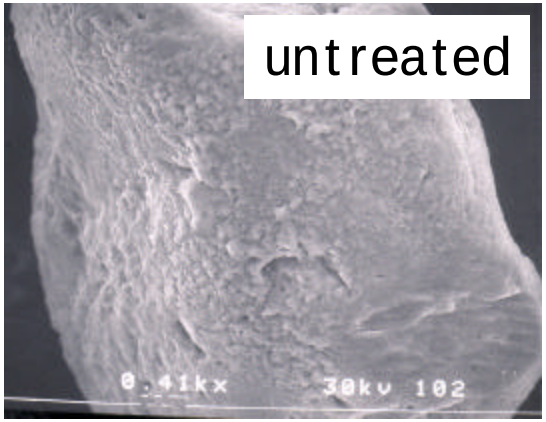
Beneath the tanks:

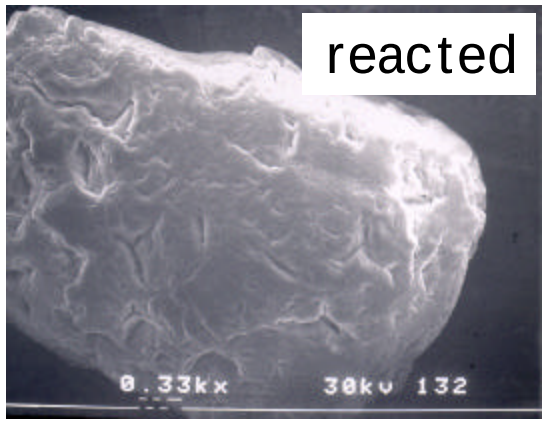
- Reactions between bulk chemical composition of leaking tank fluids and sediment minerals.
  - Dissolution rates
  - Precipitation rates
  - Characterization of precipitates

Inside (& outside?) the tanks:

- Aging of simplified sludges.
  - Fe/Al ratios typical of tanks
  - Effects of Si and Ni on aging
- Incorporation of Re (^{99}Tc analogue) in solids.







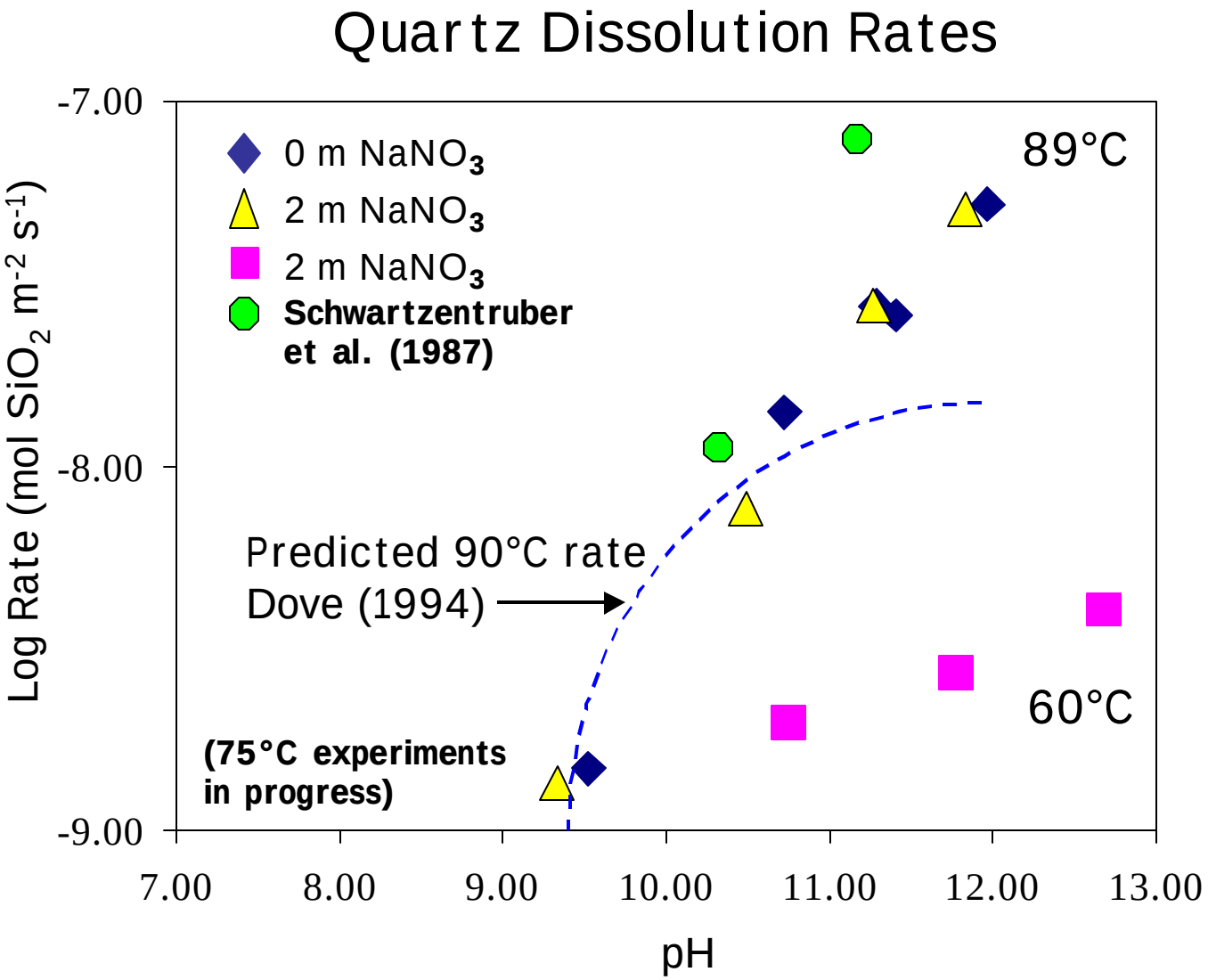
Quartz: (Aldrich)
pretreated (magnetic separation/sulfuric acid wash)

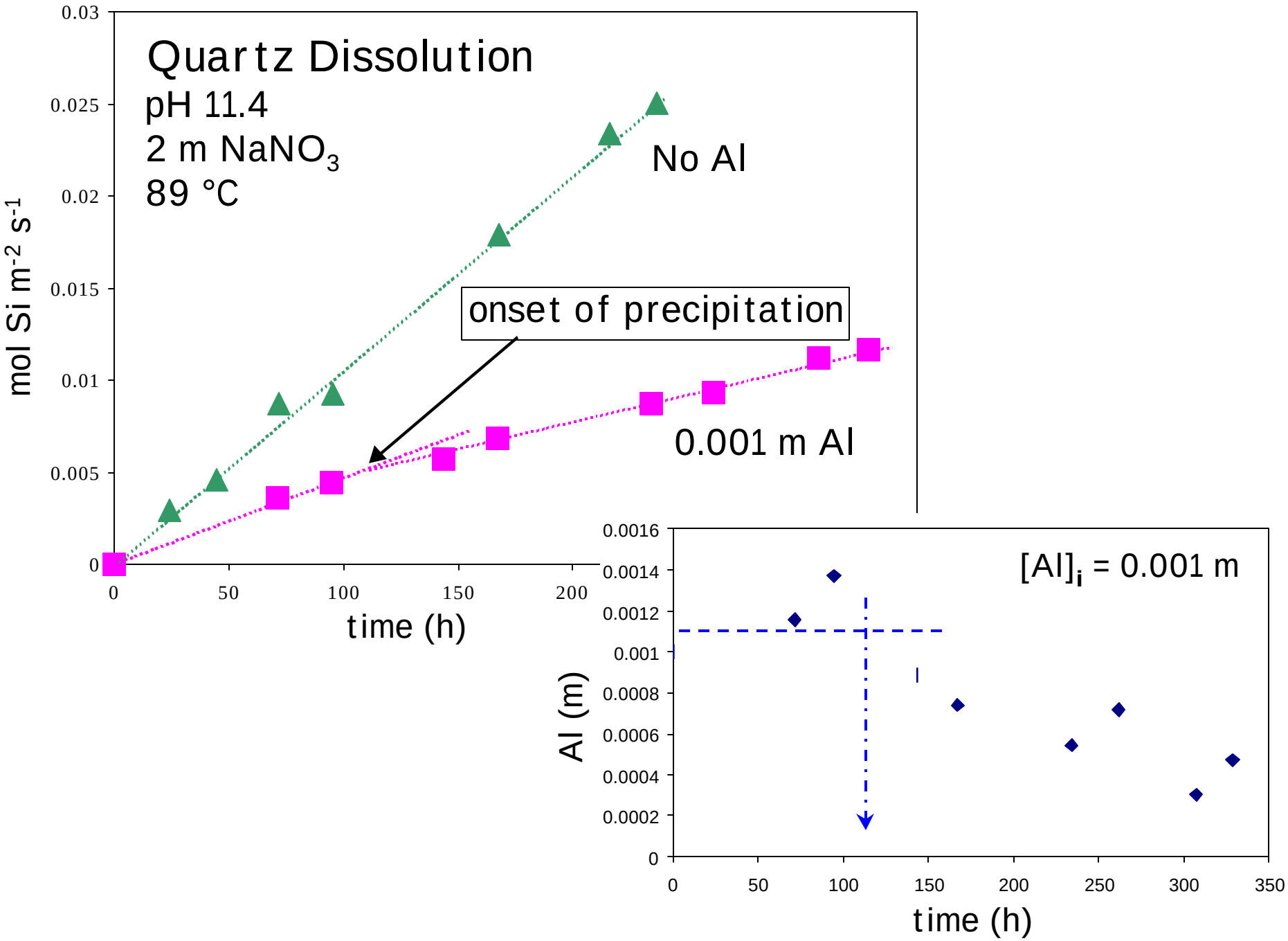
Solutions: ($NaNO_3$, $Al(NO_3)_3$, NaOH)
No CO_2 (purged with high purity Ar); collapsible bottles

