Precipitation of U(VI) in Low-Temperature Si-Na-H_2O±CO_2±Feldspar Systems

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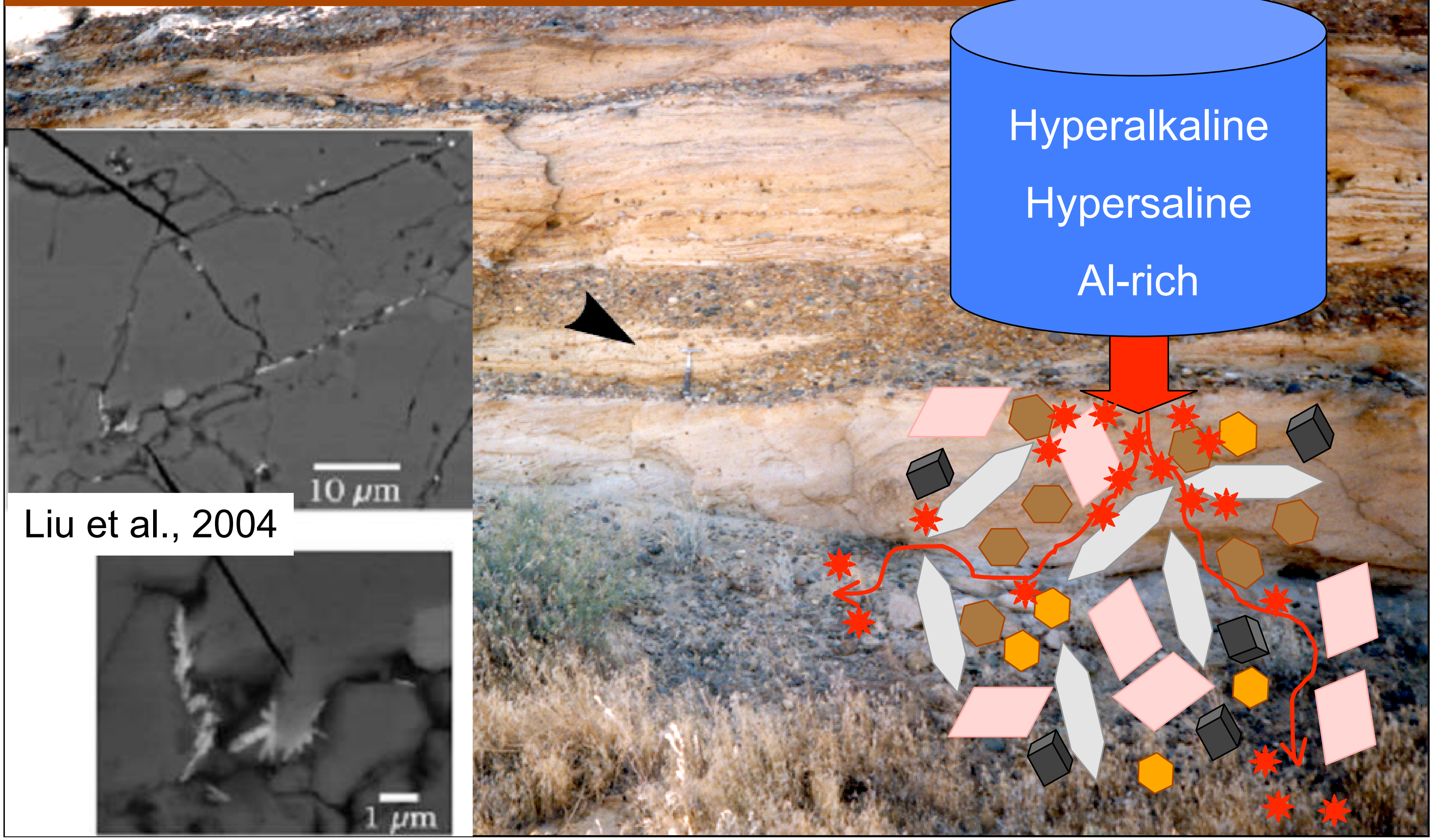
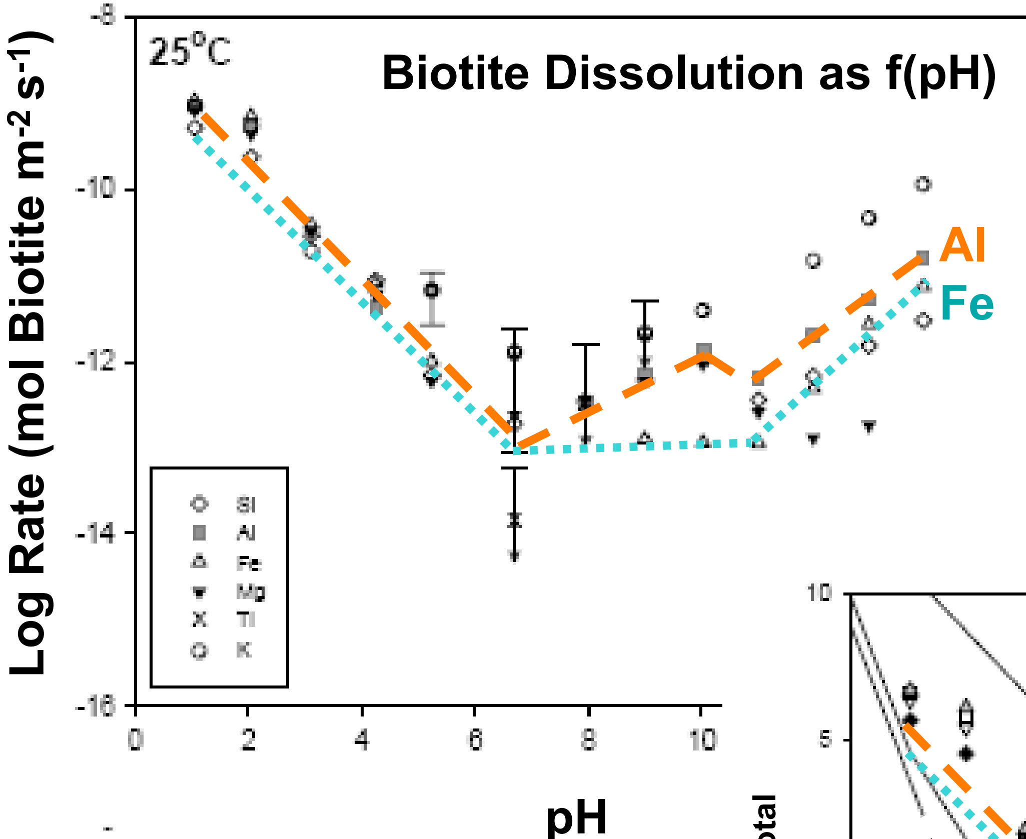
To identify and quantify processes motivated by observations from the Hanford Site

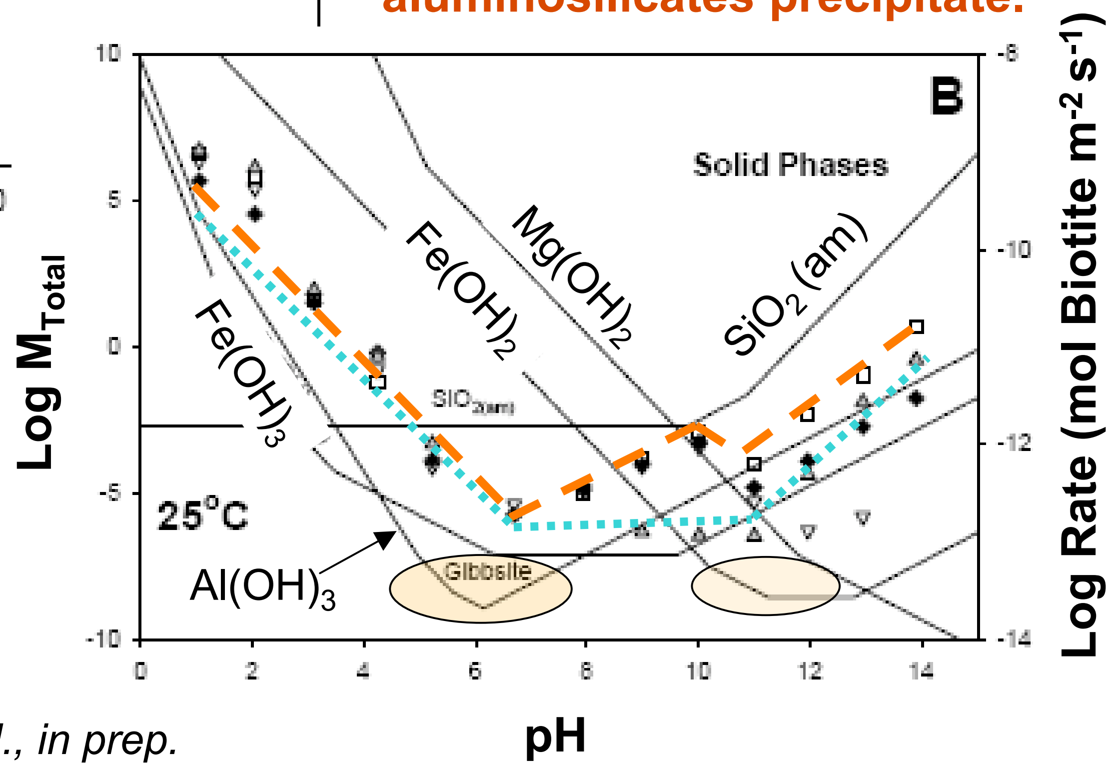




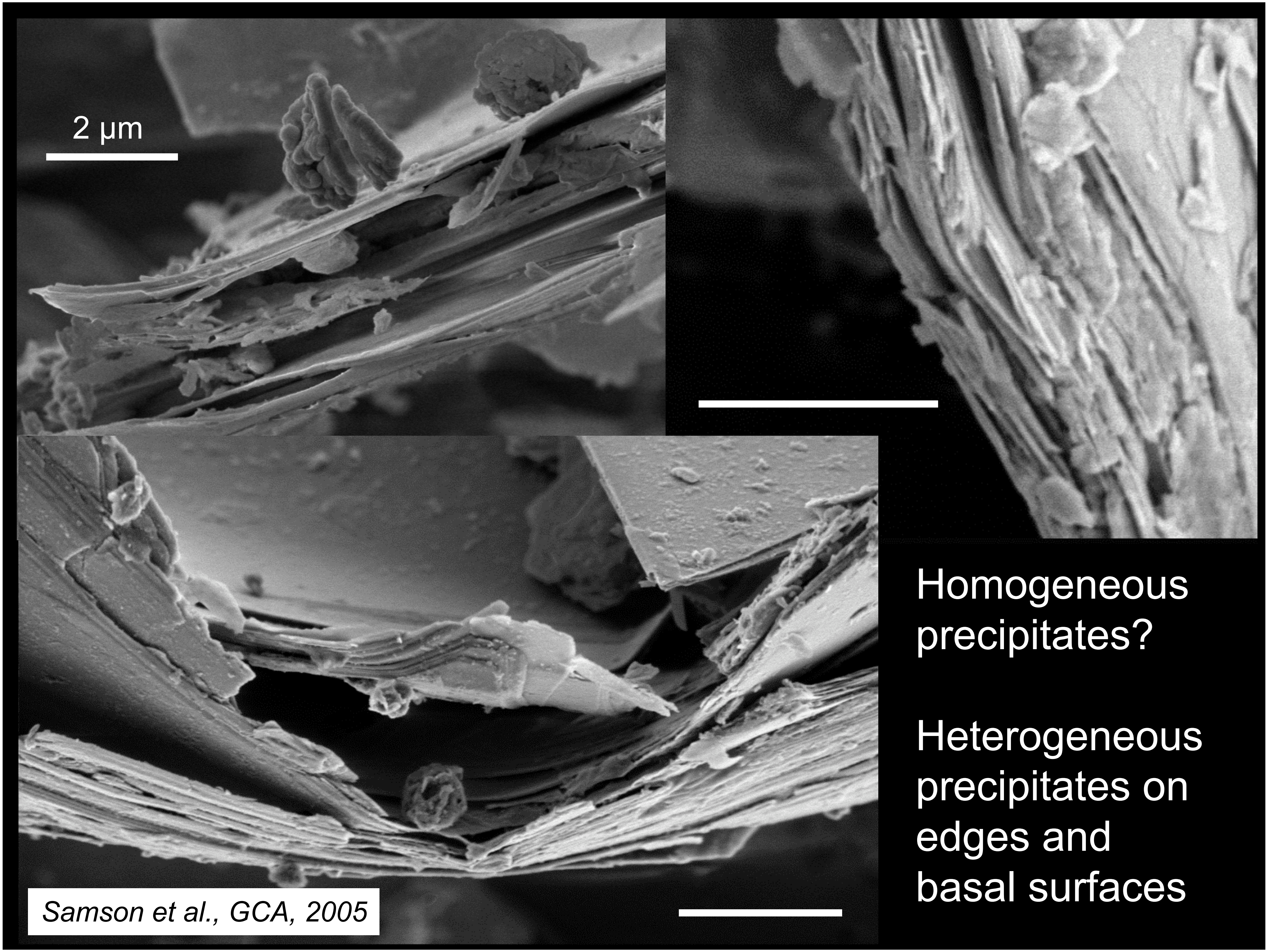
Biotite Mica Dissolution: released Fe(II) that was electron donor for Cr(VI) precipitation.

Release of Fe(II) is rate-limiting dissolution step at pH > 10.

Fe(III)-oxide and aluminosilicates precipitate.



Samson et al., GCA, 2005; Nagy et al., in prep.

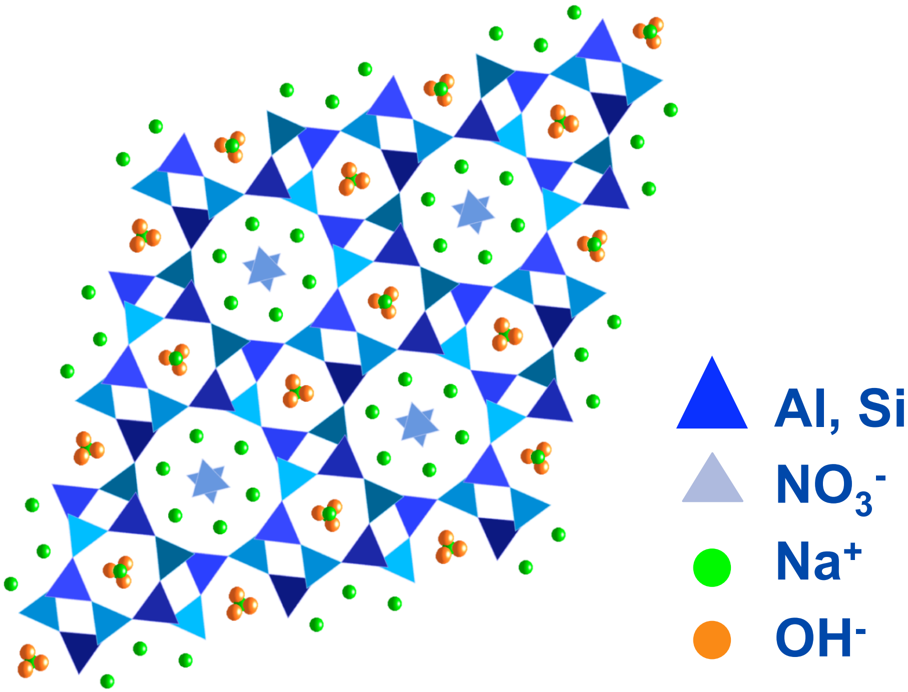

2 µm
Samson et al., GCA, 2005
Homogeneous precipitates?
Heterogeneous precipitates on edges and basal surfaces

Quartz Dissolution at 90°C, high pH:

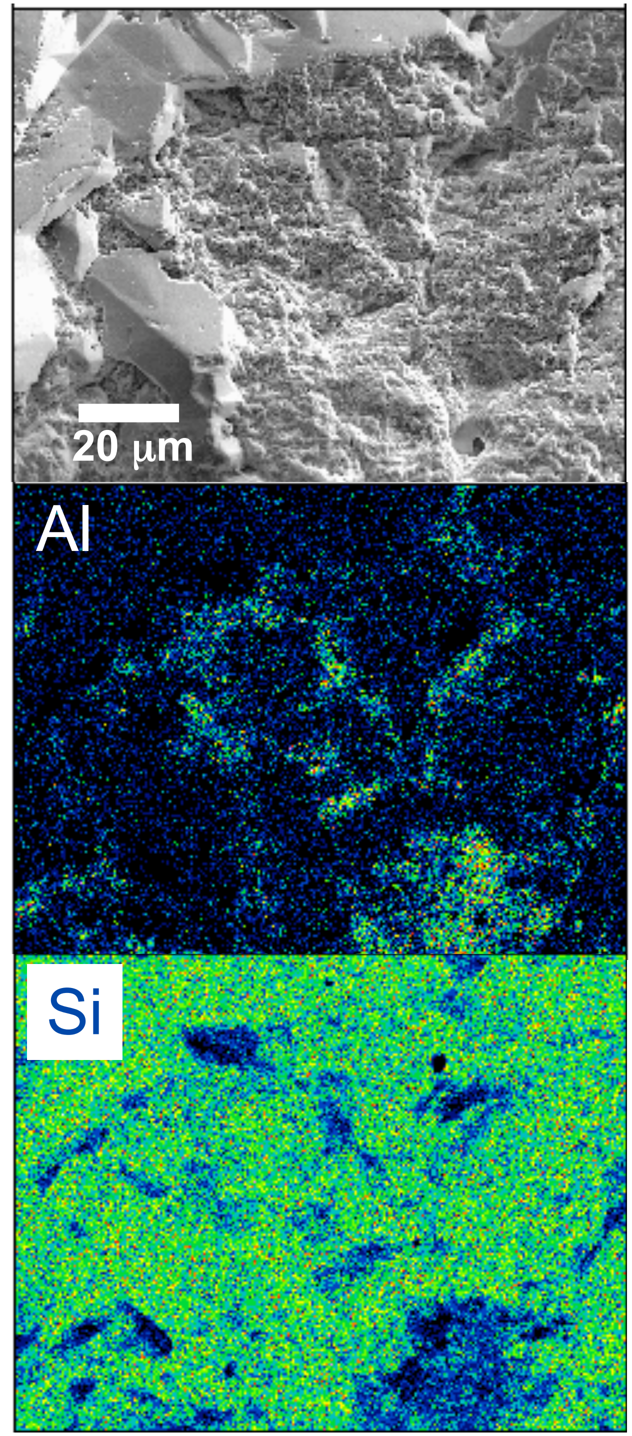
Nitrate Cancrinite precipitates;

Starts as a film in more recessed areas in quartz surface.

