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Impact of Iron Sulfide on the Oxidative Dissolution of Reduced Uranium

Co-PI: Bruce Rittmann-ASU, Co-I James Davis-LBNL
Rifle Site, CO

Rifle CO UMTRA (uranium mill tailing remedial action) site – biostimulation for U(VI) reduction to U(IV)
Project Background

Abiotic U Remobilization

After U bio-remediation stops...

DO + \(N_xO_x\) oxidants

Biostimulation Zone
Sparingly Soluble
U(IV)

Soluble
U(VI)

REDUCTION

U(VI)
Fe(III)
S(0)

UO_2

DO

FeS

\(SO_4^{2-}\)

S(-II)

Elec donor

U bio-remediation scenario
## Abiotic Studies of Uraninite Oxidation in the Presence of FeS (mackinawite)

### Hypothesis:

FeS can abiotically inhibit $\text{UO}_2$ from rapid oxidation by serving as an oxidant scavenger.

### Objectives:

- Examine rates and mechanisms of $\text{UO}_2$ oxidation and mobilization in the presence of iron sulfide (mackinawite).
- Characterize the solid phase products formed and impact on U(VI) mobilization.

### Approach:

- Perform batch, completely-mixed flow, and column reactor studies of uraninite oxidation in presence and absence of FeS.
Biogenic Production of FeS and UO$_2$ under Sulfate Reducing Conditions

**Hypothesis:**
SRB can produce FeS (mackinawite) and UO$_2$ with reactivities that mimic abiotic analogues

**Objectives:**
- Examine FeS and UO$_2$ formation over a range of conditions (pH, electron donors, electron donor/acceptor ratio, SO$_4$/Fe ratio, iron source)
- Characterize crystallite size and reactivity of biogenic FeS and UO$_2$ in comparison to abiotically produced FeS and UO$_2$

**Approach:**
- Perform batch microcosm studies using pure and mixed SRB cultures
SRB can produce mackinawite
- *D. vulgaris, D. nigrificans* produce mackinawite
- crystallite size depends on geochemical conditions
- smaller crystallite sizes are favored in systems which are more locally oversaturated (rate of production of [S(-II)] and [Fe(II)] available)
  - higher [Fe(II)]:[SO$_4$] ratio, larger crystallite size
  - lower [Fe(II)], smaller crystallite size
  - faster rate of [S(-II)] increase, larger crystallite size (e.g., lactate vs pyruvate)
- Chen et al. 2011 (in review); Chen et al. 2012 (to be submitted)
- Aging and temperature play a role in crystallite size but after 3 days remains stable (months to one year?) at low temperatures

SRB can produce uraninite
- Rizlan Bernier-Latmani et al. (*ES&T* 2010)
- But also monomeric U(IV) → geochemical conditions matter
UO₂ Synthesis

Synthesis
Reductive precipitation of uranyl nitrate solution by sulfide at pH = 7.0. Beyenal et al. (2004).
SA: ~140 m²/g (FWHM: 5 nm); similar by TEM (~5 nm)

<table>
<thead>
<tr>
<th>Source</th>
<th>a (Å)</th>
<th>crystal size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Schofield 2008, biogenic</td>
<td>5.430 – 5.467</td>
<td>2.85 – 3.03</td>
</tr>
<tr>
<td>Wyckoff 1978, abiotic</td>
<td>5.4682</td>
<td>--</td>
</tr>
<tr>
<td>Sharp 2009, biogenic</td>
<td>5.465 – 5.472</td>
<td>2.20 – 3.23</td>
</tr>
<tr>
<td>This study</td>
<td>5.408</td>
<td>3.47</td>
</tr>
</tbody>
</table>

Two-Theta (deg)

Intensity(Counts)
Mackinawite (FeS) Synthesis

**Synthetic mackinawite (FeS)**
- Precipitated from Na$_2$S and FeCl$_2$ solutions, rinsed and freeze dried (Jeong et al. 2008);
- SA: $\sim 120 \text{ m}^2/\text{g}$ ($\sim 5\text{nm}$)