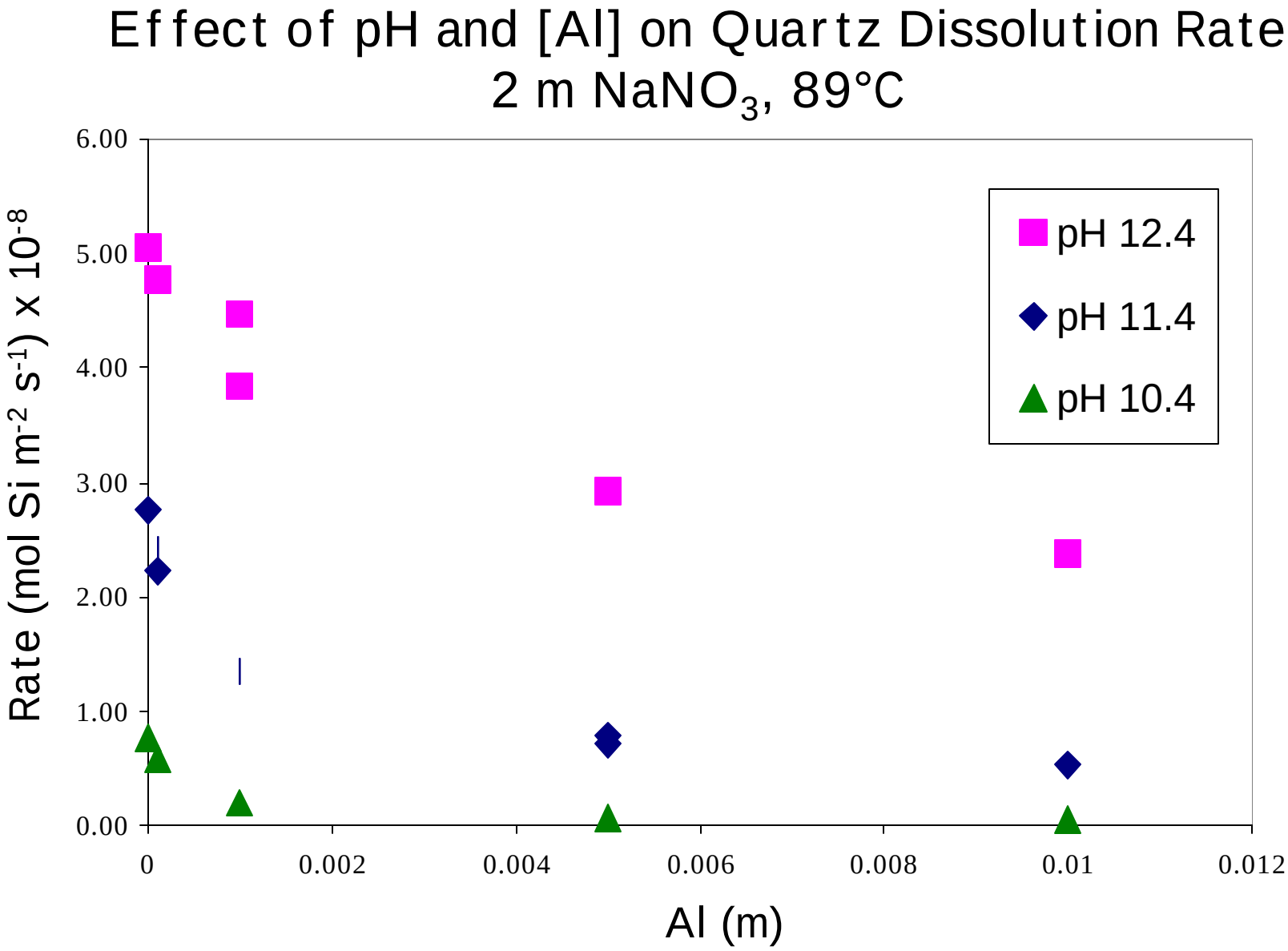
Experiments: Mass quartz = 2 g
Volume solution = 65 g
Time series: 8 bottles/expt.

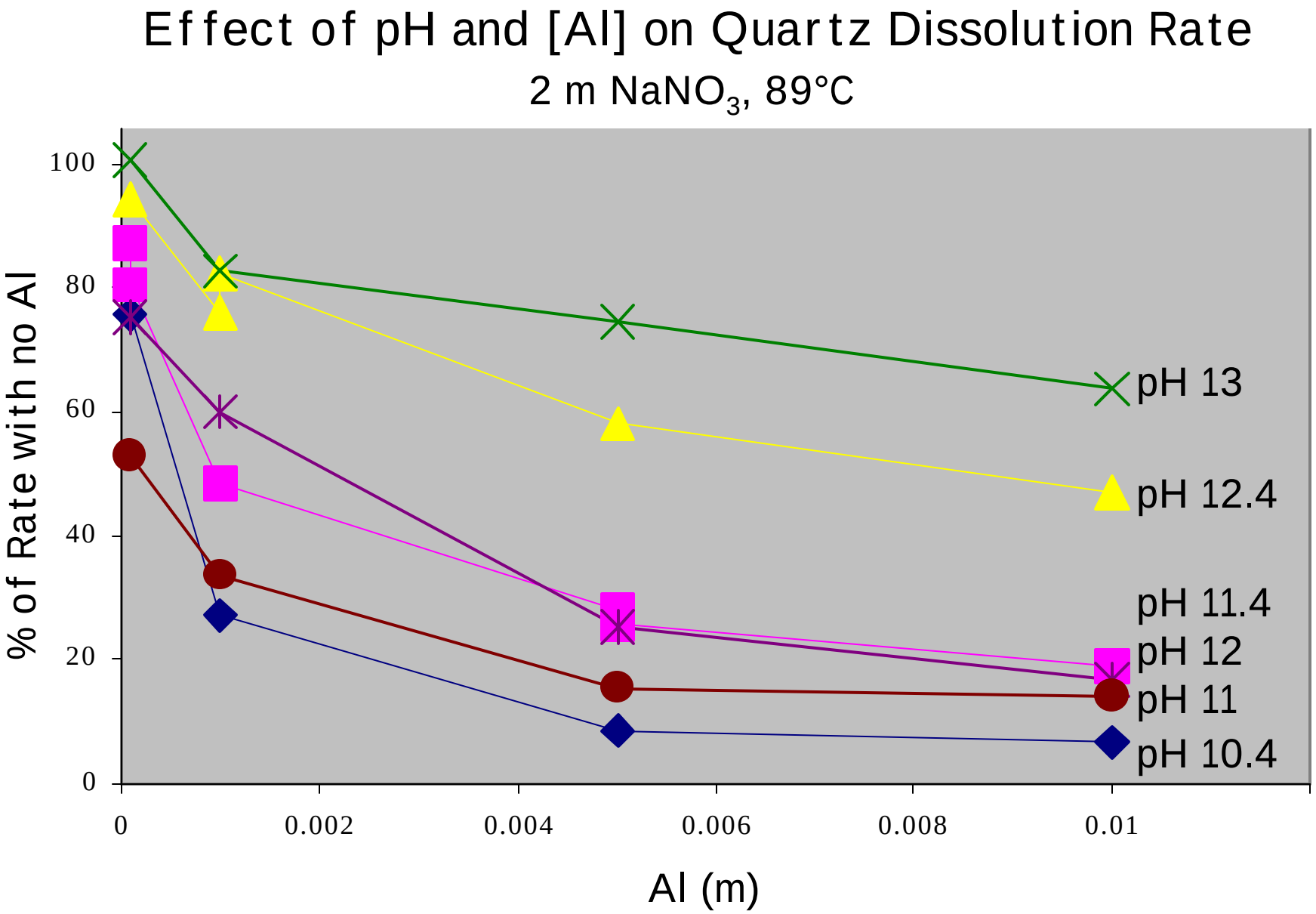
Analyses: Al & Si (UV-Vis); pH (solid-state electrode)
(measured pH up to 0.3 pH units < calculated pH)

Speciation: Pitzer model (no polysilicate species)


Quartz Dissolution Rates
-7.00
-8.00
-9.00
Log Rate (mol SiO2 m-2 s-1)
0 m NaNO3
2 m NaNO3
2 m NaNO3
Schwartzentruber et al. (1987)
89°C
Predicted 90°C rate
Dove (1994)
60°C
(75°C experiments in progress)
7.00
8.00
9.00
10.00
11.00
12.00
13.00
pH

