Reduction-Oxidation Reactions of $^{99}$Tc in Subsurface Sediments

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I. Tc(VII) reduction and Tc(IV) oxidation reactions in sediments with a lab-generated biogeochemical Fe(II) fraction

- ORNL FRC (FRC) & Hanford Ringold (RG)
- Fe and Tc spatial location and speciation
- Relative rates and controls
- Mineralogic influences

II. New experiments with anoxic, Pliocene Hanford sediments

- Tc(VII) reaction with the natural Fe(II) pool
Technetium

Fission product of $^{235}$Uranium

- Approximately 1990 kg produced at Hanford (1943-1987); world-wide inventory ~ 290 MT
- Exists in oxidation states +7 to -1
- Highly mobile as Tc(VII); pertechnetate ion $\text{TcO}_4^-$
- Biologically reactive (sulfate analogue)
- Microbial reduction to poorly soluble Tc(IV) (widespread)
Solubility of TcO$_2$$\cdot$nH$_2$O

\[
\text{Tc(IIIO}_4^- + 4\text{H}^+ + 3\text{e}^- = Tc(\text{IV})O_2\cdot nH_2O_{(s)} + (2-n)H_2O \quad E^\circ = 0.748 \text{ V}
\]

\[
[\text{Cr(VI)O}_4^{2-} + 5\text{H}^+ + 3\text{e}^- = \text{Cr(III)(OH)}_3_{(s)} + H_2O \quad E^\circ = 1.34 \text{ V}]
\]

\[
\text{Tc(IIIO}_4^- + 3\text{Fe}^{2+} + (n+7)H_2O = Tc(\text{IV})O_2\cdot nH_2O_{(s)} + 3\text{Fe(OH)}_3_{(s)} + 5\text{H}^+
\]

- Concentration of Tc(IV) fixed by solubility at reduction point
- Ionic radii and structural similarities suggest coprecipitation with Fe(III) possible
- Downgradient adsorption of Tc(IV) complexes or another reaction essential to reach MCL (900 pCi/L)
- Adsorption behavior of TcO(OH)$_2$\textsuperscript{+}$_{(aq)}$ unknown
Kinetic Pathways for Tc(VII) Reduction and Tc(IV) Oxidation

**Reduction** (Fe²⁺ or microbial)

\[ \text{Tc(VII)O}_4^{-} \text{(aq)} \]

biologic (e.g., MRB)

medium; electron donor dependent

\[ Tc(IV) \]

• speciation
• physical location

\[ \frac{\delta \text{TcO}_4}{\delta t} = k_{\text{bio}} + k_{\text{homo}} + k_{\text{het}1} + k_{\text{het}2} \]

**Oxidation** (+ O₂, Mn³⁻⁴⁺, or MOB)

\[ \frac{\delta \text{Tc(IV)}}{\delta t} = k_{\text{bio}} + k_{\text{homo}} + k_{\text{het}1} + k_{\text{het}2} \]
Oxidation of Biogenic Tc(IV)O$_2$•nH$_2$O
**Experimental Protocol for Heterogeneous Reduction and Oxidation Experiments with Sediment**

**Questions:**

Which mineral phases facilitate Tc(VII) reduction in bioreduced sediment?

How does Tc(IV) molecular speciation and mineral association effect oxidation rate?

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Bioreduction increases phyllosilicate Fe(II) and decreases goethite Fe(III)

Kukkadapu et al. 2006
Heterogeneous Reduction and Oxidation of Tc in Bioreduced Sediments

Reaction with bioreduced sediment

Oxidation by atmospheric O₂

Fredrickson et al., 2004, 2009
EXAFS Interpretation Involves Various Tc(IV)O₂ Models

Long chains: Abiotic and biotic TcO₂•nH₂O, heterogeneously reduced Tc(IV) in sediment

Dimers and trimers coordinated to Fe-O with diffuse Fe scattering: Heterogeneously reduced Tc(IV) on phyllosilicates (FRC) and diaspore/corundum