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

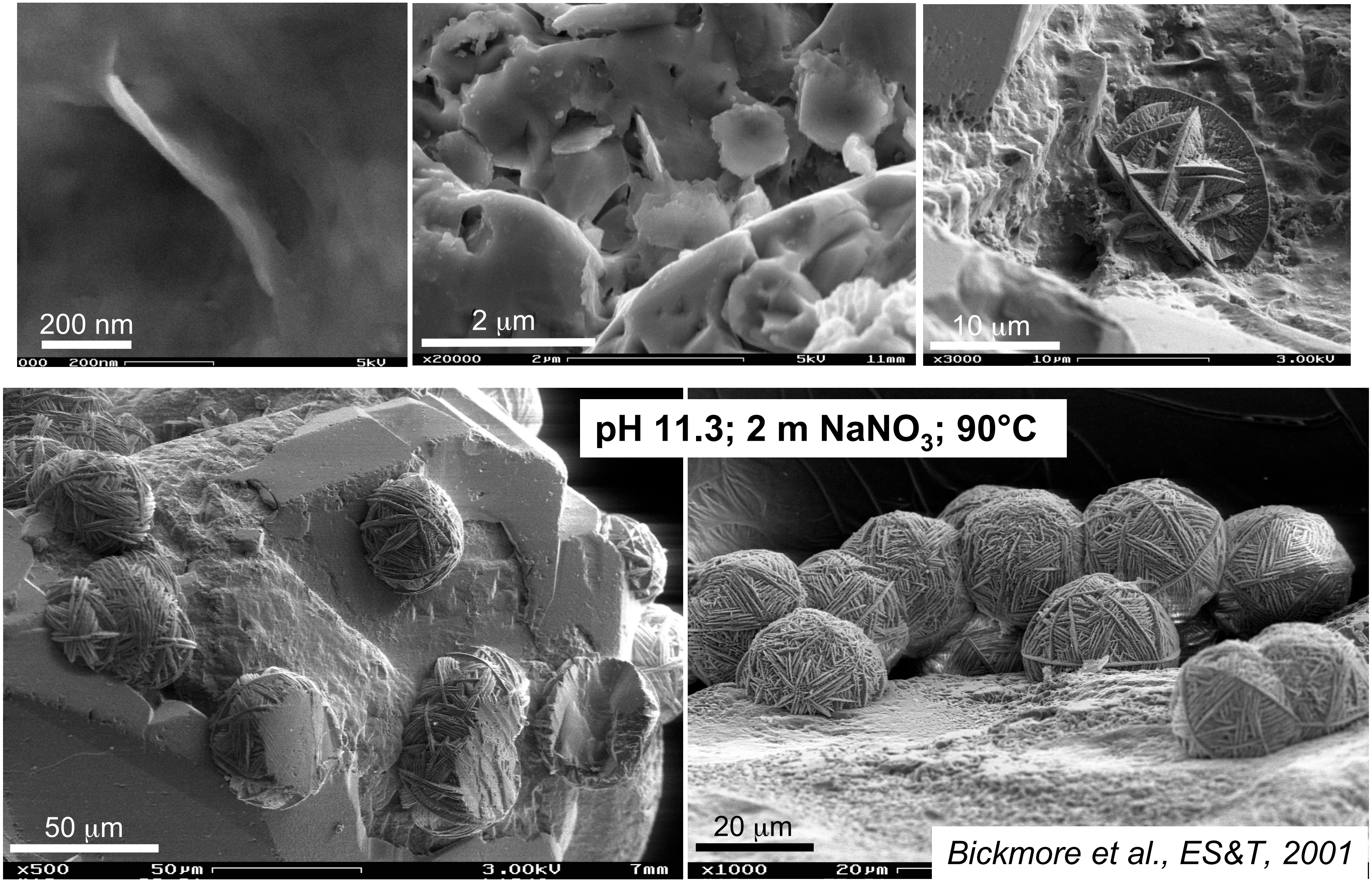


structure from Hund (1984) Z. Anorg. Atlg. Chem. 509, 153.



Bickmore et al., ES&T, 2001

Heterogeneous Precipitation of Nitrate Cancrinite on Quartz

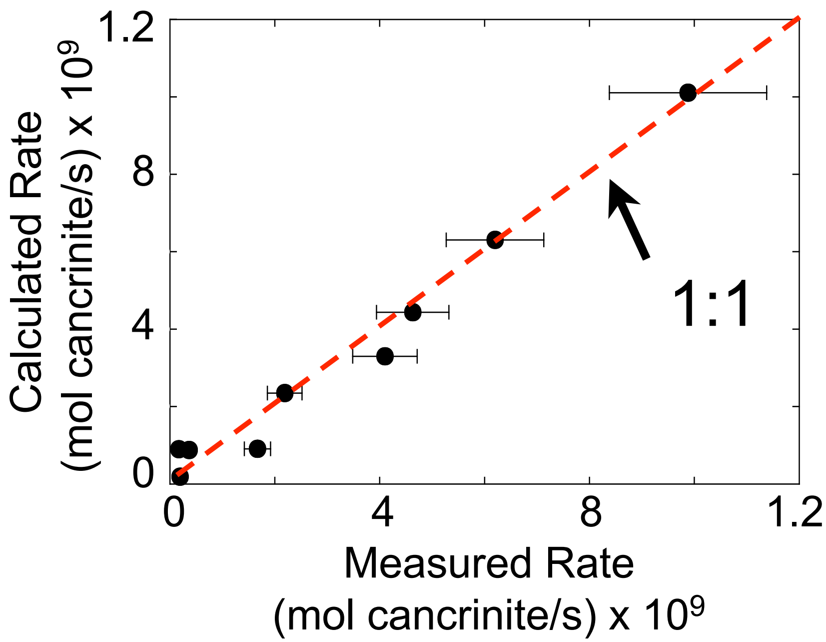


0.005 m $Al(OH)_4^-$ - 24 days

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

Initial Precipitation Rates

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



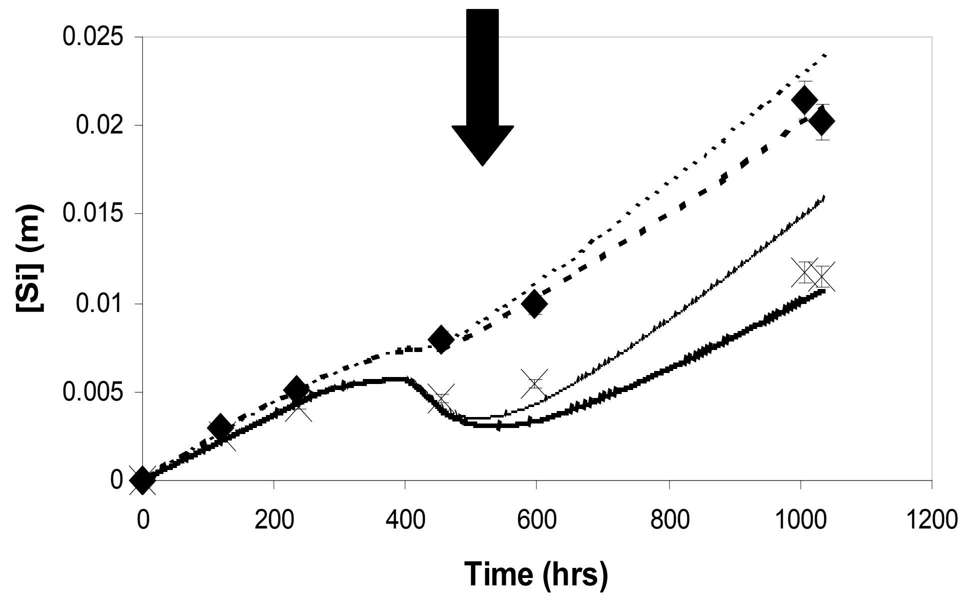
"Nitrate" Cancrinite

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

Bickmore et al., ES&T, 2001; GCA, 2006

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

+ Stoichiometric removal of Si and Al as cancrinite



NABIR Field Research Center

Oak Ridge Field Research Center

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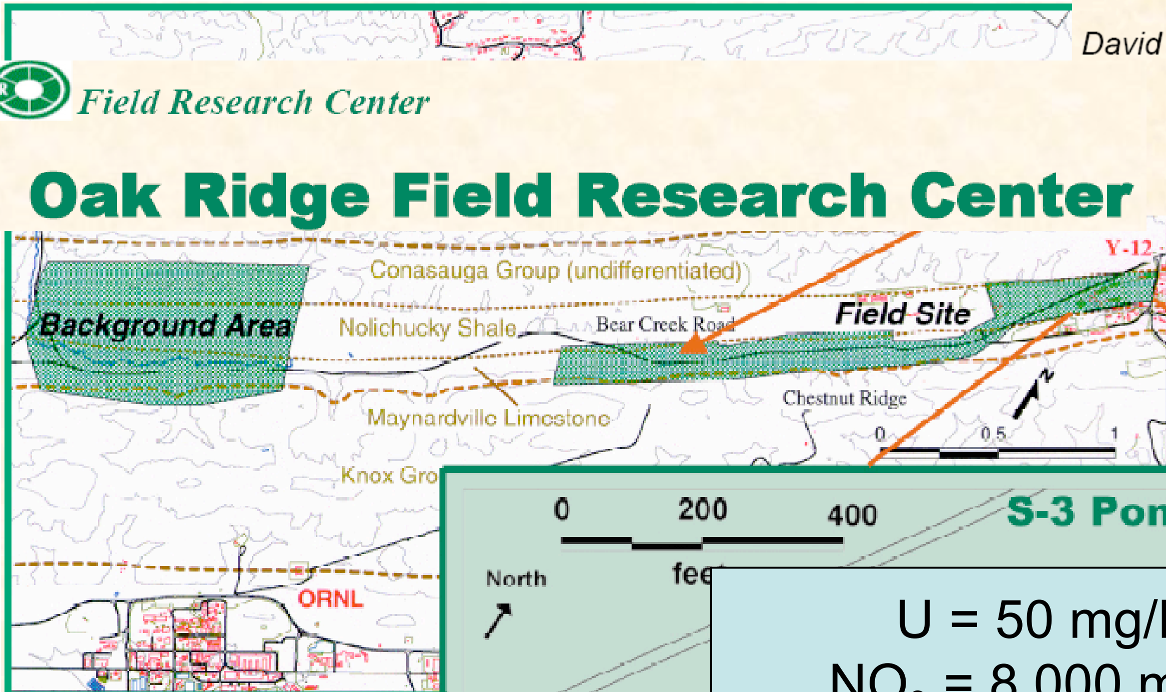
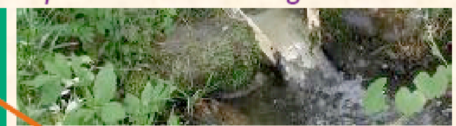
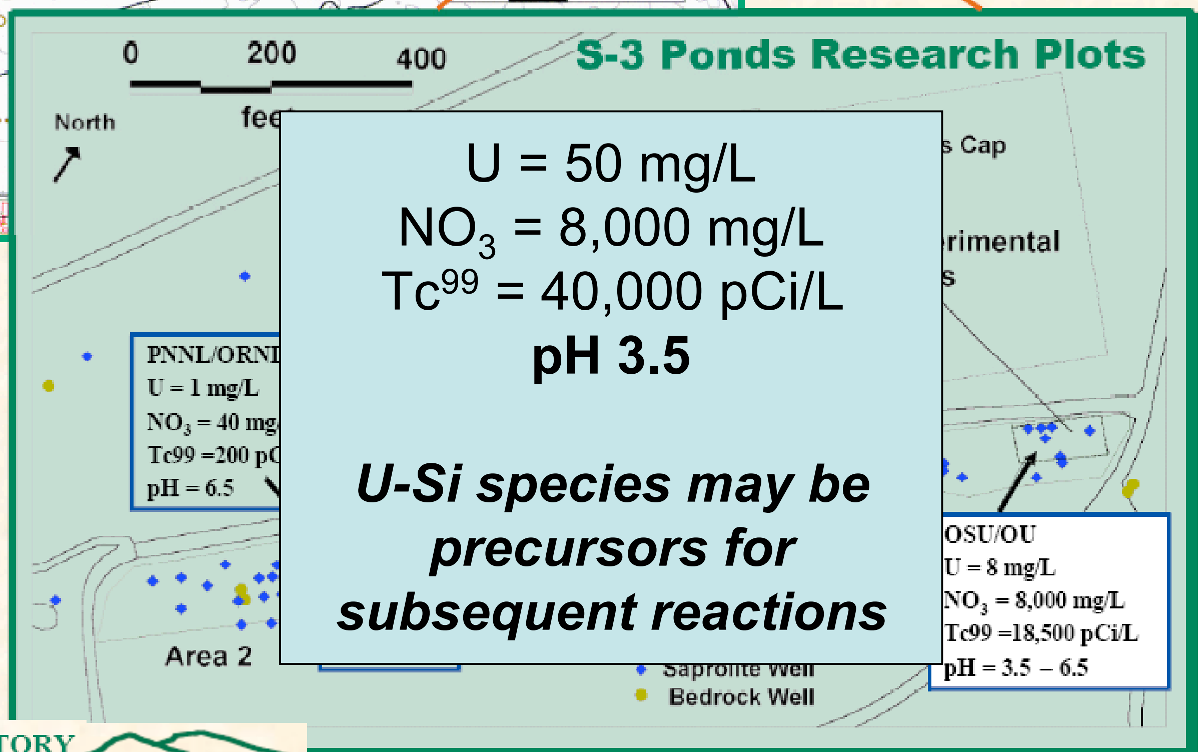