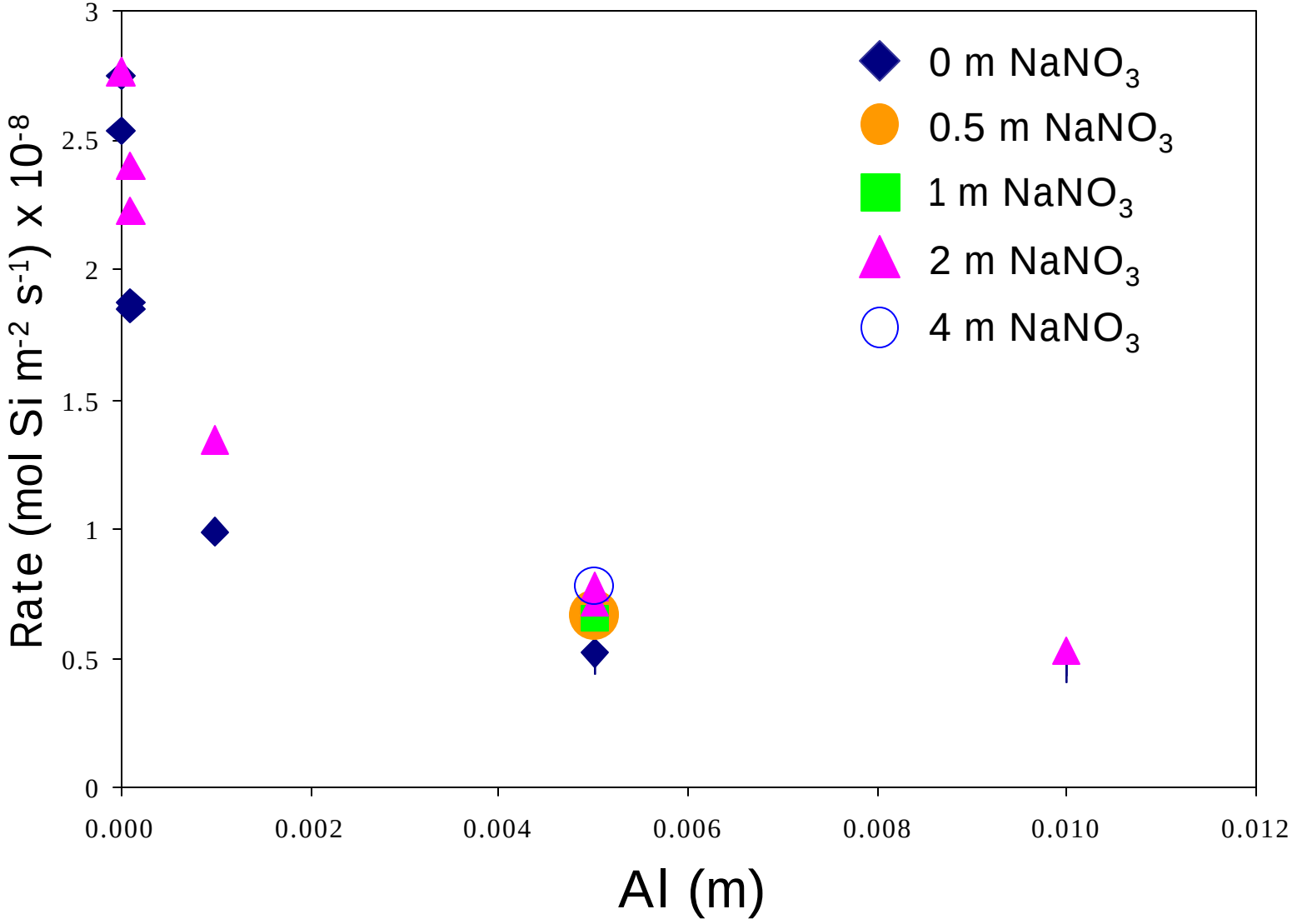

Quartz Dissolution
pH 11.4
2 m NaNO3
89 °C
No Al
onset of precipitation
0.001 m Al
mol Si m-2 s-1
time (h)
0.03
0.025
0.02
0.015
0.01
0.005
0
0
50
100
150
200
[Al]i = 0.001 m
Al (m)
time (h)
0.0016
0.0014
0.0012
0.001
0.0008
0.0006
0.0004
0.0002
0
0
50
100
150
200
250
300
350


Effect of pH and [Al] on Quartz Dissolution Rate
2 m NaNO3, 89°C
Rate (mol Si m-2 s-1) x 10-8
6.00
5.00
4.00
3.00
2.00
1.00
0.00
0
0.002
0.004
0.006
0.008
0.01
0.012
Al (m)
pH 12.4
pH 11.4
pH 10.4

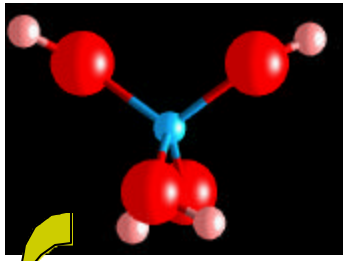

Effect of pH and [Al] on Quartz Dissolution Rate
2 m NaNO3, 89°C
% of Rate with no Al
100
80
60
40
20
0
0
0.002
0.004
0.006
0.008
0.01
Al (m)
pH 13
pH 12.4
pH 11.4
pH 12
pH 11
pH 10.4

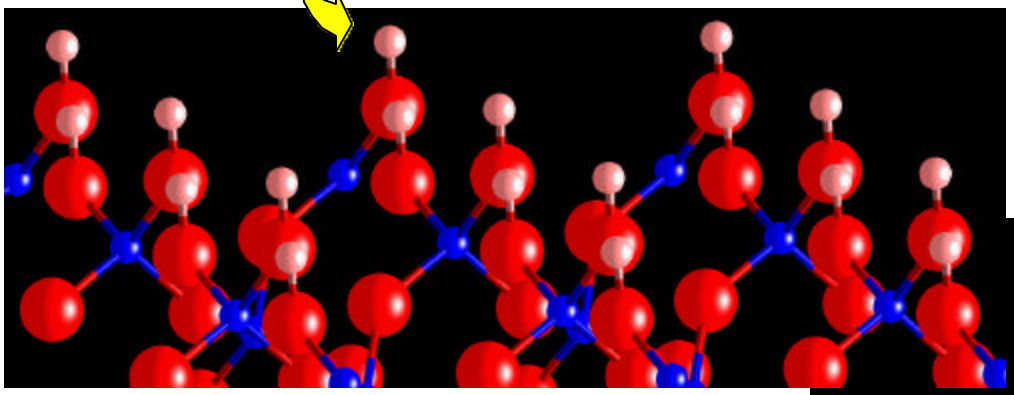
Effect of [$NaNO_3$] and [Al] on Quartz Dissolution Rate

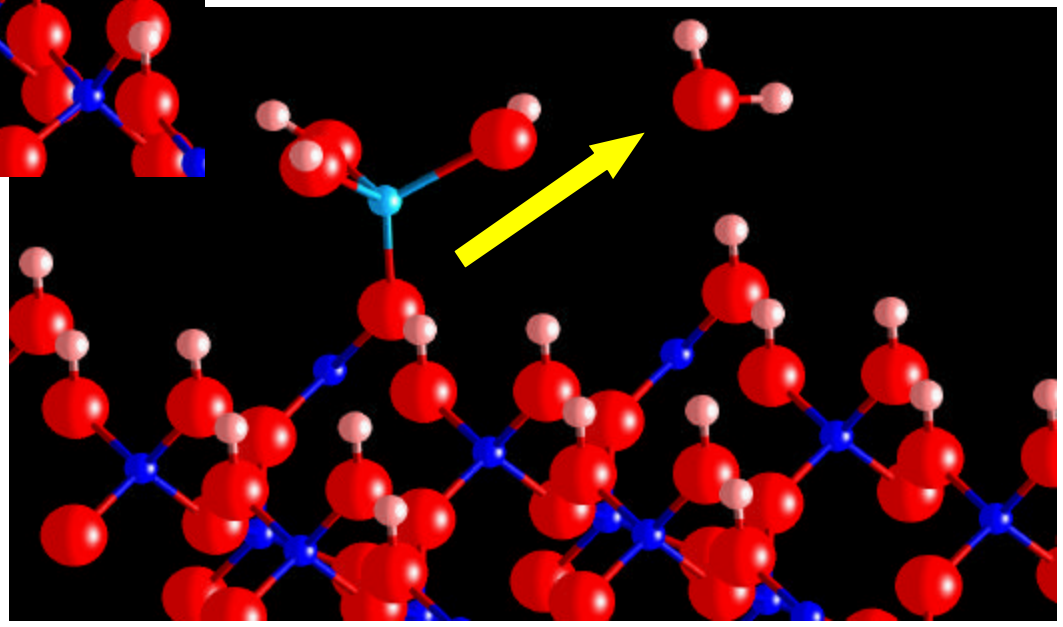
pH 11.4, 89°C



$$>Si\text{-}OH^{o} + Al(OH)_4^{-} \Rightarrow >Si\text{-}OAl(OH)_3^{-} + H_2O$$







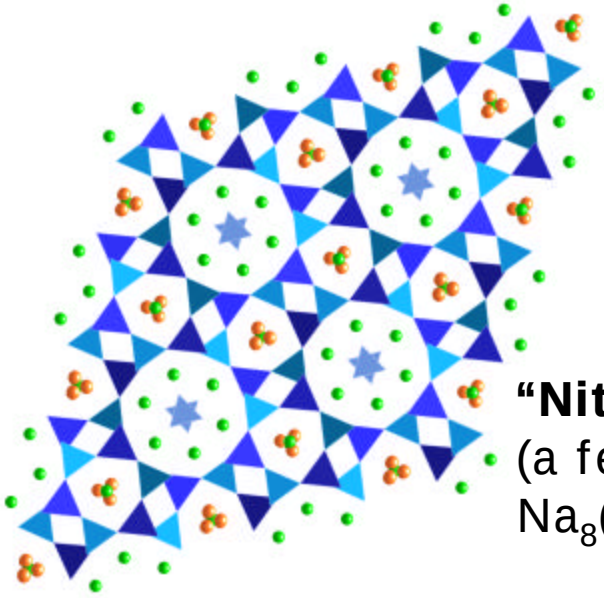
Effect of Aluminate on Quartz Dissolution Mechanism

