Precipitation of U(VI) in Low-Temperature Si-Na-H$_2$O±CO$_2$±Feldspar Systems

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

Liu et al., 2004
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.
Homogeneous precipitates?

Heterogeneous precipitates on edges and basal surfaces

Samson et al., GCA, 2005
Quartz Dissolution at 90°C, high pH: Nitrate Cancrinite precipitates; Starts as a film in more recessed areas in quartz surface.

\[ \text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} \]


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

Bickmore et al., ES&T, 2001
**Initial Precipitation Rates**

Rate\(_{ppt}\) (mol cancrinite/s) =

\[ 1.03 \pm 0.05 \times 10^{-6} \text{[Al]}^{1.22} \text{[Si]}^{0.23} \]

**“Nitrate” Cancrinite**

\[ \text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} \]

*Bickmore et al., ES&T, 2001; GCA, 2006*
$U = 50 \text{ mg/L}$

$\text{NO}_3 = 8,000 \text{ mg/L}$

$\text{Tc}^{99} = 40,000 \text{ pCi/L}$

$pH = 3.5$

**U-Si species may be precursors for subsequent reactions**
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

Na$_2$ZnSiO$_4$
Precipitated on vapor-altered glass

**Soddyite**
$(\text{UO}_2)_2(\text{SiO}_4)\cdot2\text{H}_2\text{O}$

**K-Boltwoodite**
$\text{K(UO}_2\text{(SiO}_3\text{)(OH)}\cdot1.5\text{H}_2\text{O}$
U(VI) speciated as $\text{UO}_2(\text{CO}_3)_3^{4-}$

$T = 80 \, ^\circ\text{C}; \, \text{pH} = 10$

Possible mechanism of U-Silicate formation

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)

Uranyl silicate precipitation

$\text{UO}_2^{2+} + \text{SiO}_2(aq)$
# 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

<table>
<thead>
<tr>
<th></th>
<th>$UO_2^{++}$ (M)</th>
<th>$SiO_2^{(aq)}$ (M)</th>
<th>$pH$</th>
<th>$T ^\circ C$</th>
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<tbody>
<tr>
<td>Tank Solution</td>
<td>1.03E-01</td>
<td>4.00E-03</td>
<td>10</td>
<td>80</td>
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<td>Contaminated PW</td>
<td>1.85E-03</td>
<td>7.16E-04</td>
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<tr>
<td>Uncontaminated PW</td>
<td>1.63E-07</td>
<td>4.99E-03</td>
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<td></td>
</tr>
</tbody>
</table>

Liu et al., 2004, GCA
Si Source for U-silicate formation:

Dissolution of Labradorite Feldspar: \( \text{An}_{60} \text{Ca}_{(50-70\%)} \text{Na}_{(50-30\%)} (\text{Al, Si}) \text{AlSi}_2 \text{O}_8 \)

SEM image of feldspar reacted with simulated tank waste
Bates, 2004, UIC M.S. Thesis
Si solubility changes

Na-Boltwoodite: Na[UO$_2$(SiO$_3$OH)](H$_2$O)$_{1.5}$

Soddyite: (UO$_2$)$_2$(SiO$_4$)(H$_2$O)$_2$
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 = 0.25 M, Si = 0.25 M, NaClO$_4$ = 0.5 M with CO$_2$(g), but complexation negligible
**U-silicate solution species decreases at higher pH (system with CO\(_2\))**

![Graph showing pH vs. concentration for various U-silicate species.](image)

18.3% increase in \(\text{UO}_2\text{(OH)}_2\) and decrease in \(\text{UO}_2\text{(CO}_3\text{)}_0\) at higher pH.