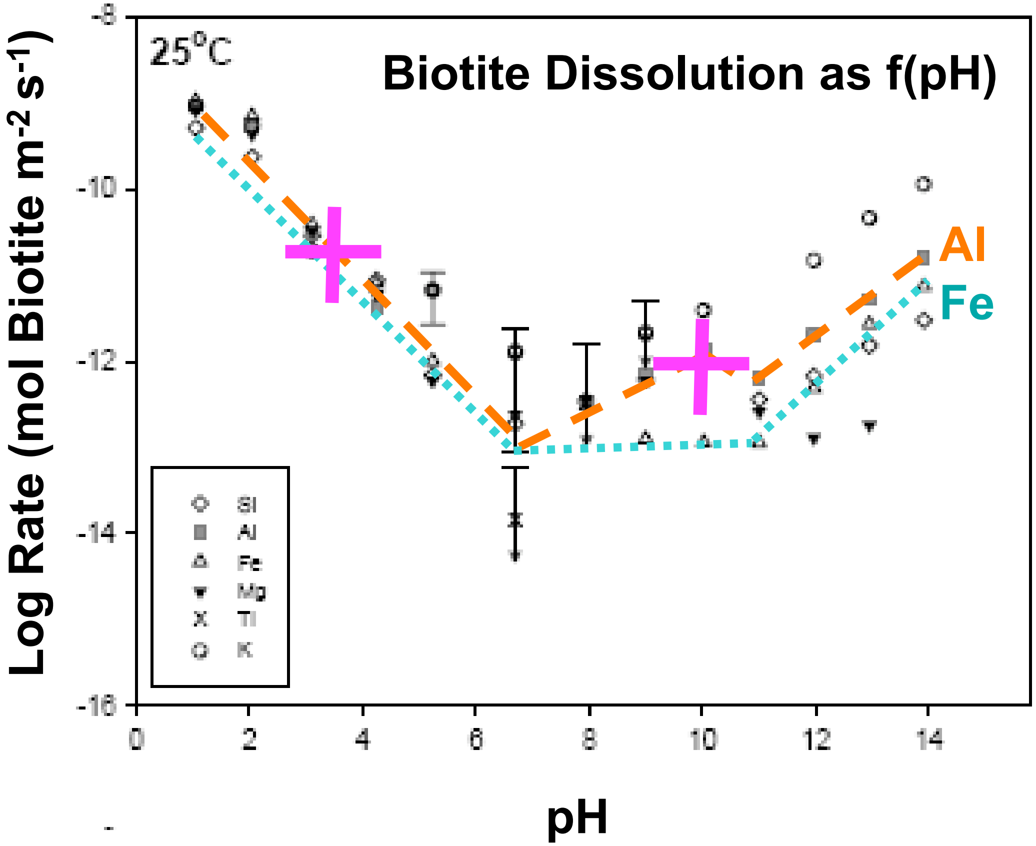




$U = 50$ mg/L
$NO_3 = 8{,}000$ mg/L
$Tc^{99} = 40{,}000$ pCi/L
pH 3.5

U-Si species may be precursors for subsequent reactions

Multiple Hydrogeologic Environments Available for Study

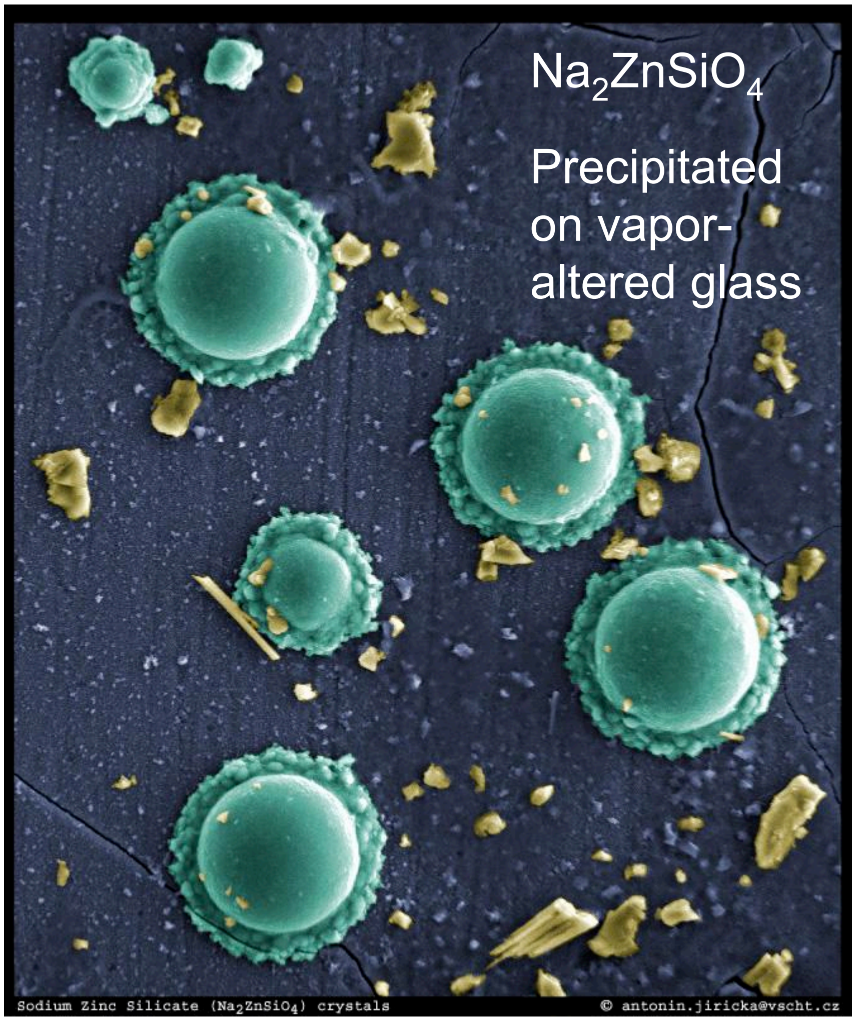


Aluminosilicate minerals dissolve faster in acidic and basic solutions than at neutral pH.

Samson et al., GCA, 2005; Nagy et al., in prep.

Uranium-silicates:

Alteration of spent fuel
Alteration of vitrified nuclear waste
Uranium mines



Soddyite

$(UO_2)_2(SiO_4)\cdot 2H_2O$

K-Boltwoodite

$K(UO_2)(SiO_3)(OH)\cdot 1.5H_2O$

Possible mechanism of U-Silicate formation

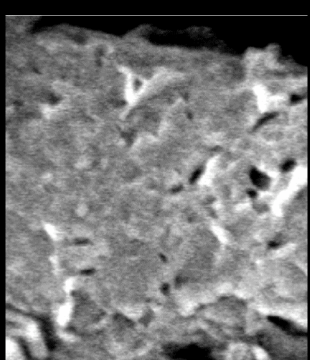
BX-102 Tank

U(VI) speciated as $UO_2(CO_3)_3^{4-}$
T = 80 °C; pH = 10

Na-boltwoodite; μ-XRD and μ-XRF (Catalano et al., 2004)

53% boltwoodite, 42% uranophane; 4% soddyite; TRLFS (time-resolved laser fluorescence spectroscopy) (Wang et al. 2005)

Na-boltwoodite or uranophane; dissolution (Liu et al. 2004)



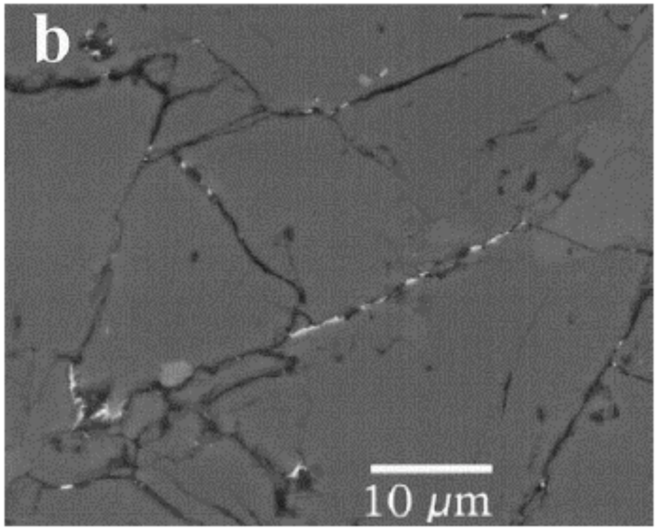
$SiO_{2(aq)}$ $SiO_{2(aq)}$ $SiO_{2(aq)}$ $SiO_{2(aq)}$ $SiO_{2(aq)}$ $SiO_{2(aq)}$

$UO_2^{2+} + SiO_2$

Uranyl silicate precipitation

Borehole Core Analysis

- Tank solutions diluted in vadose zone, but relative to background:
  - elevated concentration of uranium
  - lower concentration of silica
- T and pH decrease as the plume moves away from source

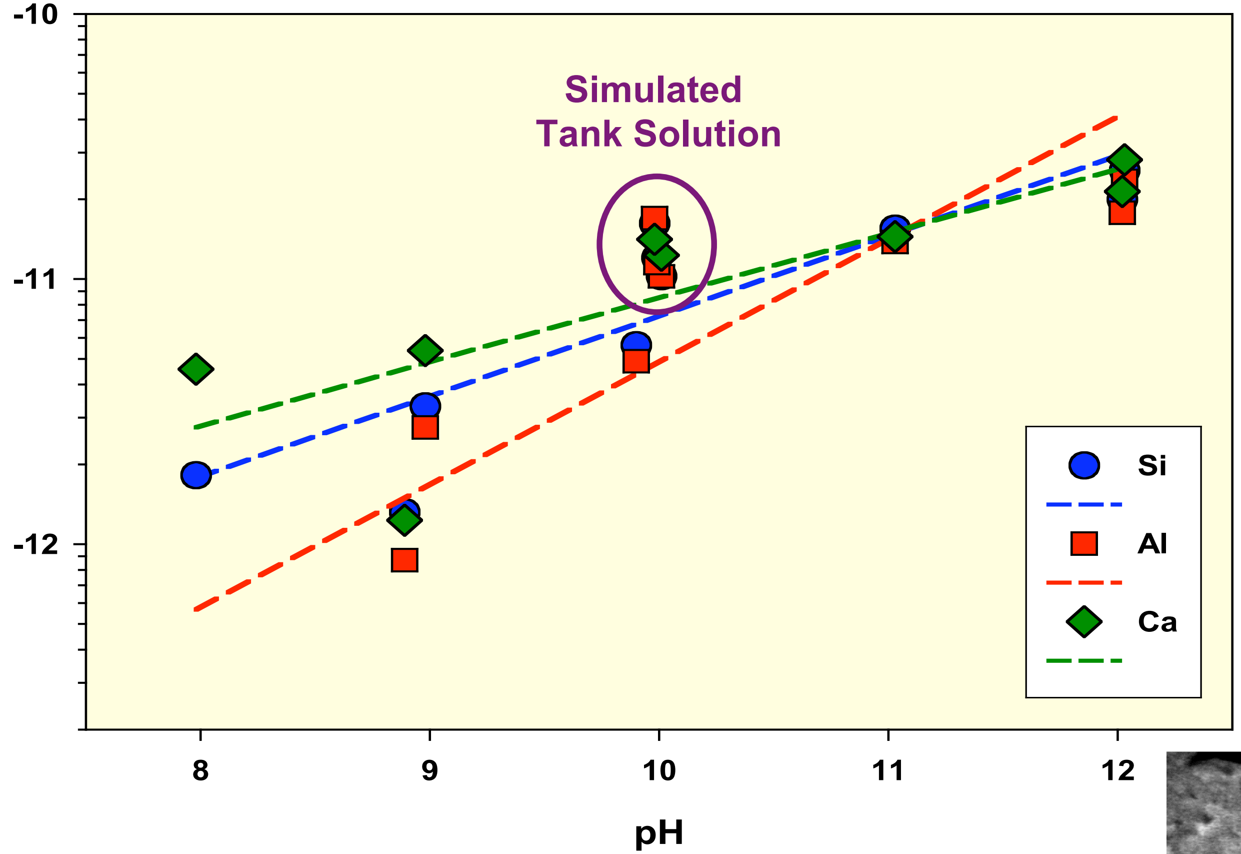


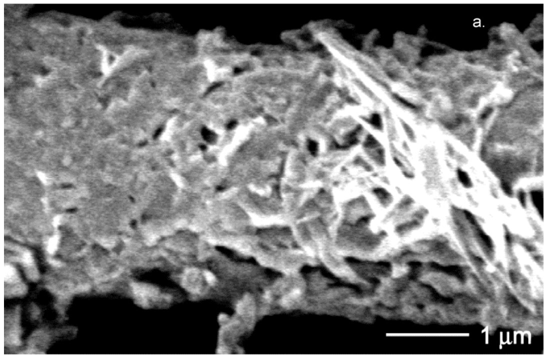
Liu et al., 2004, GCA

	UO_2^{++} (M)	$SiO_{2(aq)}$ (M)	pH	T°C
Tank Solution	1.03E-01	4.00E-03	10	80
Contaminated PW	1.85E-03	7.16E-04	9	
Uncontaminated PW	1.63E-07	4.99E-03		

Si Source for U-silicate formation:

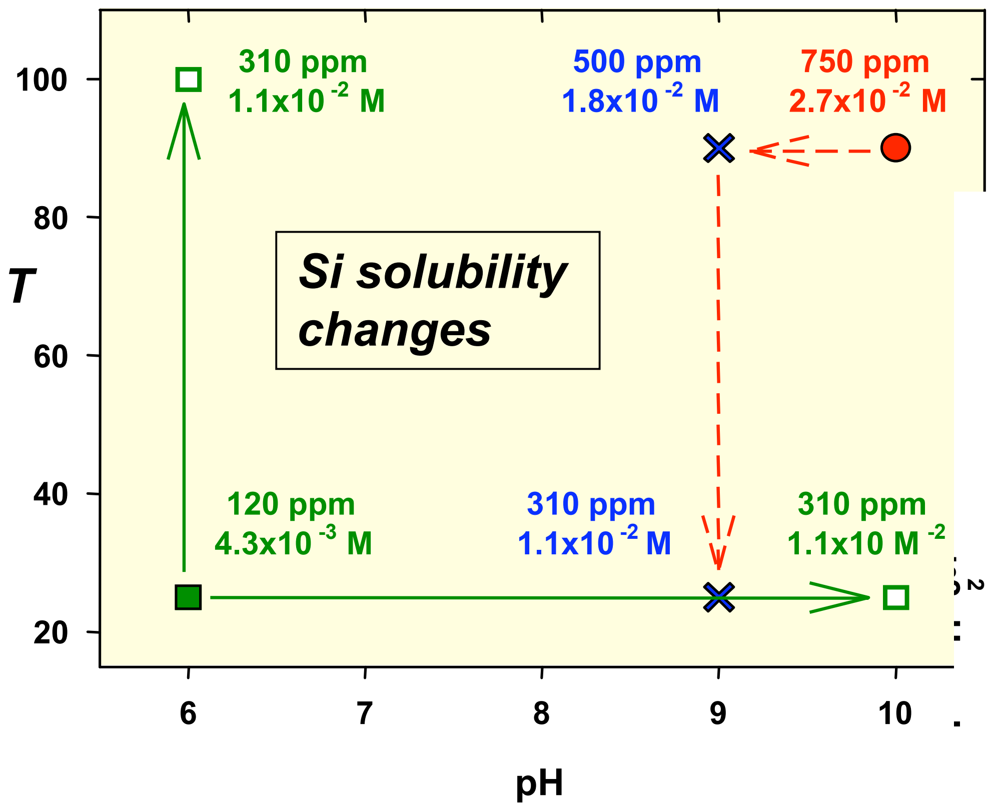
Dissolution of Labradorite Feldspar: An_{60} $Ca_{(50-70\%)}Na_{(50-30\%)}(Al,Si)AlSi_2O_8$





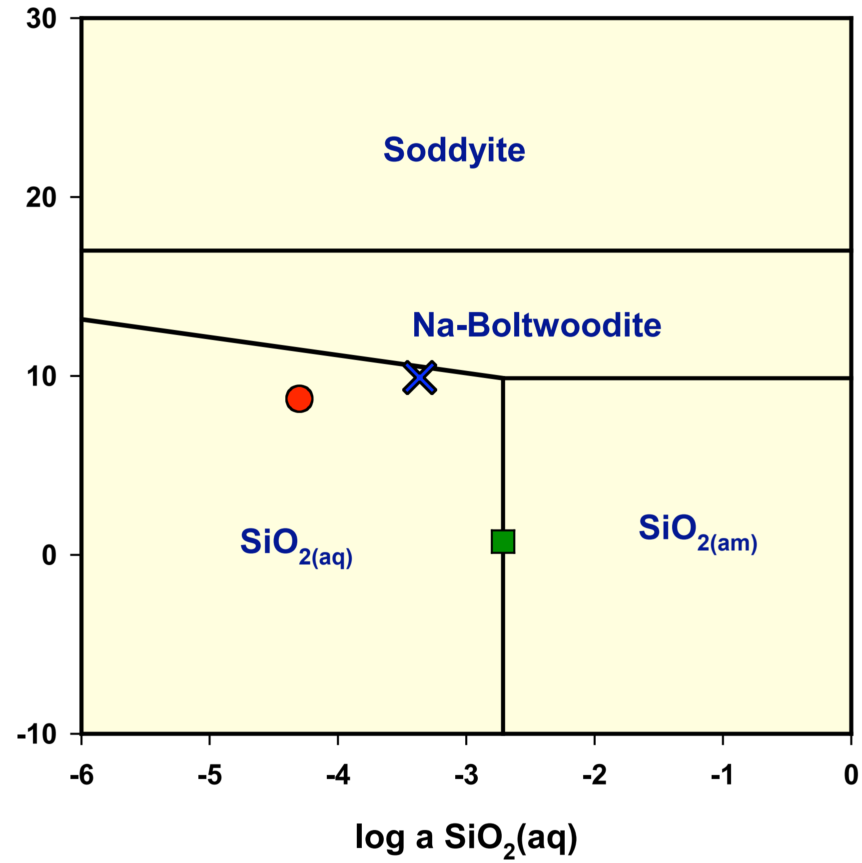
SEM image of feldspar reacted with simulated tank waste

Bates, 2004, UIC M.S. Thesis



T/pH change
Approx. Tank Solution
In-situ diluted Tank Solution?
Typical Ground Water

Activity-activity diagram for contaminated pore water



Contaminated PW
Uncontaminated PW
TS

Na-Boltwoodite: $Na[UO_2(SiO_3OH)](H_2O)_{1.5}$

Soddyite: $(UO_2)_2(SiO_4)(H_2O)_2$

What U-silicates form at low temperatures as a function of:

pH, U concentration, Si concentration ?

What controls homogeneous vs. heterogeneous nucleation?

What factors control and what are the kinetics?