Monomers and dimers coordinated to Fe-O with more intense Fe scattering: Homogeneous Tc(IV); heterogeneous Tc(IV) on goethite/hematite, and magnetite; biotransformation products of ferrihydrite; Tc(IV)-ferrihydrite; and Tc(IV)-celadonite

Dimeric surface complex
Bulk EXAFS Analyses of Tc(IV) Resulting from Heterogeneous Reduction by Biogenic Fe(II)

Peretyazhko et al. 2008; Fredrickson et al. 2009
XRM Mapping of Bioreduced Tc(VII)-Reacted FRC Sediment
Micro-XANES Analyses of Tc Hot-Spots in Oxidized FRC Thin Section

![Graph showing normalized absorption vs. energy (E, eV)]
Isolated 50-100 μm Particles from Oxidized Tc-Containing FRC Sediment for Micro-Analyses

Number Key for Sample

FRC 4M Washed

Probable

Other
XRM Analyses of Tc-Containing Particles from Oxidized FRC Sediment

a.) Particle #7

b.) Particle #15

c.) Particle #13
Micro-EXAFS of Isolated Particles Containing Oxidation Resistant Tc(IV)
BSE, XRM, and EMP Analyses of Tc-particle #7
Micro-XRD of Oxidation Resistant Tc(IV) Particles is Consistent With Celadonite

00-006-0263> Muscovite-2M1 - KAl₂(Si₃Al)O₁₀(OH,F)₂
00-017-0521> Celadonite-1M - K(Mg,Fe,Al)₂(Si,Al)₄O₁₀(OH)₂
00-046-1045> Quartz - SiO₂
00-050-0927> C - Carbon

Two-Theta (deg)
XRM of 0.2 mm FRC Tc(IV)-Containing Mica
Key Findings

- Heterogeneous reduction products similar in both sediments, but red/ox rates differ by 10x
- Initial heterogeneous Tc(IV) speciation is dominated by clusters of TcO$_2$•nH$_2$O
- Diffuse intra-aggregate Tc(IV) oxidizes slowly in FRC, while localized Tc(IV) is recalcitrant (no recalcitrance in RG)
- Oxidation resistant Tc(IV) associates with the surface of 50-100 μm celadonite particles
- The EXAFS spectra of oxidation resistant Tc(IV) is similar to that of dimeric surface complexes on goethite and hematite, and high Fe(II) ferrihydrite with unresolved implications
Ringgold Formation Sediments from Hanford’s Unconfined Aquifer (C6209)
Tc(VII) Reduction: Constant Fe(II) [all C6209 samples, Zachara SFA poster]

- 59-60', 66.25 g/l, ext Fe(II) 0.46 +/-0.06 mM; pH 8.5-8.2
- 60-61', 9.1 g/l, ext Fe(II) 0.45 +/-0.04 mM; pH 9.2-9.0
- 101-102', 1.5 g/l, ext Fe(II) 0.52 +/-0.08 mM; pH 8.2-7.8
- 128-129', 8.4 g/l, ext Fe(II) 0.55 +/-0.10 mM; pH 9.2-9.1
- 155-156', 8.6 g/l, ext Fe(II) 0.71 +/-0.10 mM; pH 8.9-8.7
- 169-170', 2.5 g/l, ext Fe(II) 0.057 +/-0.01 mM; 9.2-8.2
Developing rigorous models for redox reactivity of (bio)geochemical Fe(II) forms challenging in sediments

- Difficult to establish identity, concentrations, and unique thermodynamic properties of both reactants and products
- A range of Fe(II) forms with variable properties often exists
- Complex biologic and chemical linkages

Coupling between chemical, biological, and physical environments

- Mass transfer as a control on oxidant fluxes
- Surface and intragrain environments (“microenvironments”)
- Interaction between surface and bulk mineral redox properties