Heterogeneity in Bioreduction and Resulting Impacts on Contaminant Dynamics

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Changes in iron phases will impact both contaminant sorption and reduction (oxidation).
Reductive Transformation of Iron

- *S. putrefaciens* strain CN32 inoculated ferrihydrite coated quartz-sand
- pH 7, 3 mM lactate
Solid-phase Distribution

- **Ferrihydrite**
- **Goethite**
- **Magnetite**

Green Rust < 4%

Flow vs. Mole % Fe graph:
- Black line for Ferrihydrite
- Orange line for Goethite
- Blue line for Magnetite

Image of a material with a black and orange section.
Iron Biomineralization

Fe(OH)$_3$$\cdot$$_n$H$_2$O
goethite

siderite

decay

Fe(II) aq

Low
(< 0.3 mM)

Medium
(> 0.3 mM)

goethite

conversion

Fe(II) aq + S(-II)  \rightarrow  IRB

Fe(II) aq + HCO$_3^-$  \rightarrow  IRB

iron sulfide

green rust

magnetite
Alteration in Surface Composition

\[
\begin{align*}
\text{Org} & \rightarrow \text{RED} \\
\text{Cox} & \rightarrow \text{IRB} \\
\text{Fe(II)}_{aq} & \rightarrow \text{Fe(OH)\textsubscript{3} \cdot nH}_2\text{O} \\
\text{PO}_4^{3-} & \rightarrow \text{Chemi-sorption}
\end{align*}
\]
Ferrihydrite Reduction: Impact of Phosphate

\[ \text{Fe}^{2+}(\text{aq}) \text{ (uM)} \]

\[ \% \Gamma_{\text{max}} \quad (\text{P surface coverage}) \]

\[ \text{Acetate (uM)} \]

\[ \% \Gamma_{\text{max}} \]
Alteration of Ferrihydrite Reactivity by Phosphate

![Graph showing the alteration of ferrihydrite reactivity by phosphate. The graph plots phosphate coverage (%) on the x-axis and Fe(II) (umoles g⁻¹) on the y-axis. Three lines represent Fe(II) total, Fe(II) solid, and Fe(II) aqueous, each declining as phosphate coverage increases.]
Fe Biomineralization: Impact of Phosphate

Day 1

Day 17
with P

Day 17
without P
Biomineralization Products with Phosphate

Fe EXAFS

Column Day 17

Flow Direction

Distance (cm)
mole % Fe
Iron Biomineralization with P

Fe(OH)$_3$•nH$_2$O

vivianite
Fe$_3$(PO$_4$)$_2$•8H$_2$O

siderite

Fe(II) aq

IRB

Fe(OH)$_3$•nH$_2$O

+ PO$_4^{3-}$

magnetite

green rust

+ HCO$_3$-

conversion
Impacts of Iron Transformation:

Reduction of Uranium

U(IV) → U(VI) → Reduction → Oxidation → U(IV)
Uranyl Reduction by *Shewanella alga*

![Graph showing uranyl reduction over time with markers for ferrihydrite and goethite, hematite.]
U(VI)-Fe(III) Reduction

Nutrient-rich

Nutrient-poor

**Graphs**

- **Top Graph**: Bar chart showing the percent of electrons transferred from 0-24, 24-72, 72-168, and 168-408 time segments.
- **Bottom Left Graph**: Image of nutrient-rich environment with a scale of 10 µm.
- **Bottom Right Graph**: Image of nutrient-poor environment with a scale of 10 µm.
Uranyl Reduction by *Shewanella* sp.
Reactive Transport of Uranium

Uranium(VI) (µM)

Time (d)

Sorption

Desorption

Calcite buffered uranyl/lactate feed solution

influent

effluent
Transport of Uranium: Pore-water Concentration

**Ca$_2$UO$_2$(CO$_3$)$_3$**

- **4 mM Ca**
- **0 mM Ca**

**UO$_2$(CO$_3$)$_2^{2-}$**

Column Length (cm)