APPROACH:

Synthesis experiments:

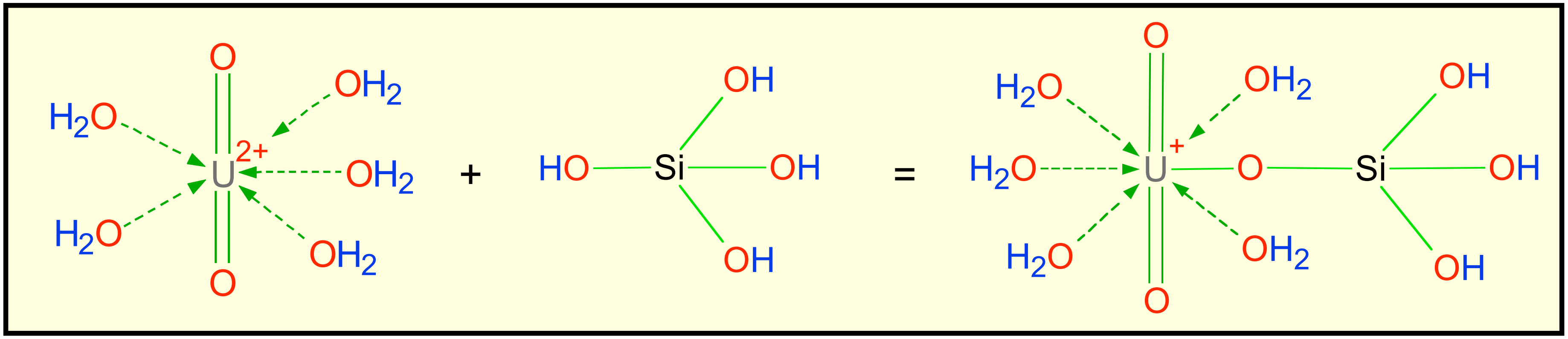
- with and without CO_2
- varying pH, U, Si concentrations
- presence or absence of feldspar
- effect of drying, time, and temperature

Structural & compositional analyses:

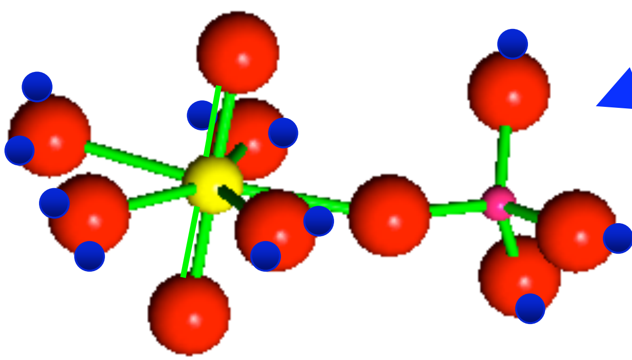
- HEXS & SAXS
- EXAFS spectroscopy
- FTIR, XRD
- Solid & solution compositions

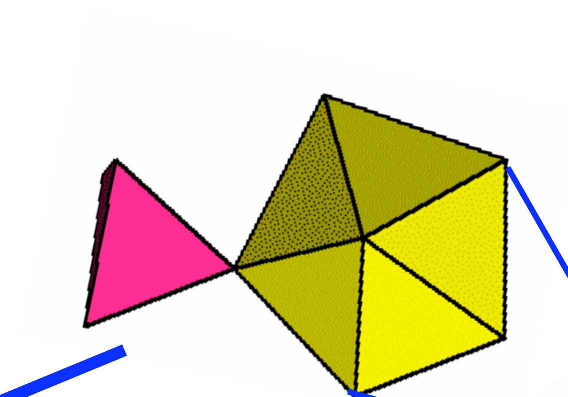
Unifying predictive equations

The uranyl-silicato monomer complex

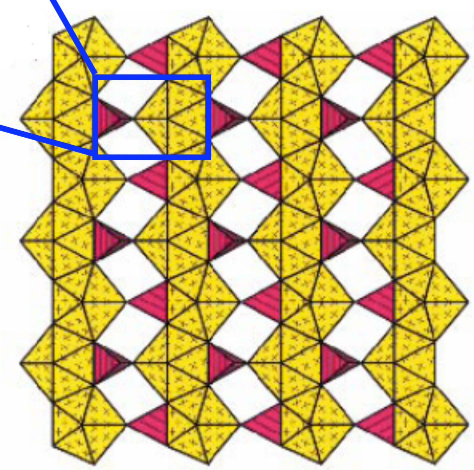


Possible structure of the complex



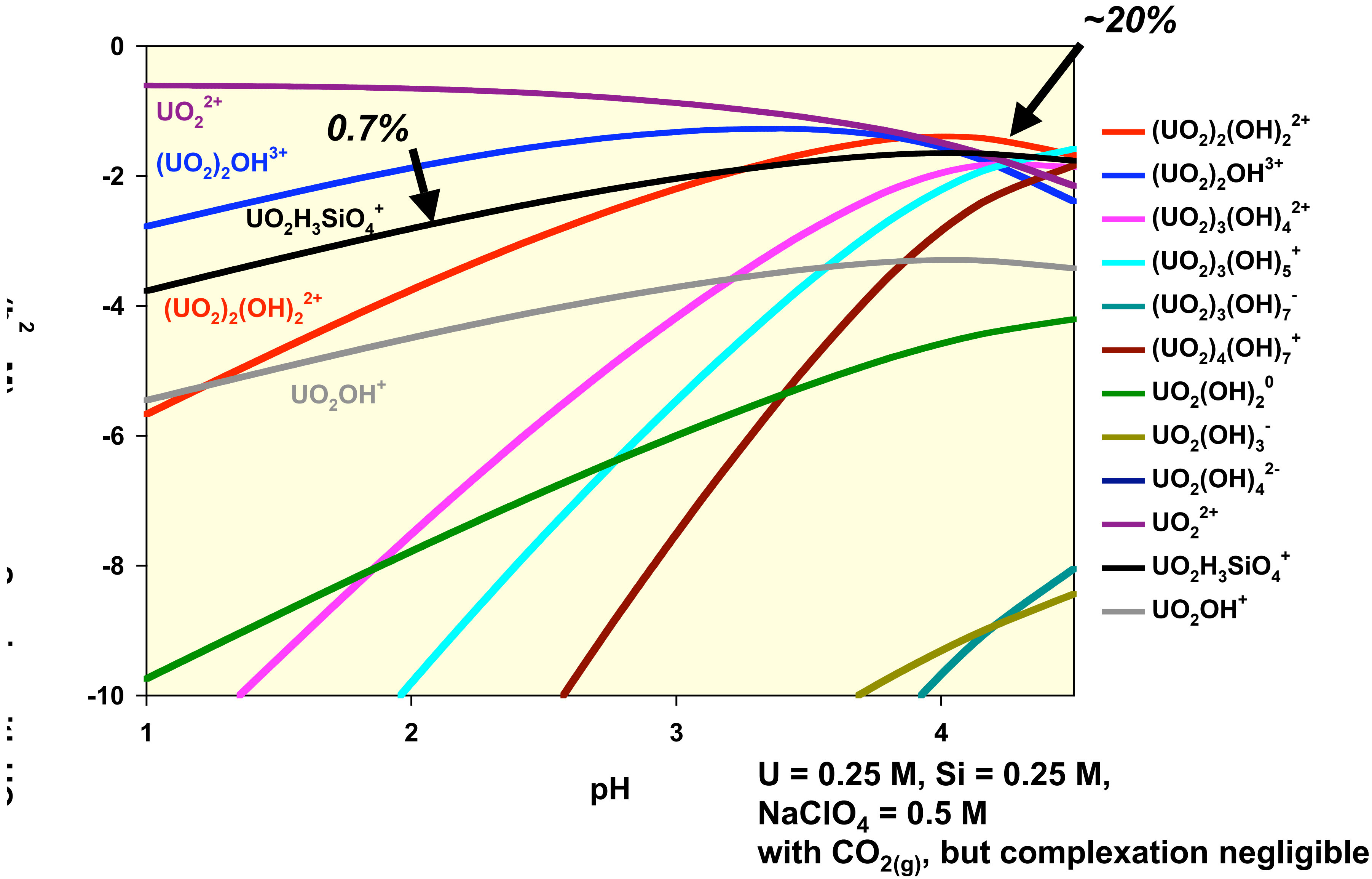


Uranyl silicate sheet in uranophane and boltwoodite. U:Si =1:1 (Burns, 2001)

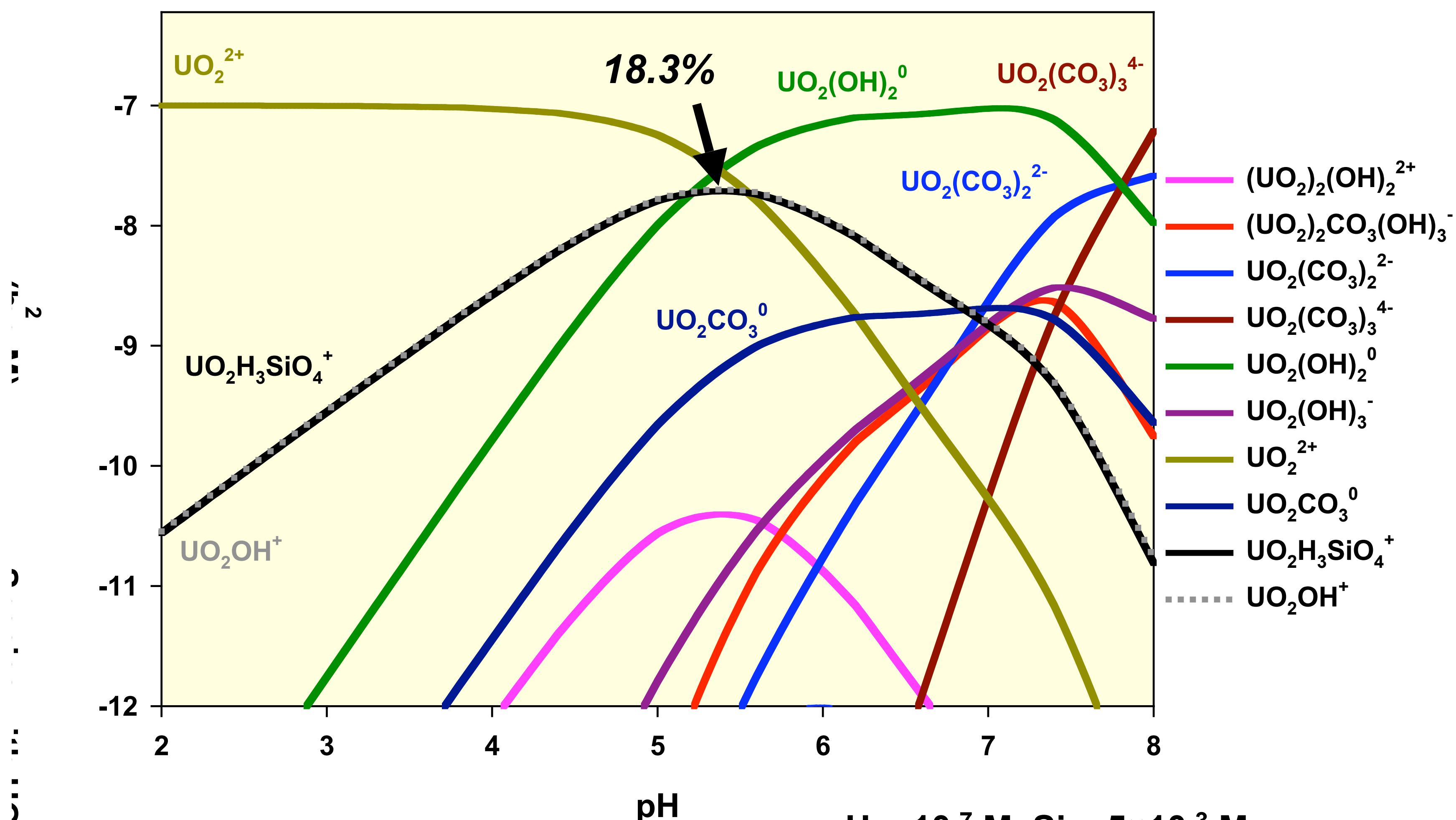


May be correlated with structures observed for uranyl silicates

U-silicate solution species highest at lower pH (system without CO_2)



U-silicate solution species decreases at higher pH (system with CO_2)

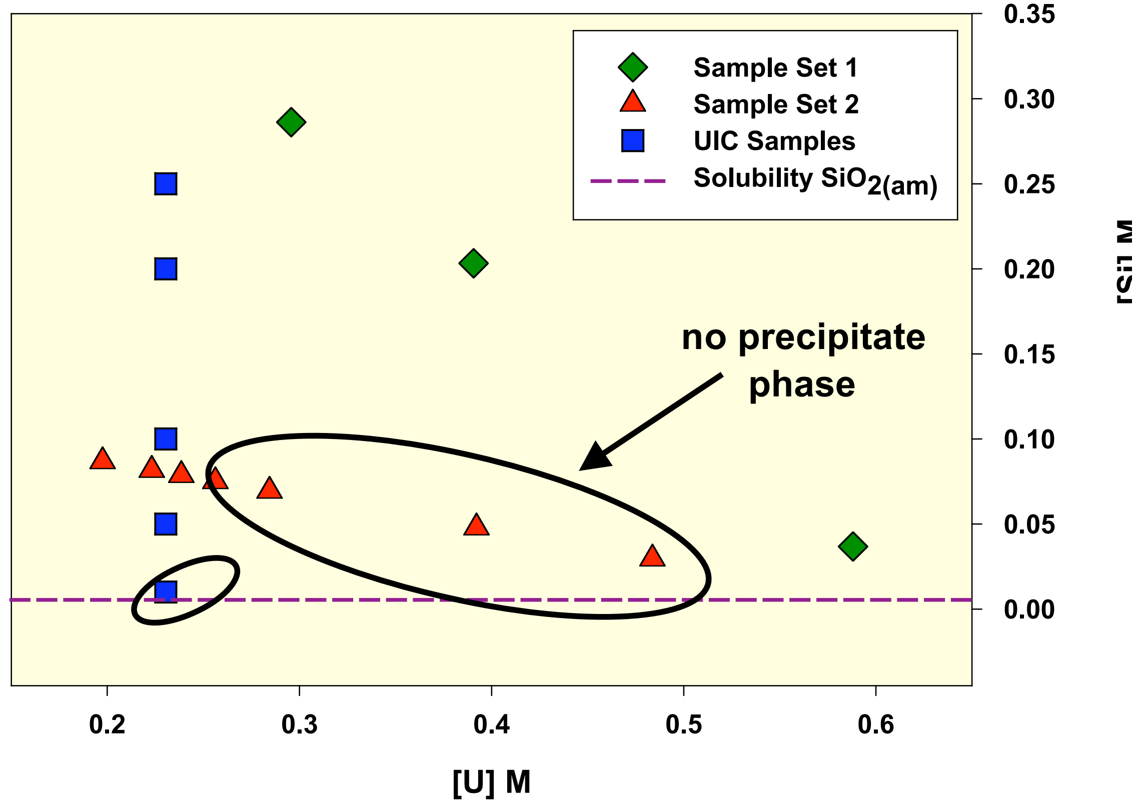


U = 10^{-7} M, Si = 5×10^{-3} M,
$NaNO_3$ = 0.1 M, $PCO_{2(g)}$ = $10^{-3.5}$ atm

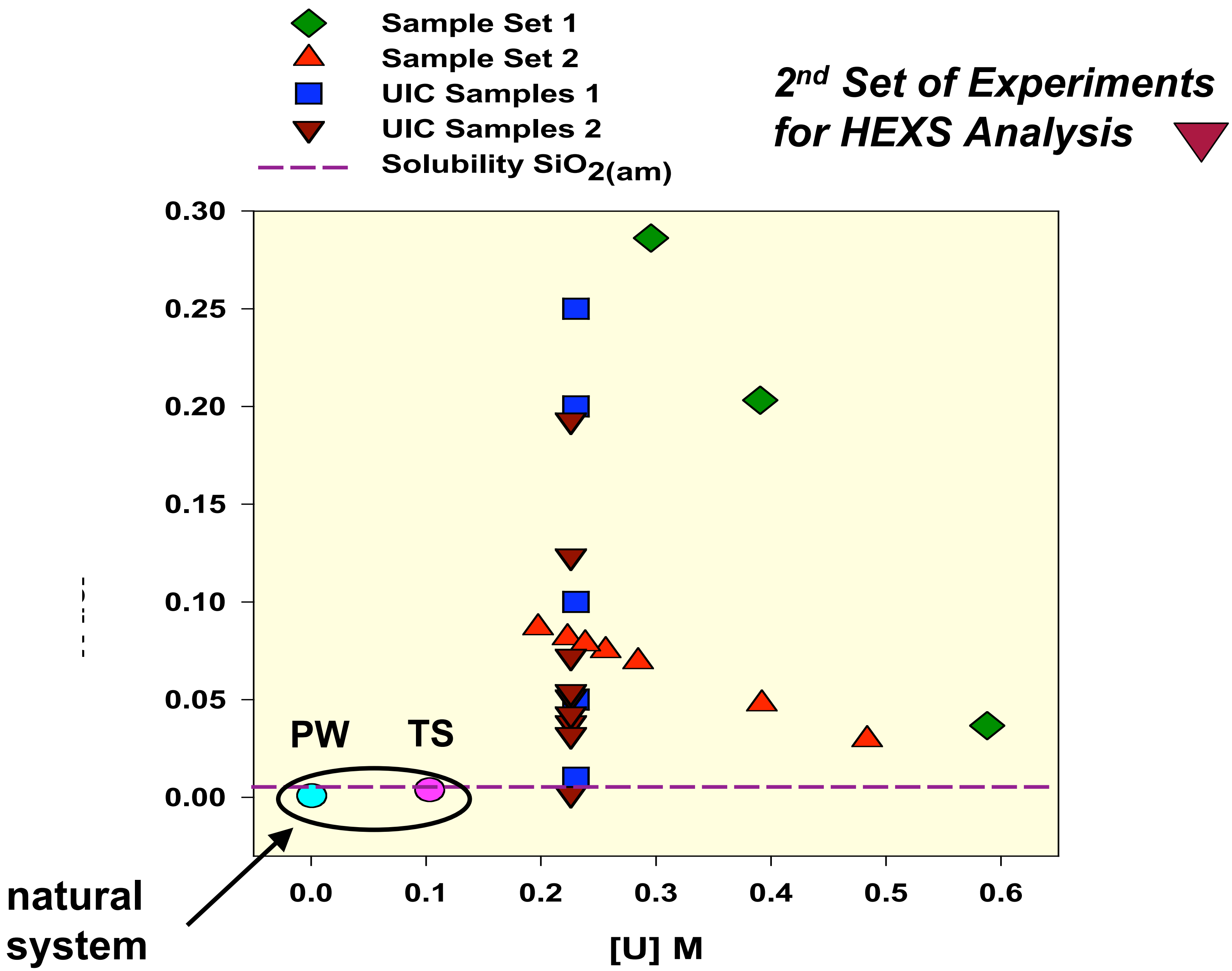
Solution compositions for initial scattering experiments:

