Aqueous Complexation Reactions Governing the Rate and Extent of Biogeochemical U(VI) Reduction

Scott C. Brooks*1, Wenming Dong1, Sue Carroll1, James K. Fredrickson2, Kenneth M. Kemner3, Shelly Kelly3
Collaborators: Kent Orlandini3, John Zachara2

1 Oak Ridge National Laboratory
2 Pacific Northwest National Laboratory
3 Argonne National Laboratory

DOE-ERSP Spring PI Meeting 4 April 2006
The effect of Ca did not depend on:

- Bacterial strain:
  - *S. algae* BrY
  - *S. putrefaciens* SN32
  - *Desulfovibrio desulfuricans*
  - *Geobacter sulfurreducens*
  - *G. metallireducens* GS-15

- Antecedent culture conditions: aerobic, anaerobic.

- Electron donor: Lactate, Acetate, H₂.

The effect of Ca did depend on:

Electron acceptor:

- ✓ U(VI)
- ✗ Tc(VII)
- ✓ Fumarate
- ✗ Co(III)EDTA

(Brooks et al., 2003)
Link between U(VI) speciation and direct bacterial reduction

Implications for Biogeochemical U(VI) Reduction:

Ternary Complex Formation:
Other M-UO$_2$-CO$_3$ complexes exist. Their influence on rate and extent of bacterial U(VI) reduction will be a function of their net charge and stability.

Abiotic Reduction:
Indirect reduction of U(VI) (e.g., surface associated Fe(II)) is inhibited by formation of M-UO$_2$-CO$_3$ complexes. Effect proportional to stability constants.

Microbial Reduction:
Retardation of microbial metal reduction activity will be restricted to M-UO$_2$-CO$_3$ complexes (i.e., no effect on Fe(III) reduction).

[Graphs and diagrams illustrating the temporal changes in [U(VI)] and the influence of different conditions on U(VI) reduction]
Determination of the formation constants of ternary complexes of uranyl and carbonate with alkaline earth metals (Mg$^{2+}$, Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$) using an anion exchange method (Dong and Brooks, in review)

\[
\frac{D_0}{D_M} - 1 = K_1 [M^{2+}]_{aq} + K_2 [M^{2+}]_{aq}^2
\]

- $D_0$, $D_M$, $[M]$ measured by experiment.
- $K_1$ and $K_2$ determined from fit to data.
- F-test to determine the more appropriate model.
Formation constants of the $\text{MUO}_2(\text{CO}_3)_3^{2-}$ (aq) and $\text{M}_2\text{UO}_2(\text{CO}_3)_3^{0}$ (aq) complexes.

<table>
<thead>
<tr>
<th>$\text{M}^{2+}$</th>
<th>$\log \beta_{113} (I = 0)$</th>
<th>$\log \beta_{213} (I = 0)$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Mg}^{2+}$</td>
<td>26.11 ± 0.04</td>
<td>---</td>
<td>This work</td>
</tr>
<tr>
<td>$\text{Ca}^{2+}$</td>
<td>27.18 ± 0.06</td>
<td>30.70 ± 0.05</td>
<td>This work</td>
</tr>
<tr>
<td></td>
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<td>29.41 ± 0.7$^b$</td>
<td>Bernhard et al., 1996</td>
</tr>
<tr>
<td></td>
<td>25.6 ± 0.25$^b$</td>
<td>30.79 ± 0.25$^b$</td>
<td>Bernhard et al., 2001</td>
</tr>
<tr>
<td>$\text{Sr}^{2+}$</td>
<td>26.86 ± 0.04</td>
<td>---</td>
<td>This work</td>
</tr>
<tr>
<td>$\text{Ba}^{2+}$</td>
<td>26.68 ± 0.04</td>
<td>29.75 ± 0.07</td>
<td>This work</td>
</tr>
</tbody>
</table>

$^a$ = marginally significant at $P = 0.0496$ and therefore not accepted.