Time (d)

Uranium (µM)

Fe Coated Sand

Uncoated Sand

- pH 2 3 4 5 6 7 8 9 10
- Concentration (log molal)

- $\text{CaUO}_2\text{(CO}_3\text{)}_3$
- $\text{UO}_2\text{(CO}_3\text{)}_3^4^-$
- $\text{UO}_2^{2+}$
- $\text{UO}_2\text{CO}_3$
- $\text{UO}_2\text{OH}^+$
- $\text{CaUO}_2\text{(CO}_3\text{)}_3^{2-}$
Uranium Sequestration

Graph showing uranium sequestration with and without calcium. The graph compares the uranium (mg/Kg) levels under different conditions.

- **no Ca**
- **with Ca**

Graph on the right shows the derivative intensity of uranium (VI) and (IV) with and without calcium. The energy (keV) ranges from 17.160 to 17.190 keV.
Uraninite Deposition
Physical-Biogeochemical Linkage
Iron Biomineralization

Fe(OH)$_3$$\cdot$$n$H$_2$O  
**goethite**

Fe(II)$_{aq}$

**magnetite**

Fe(II)$_{aq}$

Low  
(< 0.3 mM)

Medium  
(> 0.3 mM)

IRB + S(-II)  
iron sulfide

+ HCO$_3^-$  
siderite

conversion  
green rust

+ Fe(II)$_{aq}$  
goethite

iron sulfide

siderite

green rust
Spatial Heterogeneity in Biogeochemical Processes

Ferrihydrite
Goethite
Magnetite

Mole % Fe
Solid-Phase Evolution

Mole % Fe vs Time (d)

- Magnetite (red diamonds)
- Ferrihydrite (red triangles)
- Goethite (yellow squares)

Down Gradient (17 cm)
- Magnetite
- Ferrihydrite
- Goethite

Up Gradient (3 cm)
- Magnetite
- Ferrihydrite
- Goethite
Heterogeneity in Iron Biomineralization

Flow Field
Box: Zone of low conductivity

Magnetite (Vol. Fraction)
- 1.9E-03
- 1.3E-03
- 7.2E-04
- 1.5E-04

Goethite (Vol. Fraction)
- 4.3E-04
- 2.9E-04
- 1.4E-04
- 0.0E+00
Biomineralization within Physically Complex Media

Advective flow

Ferrihydrite
Goethite
Magnetite

diffusion

I.D. 0.5 mm
Pore-scale Heterogeneity in Uranium Dynamics

Phase | Process
--- | ---
Fernhydrite | U\(^{VI}\) retention
Goethite | U\(^{VI}\) desorption and reduction
Magnetite | U\(^{VI}\) desorption
Bacteria | U\(^{VII}\)-reduction
Mn
Mn+x
Reduction Oxidation
Impacts of Iron Transformation:

Reduction of Chromium

Cr(III) → Cr(VI) (Oxidation)
Cr(VI) → Cr(III) (Reduction)
Reductants of Chromate

- Dissolved Fe(II)
- Dissolved (S-II)
- Soluble and particulate organic molecules/material
  - mineral catalyzed
  - photoinduced
- ‘Reduced’ Minerals
  - Fe(II) bearing
  - ‘reduced’ sulfur (-II, 0, …)
- Bacteria (enzymatic reduction)
Impact of Biomineralization on Chromium Dynamics

Cr(VI) → IRB → Fe(OH)₃•nH₂O → Fe(II) aq → goethite

Cr(III) ← IRB ← Fe(OH)₃•nH₂O ← Fe(II) aq ← magnetite

green rust
Comparative Rates of Reduction

- Fe(II) \_\text{aq}
- Fe(II)-FeOOH
- Green Rust
- Other Reductants

\( \text{pH} \):

- \(3\)  \(4\)  \(5\)  \(6\)  \(7\)  \(8\)  \(9\)  \(10\)