- UIC samples
  - 0.23 M $UO_2(NO_3)_2$
  - 0.01-0.25 M $Na_2SiO_3 \bullet 9H_2O$
  - U added to Si stock
  - U analysis by α-counting
  - Not analyzed by scattering
- Sample Set 1
  - 0.30-0.59 M $UO_2(ClO_4)_2$
  - 0.04-0.29 M $Na_2SiO_3 \bullet 9H_2O$
  - Si added to U stock
- Sample Set 2
  - 0.20-0.48 M $UO_2(ClO_4)_2$
  - 0.03-0.09 M $Na_2SiO_3 \bullet 9H_2O$
  - Si reagent added incrementally

Open to atmosphere; pH ~ 2-4



Precipitate increases with ↑ [Si] & ↓ [U]

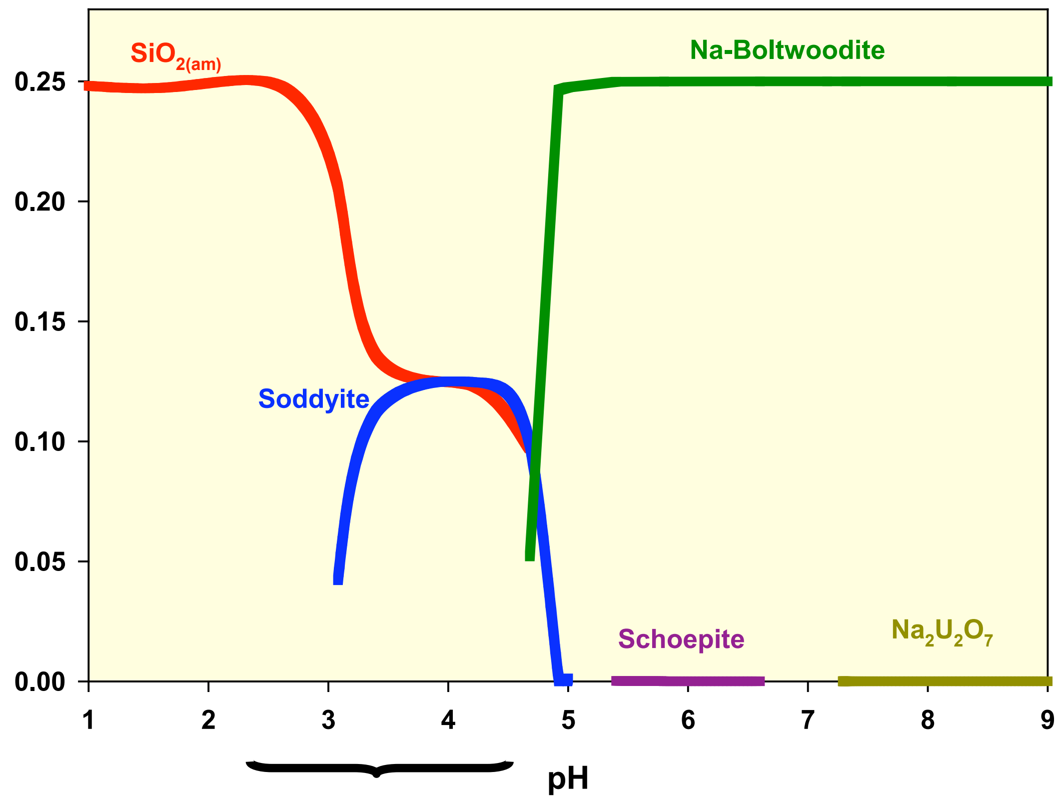


Sample Set 1
Sample Set 2
UIC Samples 1
UIC Samples 2
Solubility $SiO_{2(am)}$
2nd Set of Experiments for HEXS Analysis
0.30
0.25
0.20
0.15
0.10
0.05
0.00
PW
TS
natural system
0.0
0.1
0.2
0.3
0.4
0.5
0.6
[U] M

SYNTHESIS EXPERIMENTS
without CO_2
for initial HEXS analysis

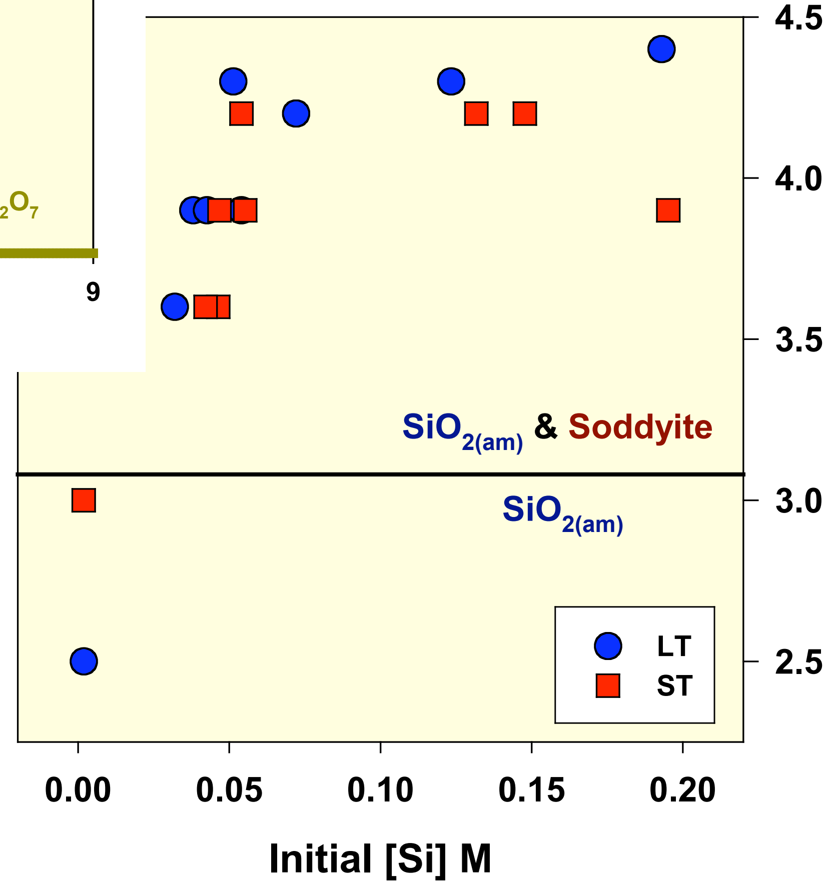
- **Prepared in glove box under $Ar_{(g)}$ atmosphere**
- **0.25 M $UO_2(ClO_4)_2$**
- **0.01-0.25 M $Na_2SiO_3 \bullet 9H_2O$**
- **Si added incrementally to U stock**
- **pH measured (~2.5-4)**
- **Sampled for analysis**
  - **U: α-counting**
  - **Si: UV-Vis & ICP-OES**
- **2 sample sets:**
  - **LongTerm: 8 weeks**
  - **ShortTerm: 2 weeks**