Previous Model of Rate-Determining Sites

$$>Si\text{-}OH^{o} + Na^{+} \Rightarrow >SiO\text{-}Na + H^{+}$$

$$>Si\text{-}OH^{o} \Rightarrow >SiO^{-} + H^{+}$$

(Dove, 1994)



Al, Si

NO_3^-

Na^+

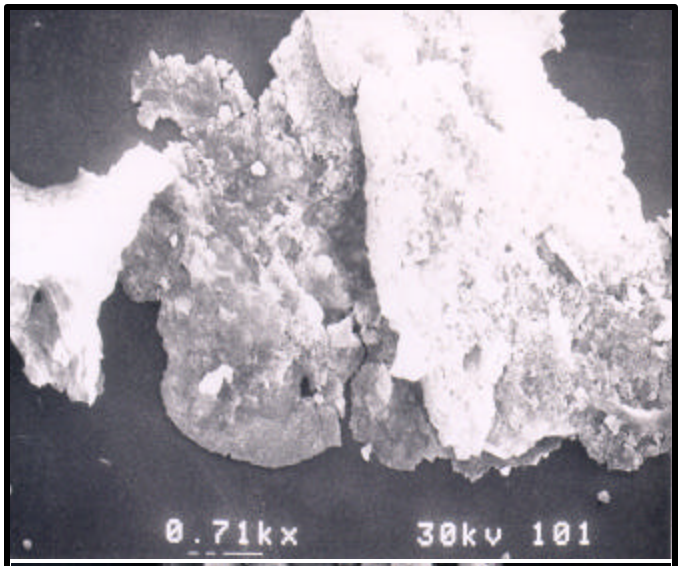
OH^-

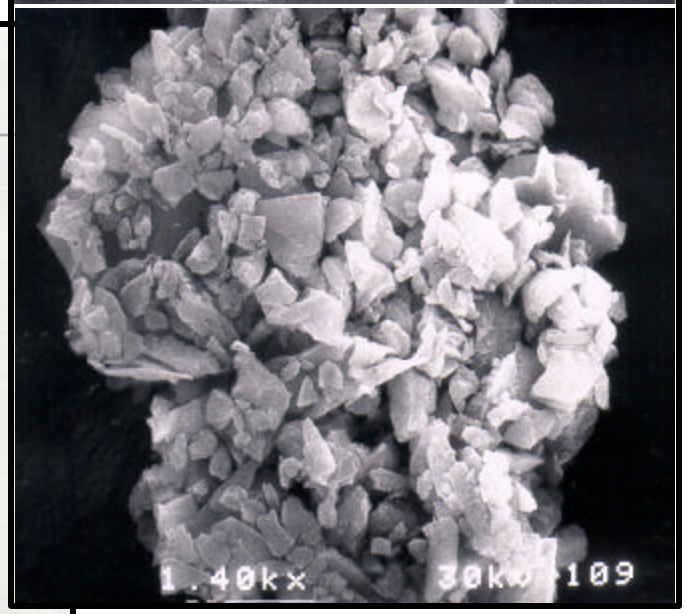
“Nitrate” Cancrinite

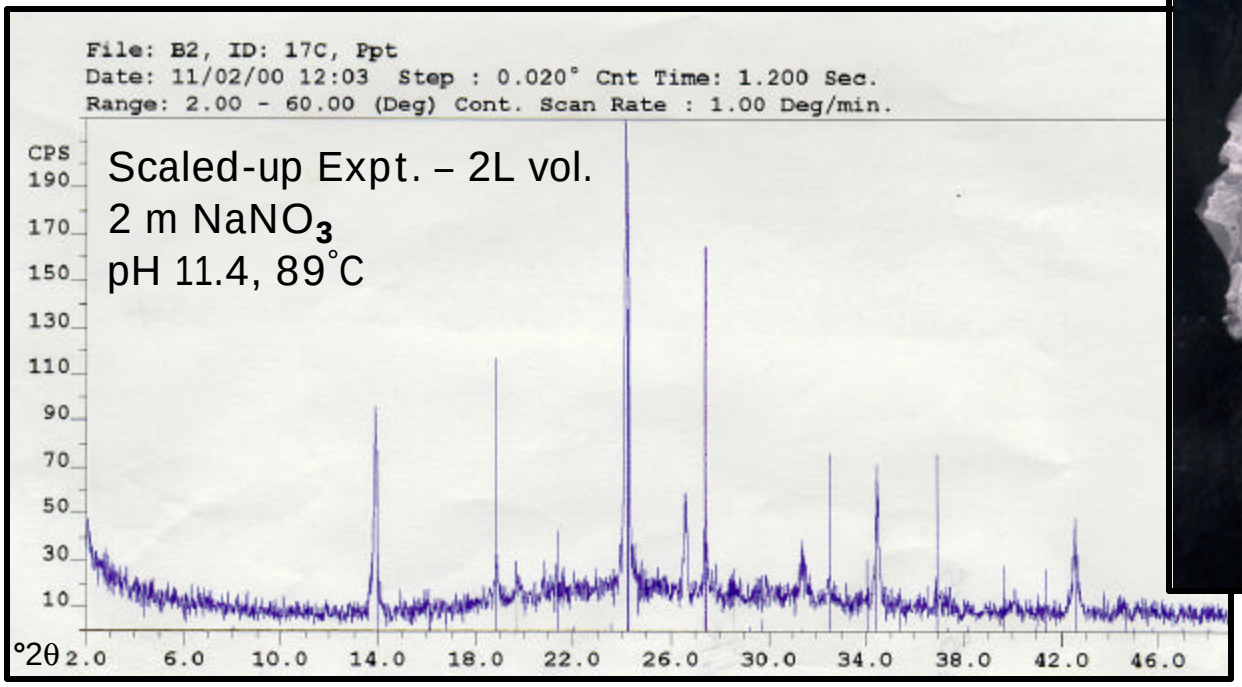
(a feldspathoid)

