Reactions of Tc with Fe(II) and O_2 in Hanford Redox-Sensitive Sediments

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Introduction and Objectives

Motivation

400 Ci of ^{99}Tc were released to Hanford's BC cribs/trenches complex

- ^{99}Tc(VII) is a major risk-driving contaminant at Hanford because of high vadose zone inventory, significant mobility, and long half-life.
- ^{99}Tc(VII) is mobile and poorly reactive in the Hanford vadose zone, but localized anoxic, potentially reactive domains exist in groundwater.
- Understanding natural attenuation processes can provide insights for sustainable remediation.

Technetium Properties

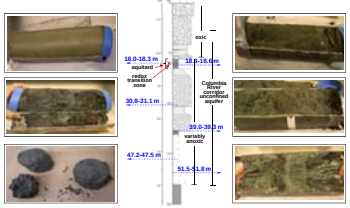
- Fission product of ^{235}Uranium (^{235}U) and ^{239}Plutonium (^{239}Pu).
- Exists in oxidation states +7 to -1.
- Highly mobile as Tc(VII) [pertechnetate TcO_4^-]; exists under oxic condition.
- Insoluble Tc(IV); stable in anoxic environments.
- Tc(VII) to Tc(IV) reduction: biotic (microbial enzymatic reduction) and/or abiotic [reduction by Fe(II)].

The objectives of this PNNL SFA research are to (1) investigate abiotic electron transfer reactions of Fe, O_2, and Tc in mineralogically heterogeneous sediment obtained from a subsurface redox transition zone including their reaction products and kinetics, (2) identify the reactive ferrous mineral forms and associated reaction networks that control sediment reduction and/or oxidation, and (3) formulate rate expressions for describing the potentially multi-component redox reaction network.

Here we present research results on the reactions of Tc with Fe(II) and O_2 in Ringold Formation sediments recovered from a redox transition zone in Hanford's unconfined aquifer in the Columbia River corridor.

Sediment Cores from Hanford's Unconfined Aquifer

A deep borehole (C6209) that sampled the entire depth sequence of Hanford's Columbia River corridor unconfined aquifer was completed in August 2008 as part of the Hanford IFRC well installation program.



- The aquifer sediments below 18 m are variably anoxic, and range significantly in texture and chemistry.
- Ringold Formation sediments at and below a redox transition zone at 18 m were selected for Tc reduction/oxidation studies.
- All samples were dried in an anaerobic chamber (100 % Ar), ground and passed through a 0.5-mm sieve prior to characterization and Tc experiments.

Sediment Characterization

Sediments chemical composition, mineralogy and morphology were characterized using chemical extractions, X-ray diffraction, Mössbauer spectroscopy and electron microscopy.

Selected Sediment Properties

Sample	pH_w[1]	Extracted $Fe(II)_{aq}$[2] (µmol/g)	Extracted $Fe(II)_{acid}$[3] (µmol/g)	$Fe(II)_{aq}/Fe(II)_{acid}$ (%)	Fe_{total} (µmol/g)	$Fe(II)_{acid}/Fe_{total}$ (%)	C_{inorg} (%)	C_{org} (%)	Surface area (m^2/g)
18.0-18.3 m	7.92	9.4±0.4	143.0±7.6	6.6	671	21.3	<0.02	<0.05	25.6
18.3-18.6 m	8.60	85.1±0.5	276.0±7.9	30.8	679	40.6	<0.02	0.08	37.1
30.8-31.1 m	8.84	370.9±7.0	502.7±16.4	73.8	862	58.3	0.42	0.05	13.8
39.0-39.3 m	8.52	72.7±1.9	371.1±3.5	19.6	1000	37.1	<0.02	0.21	49.0
47.2-47.5 m	8.44	70.1±2.0	321.3±8.9	21.8	766	41.9	<0.02	1.33	55.4
51.5-51.8 m	8.93	243.4±15.6	398.3±13.5	61.1	1420	28.0	2.65	0.30	47.3

[1]pH measured in sediment suspension (1g sediment+1 g deoxygenated water); [2] 1h 0.5 M HCl extracted Fe(II); [3]16h 0.5 M HCl extracted Fe(II)

- 0.5 M HCl extraction was used to quantify reactive Fe(II).
- Sediments have different 0.5 M HCl extracted Fe(II) content (168h):
  Fe(II) (30.8-31.1 m)> Fe(II) (51.5-51.8 m)>Fe(II) (39.0-39.3 m)>Fe(II) (47.2-47.5 m)>Fe(II) (18.3-18.6 m)>Fe(II) (18.0-18.3 m)

X-ray Diffraction

X-ray diffraction analysis of the <0.5 mm and clay fractions revealed very similar mineralogy of all sediment samples:

<0.5 mm fraction: quartz, feldspar.
<2 µm fraction: Fe(II)-containing dioctahedral smectite.