Thermodynamic modeling tells us…

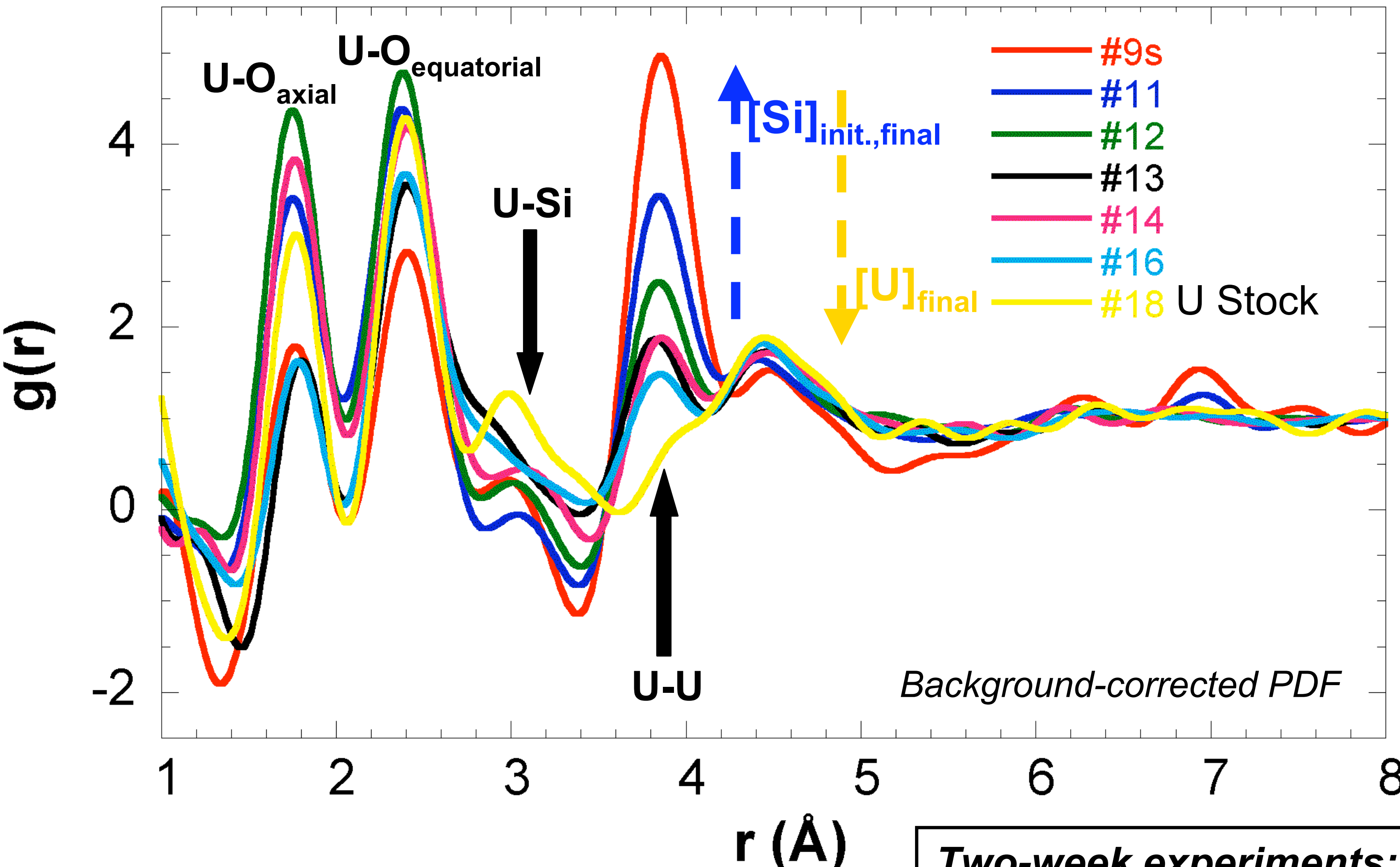


experimental conditions

U = 0.25 M, Si = 0.25 M, $NaClO_4$ = 0.5 M, $CO_{2(g)}$ excluded



High Energy X-ray Scattering: Pair Distribution Function

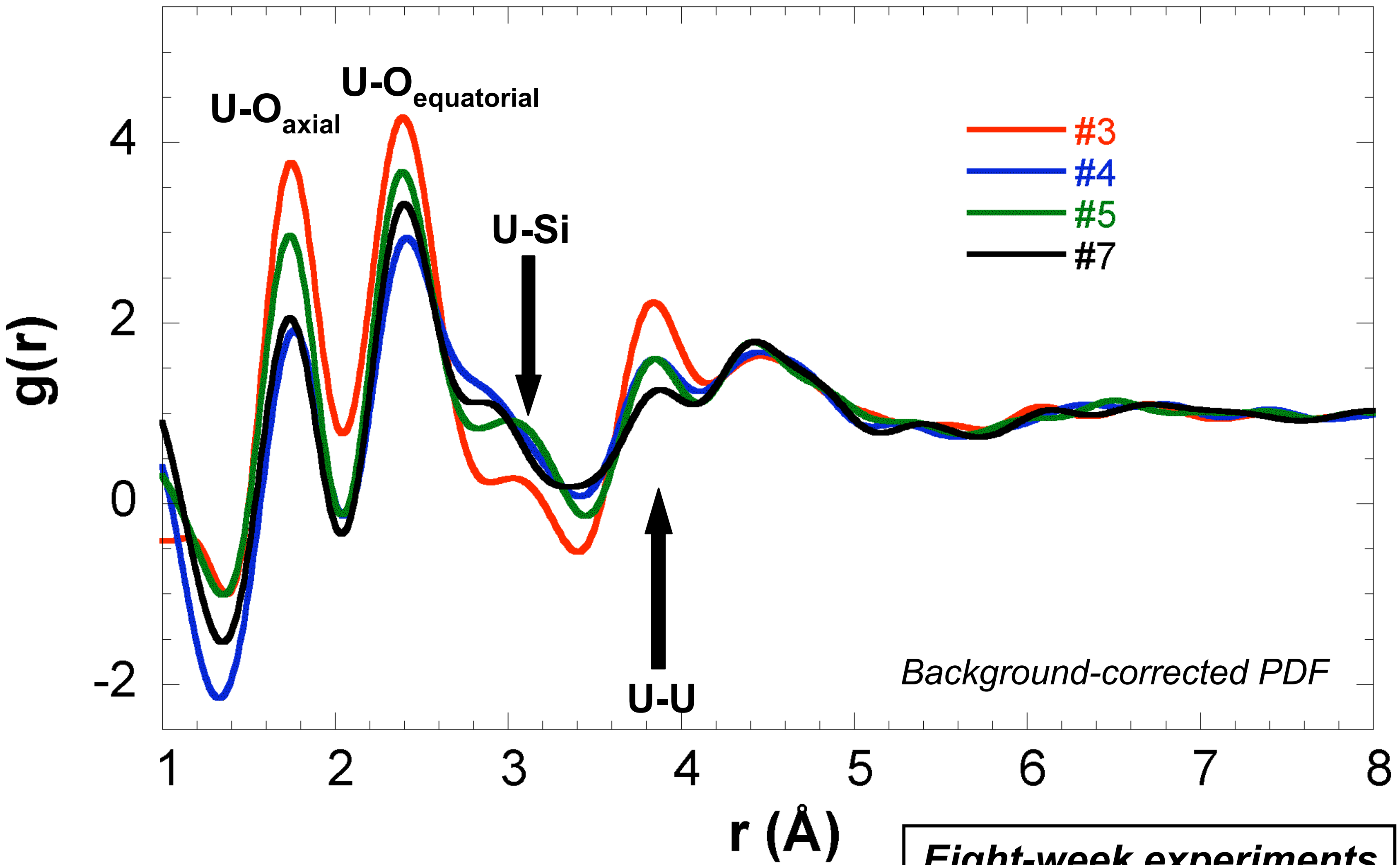


Two-week experiments: Evidence for U-oligomers

11-ID-C, 91 keV
Advanced Photon Source

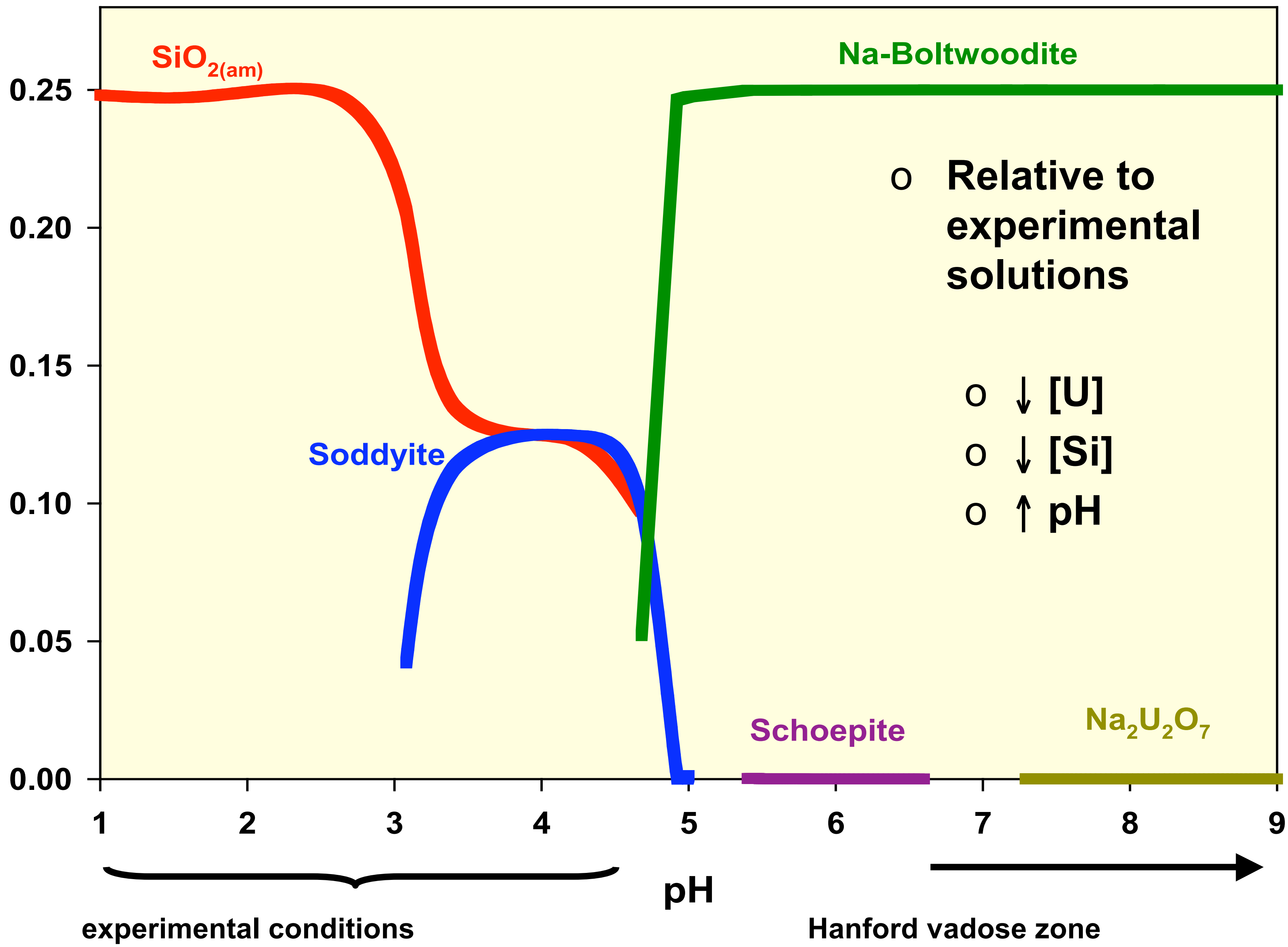
HEXS: Pair Distribution Function

Similar results - Little effect of time visible in the data



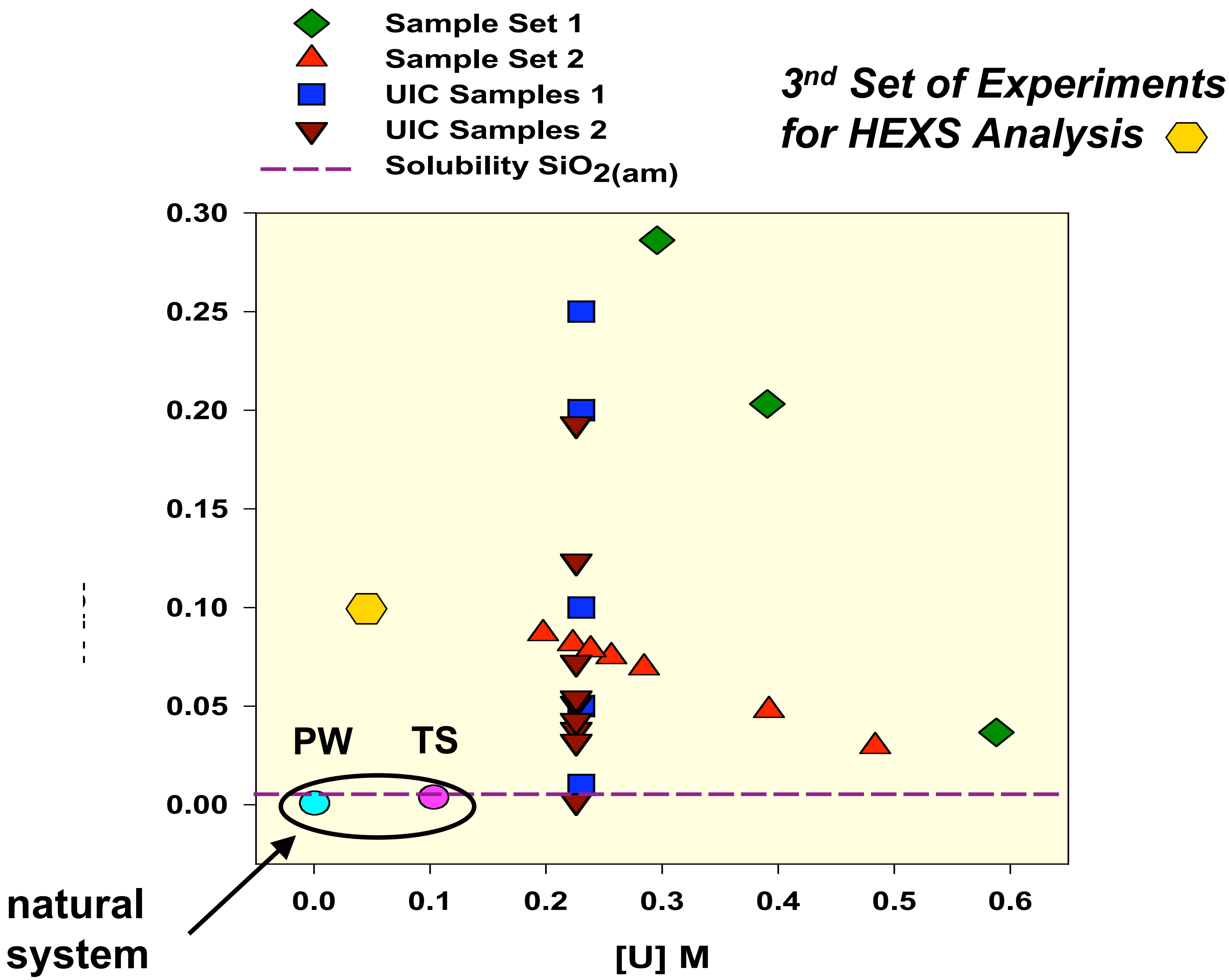
Eight-week experiments

Comparison with Hanford vadose zone:

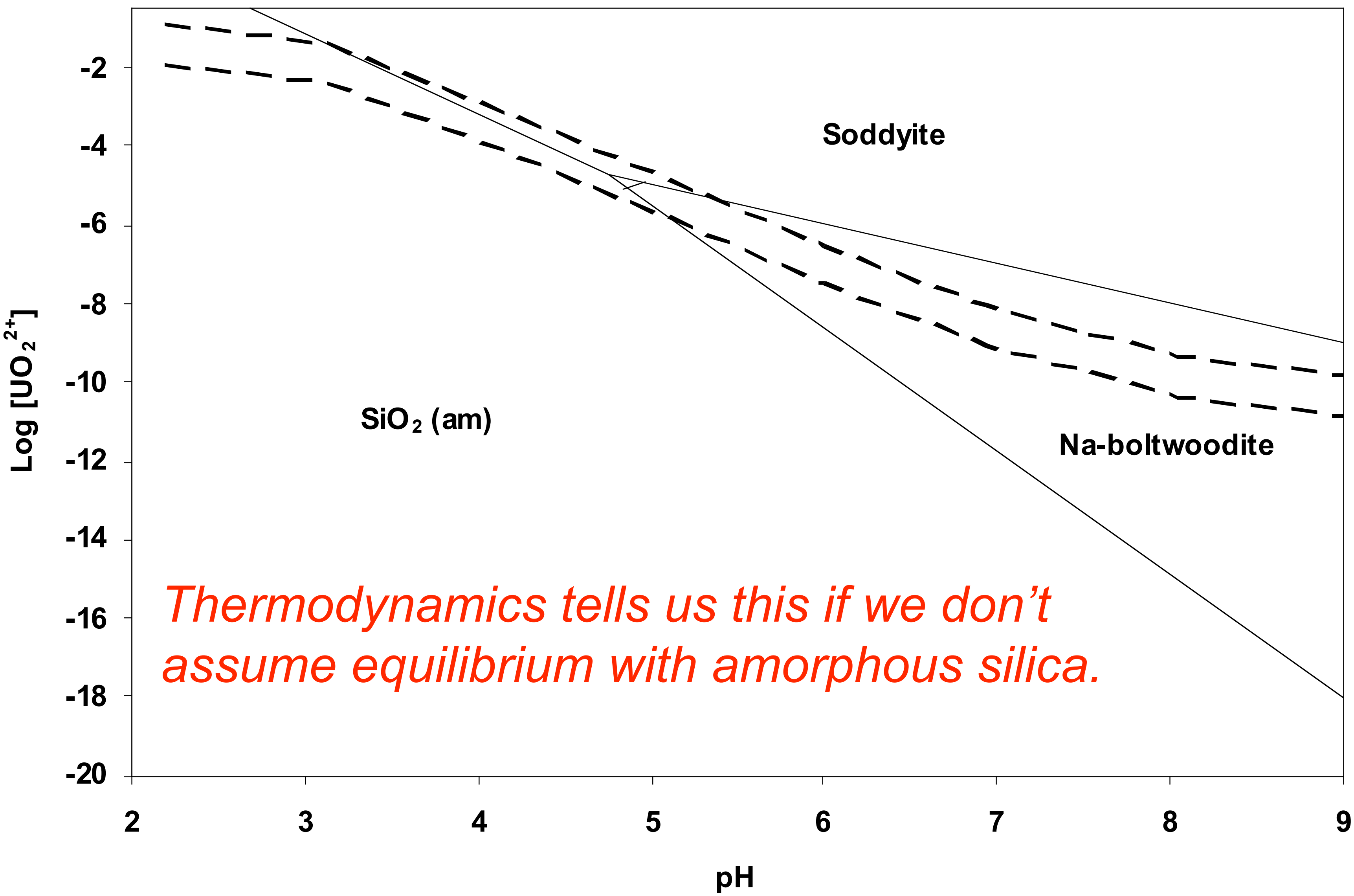


SYNTHESIS EXPERIMENTS with CO_2 HEXS, FTIR, XRD analysis

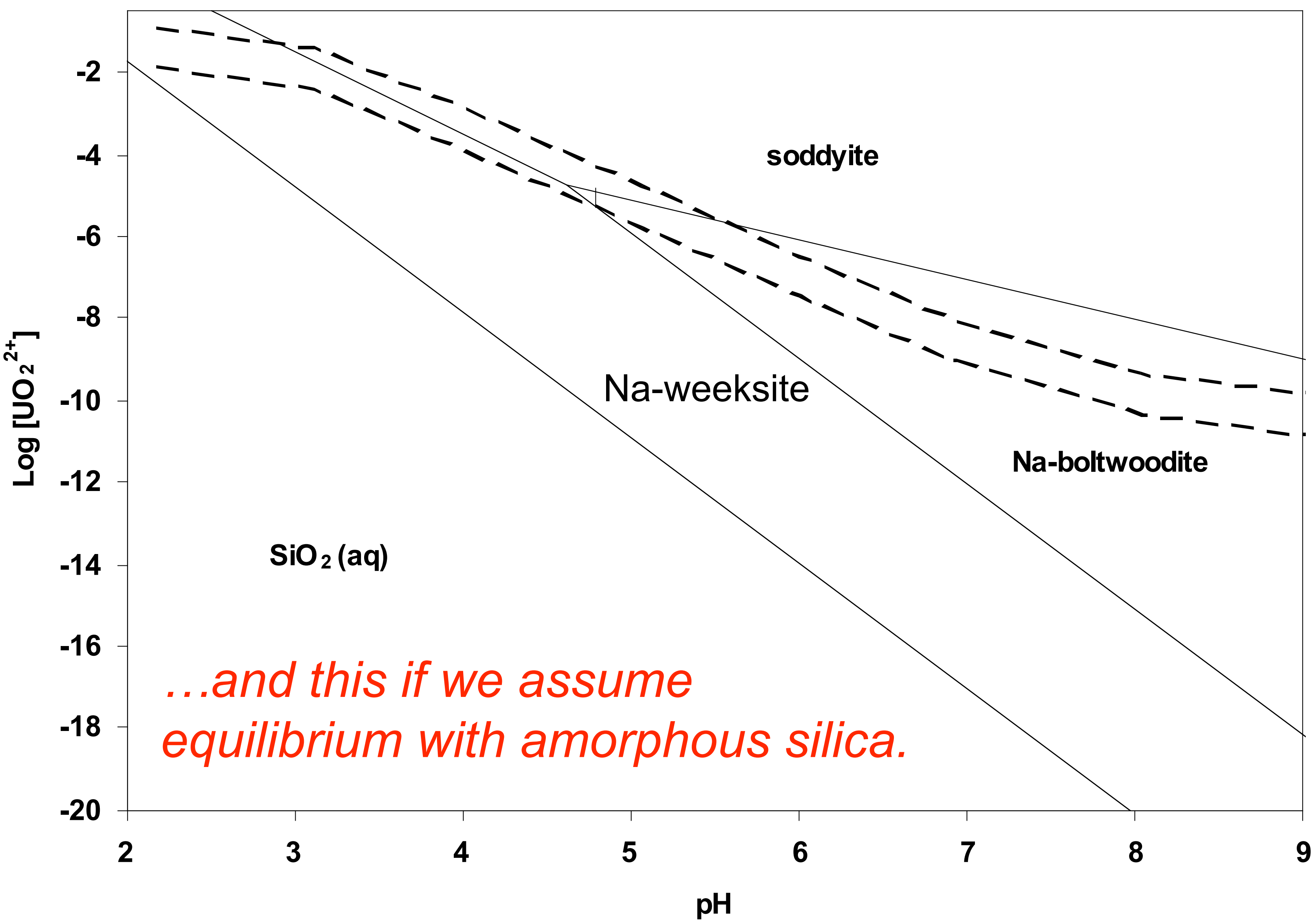
- Prepared on benchtop open to the atmosphere
- 0.990 M $UO_2(ClO_4)_2$
- 0.105 M $Na_2SiO_3 \bullet 9H_2O$
- 50 µL U-solution (0.05 M U_f)
  950 µL Si-solution (0.1 M Si_f)
- pH adjusted from 2.2 to 9.0
- 4 da @ 150°C for similar pH 5.1 to 9.1 samples
- Solids analyzed for U & Si by spectrophotometry
- Solids analyzed by XRD, FTIR, and HEXS