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

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



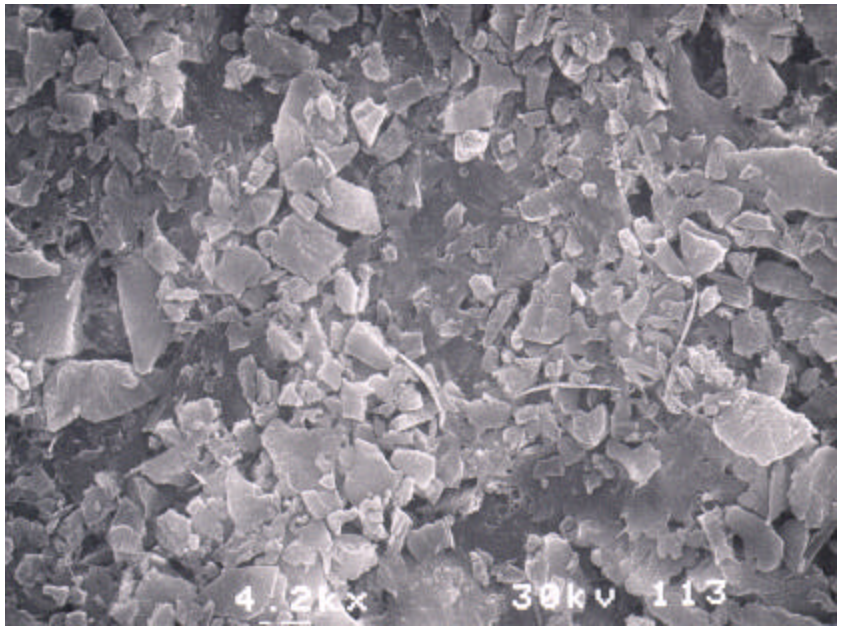


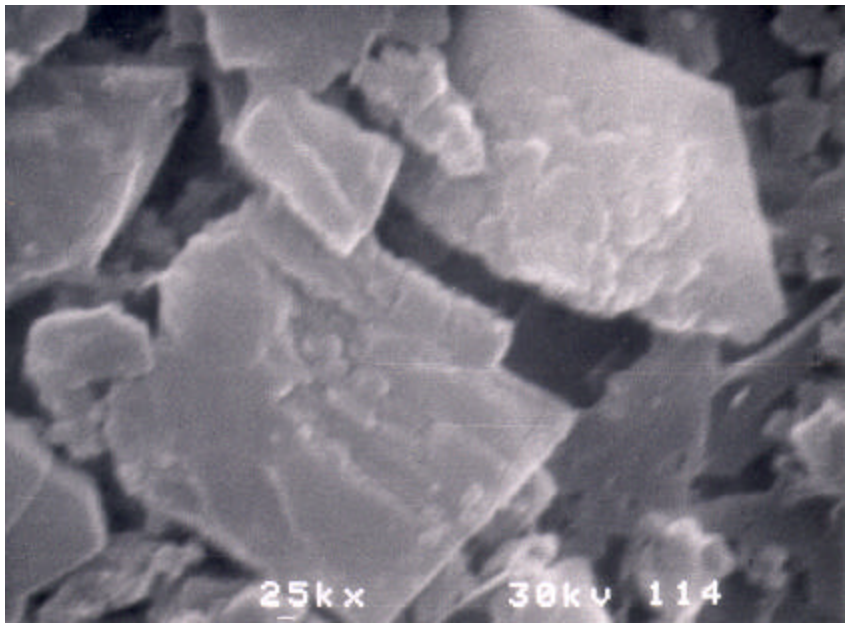


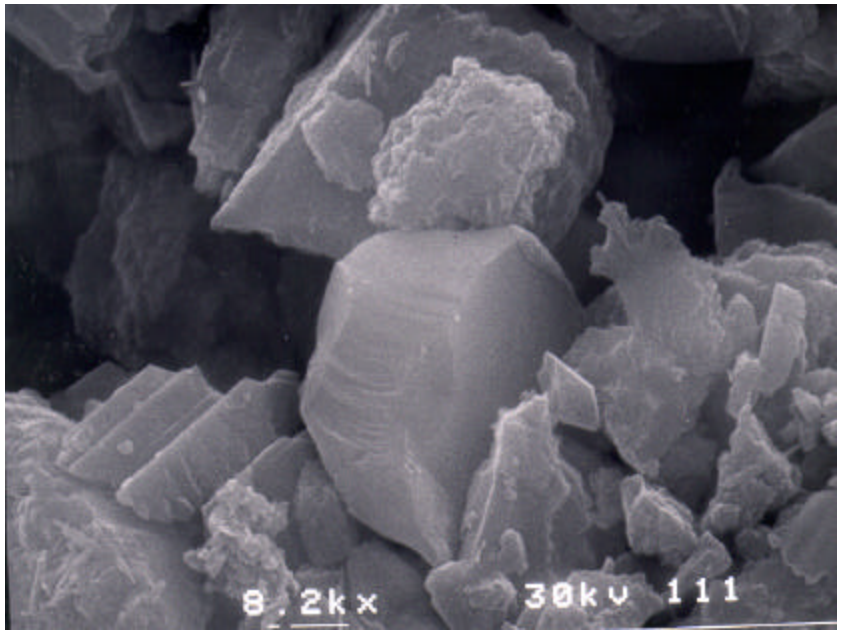
Scaled-up Expt. – 2L vol.

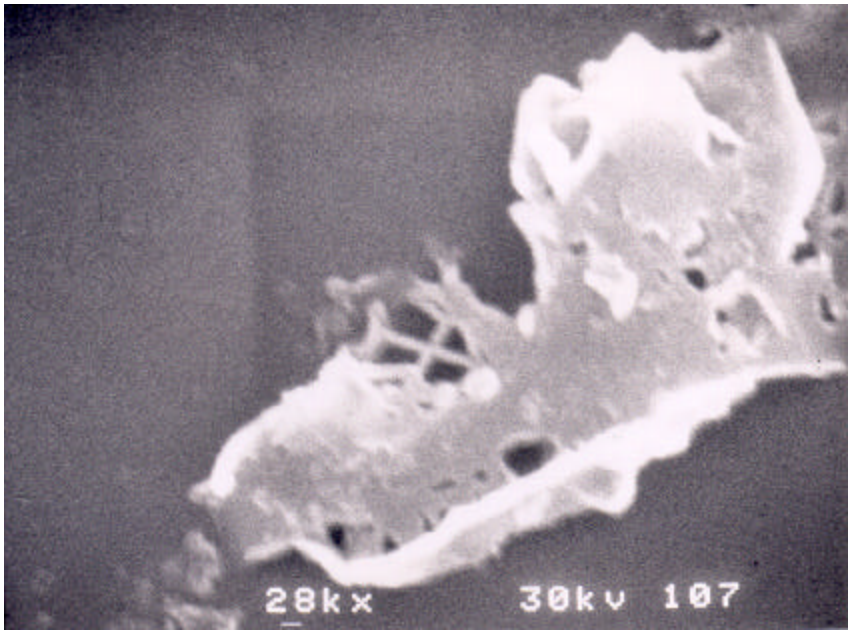
2 m $NaNO_3$

pH 11.4, 89°C


4.2kx 30kv 113


25kx 30kv 114

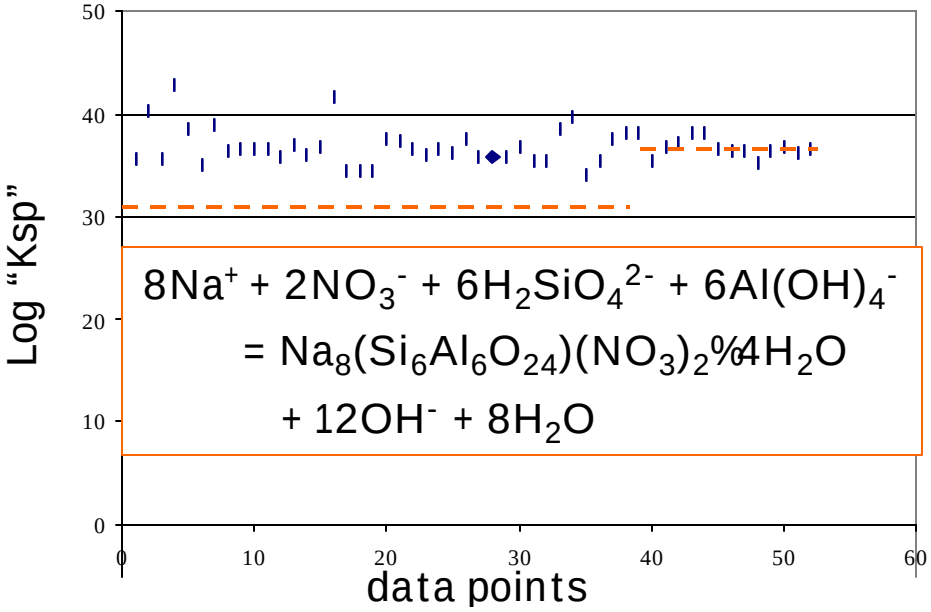

8.2kx 30kv 111

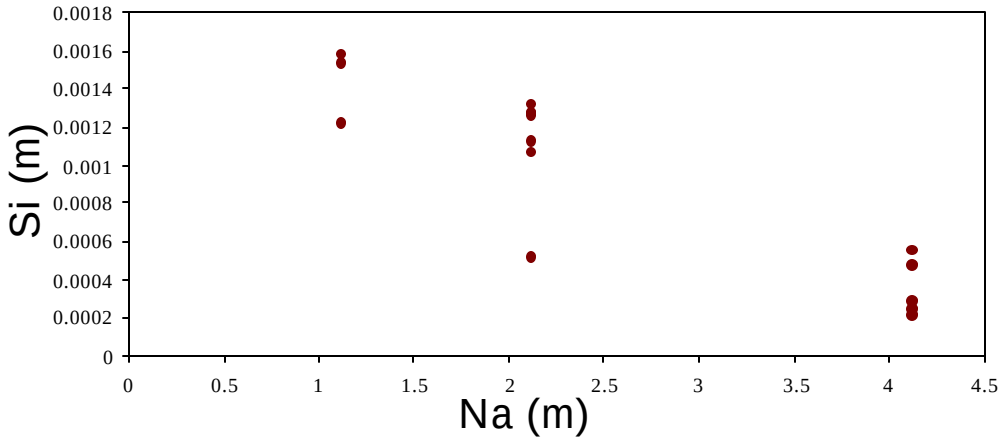

28kx 30kv 107

Cancrinite Phase Solubility: speculative!

$8Na^+ + 2NO_3^- + 6AlSiO_2(OH)_5^{2-} =$

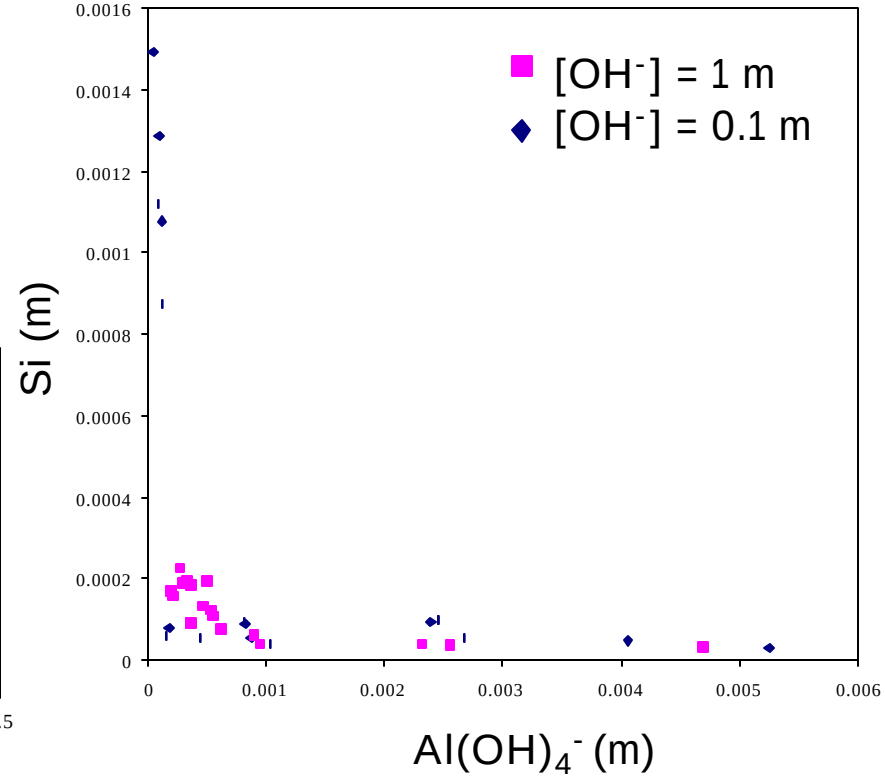
$Na_8(Si_6Al_6O_{24})(NO_3)_2 \cdot 4H_2O + 6OH^- + 16H_2O$