\( \log \text{Rate (M/h)} \):

- \(-5\)
- \(-4\)
- \(-3\)
- \(-2\)
- \(-1\)
- \(0\)
• Ferrihydrite transformation proceeds rapidly
  – Coupled biotic-abiotic reaction path
  – Generation of goethite and magnetite (lepidocrocite and green rust)
• Chromate reduction is dominated by Fe(II) (sorbed and aqueous) and green rust.
• Uranyl reduction is dependent on aqueous speciation and active metal reducing bacteria
• Biomineralization of ferric hydroxide, a ubiquitous and reactive aerobic iron phase, results dominantly in goethite and magnetite

• Biomineralization occurs via a coupled, biotic-abiotic process that results in solids with constrained size and morphology

• Physical complexity will result in biomineralization heterogeneity

• Iron transformations in natural systems will impact contaminant dynamics and Fe availability
  - alter magnitude and retention strength of contaminants
  - impart reductive capacity
Reaction Progression

\[ \frac{1}{4} \text{C}_3\text{H}_5\text{O}_3^- + \text{Fe(OH)}_3 \rightarrow \frac{1}{4} \text{C}_2\text{H}_3\text{O}_2^- + \text{Fe}^{2+} + \frac{1}{4} \text{HCO}_3^- + \frac{2}{3} \text{H}_2\text{O} + \frac{7}{4} \text{OH}^- \]
Processes Controlling Uranium Reduction

Fe(OH)$_3$•nH$_2$O  IRB  Fe$^{2+}$

U(VI)  U(IV)

green rust

U(VI)  U(IV)

goethite
Physical-Chemical/Mineralogical Challenges

Defining reactive constituents within innately heterogeneous media

Chromium(VI) Transport at the Hanford Reservation

Near-Field Conditions

Far-Field Conditions
Cr(VI) Reactions within Hanford Sediments

Defining reactive constituents within innately heterogeneous media
Cr(VI) (0.2 mM, pH 8) was reacted with Hanford sediments. Cr breakthrough was retarded in acid treated sediment. 300 mg/Kg Cr retained within sediment. What are the specific reductants?
Pore-scale Uranium Reduction

after Tokunaga et al., 2005
Reductants of Uranium

$\text{Fe(OH)}_3 \cdot n\text{H}_2\text{O}$

$\text{MRB/SRB}$

$\text{U(IV)}$ $\text{U(VI)}$

$\text{Fe}^{2+}$

$\text{goethite}$

$\text{green rust}$

$\text{U(IV)}$ $\text{U(VI)}$
Localized Biogeochemical Processes
Ferrihydrite Transformation Upon Reaction with Fe(II)

![Graph showing the transformation of ferrihydrite to goethite and magnetite over time.](image-url)
Changing Reactivity of Ferrihydrite

\[
C_3H_5O_3^- + 4\text{Fe(OH)}_3 \rightarrow C_2H_3O_2^- + 4\text{Fe}^{2+} + \text{HCO}_3^- + \frac{8}{3}\text{H}_2\text{O} + 7\text{OH}^- 
\]

![Images of ferrihydrite, goethite, and hematite with concentration vs. time graphs showing changes over time.](attachment:image.png)
Rate of Mineralogical Transformation

2 mM FeSO₄

% Mineral Phase (mole % Fe)

Time (h)

- goethite
- magnetite
- ferrihydrite
Comparative Rates of Chromate Reduction

D. vulgaris

Fe(II) (aq)

S(-II) (aq)

2,6 dimethoxyphenol

Soil Fulvic Acid

Oxalate/Fe(III)
Controlling Factor in U(VI) Reduction

![Diagram showing uranium concentration over time with different calcium concentrations and pH levels.](image)

- *0 mM Ca*
- *4 mM Ca*
- *Feed*

**Uranium (µM)**

**Time (d)**

**Concentration (log molal)**