Mössbauer Spectroscopy

Variable temperature Mössbauer spectroscopy measurements of the <0.5 mm size fraction revealed that Fe(II) and Fe(III) mineralogical forms differed significantly between the samples:

a. 18.0-18.3 m (data not shown)

- Fe(II)/Fe(III) < 0.15.
- Primary structural environment is phyllosilicate Fe(III).
- No evidence for Fe(III) oxides based on 12K.

b. 18.3-18.6 m (data not shown)

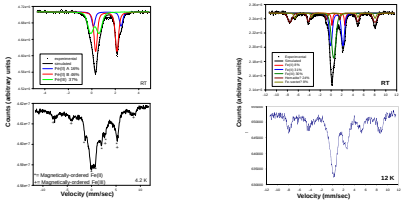
- Reduced version of 18.0-18.3 m, Fe(II)/Fe(III) = 0.58.
- Primary structural environments are phyllosilicate Fe(II) and Fe(III).

c. 30.8-31.1 m

- Fe(II)/Fe(III) = 1.68.
- Complex and unusual Mössbauer spectra.
- Fe(II) ordering only below 12K; no Fe(III) oxides.
- Two Fe(II) phases (not siderite or GR).
- Discrete Fe(II) phase with magnetic ordering at <12K.

d. 51.5-51.8 m

- Fe(II)/Fe(III) = 0.64.
- Magnetically ordered phase at RT = crystalline Fe(III) oxides.
- Two ferrous forms, phyllosilicate Fe(II) (blue) and possibly adsorbed Fe(II) (red).

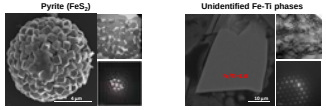


Electron Microscopy

Electron microscopy analysis of selected sediments showed the presence of different Fe-containing phases: pyrite (18.3-18.6 m and 30.8-31.1 m), unidentified Fe-Ti phases with different Fe/Ti ratio (18.3-18.6 m and 30.8-31.1 m), and magnetite (30.8-31.1 m).

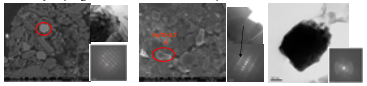
a. 18.0-18.3 m: Fe-containing phases

Pyrite (FeS_2) — Unidentified Fe-Ti phases



b. 30.8-31.1 m: Fe-containing phases

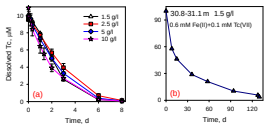
Pyrite (FeS_2) — Unidentified Fe-Ti phases — Magnetite (Fe_3O_4)



Tc(VII) Reduction (Kinetic Batch Experiments)

10 or 100 µM Tc(VII) Reduction in 30.8-31.1 m Sediment

30.8-31.1 m sediment suspensions containing different concentrations of 0.5 M HCl extracted $Fe(II)_{ex}$ were prepared using deoxygenated water (0.6 mM, 1 mM, 2 mM and 4 mM extracted $Fe(II)_{ex}$; 1.5 g/l, 2.5 g/l, 5 g/l and 10 g/l solid concentration, respectively). The suspensions were pasteurized by heating in 80 °C water bath for 1 h then cooled down to room temperature. An aliquot of Tc(VII) stock solution was added to the suspensions to obtain a final concentration of 10 or 100 µM.



(a) 10 µM Tc(VII) reduction at different 1h-extracted Fe(II) content (30.8-31.1 m):

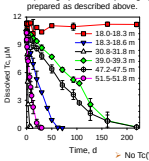
- no rate dependence on $[Fe(II)_{ext}]$.
- Tc-reduced sample (10 g/l solid concentration) was used in stir-flow oxidation experiment.