$Al(OH)_4^- + H_2SiO_4^{2-} =$

$AlSiO_2(OH)_5^{2-} + OH^-$



Fe(III)-Al-NO_3 solutions (initial pH < 1)
Neutralized to pH > 13 with 15 M NaOH at room T

Resulting caustic suspensions submerged in 90°C water bath and allowed to age

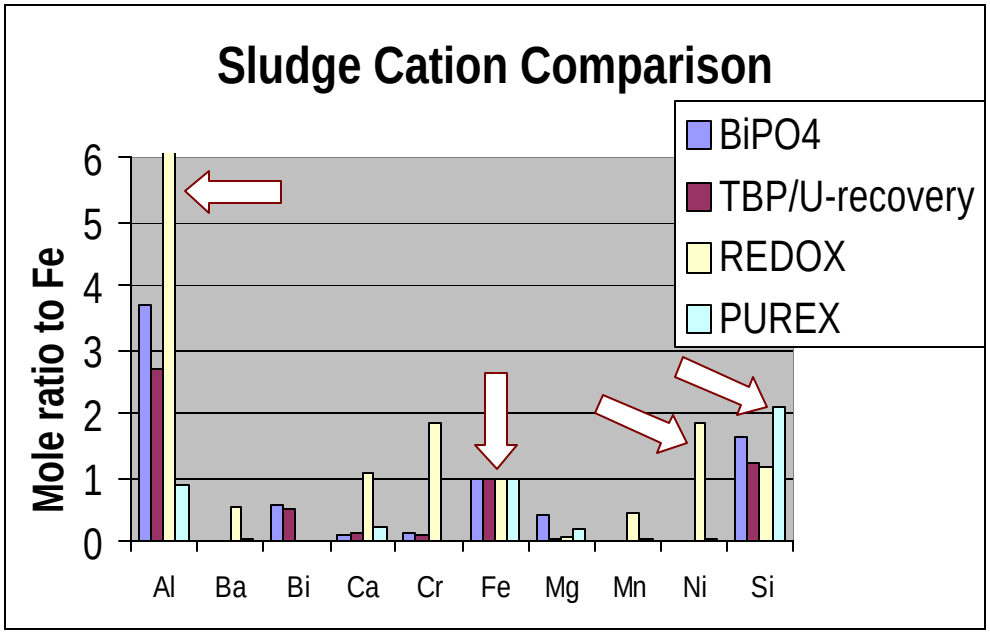
Sample aliquots of suspension removed and centrifuged

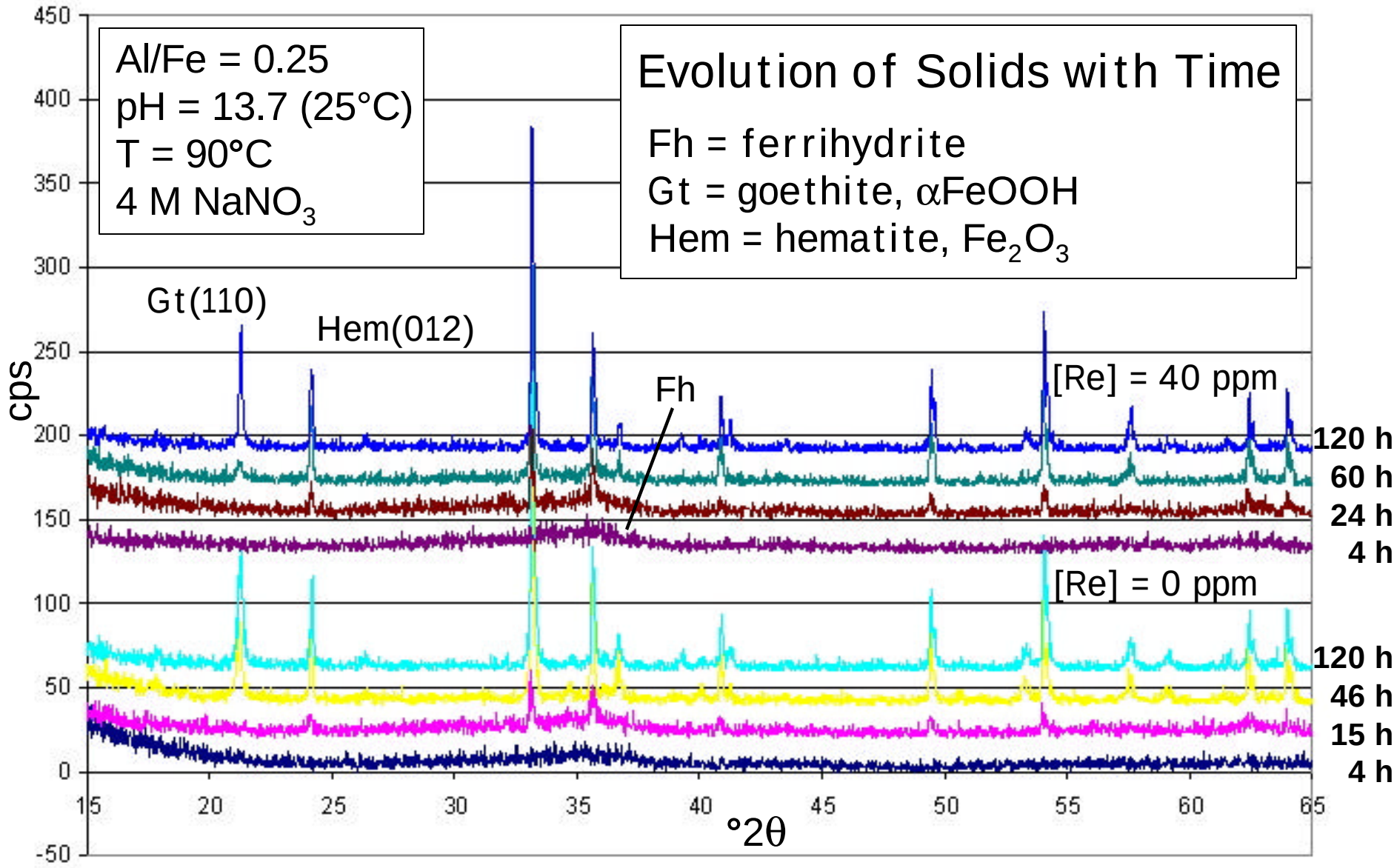
Supernatants decanted and filtered (0.45 µm)