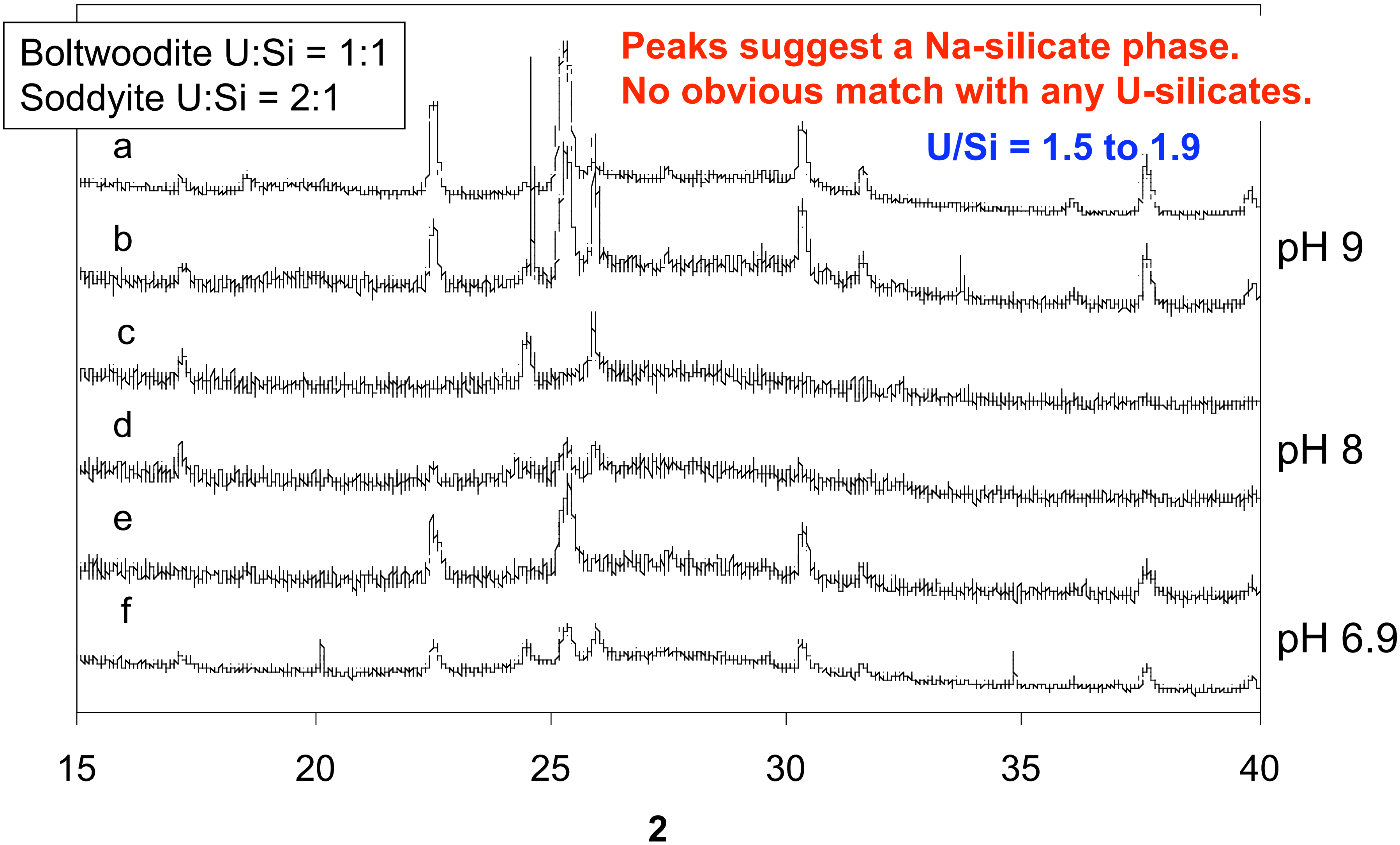
Sample Set 1
Sample Set 2
UIC Samples 1
UIC Samples 2
Solubility $SiO_{2(am)}$
3rd Set of Experiments for HEXS Analysis
0.30
0.25
0.20
0.15
0.10
0.05
0.00
PW
TS
0.0
0.1
0.2
0.3
0.4
0.5
0.6
[U] M
natural system



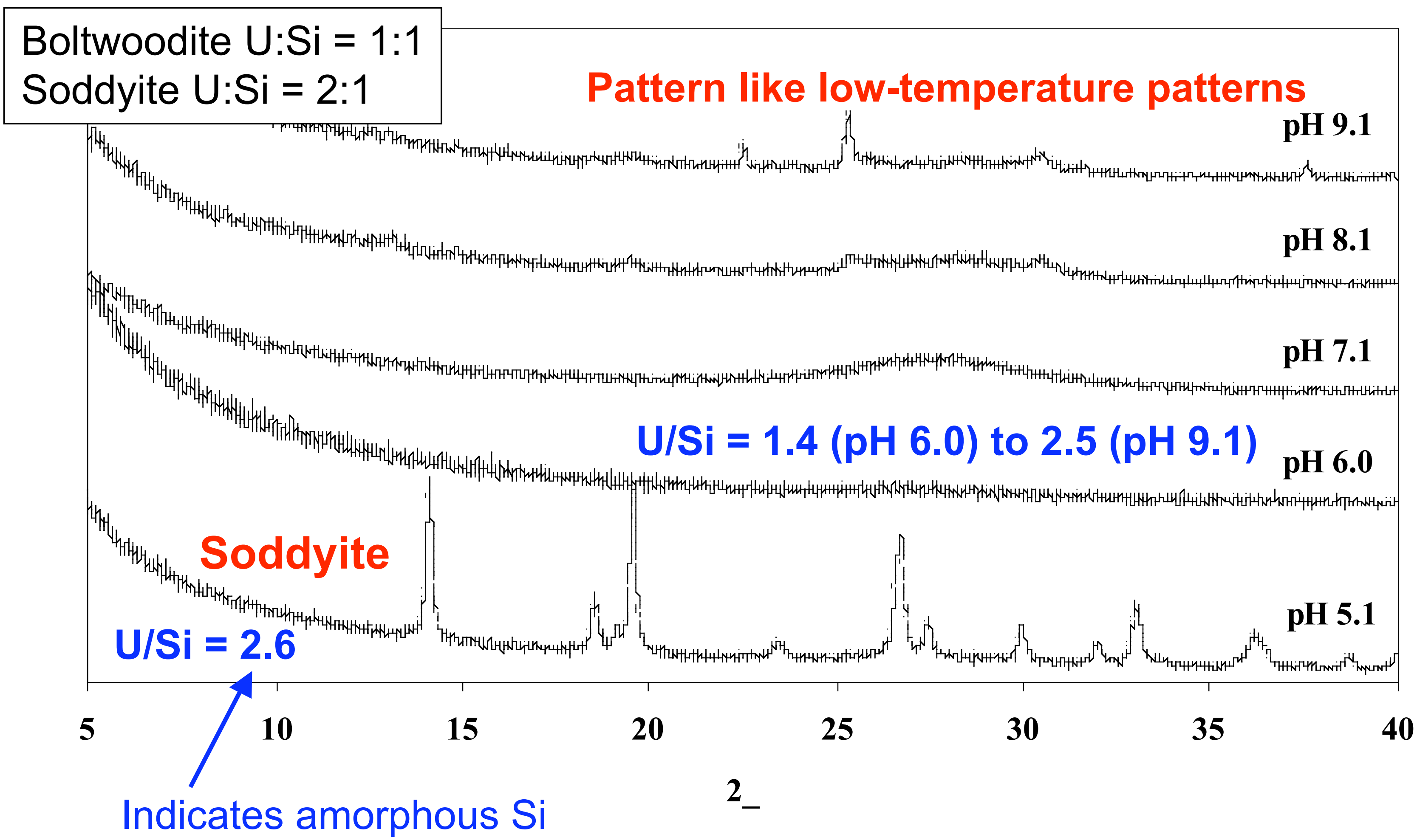
Thermodynamics tells us this if we don't assume equilibrium with amorphous silica.


soddyite
Na-weeksite
Na-boltwoodite
SiO2 (aq)
…and this if we assume
equilibrium with amorphous silica.
Log [UO2 2+]
pH
-2
-4
-6
-8
-10
-12
-14
-16
-18
-20
2
3
4
5
6
7
8
9

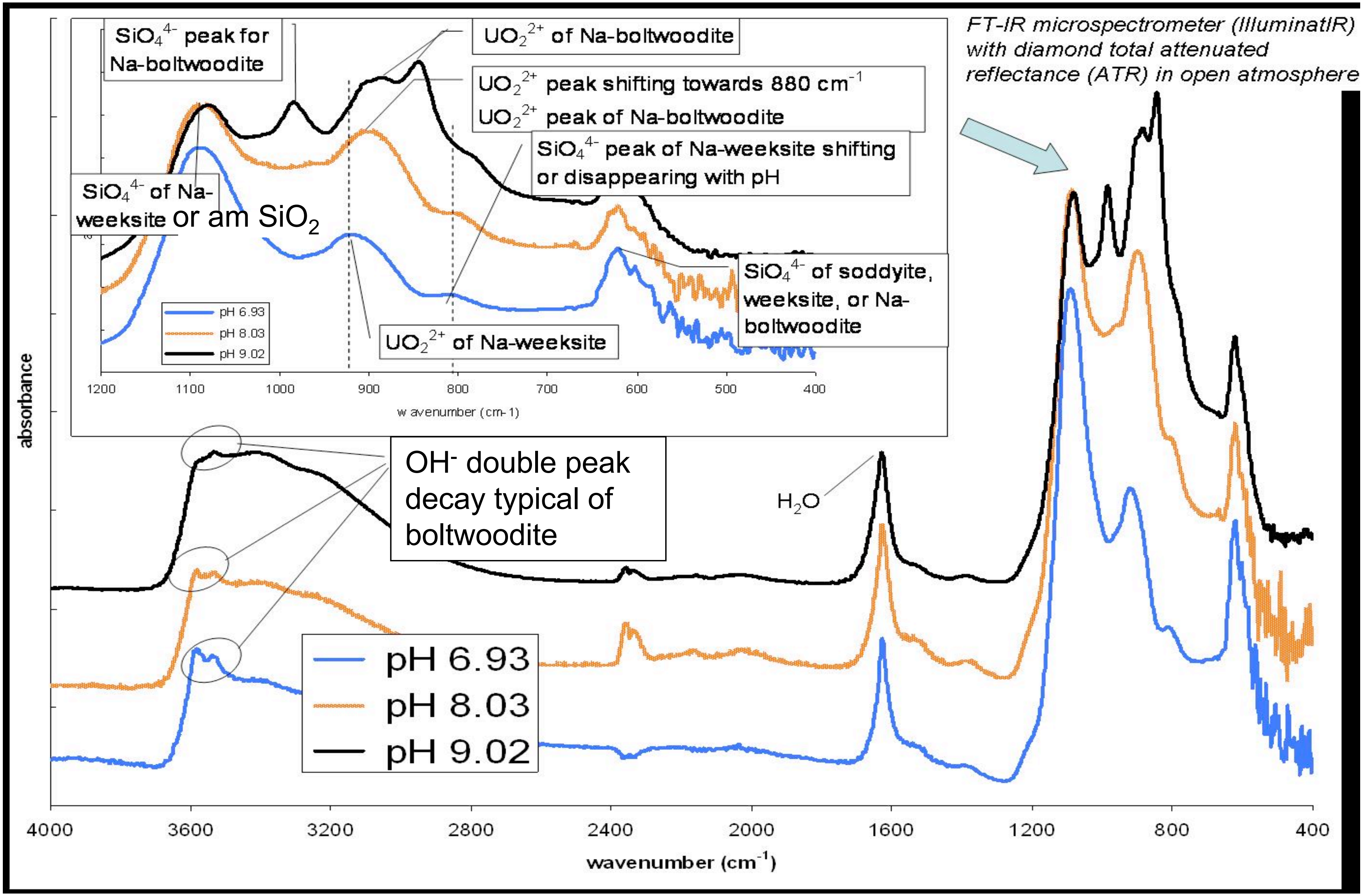
X-ray Diffraction of Room Temperature Solids – air-dried



X-ray Diffraction of Solids heated at 150°C for 4 days

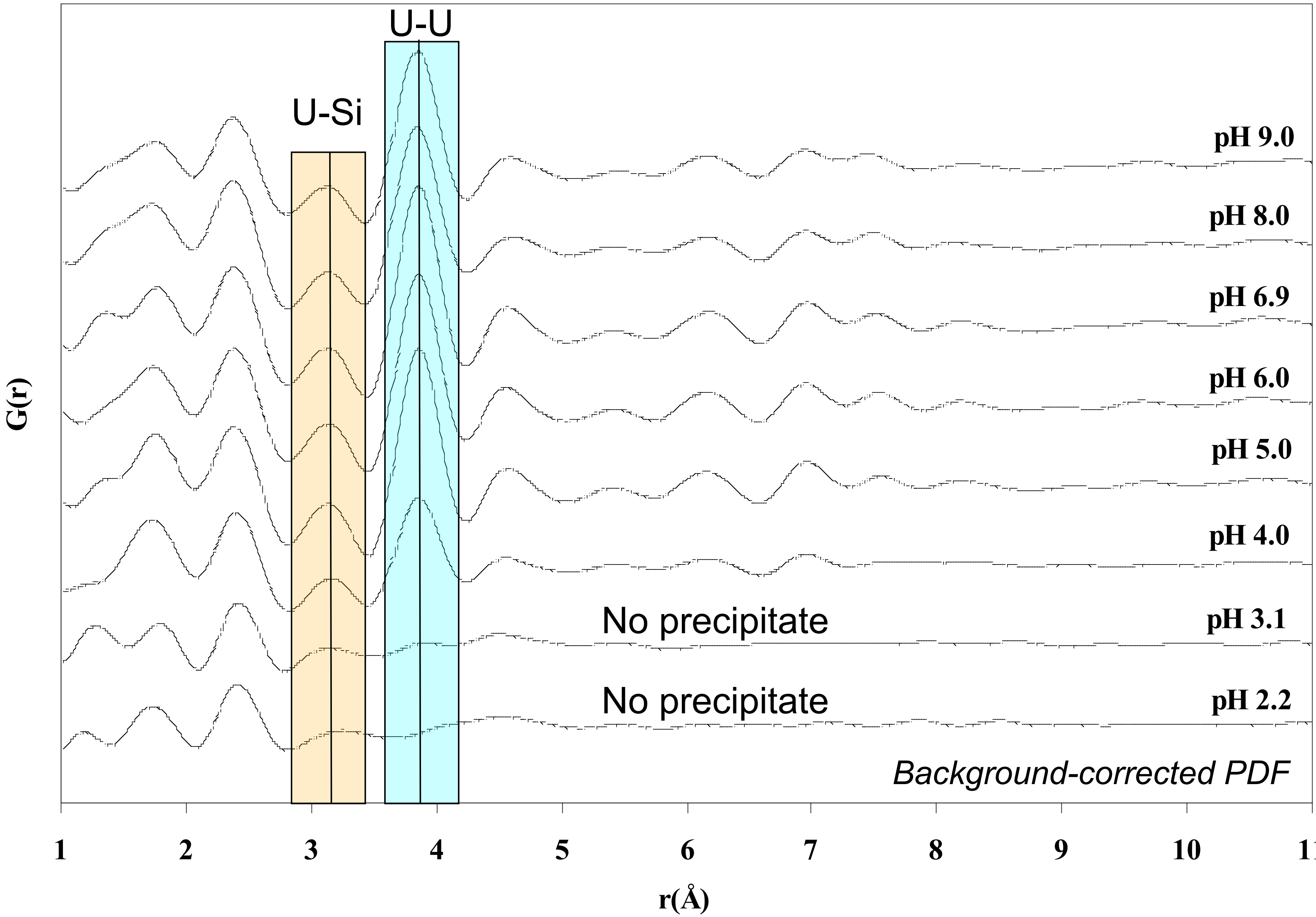


FTIR on Room T samples, aged for 6 weeks and air-dried



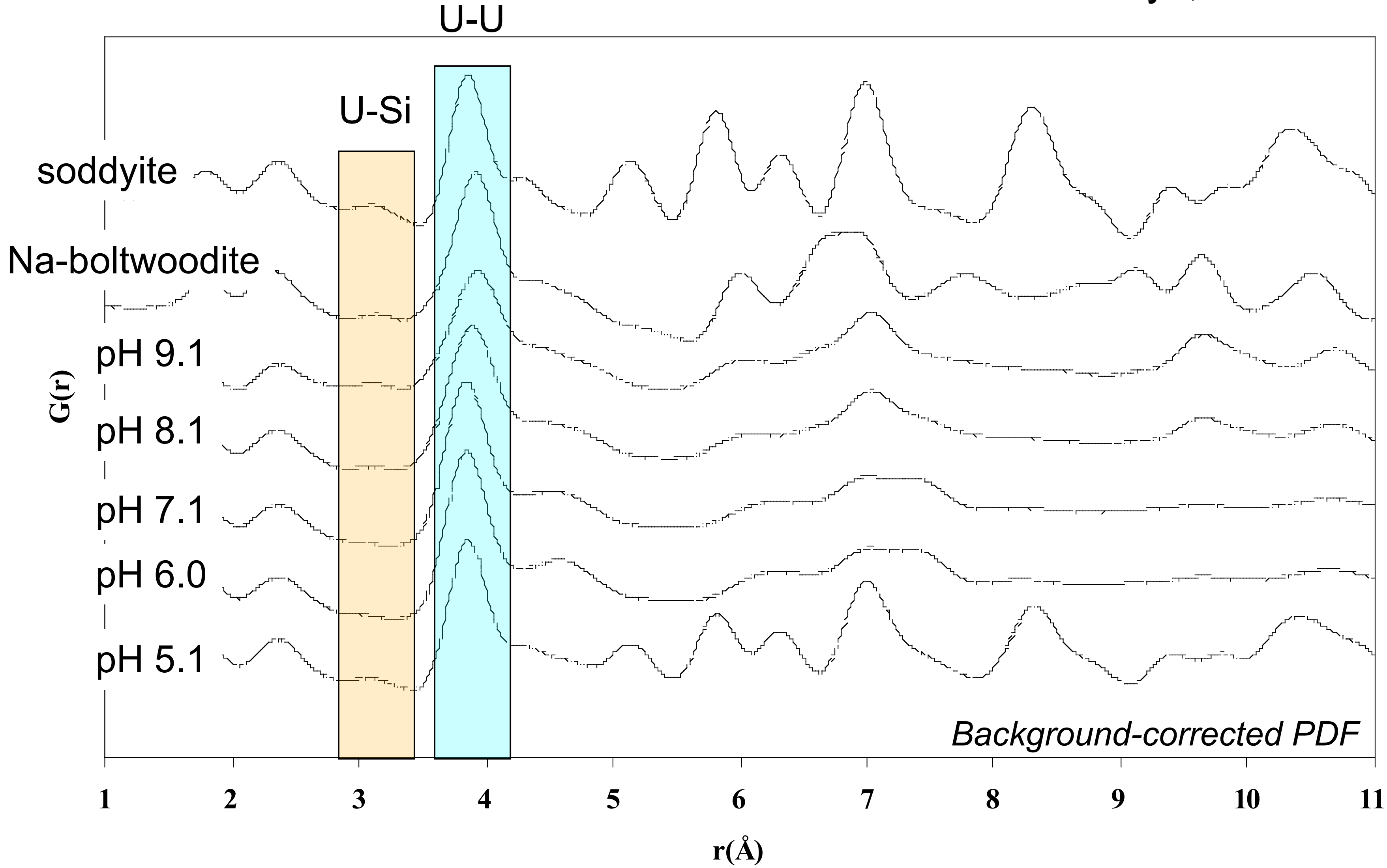
HEXS: Pair Distribution Function – Room T Precipitates