(b) 100 µM Tc(VII) reduction in 30.8-31.1 m sediments:

- final Tc-containing sample was analyzed by Mössbauer spectroscopy.

10 µM Tc(VII) Reduction in Sediments at Constant 1h-Extracted Fe(II) (~0.6 mM)

Extracted $Fe(II)_{ex}$ concentration was adjusted to ~0.6 mM in all sediments. Sediment suspensions of 66.2 g/l (18.0-18.3 m), 9.1 g/l (18.3-18.6 m), 1.5 g/l (30.8-31.1 m), 8.4 g/l (39.0-39.3 m), 8.6 g/l (47.2-47.5 m) and 2.5 g/l (51.5-51.8 m) were prepared as described above.



Summary of experimental conditions and kinetic analysis

Sample	Solid concentration (g/l)	$Tc(VII)_{added}$ (µM)	Extracted $Fe(II)_{acid}$[1] (mM)	Extracted $Fe(II)_{aq}$[2] (mM)	Reaction time (d)	k_{obs} (d^{-1})
18.0-18.3 m	66.2	11.30±0.03	0.46±0.06	0.40±0.10	no reduction	
18.3-18.6 m	9.1	10.48±0.02	0.45±0.04	0.82±0.03	71	0.038
30.8-31.1 m	1.5	9.51±0.07	0.47±0.04	0.52±0.08	8	0.38
39.0-39.3 m	8.4	10.52±0.04	0.55±0.10	0.72±0.06	219	0.0081
47.2-47.5 m	8.6	10.40±0.10	0.71±0.10	0.69±0.04	219	0.012
51.5-51.8 m	2.5	10.23±0.22	0.57±0.01	0.63±0.03	30	0.11

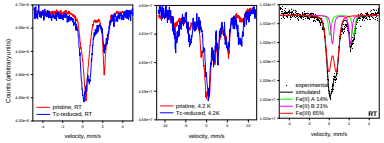
[1] 1h 0.5 M HCl extracted Fe(II) before Tc(VII) addition; [2] 1h 0.5 M HCl extracted Fe(II) at the end of reaction with Tc(VII).

- No Tc(VII) reduction in oxic sample (18.0-18.3 m).
- All anoxic sediments (>18.3 m) reduced Tc(VII) to Tc(IV) with reaction time from 8d to 219d.
- Reduction rates: (30.8-31.1 m)>> (51.5-51.8 m)> (18.3-18.6 m)> (47.2-47.5 m)>(39.0-39.3 m).
- Difference in reduction rates indicated significant difference in Fe(II) reactivity.
- Final Tc-containing sediments were analyzed by X-ray absorption spectroscopy (Tc-XAS).

Tc(VII) Reduction (Mössbauer and Tc-XAS)

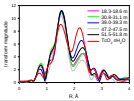
Mössbauer Analysis of Tc-Reduced 30.8-31.1 m Sediment

Mössbauer spectroscopy measurements of 30.8-31.1 m sediment after reaction with 100 µM Tc(VII) revealed significant changes in the Mössbauer spectra.



- Fe(II) content decreased after Tc reduction: *62% Fe(II) pristine sediments; 35% Fe(II) Tc-reduced sediments.*
- Fe(II) decrease was in good agreement with stoichiometric amount of Fe(II) required for the reduction of 100 µM Tc(VII) to Tc(IV):
  Mössbauer: 348 µM Fe(II)
  Stoichometric demand: 300 µM Fe(II) [Fe(II)/Tc(VII)=3/1]

Tc-XAS



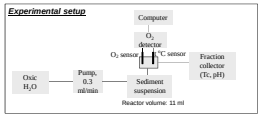
Summary of EXAFS fit parameters

Sample	N (O)	R (O)	σ^2 (O)	Tc-Tc chain length	R (Tc)	σ^2 (Tc)
30.8-31.1 m	5.0 (0.3)	2.00 (0.01)	0.0038 (0.001)	2.0 (0.5)	2.57 (0.02)	0.0019 (0.0015)
51.5-51.8 m	4.8	2.01	0.0032	2.9	2.56	0.0033
18.3-18.6 m	4.8	2.01	0.0034	2.5	2.57	0.0035
39.0-39.3 m	4.6	2.02	0.0026	2.8	2.58	0.0022
47.2-47.5 m	4.6	2.00	0.0037	2.2	2.57	0.0039
TcO_4 std,O	4.6	2.01	0.0042	10.3	2.56	0.0034

- **Tc-XANES**: Tc(IV) valence state after reaction with sediments (data not shown).
- **Tc-EXAFS**: TcO_2-like final phases formed in all sediments.
- Average Tc-Tc chain length varied from 2 to 3; Tc(IV) chain length not proportional to reduction rate.

