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Technetium and Iron Biogeochemistry in Suboxic Subsurface Environments with Emphasis on the Hanford Site

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Environmental Remediation Sciences

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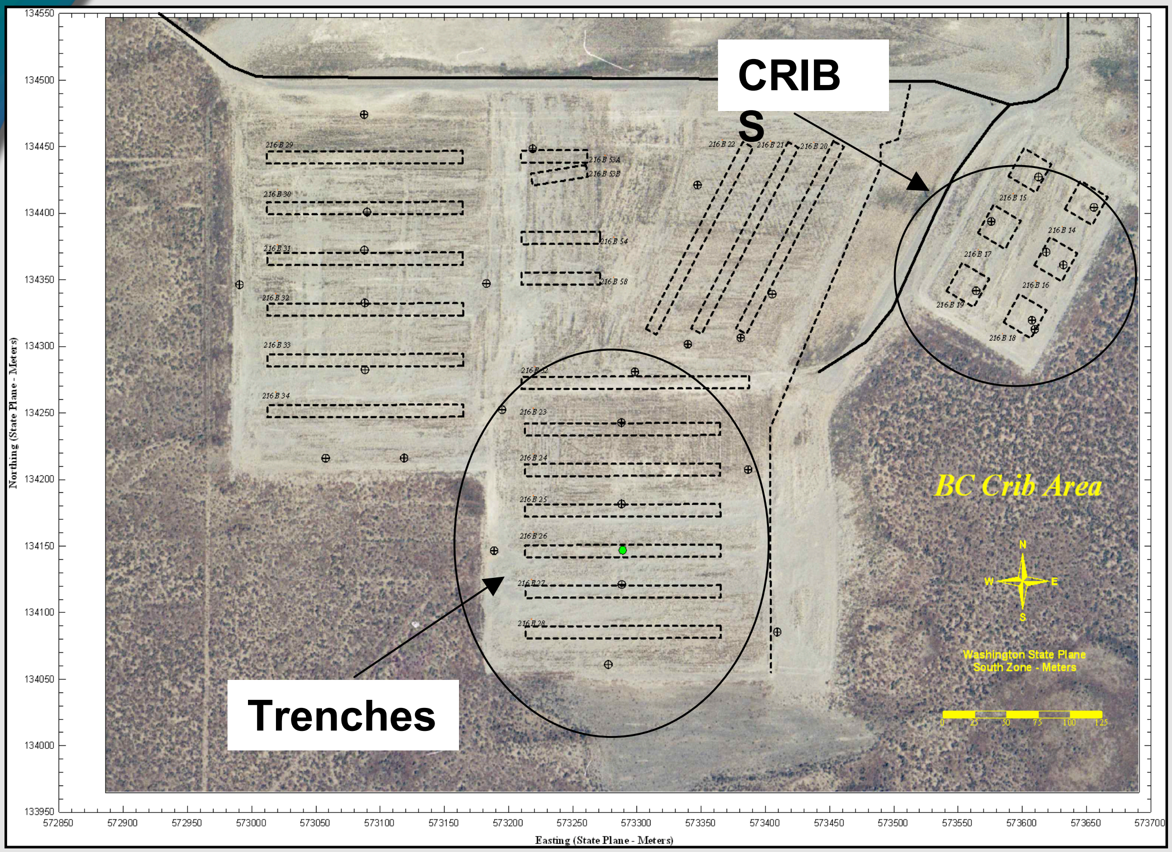
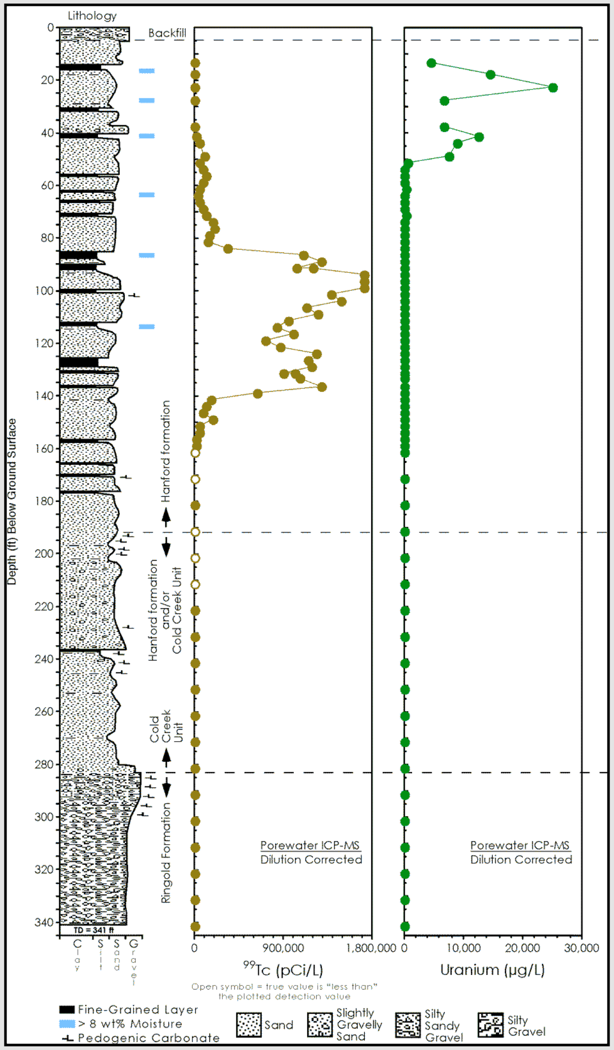
- EMSL and APS user facilities
- Alex Beliaev and Frank Loeffler ERSP project for *Anaeromyxobacter* culture and conditions