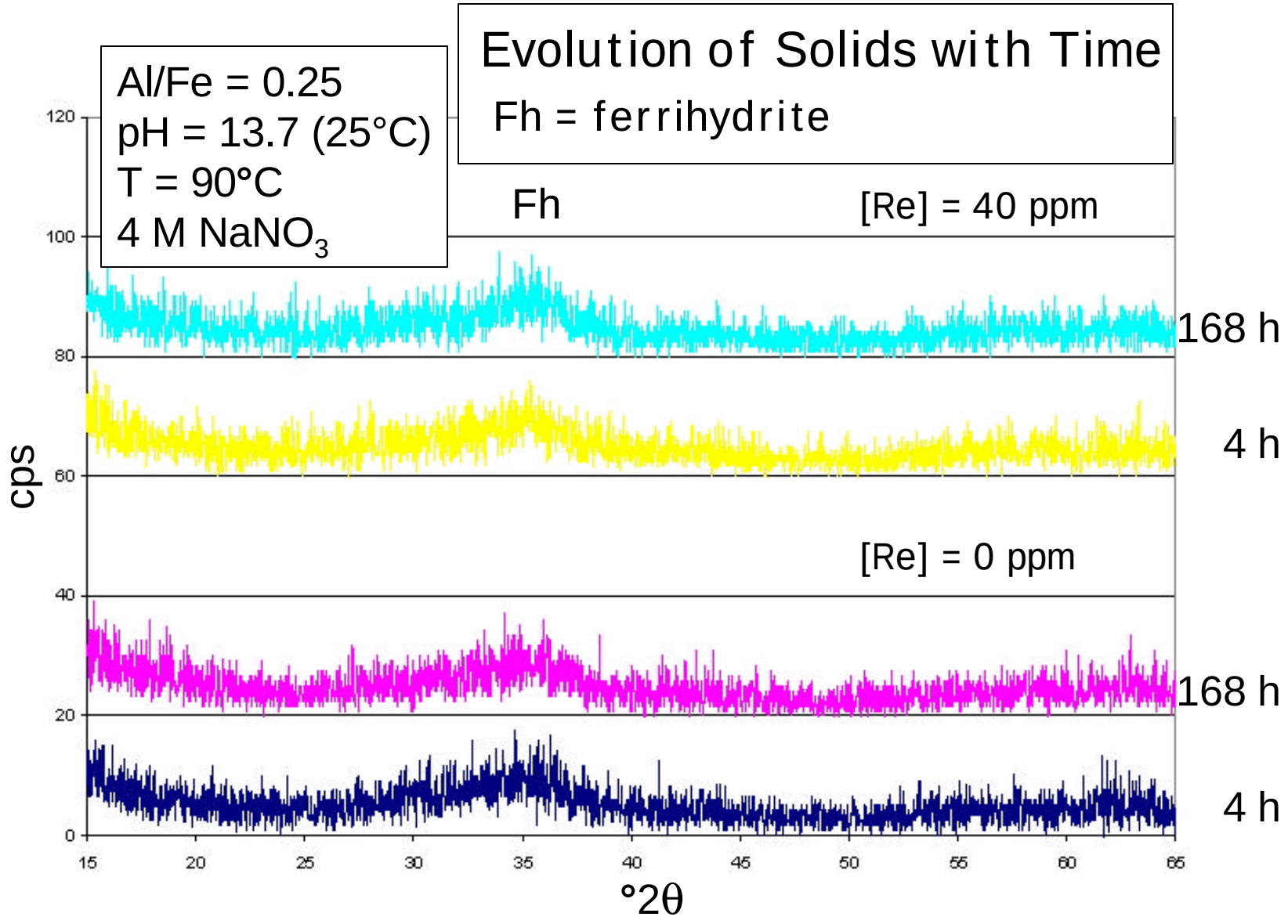
Solutions analyzed for Al, pH, and Re

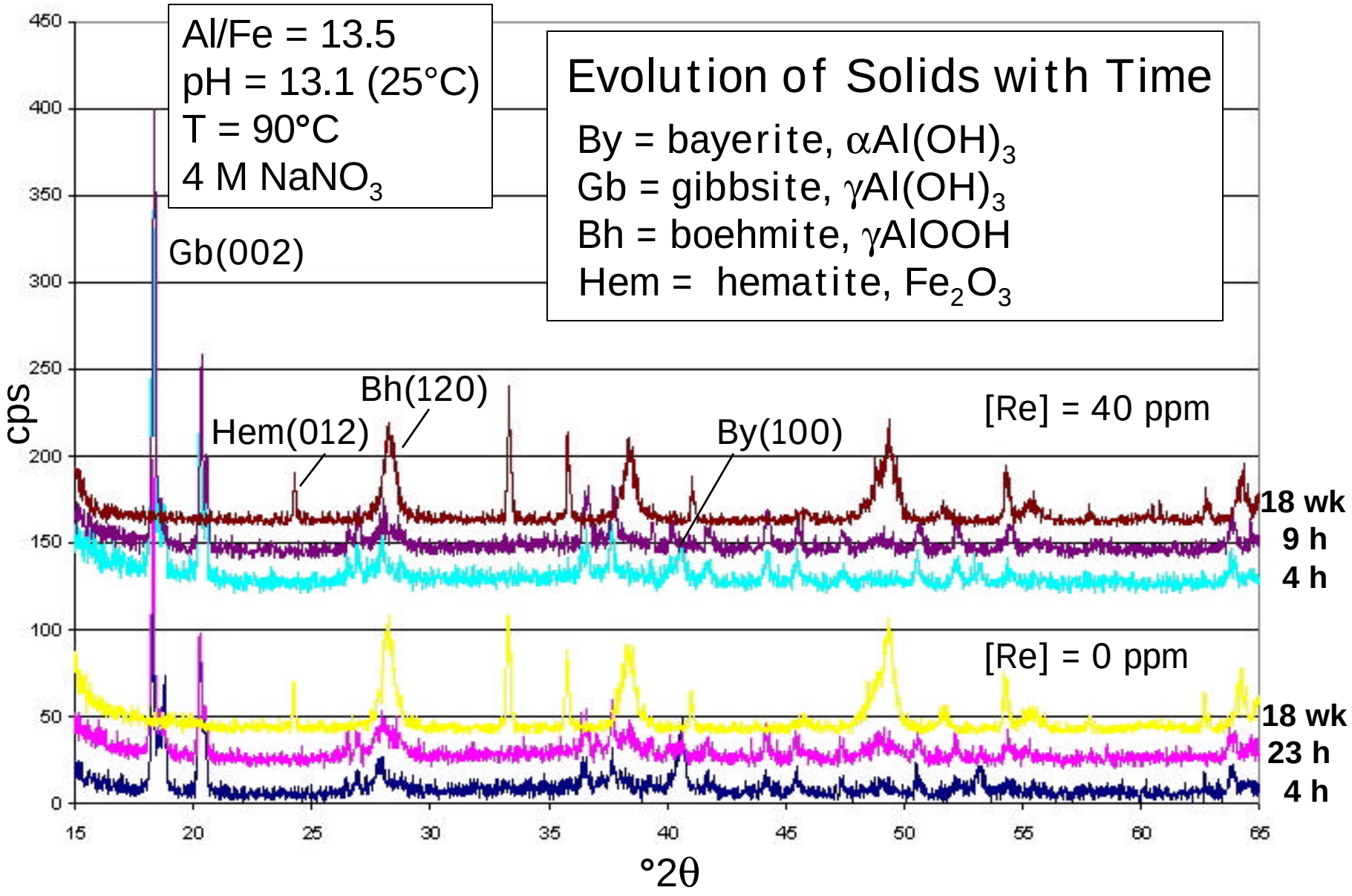
Solids dialyzed to remove excess salts, then freeze-dried

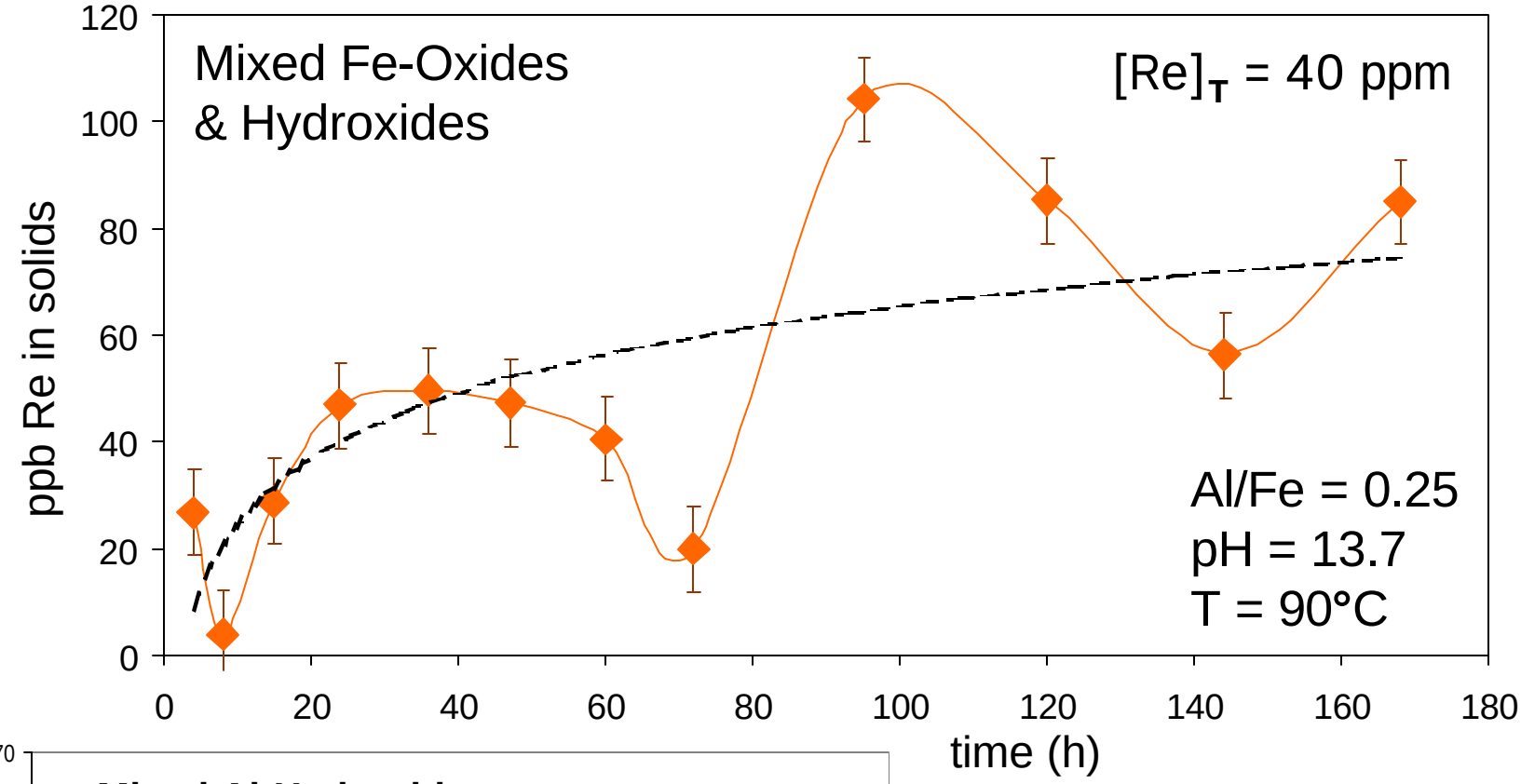
Solids X-rayed and analyzed for Re using ICP-MS