<table>
<thead>
<tr>
<th>Source</th>
<th>$a = b$ (Å)</th>
<th>$c$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthetic Mk$^a$</td>
<td>3.67</td>
<td>5.20</td>
</tr>
<tr>
<td>Synth MkA$^b$</td>
<td>4.02</td>
<td>6.60</td>
</tr>
<tr>
<td>Synthetic MkB$^b$</td>
<td>3.65</td>
<td>5.48</td>
</tr>
<tr>
<td>Crystalline Mk$^c$</td>
<td>3.6735(4)</td>
<td>5.0328(7)</td>
</tr>
<tr>
<td>Mullet 2002</td>
<td>3.37</td>
<td>5.05</td>
</tr>
<tr>
<td>Evans 1965</td>
<td>3.66-68</td>
<td>5.03</td>
</tr>
<tr>
<td>Berner 1962</td>
<td>3.68</td>
<td>5.03</td>
</tr>
<tr>
<td><strong>This Study</strong></td>
<td><strong>3.668</strong></td>
<td><strong>5.107</strong></td>
</tr>
</tbody>
</table>
What if FeS is present?

**Mackinawite (FeS)**

**Surface complexes**

**Passivated UO$_2$(s)**

**UO$_2$(CO$_3$)$_{aq}$**

**UO$_2^{2+}$**

**O$_2$, NO$_2$**

**UO$_2$(solid)**
Batch Studies for UO$_2$ Oxidative Dissolution

Features:

- Fixed partial pressure of gas
- pH 7 controlled by carbonate buffer
- Artificial groundwater
- 5 g FeS/L loading
- Varied UO$_2$ loading
- Temp control @ 25°C
Aqueous U(VI) Species Distribution

Simulation Conditions

- pH = 3 to 9
- $U_T = 1.7$ mM
- 5% CO$_2$
- $Ca_T = 2$ mM

- U(VI) is greatly under-saturated to any U(VI) solids at pH = 7
- The predominant U(VI) species: $Ca_2UO_2(CO_3)_3^0$ and $CaUO_2(CO_3)_3^{2-}$
- $Ca^{2+}$ is under-saturated to calcite
General Sample Analyses

- Aqueous phase
  - **ICP-MS**: Dissolved Fe$_T$, U$_T$, and Ca$_T$;
  - **IC**: $S_2O_3^{2-}$, $SO_4^{2-}$;
  - **LC**: Elemental $S$;
  - pH, DO, and ORP

- Solid phase
  - **XRD**: selected bulk samples;
  - **XANES**: U $L_{III}$-edge and S $K$-edge;
  - **EXAFS**: U $L_{III}$-edge.
Batch Results: Oxidative Dissolution of UO$_2$

**Experimental Conditions**
- pH = 7
- Fe: U (molar) = 30:1
- 5% CO$_2$ and 2% O$_2$

- Control with only UO$_2$

- FeS inhibits UO$_2$ oxidation until it is completely consumed by oxygen
- After 60 hrs. UO$_2$ begins significant oxidation

Bi et al. 2011 (in revision)
Oxidative Dissolution Rates

- Dissolution rate of UO$_2$ from linear regression are close to biogenic UO$_2$ Ulrich et al. 2009 under similar conditions

- Slightly faster rate in the presence of Fe

- The oxidative dissolution of UO$_2$ is closely tracked by the change of Eh

Bi et al. 2011 (in revision)

<table>
<thead>
<tr>
<th>Mass-normalized Initial Rate (mol/g-s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Syn-UO$_2$ only</td>
</tr>
<tr>
<td>5.4 ± 0.2 ×10$^{-9}$</td>
</tr>
<tr>
<td>Syn-UO$_2$ w/ FeS</td>
</tr>
<tr>
<td>1.2 ± 0.4 ×10$^{-8}$</td>
</tr>
</tbody>
</table>
Oxidative Dissolution Rates

- The absence of FeS results in slower rate and incomplete oxidation of UO₂
- UO₂ presence at 200 hr confirmed by XRD

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<thead>
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<th>Mass-normalized Initial Rate (mol/g-s)</th>
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<td>Syn-UO₂ only</td>
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<tr>
<td>5.4 ± 0.2 \times 10^{-9}</td>
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<tr>
<td>Syn-UO₂ w/ FeS</td>
</tr>
<tr>
<td>1.2 ± 0.4 \times 10^{-8}</td>
</tr>
</tbody>
</table>
Oxidative Dissolution Rates

- The presence of FeS results in faster rate and complete oxidation of UO₂.