400 Ci of ^{99}Tc was Released to the BC-Crib Area: Where is it?





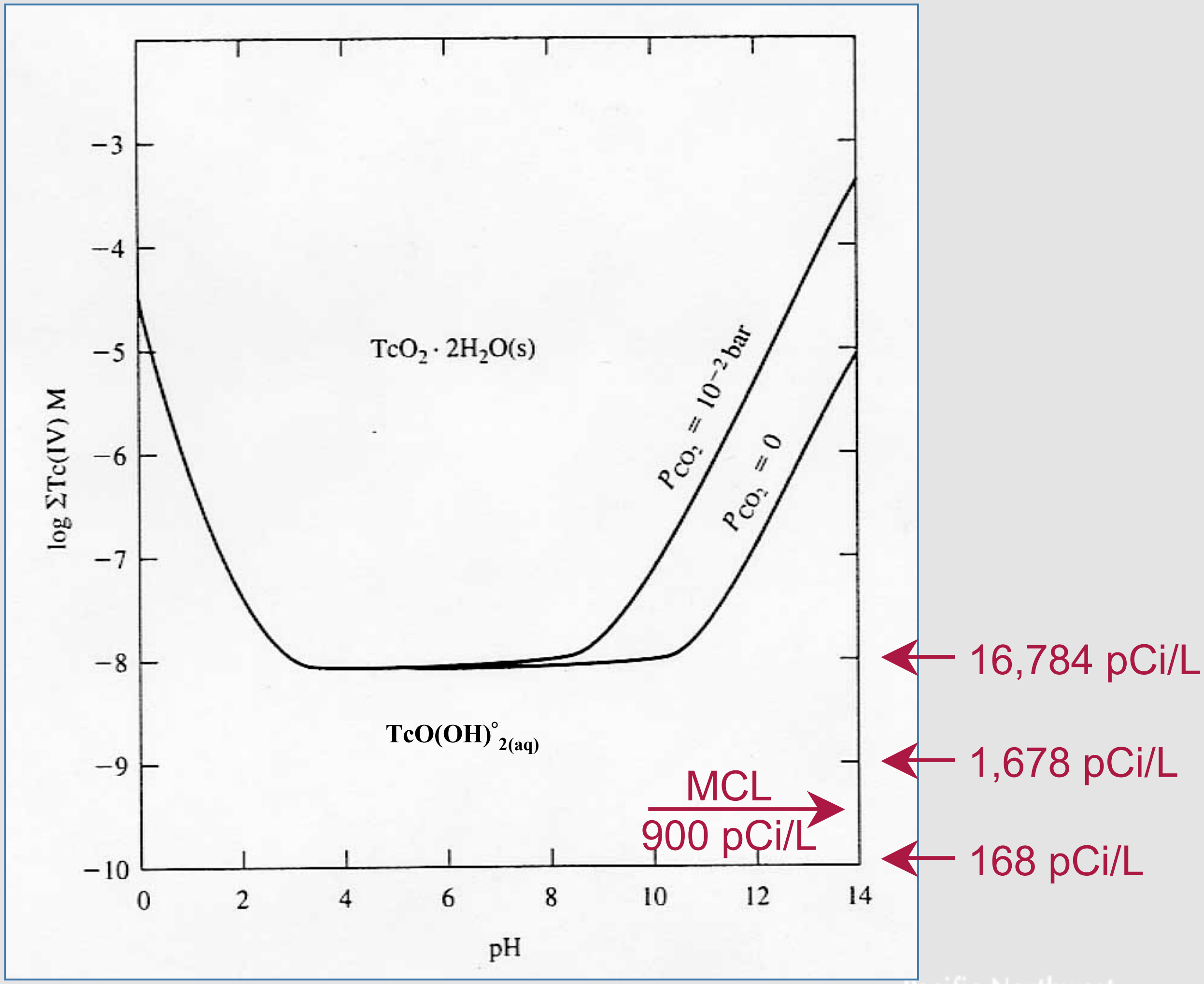
- The SAC model forecasts that a growing plume of ^{99}Tc should exist beneath the BC-cribs