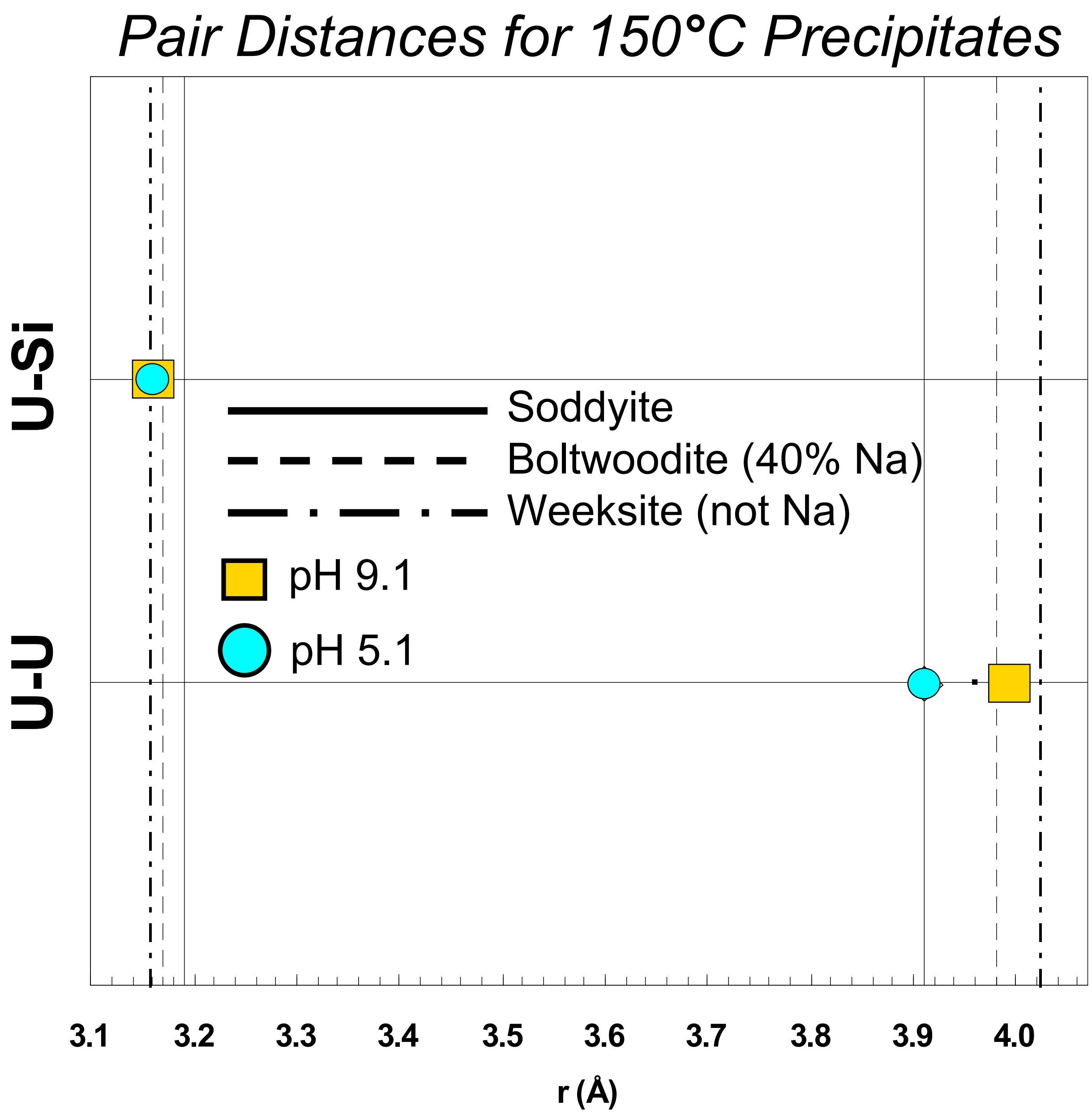
Mounted after 60 minutes; analyzed within 24 hours



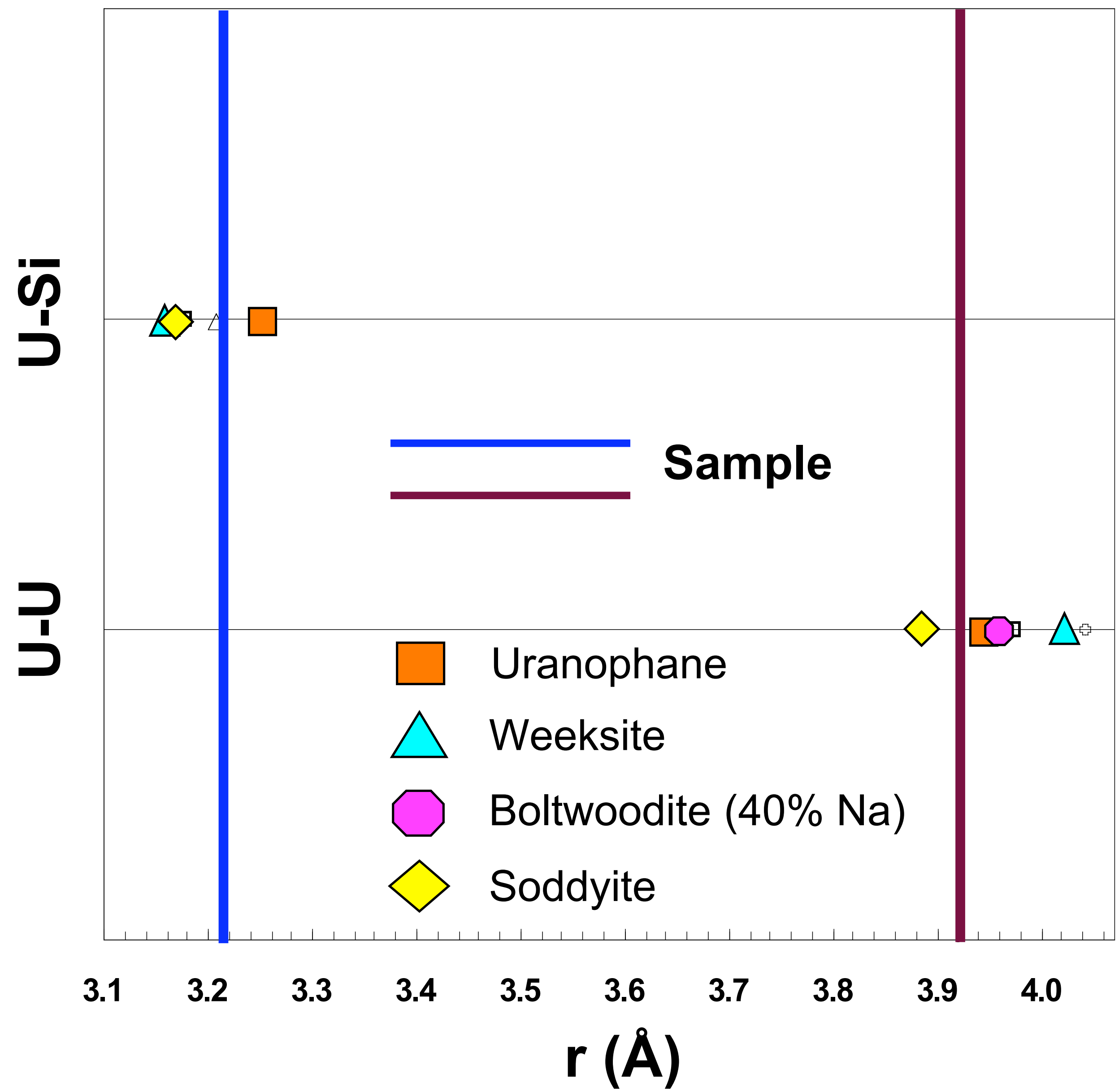
HEXS: Pair Distribution Function – 150°C Precipitates

Reacted 4 days; air-dried




Pair Distances for 150°C Precipitates
U-Si
U-U
Soddyite
Boltwoodite (40% Na)
Weeksite (not Na)
pH 9.1
pH 5.1
3.1
3.2
3.3
3.4
3.5
3.6
3.7
3.8
3.9
4.0
r (Å)

Average Pair Distances for Room T Precipitates

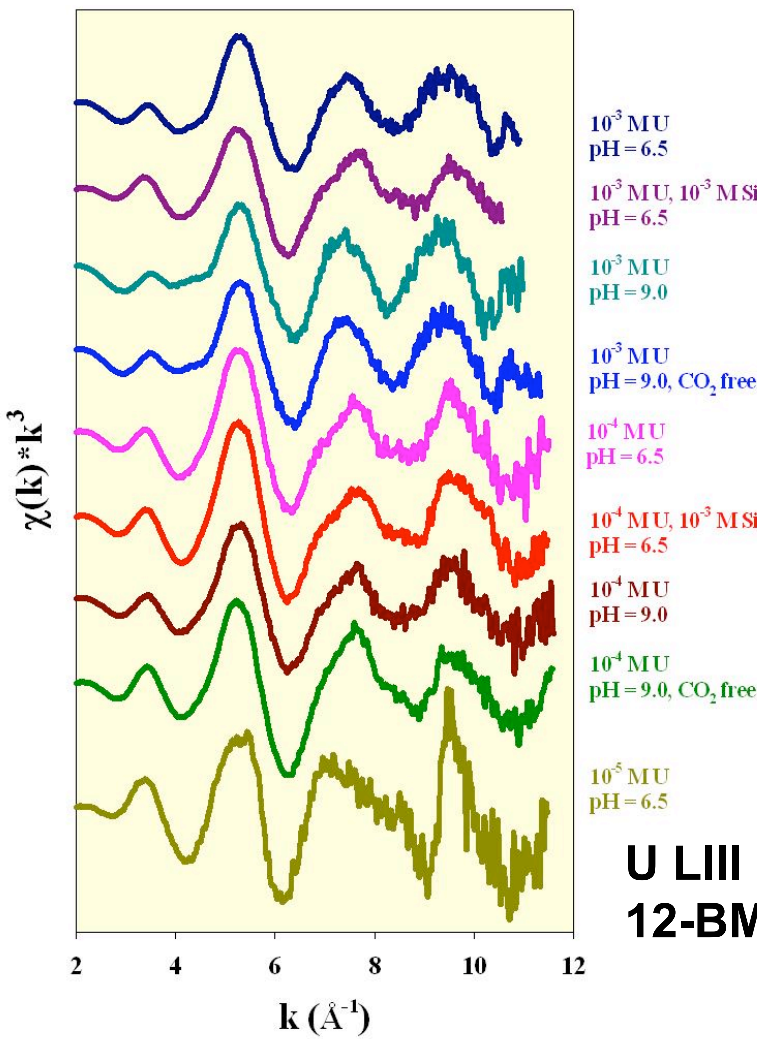


Other work in progress:

	U [M]	Si [M]	CO2	pH
1	1.0E-03		atm	6.5
2	1.0E-03	1.0E-03	atm	6.5
3	1.0E-03		atm	9.0
4	1.0E-03		N/A	9.0
5	1.0E-04		atm	6.5
6	1.0E-04	1.0E-03	atm	6.5
7	1.0E-04		atm	9.0
8	1.0E-04		N/A	9.0
9	1.0E-05		atm	6.5
10	1.0E-05		atm	6.5
11	1.0E-05	1.0E-03	atm	6.5
12	1.0E-05		atm	9.0
13	1.0E-05		N/A	9.0
14	1.0E-06		atm	6.5
15	1.0E-06	1.0E-03	atm	6.5
16	1.0E-06		atm	9.0
17	1.0E-06		N/A	9.0
18	1.0E-07		atm	6.5
19	1.0E-07	1.0E-03	atm	6.5
20	1.0E-07		atm	9.0
21	1.0E-07		N/A	9.0

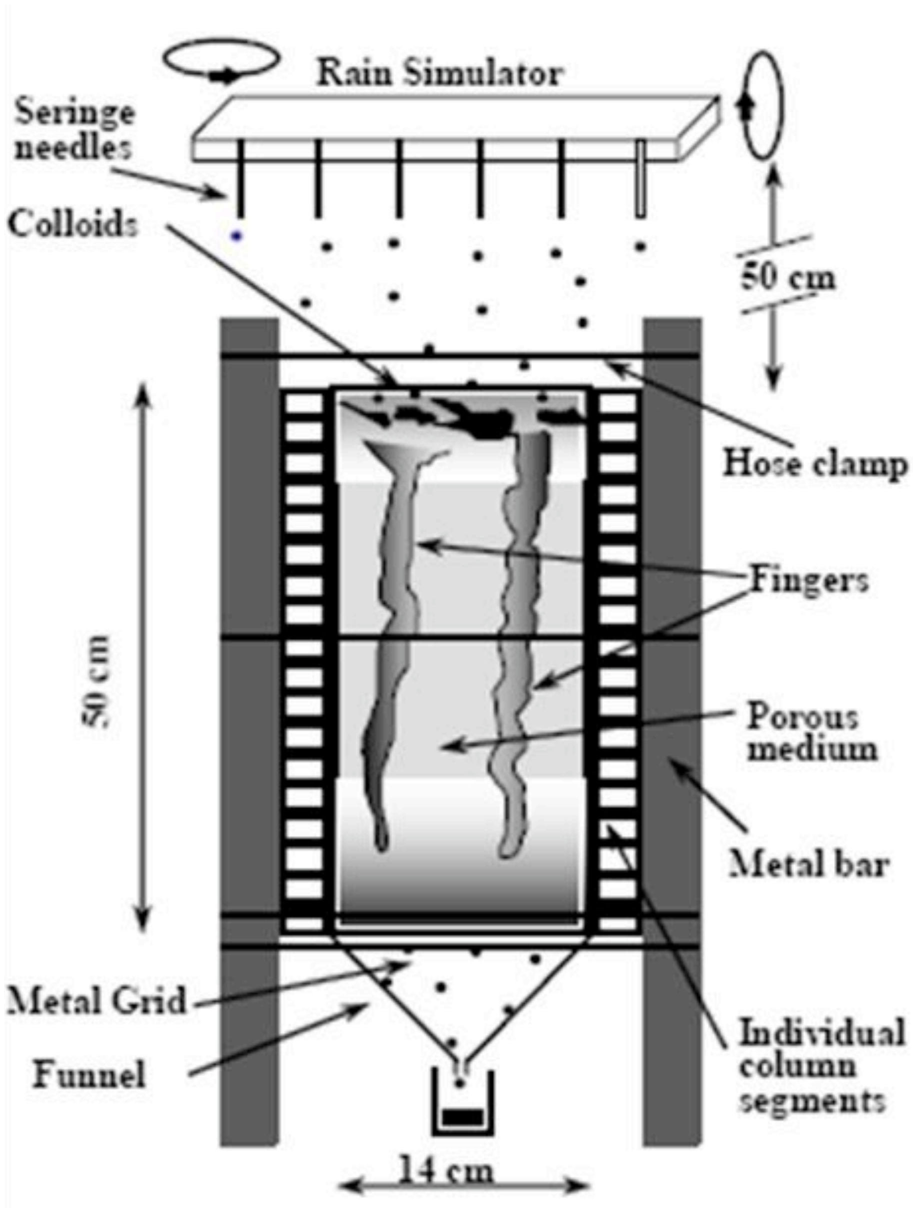
EXAFS spectroscopic analysis of U uptake on labradorite feldspar

- at pH 6.5 and 9.0
- with and without CO_2
- with and without added Si



U LIII edge
12-BM, APS

Other work in progress:



1-D and 2-D column flow:

feldspar & quartz substrates

U-solutions guided by experiments

Image analysis of flow (fluorescence, luminescence)

Summary: U-Silicate Nucleation and Precipitation

Solution compositional space is being refined with respect to merging experimental and analytical needs with simulation of reality

High Energy X-ray Scattering (HEXS) shows systematic, reproducible, but subtle changes in U-Si and U-U pair distances with changes in pH, [U], and [Si]

FTIR is sensitive to subtle changes in bonding environment of U in mixed precipitates

Little change in precipitate structures is observed at short times (to 8 weeks)

Precipitate structures are changed upon drying

Increasing temperature, thought to accelerate rates of crystallization, does not appear to have equal effect at all pHs.