- U(VI) and no detectable U(IV) confirmed by XAS.

<table>
<thead>
<tr>
<th></th>
<th>Syn-UO₂ only</th>
<th>Syn-UO₂ w/ FeS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass-normalized Initial Rate (mol/g-s)</td>
<td>5.4 ± 0.2 ×10⁻⁹</td>
<td>1.2 ± 0.4 ×10⁻⁸</td>
</tr>
</tbody>
</table>
Phase 1: Fe(II) dissolution formation of ferrihydrite

Phase 2: S(-II) oxidation to elemental S$_8$; formation of nano-goethite

Phase 3: FeS completely oxidized to Fe(III) solids; U(IV) oxidation to U(VI)

FeS(s) + $\frac{3}{4}$O$_2$ + $\frac{1}{2}$H$_2$O = $\frac{1}{8}$S$_8$(s) + FeOOH(s)

$U_T = 1.7$ mM ~65% sorbed
Solid Phase S: XANES of K-edge Sulfur

- Transformation of structural sulfide [S(-II)] into elemental S over oxidation reaction.
- $S_8^0$ is the dominant oxidation product in the abiotic system.
- S(-II) oxidation to $S_8^0$ consumes oxygen and controls Eh.
Solid Phase FeS Oxidation Products

- Fe(III) hydroxides (i.e., ferrihydrite to nano-goethite and lepidocrocite) as final oxidation products

- Mössbauer confirms ferrihydrite to nano-goethite at earlier times (not shown)
Solid-Associated U $L_{III}$-edge EXAFS

Trend of U structure as a function of time:

- Uranium mainly remains as U(IV) before 48 hr reaction.
- At 87 hr, mixed U(VI) and U(IV) species exist, with uranyl ions bound to UO$_2$ core.
- U dominantly in a hexavalent form at 144 hr reaction, as surface-adsorbed uranyl complexes $\rightarrow$ completely oxidized.
Varying Fe:U Molar Ratios

Comparing 100:1 and 30:1 Fe:U (molar)

- Consistent inhibition period by FeS (~60 hr)
- Rate increase with molar ratio
- Adsorption of U(VI) controls ~30-40% of total U in batch reactors at 250 hr

<table>
<thead>
<tr>
<th>Mass-normalized Initial Rate (mol/g-s)</th>
<th>100:1 (Fe:U)</th>
<th>30:1 (Fe:U)</th>
<th>UO₂ only (1.7 mM U)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.4 ± 0.3 × 10⁻⁸</td>
<td>1.2 ± 0.4 × 10⁻⁸</td>
<td>5.4 ± 0.2 × 10⁻⁹</td>
<td></td>
</tr>
</tbody>
</table>

Bi et al. 2012 (in prep)
After depletion of FeS

Iron oxidation products serve as shuttle and sink to reduce passivation layer?

Bi et al. 2011 (in revision)
### Abiotic Batch Studies Results

- The stability of U(IV) solid phases is maintained in the presence of FeS as a result of the preferential reaction of DO with FeS before reacting with U(IV).

- Elemental sulfur and Fe(III) hydroxides are the end oxidation products of FeS by O$_2$ in the abiotic systems.

- The extent of FeS protection of U(IV) solids depends on O$_2$ concentration and the relative amount of FeS to reduced U(IV).