Solubility of TcO_2

$$Tc(VII)O_4^- + 4H^+ + 3e^- = Tc(IV)O_2 \cdot nH_2O_{(s)} + (2-n)H_2O \qquad E^o = 0.748\ V$$

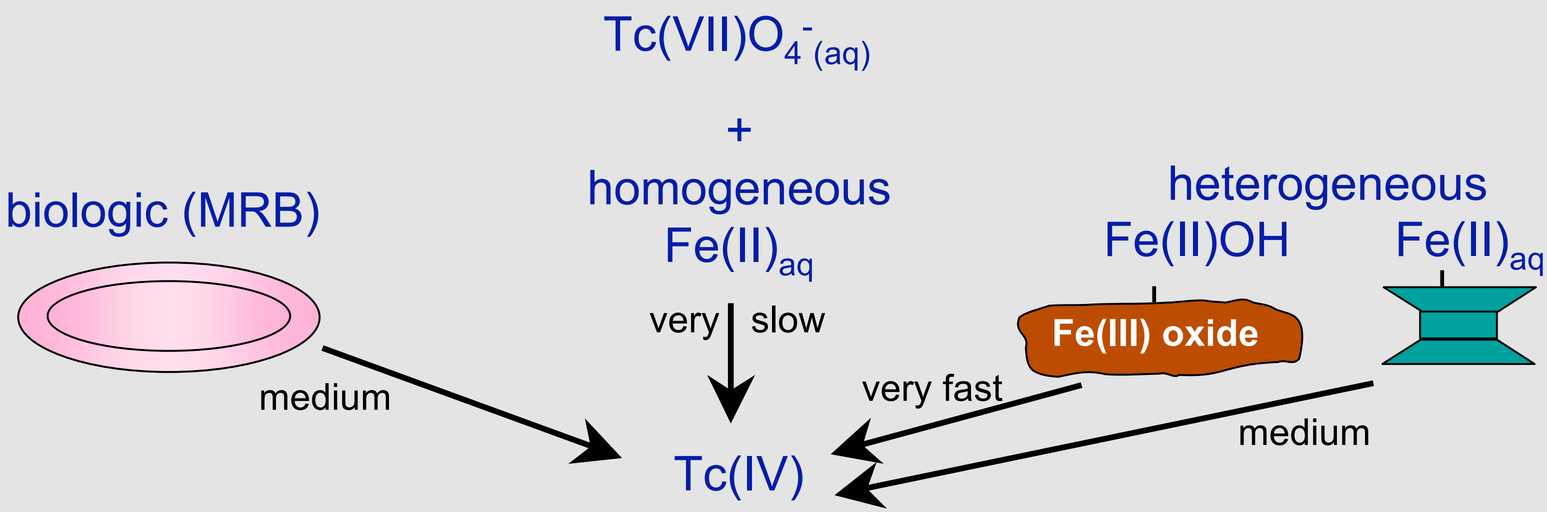
$$Tc(VII)O_4^- + 3Fe^{2+} + (n+7)H_2O = Tc(IV)O_2 \cdot nH_2O_{(s)} + 3Fe(OH)_{3(s)} + 5H^+$$