- **Conditions:** \(U = 10^{-7}\) M, \(Si = 5\times10^{-3}\) 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$_2$SiO$_3$·9H$_2$O
  - 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$_2$SiO$_3$·9H$_2$O
  - Si added to U stock

- **Sample Set 2**
  - 0.20-0.48 M UO$_2$(ClO$_4$)$_2$
  - 0.03-0.09 M Na$_2$SiO$_3$·9H$_2$O
  - Si reagent added incrementally

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

Open to atmosphere; pH ~ 2-4
Sample Set 1
Sample Set 2
UIC Samples 1
UIC Samples 2
Solubility SiO$_2$(am)

$2^{nd}$ Set of Experiments for HEXS Analysis

natural system

[U] M
SYNTHESIS EXPERIMENTS
without CO₂
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\(_2\)SiO\(_3\)●9H\(_2\)O
- 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

Graphs show the pH scale with minima and maxima for different minerals:
- SiO$_2$(am)
- Na-Boltwoodite
- Na$_2$U$_2$O$_7$
- Schoepite Na$_2$U$_2$O$_7$

Lists of minerals with moles:
- SiO$_2$(am)
- Soddyite
- Na-Boltwoodite
- Schoepite Na$_2$U$_2$O$_7$

Graph with pH on the x-axis and mole fractions on the y-axis.
High Energy X-ray Scattering: Pair Distribution Function

11-ID-C, 91 keV
Advanced Photon Source

Two-week experiments: Evidence for U-oligomers
HEXS: Pair Distribution Function

Similar results - Little effect of time visible in the data

Eight-week experiments
Comparison with Hanford vadose zone:

Relative to experimental solutions

- ↓ [U]
- ↓ [Si]
- ↑ pH

Experimental conditions

Hanford vadose zone
SYNTHESIS EXPERIMENTS
with CO₂
HEXS, FTIR, XRD analysis

- Prepared on benchtop open to the atmosphere
- 0.990 M \( \text{UO}_2(\text{ClO}_4)_2 \)
- 0.105 M \( \text{Na}_2\text{SiO}_3\cdot9\text{H}_2\text{O} \)
- 50 µL U-solution (0.05 M \( \text{U}_3 \))
  950 µL Si-solution (0.1 M \( \text{Si}_1 \))
- 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 SiO₂(am)

3rd Set of Experiments for HEXS Analysis

natural system
Thermodynamics tells us this if we don’t assume equilibrium with amorphous silica.
...and this if we assume equilibrium with amorphous silica.
Peaks suggest a Na-silicate phase. No obvious match with any U-silicates.

U/Si = 1.5 to 1.9

Boltwoodite U:Si = 1:1
Soddyite U:Si = 2:1
**X-ray Diffraction of Solids heated at 150°C for 4 days**

Boltwoodite $U:Si = 1:1$
Soddyite $U:Si = 2:1$

Pattern like low-temperature patterns

- pH 9.1
- pH 8.1
- pH 7.1
- pH 6.0
- pH 5.1

U/Si = 1.4 (pH 6.0) to 2.5 (pH 9.1)

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

SiO$_4^{4-}$ peak for Na-boltwoodite
SiO$_4^{4-}$ of Na-weeksite or am SiO$_2$
UO$_2^{2+}$ of Na-boltwoodite
UO$_2^{2+}$ peak shifting towards 880 cm$^{-1}$
UO$_2^{2+}$ peak of Na-boltwoodite
SiO$_4^{4-}$ peak of Na-weeksite shifting or disappearing with pH
SiO$_4^{4-}$ of soddyite, weeksite, or Na-boltwoodite
OH$^-$ double peak decay typical of boltwoodite

FT-IR microspectrometer (IlluminatIR) with diamond total attenuated reflectance (ATR) in open atmosphere

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

Background-corrected PDF
**HEXS: Pair Distribution Function – 150°C Precipitates**

Reacted 4 days; air-dried

[Graph showing pair distribution function for various pH values and minerals]
Average Pair Distances for Room T Precipitates

- U-U
- U-Si

Sample

- Uranophane
- Weeksie
- Boltwoodite (40% Na)
- Soddyite

r (Å)

3.1 3.2 3.3 3.4 3.5 3.6 3.7 3.8 3.9 4.0
**Other work in progress:**

<table>
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<th>U [M]</th>
<th>Si [M]</th>
<th>CO2</th>
<th>pH</th>
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<td>1.0E-07</td>
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</tbody>
</table>

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
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.