- Uraninite oxidation rate may be enhanced by the production of Fe(III) (hydr)oxides, after FeS is depleted.
Future Plans

• Perform studies over a range of geochemical conditions including pH, carbonate, and calcium concentrations

• Conduct studies using biogenically produced FeS and UO$_2$(s)

• Examine the effects of FeS post oxidation products on UO$_2$ oxidative dissolution and long-term uranium stability - see poster 145

• Investigations of abiotic oxidation rates in column reactor systems using gamma irradiated sediments (RABS) - see poster 146

Carpenter et al. 2012 (to be submitted)
Acknowledgements

**UM Research group:** Yuqiang Bi, Julian Carpenter, Tara Clancy, Sung Pil Hyun.

**Co-PIs:** Bruce E. Rittmann (Arizona State University) and James Davis (LBNL)

**Collaborators:** Raveender Vannela (ASU), John Bargar (SSRL), and Ravi K. Kukkadapu (PNNL)

**Funding:** Office of Science (BER), U.S. Department of Energy, Grant No. DE-FG02-09ER64803. Thank you!!
Questions?
Experimental Conditions

<table>
<thead>
<tr>
<th>Artificial G.W. recipe</th>
<th>Concentration (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaHCO₃</td>
<td>4.0</td>
</tr>
<tr>
<td>KCl</td>
<td>0.4</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>2.0</td>
</tr>
</tbody>
</table>

This g.w. composition applies to all the experiments listed below.

<table>
<thead>
<tr>
<th>pH</th>
<th>DO  (mg/L)</th>
<th>[Ca] (mM)</th>
<th>Fe:U (molar)</th>
<th>Gas mixture</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.0</td>
<td>0.7</td>
<td>2.0</td>
<td>30:1</td>
<td>5% CO₂ &amp; 2% O₂</td>
<td>DO is controlled by O₂ gas partial pressure</td>
</tr>
<tr>
<td>7.0</td>
<td>~7.0</td>
<td>2.0</td>
<td>30:1</td>
<td>5% CO₂ &amp; 20% O₂</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>pH</th>
<th>DO  (mg/L)</th>
<th>[Ca] (mM)</th>
<th>Fe:U (molar)</th>
<th>Gas mixture</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.0</td>
<td>0.7</td>
<td>2.0</td>
<td>100:1</td>
<td>5% CO₂ &amp; 2% O₂</td>
<td>Keeping FeS = 5.0 g/L (0.056 mol/L) while changing UO₂ input.</td>
</tr>
<tr>
<td>7.0</td>
<td>0.7</td>
<td>2.0</td>
<td>30:1</td>
<td>5% CO₂ &amp; 2% O₂</td>
<td></td>
</tr>
</tbody>
</table>

The experimental results discussed here will focus on the first set.
Supplementary EXAFS Data

Structural parameters extracted from U $L_{III}$-edge EXAFS data from the batch reactor.

<table>
<thead>
<tr>
<th>Sample</th>
<th>0 hr</th>
<th>48 hr</th>
<th>87 hr</th>
<th>144 hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_O$</td>
<td>6.6 (U$^{IV}$-O)</td>
<td>6.8 (U$^{IV}$-O)</td>
<td>2.1 (U$^{VI}$-O)</td>
<td>1.4 (U$^{VI}$-O)</td>
</tr>
<tr>
<td>$R_O$ (Å)</td>
<td>2.34(2)</td>
<td>2.34(1)</td>
<td>1.83(6)</td>
<td>1.84(4)</td>
</tr>
<tr>
<td>$\sigma^2_O$</td>
<td>0.0091</td>
<td>0.0096</td>
<td>0.0113</td>
<td>0.0033</td>
</tr>
<tr>
<td>$N_O$</td>
<td>9.7 (U$^{IV}$-O)</td>
<td>2.2 (U$^{VI}$-O)</td>
<td>2.28(3)</td>
<td>2.45(6)</td>
</tr>
<tr>
<td>$R_O$ (Å)</td>
<td></td>
<td></td>
<td>0.0295</td>
<td>0.0868</td>
</tr>
<tr>
<td>$\sigma^2_O$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$N_U$</td>
<td>4.7</td>
<td>5.8</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>$R_U$ (Å)</td>
<td>3.85(5)</td>
<td>3.83(2)</td>
<td>3.84(3)</td>
<td></td>
</tr>
<tr>
<td>$\sigma^2_U$</td>
<td>0.0044</td>
<td>0.0057</td>
<td>0.0083</td>
<td></td>
</tr>
</tbody>
</table>

$N_O$: coordination number of U-O bond; $R_O$: interatomic distance of the U-O bond; $\sigma^2_O$: Debye-Waller factor of the U-O bond, etc.