- Concentration of Tc(IV) fixed by solubililty at reduction point
- Downgradient adsorption of Tc(IV) complexes or another reaction essential to reach MCL (900 pCi/L)
- Adsorption behavior of $TcO(OH)_2°_{(aq)}$ unknown



Kinetic Pathways for Tc(VII) Reduction and Tc(IV) Oxidation

Reduction (+ Fe(II) or MRB)



- speciation
- physical location

$$\frac{\delta TcO_4}{\delta t} = k_{bio}[\quad] + k_{homo}[\quad] + k_{het1}[\quad] + k_{het2}[\quad]$$

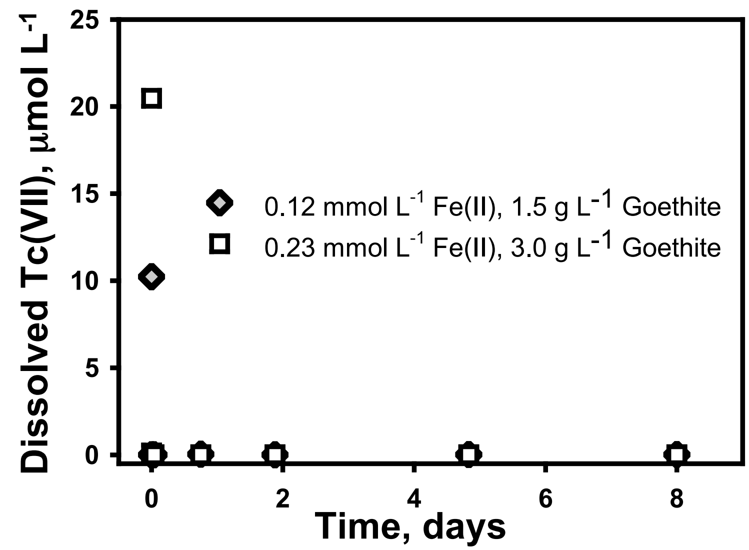
Oxidation (+ O_2 or MOB)

$$\frac{\delta Tc(IV)}{\delta t} = k_{bio}[\quad] + k_{homo}[\quad] + k_{het1}[\quad] + k_{het2}[\quad]$$

Heterogeneous Reduction of Pertechnetate $[Tc(VII)O_4^-]$ by Surface Complexed Fe(II) at pH = 7

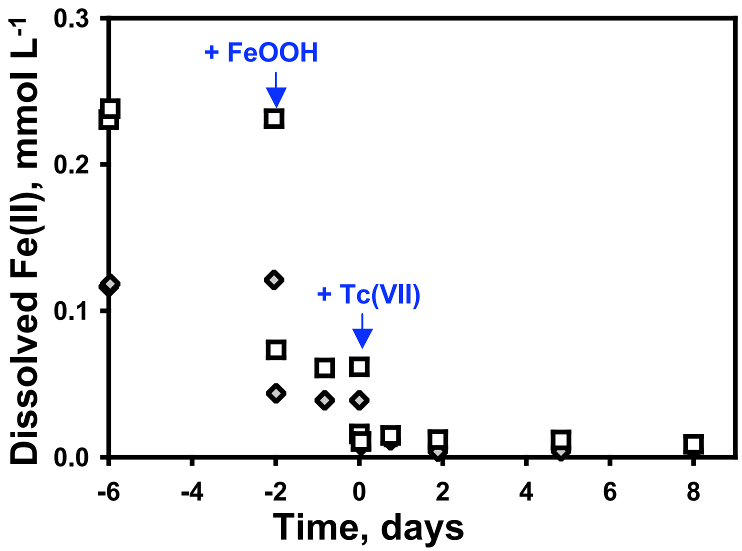
$$3FeO\text{-}Fe(II)OH + Tc(VII)O_4^- = 3FeO\text{-}Fe(III)OH_2\ [?] + Tc(IV)O_2H_2O\ [?]$$