Tc(IV) Oxidation (Stir-Flow Experiments)

Experimental setup

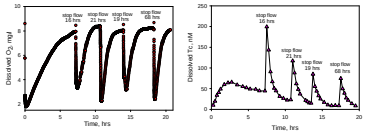


Experimental conditions:

Tc(IV)-sediment: 30.8-31.1 m, 10 g/l;
Suspension added to the reactor: 7 ml;
Final Tc(IV) concentration: 0.7 µmol/g;
Experiment duration: 7 days.

Dissolved Oxygen and Tc in 30.8-31.1 m Sediment

The influx of O_2-saturated deionized MilliQ water (e.g., 8.6 mg/l) resulted in release of 10-50 nM Tc into effluent solu



- Total O_2 consumed during 7d experiment: ~1.3 mM.
- Total Tc released into solution: 770 nM or 16% of total Tc. Reduction of 770 nM Tc(IV) required <0.6 µM O_2.
- O_2 reacted preferentially [over Tc(IV)] with sediment Fe(II).

Tetraphenyl Arsonium Chloride (TPAC) Extraction

TPAC extraction was performed to separate Tc(VII) and Tc(IV) in selected samples.

Time, hrs	Tc(VII), nM	Tc(IV), nM
3.5	60.4	4.75
7.25	47.0	3.37
10.25	25.3	2.45

- Both Tc(VII) and Tc(IV) were released into solution.

Summary and Conclusions

- X-ray diffraction, Mössbauer and electron microscopy analysis revealed complex Fe mineralogy: Fe(II)-containing smectites (all samples), unidentified Fe(II) phases (18.0-18.3 m, 30.8-31.1 m), pyrite (18.0-18.3 m, 30.8-31.1 m), magnetite (30.8-31.1m), adsorbed Fe(II) (51.5-51.8 m).
- Tc reduction experiments at constant 0.5 M 1h-extracted Fe(II) content revealed that anoxic sediments (>18.3 m) had different reactivity towards Tc(VII) reduction with reaction time from 8d to 219d. No Tc(VII) reduction occurred in the oxic sample (18.0-18.3 m).
- Tc(VII) reduction rates: separate Fe(II) phase + magnetite+ Fe(II)-smectite (30.8-31.1 m) > Fe(II)-sorbed Fe(III) oxide + Fe(II)-smectite (51.5-51.8 m) >> Fe(II)-smectite.
- Tc-XAS analysis demonstrated that TcO_2-like final phases were formed in all sediments; No Fe in Tc(IV) second shell.
- Mössbauer analysis revealed a decrease in sediment Fe(II) concentration (30.8-31.1 m) after reduction of 100 µM Tc(VII).
- Tc(IV) oxidation was slow. Dissolved O_2 reacted preferentially with sediment Fe(II) in stir-flow experiments.
- Both Tc(VII) and Tc(IV) (up to 5%) were released in stir-flow oxidation experiments.

Future Research

- Further Mössbauer and XAS characterization, quantification, and modeling of reactive sediment Fe(II) phases.
- Stir-flow studies of oxygen consumption with the various sediments.
- Evaluation of Tc(IV) oxidation rates in different sediments using stir-flow reactors.
- Characterization of molecular nature, physicochemical environment, and mineral residence of oxidation resistant Tc(IV).
- Development of kinetic models that describe the observed redox reactions between the various valence states and mineral forms of Tc, Fe, and O_2.

U.S. DEPARTMENT OF ENERGY — Office of Science

Research performed through PNNL's Scientific Focus Area (SFA)
Supported by DOE Office of Science
Office of Biological and Environmental Research (BER)
Climate and Environmental Sciences Division (CESD)

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