$^b$ = revised to reflect the new recommended value for formation constant of $\text{UO}_2(\text{CO}_3)_3^{4-}$ in Guillaumont et al. (2003).
Implications of our estimated stability constants 1: Speciation as f(pH)
Implications of our estimated stability constants 2: Speciation as f([Ca])

**NEA suggested values**

<table>
<thead>
<tr>
<th>[Ca] (mM)</th>
<th>Species Concentration (µM)</th>
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<tbody>
<tr>
<td>0.0</td>
<td>0</td>
</tr>
<tr>
<td>0.5</td>
<td>2</td>
</tr>
<tr>
<td>1.0</td>
<td>4</td>
</tr>
<tr>
<td>1.5</td>
<td>6</td>
</tr>
<tr>
<td>2.0</td>
<td>8</td>
</tr>
<tr>
<td>2.5</td>
<td>10</td>
</tr>
</tbody>
</table>

- $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$
- $\text{CaUO}_2(\text{CO}_3)_3^{2-}$
- $\text{UO}_2(\text{CO}_3)_2^{2-}$
- $\text{UO}_2(\text{CO}_3)_3^{4-}$
- $\text{UO}_2\text{CO}_3(\text{aq})$

**This study**

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I = 0.05; pH 8
TIC = 10 mM
$U_{TOT} = 10 \mu M$
U(VI) uptake by anion exchange resins inhibited by formation of neutral \( \text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0 \)
Summary 1:

- Identified and quantified alkaline earth-uranyl-carbonate complexes.
  - Mg & Sr : $\text{MUO}_2(\text{CO}_3)_3^{2-}$ **
  - Ca & Ba : $\text{MUO}_2(\text{CO}_3)_3^{2-}$, $\text{M}_2\text{UO}_2(\text{CO}_3)_3^{0}$
  - Ca > Ba = Sr > Mg
- $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ complex more important than previously suggested
- Decreased U partitioning to anion exchange resins correlate with predicted species distribution.
Influence of EDTA and pH on Bioreduction of Uranium(VI) in the Presence of Calcium Ions (Dong et al., in prep)

U(VI) Speciation: Implications for Bioreduction?

- **Thermodynamic considerations**
  - U(VI) speciation affects reduction potential → energy available to microorganisms.

- **Kinetic considerations**
  - Synthesis of new cell components?
  - Speciation kinetics?

![Eh (Volts) vs. pH diagram](attachment:image.png)

- pH 6.5, 25°C, 20% CO₂, [U(VI)] = 50 µM

U(VI) Speciation:
- $\text{UO}_2(\text{CO}_3)_3^{4-}/\text{Uraninite}$
- $\text{UO}_2(\text{CO}_3)_2^{2-}/\text{Uraninite}$
- $\text{CaUO}_2(\text{CO}_3)_3^{2-}/\text{Uraninite}$
- $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^+/\text{Uraninite}$
- $\text{UO}_2\text{EDTA}^{2-}/\text{U(IV)EDTA}$
- $\text{UO}_2\text{EDTA}^{2-}/\text{Uraninite}$
Influence of EDTA and pH on Bioreduction of Uranium(VI) in the Presence of Calcium Ions (Dong et al., in prep)

U(VI) Speciation as f([EDTA]) at pH 6.5

11 mM NaHCO₃, 20% CO₂, pH 6.5, 2.5 mM Ca

UO₂(CO₃)₃⁴⁻ and UO₂(CO₃)₂²⁻ constitute the balance of U(VI) species.
Influence of EDTA and pH on Bioreduction of Uranium(VI) in the Presence of Calcium Ions

- **S. putrefaciens CN32**
  - 11 mM NaHCO$_3$
  - 20% CO$_2$(g)
  - pH 6.5
  - 2.5 mM CaCl$_2$

- **Increasing [EDTA]:**
  - Decreased fraction Ca-U(VI)-CO$_3$ species.
  - Increased reduction rate.
  - Decreased lag phase.
  - More complete reduction.
  - Lines = pseudo 1° model

- **When EDTA present** U$_{\text{TOT}}$ constant in filtered fraction.