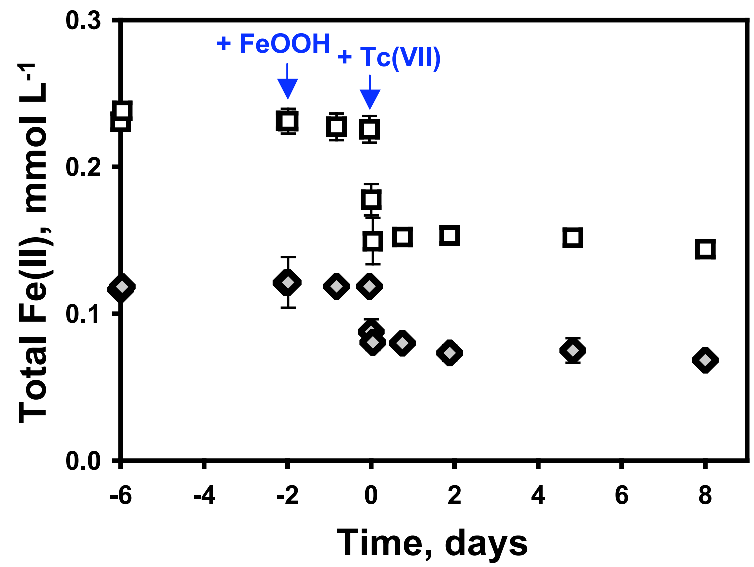
-6 to -2 day	$Fe(II)_{aq}$
-2 to 0 day	FeO-Fe(II)OH
0 day +	FeO-Fe(II)OH+Tc(IV)/Fe(III)



Issues:

- Stoichiometry of Fe(III) and Tc(IV)
- Nature of Fe(III) and Tc(IV) phases
- Location and association of Fe(II)
- Speciation effects on heterogeneous oxidation



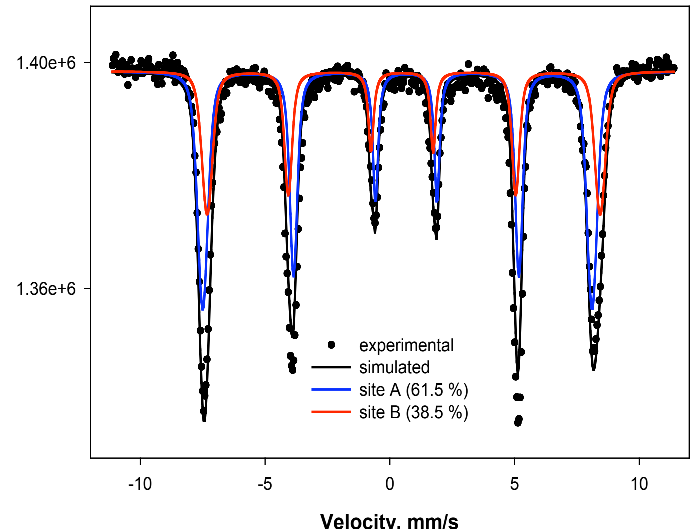


Products of Heterogeneous $Tc(VII)O_4^-$ Reduction by Fe(II) on Goethite

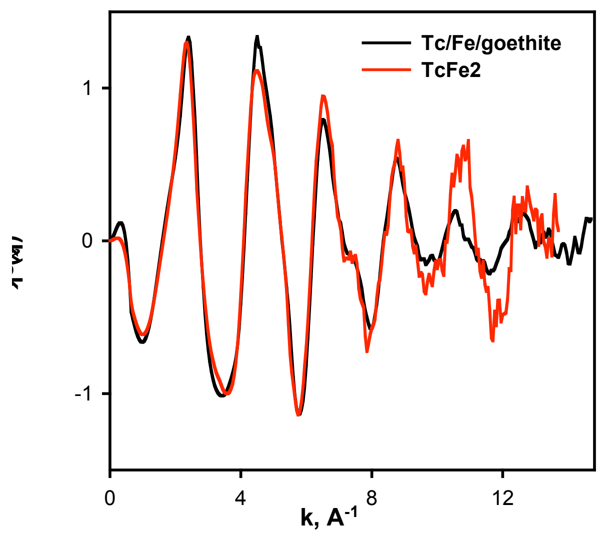
What is $Fe(III)/Tc(IV)O_x$? Where is readsorbed Fe(II)?

