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.

Na₈(Al₆Si₆O₂₄)(NO₃)₂ • 4H₂O


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

pH 11.3; 2 m NaNO$_3$; 90°C

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

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

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

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**‘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 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
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

**Na₂ZnSiO₄**
Precipitated on vapor-altered glass

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

**K-Boltwoodite**
\(\text{K(UO}_2)(\text{SiO}_3)(\text{OH})\cdot1.5\text{H}_2\text{O}\)
**Possible mechanism of U-Silicate formation**

U(VI) speciated as $\text{UO}_2(\text{CO}_3)_3^{4-}$; $T = 80 \, ^\circ\text{C}$; $\text{pH} = 10$

Na-boltwoodite; $\mu$-XRD and $\mu$-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**
**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°C</th>
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<td>Uncontaminated PW</td>
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<td>4.99E-03</td>
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</table>

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

Dissolution of Labradorite Feldspar: An\textsubscript{60} Ca\textsubscript{(50-70\%)} Na\textsubscript{(50-30\%)}\textsubscript{(Al,Si)}AlSi\textsubscript{2}O\textsubscript{8}

SEM image of feldspar reacted with simulated tank waste
Bates, 2004, UIC M.S. Thesis
Activity-activity diagram for contaminated pore water

Silica solubility changes

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

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

Soddyite: \( (\text{UO}_2)_2(\text{SiO}_4)(\text{H}_2\text{O})_2 \)
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 CO₂
  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$_2$)

$U = 10^{-7}$ M, $Si = 5 \times 10^{-3}$ M, $NaNO_3 = 0.1$ M, $PCO_2(g) = 10^{-3.5}$ atm
Solution compositions for initial scattering experiments:

- **UIC samples**
  - 0.23 M $\text{UO}_2(\text{NO}_3)_2$
  - 0.01-0.25 M $\text{Na}_2\text{SiO}_3\cdot9\text{H}_2\text{O}$
  - U added to Si stock
  - U analysis by $\alpha$-counting
  - Not analyzed by scattering

- **Sample Set 1**
  - 0.30-0.59 M $\text{UO}_2(\text{ClO}_4)_2$
  - 0.04-0.29 M $\text{Na}_2\text{SiO}_3\cdot9\text{H}_2\text{O}$
  - Si added to U stock

- **Sample Set 2**
  - 0.20-0.48 M $\text{UO}_2(\text{ClO}_4)_2$
  - 0.03-0.09 M $\text{Na}_2\text{SiO}_3\cdot9\text{H}_2\text{O}$
  - Si reagent added incrementally

Open to atmosphere; pH ~ 2-4

Precipitate increases with $\uparrow [\text{Si}]$ & $\downarrow [\text{U}]$
2nd Set of Experiments for HEXS Analysis

Sample Set 1
Sample Set 2
UIC Samples 1
UIC Samples 2
Solubility SiO2(am)

natural system

[U] M
0.0 0.1 0.2 0.3 0.4 0.5 0.6
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$_2$SiO$_3$$\cdot$9H$_2$O
- Si added incrementally to U stock
- pH measured (~2.5-4)
- Sampled for analysis
  - U: $\alpha$-counting
  - Si: UV-Vis & ICP-OES
- 2 sample sets:
  - LongTerm: 8 weeks
  - ShortTerm: 2 weeks
Thermodynamic modeling tells us...

Experimental conditions:

$U = 0.25 \text{ M, } Si = 0.25 \text{ M, } NaClO_4 = 0.5 \text{ M, } CO_2(g)$ excluded.

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

Background-corrected PDF

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

Background-corrected PDF
Comparison with Hanford vadose zone:

- Relative to experimental solutions:
  - $\downarrow$ [U]
  - $\downarrow$ [Si]
  - $\uparrow$ pH

Experimental conditions in the Hanford vadose zone:

- $\text{SiO}_2\text{(am)}$
- Soddyite
- Na-Boltwoodite
- Schoepite $\text{Na}_2\text{U}_2\text{O}_7$
SYNTHESIS EXPERIMENTS
with CO₂
HEXS, FTIR, XRD analysis

- Prepared on benchtop open to the atmosphere
- 0.990 M UO₂(ClO₄)₂
- 0.105 M Na₂SiO₃•9H₂O
- 50 µL U-solution (0.05 M Uᵣ)
- 950 µL Si-solution (0.1 M Siᵣ)
- 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
3rd Set of Experiments for HEXS Analysis

Sample Set 1
Sample Set 2
UIC Samples 1
UIC Samples 2
Solubility SiO$_2$(am)

natural system

Sample

[U] M
Thermodynamics tells us this if we don’t assume equilibrium with amorphous silica.
...and this if we assume equilibrium with amorphous silica.
X-ray Diffraction of Room Temperature Solids – air-dried

Peaks suggest a Na-silicate phase. No obvious match with any U-silicates.

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

U/Si = 1.5 to 1.9
**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)

Soddyite

$U/Si = 2.6$

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

The diagram illustrates the FTIR spectra of samples aged for 6 weeks and air-dried, focusing on the wavenumber (cm⁻¹) range from 4000 to 400. The absorbance peaks are labeled for different pH conditions: pH 6.93, pH 8.03, and pH 9.02. Key features include:

- **$	ext{SiO}_4^{4-}$ peak** for Na-boltwoodite.
- **$	ext{UO}_2^{2+}$ peak** for Na-boltwoodite.
- **$	ext{SiO}_4^{4-}$ peak** of Na-weeksite shifting or disappearing with pH.
- **$	ext{SiO}_4^{4-}$ peak** of soddyite, weeksite, or Na-boltwoodite.
- **OH⁻ double peak**, indicative of Na-weeksite, begins to disappear at pH 9.
- **H₂O** peak typical of boltwoodite.

The FT-IR microspectrometer (IlluminatIR) was used with diamond total attenuated reflectance (ATR) in an open atmosphere.
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

Background-corrected PDF
Pair Distances for 150°C Precipitates

- Soddyite
- Boltwoodite (40% Na)
- Weeksite (not Na)

- pH 9.1
- pH 5.1
Average Pair Distances for Room T Precipitates

- Uranophane
- Weeksite
- Boltwoodite (40% Na)
- Soddyite
**Other work in progress:**

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<th>U [M]</th>
<th>Si [M]</th>
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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.