  (Dong et al., in prep)
Fate of Biogenic U(IV) in presence of EDTA
(*U(IV) in solution = U(IV) passing 0.2 µm pore size filter)

- Suggests that a U(IV) solid phase with a higher solubility than UO$_2$$_{am}$ (Guillaumont et al., 2003) controlled [U(IV)].
- U(IV) stable in solution for at least 5 months (...and counting).
**U-XANES** verifies that the majority of the U in the sample is in the +4 valence state.

**U-EXAFS**: No U-U backscatter – indicates dissolved U, not nanoparticles that passed 0.2 µm pores in filter.
U(VI) speciation controlled by [EDTA] pH 6.5

11 mM NaHCO₃, 20% CO₂, pH 6.5, 2.5 mM Ca
U(VI) speciation controlled by [EDTA] pH 7.1

20% CO₂, pH 7.1

Mole Fraction U(VI)

[EDTA] (mM)

0 0.2 0.4 0.6 0.8 1

Mole Fraction Ca-U-CO₃

[EDTA] mM

0 2.25 2.0 0

Pseudo 1° k (h⁻¹)

0 0.2 0.4 0.6 0.8 1

Mole Fraction Ca-U-CO₃ Species

0 1.75 2 2.25 2.5 2.5, No Ca

Ca₂UO₂(CO₃)₃

CaUO₂(CO₃)₃²⁻

UO₂EDTA²⁻

Ca₂UO₂(CO₃)₃⁰

CaUO₂(CO₃)₃²⁻
U(VI) speciation controlled by [Ca] pH 6.9
Effect of Mg on bacterial U(VI) reduction (preliminary):

- Mg slows rate of U(VI) reduction
  - Effect weaker than Ca
  - Mg complex is weaker than the Ca complexes
  - The MgUO$_2$(CO$_3$)$_3^{2-}$ complex is dominant
Summary 2:

- Rate and extent U(VI) bioreduction related predicted speciation.
  - Tentative evidence that the uncharged \( \text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0 \) complex governs the observed rate.

- EDTA additions:
  - A stable U(IV)EDTA complex generated
    - Suggests that neither \( \text{UO}_2,\text{am} \) nor Uraninite controlling U(IV) solubility.

- Nature of thermodynamic and kinetic constraints is not entirely clear:
  - Thermodynamic constraints do not seem to limit rate or extent U(VI) reduction
    - U(VI)EDTA weaker electron acceptor than the Ca-UO_2-CO_3 species yet is reduced faster and to a greater extent.
  - Analogous species exist for other alkaline earth elements
    - Impact on U(VI) bioreduction related to strength of complex

- Rate of complex dissociation?
Reduced Product Stability: Effects of pH, EDTA, and Ca\(^{2+}\) on Biogenic U(IV) solids and U(IV)-EDTA Oxidation (Dong and Brooks, in prep)

- Biogenic U(IV) samples prepared anaerobically.
- Removed from glovebox and exposed to atmosphere (21% \(O_2\)) without stirring/shaking.
- U(VI) monitored over time.

\[
\frac{C(t)}{C(0)} = 1 - \exp(-kt)
\]
The oxidation rate of U(IV) solids and U(IV)-EDTA increased with increasing pH and decreasing [Ca].
• EDTA slows the rate of biogenic U(IV) oxidation at pH 1.

• EDTA enhances the rate of biogenic U(IV) solids oxidation as pH increases.
Summary 3:

- Biogenic U(IV) oxidation
  - Increased with pH
  - Decreased with addition of Ca
- At pH 1 EDTA decreased oxidation rate
- As pH increased, EDTA enhanced U(IV) oxidation rate.
- Improved method to determine U(IV) from difference ($U_{TOT} - U(\text{VI})$) by stabilizing U(IV) in samples.