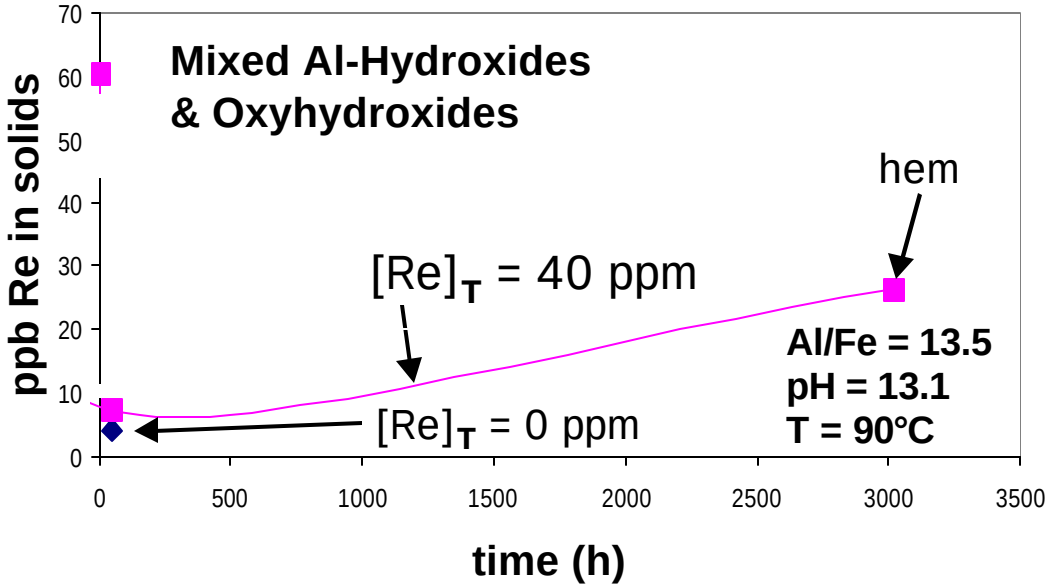


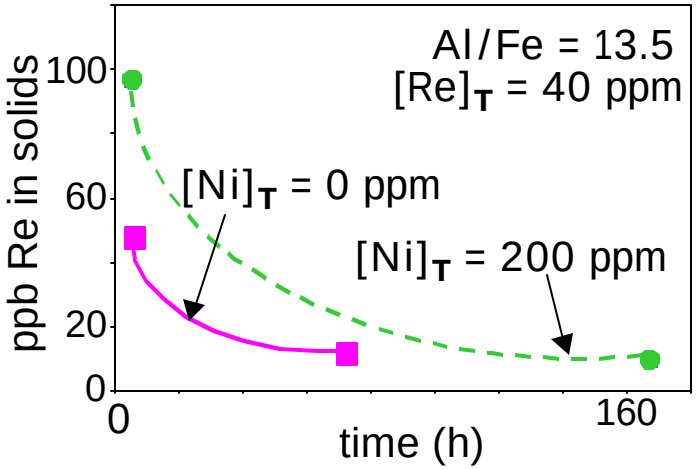

Al/Fe = 0.25
pH = 13.7 (25°C)
T = 90°C
4 M NaNO3
Evolution of Solids with Time
Fh = ferrihydrite
Gt = goethite, αFeOOH
Hem = hematite, Fe2O3
Gt(110)
Hem(012)
Fh
[Re] = 40 ppm
[Re] = 0 ppm
120 h
60 h
24 h
4 h
120 h
46 h
15 h
4 h
cps
°2θ
450
400
350
300
250
200
150
100
50
0
-50
15
20
25
30
35
40
45
50
55
60
65

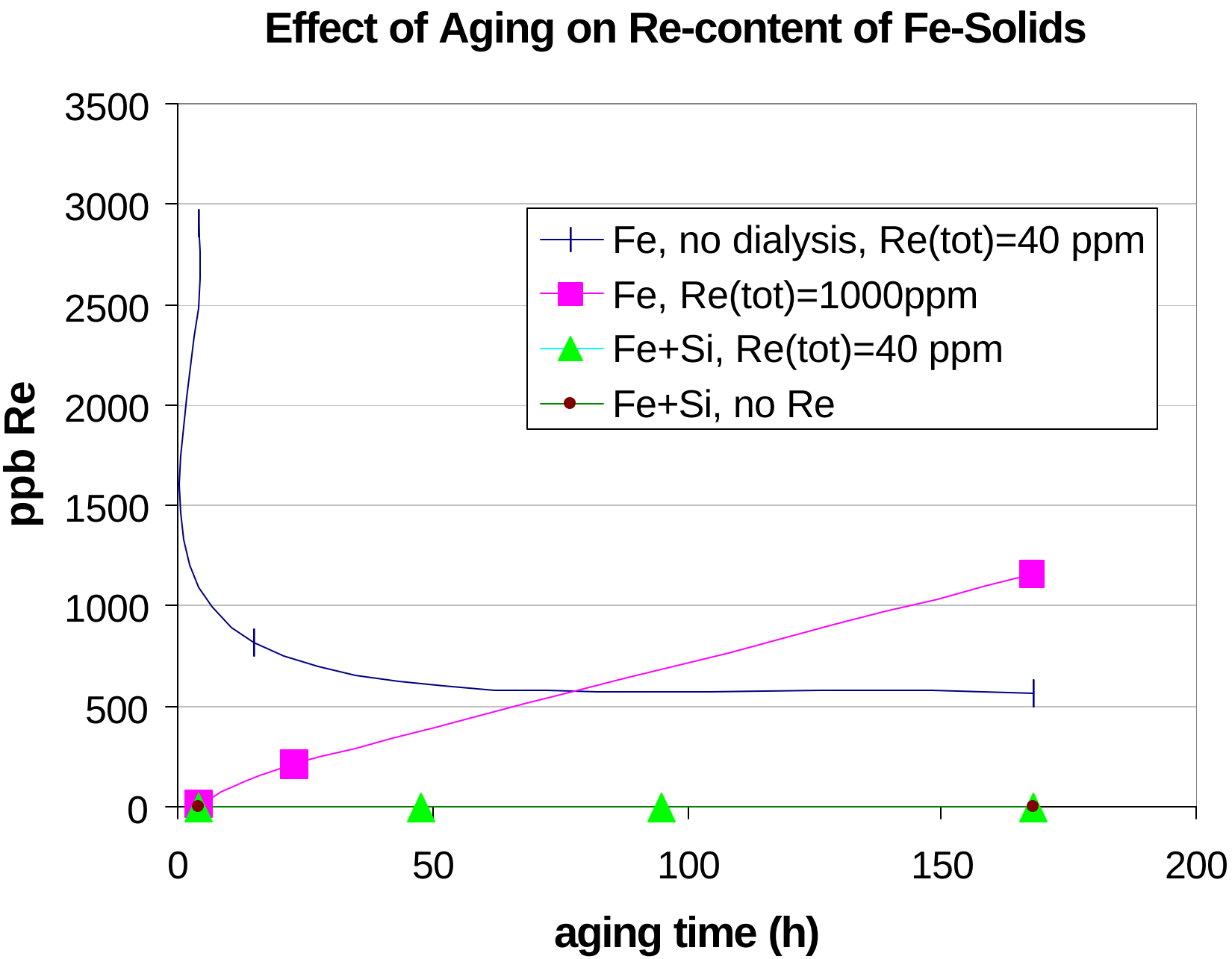

Evolution of Solids with Time
Fh = ferrihydrite
Al/Fe = 0.25
pH = 13.7 (25°C)
T = 90°C
4 M NaNO3
Fh
[Re] = 40 ppm
168 h
4 h
[Re] = 0 ppm
168 h
4 h
cps
°2θ
120
100
80
60
40
20
0
15
20
25
30
35
40
45
50
55
60
65


Al/Fe = 13.5
pH = 13.1 (25°C)
T = 90°C
4 M NaNO3
Evolution of Solids with Time
By = bayerite, αAl(OH)3
Gb = gibbsite, γAl(OH)3
Bh = boehmite, γAlOOH
Hem = hematite, Fe2O3
Gb(002)
Bh(120)
Hem(012)
By(100)
[Re] = 40 ppm
18 wk
9 h
4 h
[Re] = 0 ppm
18 wk
23 h
4 h
cps
°2θ
450
400
350
300
250
200
150
100
50
0
15
20
25
30
35
40
45
50
55
60
65


Mixed Fe-Oxides
& Hydroxides
[Re]T = 40 ppm
Al/Fe = 0.25
pH = 13.7
T = 90°C
ppb Re in solids
time (h)
0
20
40
60
80
100
120
140
160
180


Mixed Al-Hydroxides
& Oxyhydroxides
hem
[Re]T = 40 ppm
[Re]T = 0 ppm
Al/Fe = 13.5
pH = 13.1
T = 90°C
ppb Re in solids
time (h)


Al/Fe = 13.5
[Re]T = 40 ppm
[Ni]T = 0 ppm
[Ni]T = 200 ppm
ppb Re in solids
time (h)


Effect of Aging on Re-content of Fe-Solids
3500
3000
2500
2000
1500
1000
500
0
ppb Re
0
50
100
150
200
aging time (h)
Fe, no dialysis, Re(tot)=40 ppm
Fe, Re(tot)=1000ppm
Fe+Si, Re(tot)=40 ppm
Fe+Si, no Re

Schedule

Year 2:

- Perform batch experiments reacting tank simulates with Hanford sediments (PNNL)
- Increase Al concentration in fundamental kinetics experiments to determine effect of Al-phase formation on reactivity of quartz (CU)
- Continue saturated flow column experiments (PNNL)
- Conduct modeling experiments using new kinetic data (PNNL)
- Present and publish results

Year 3:

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

Information Needed

- Knowledge of secondary precipitates
  - in laboratory experiments (EMSL)
  - beneath tanks