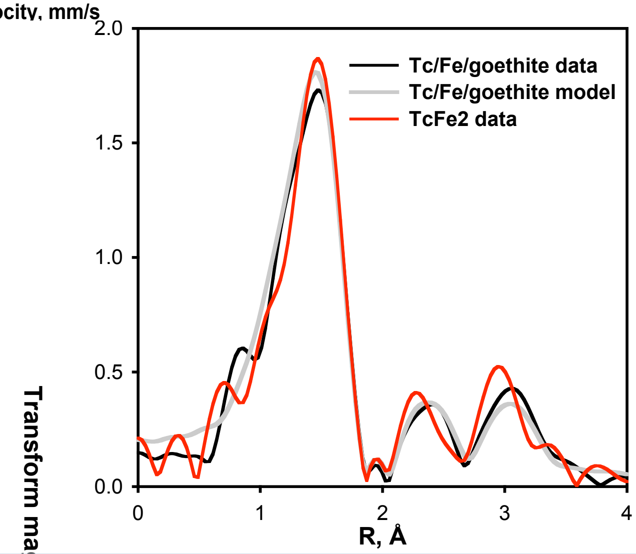
$^{56}Fe^-$ goethite (Mössbauer invisible)

$^{57}Fe(II)$ (Mössbauer visible)

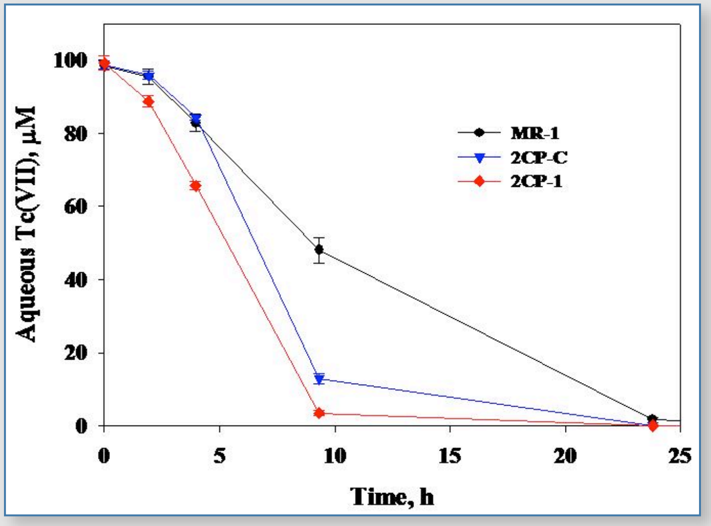


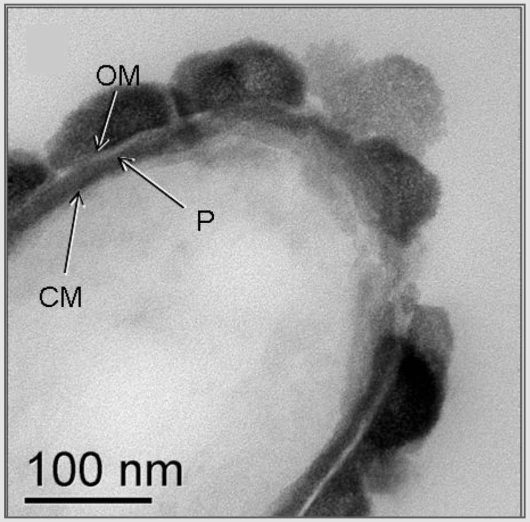
- Magnetic order and peak positions consistent with Fe(III) and goethite
- No Fe(II)
- “two” Fe(II) sites
- Spectra before Tc(IV) addition almost identical



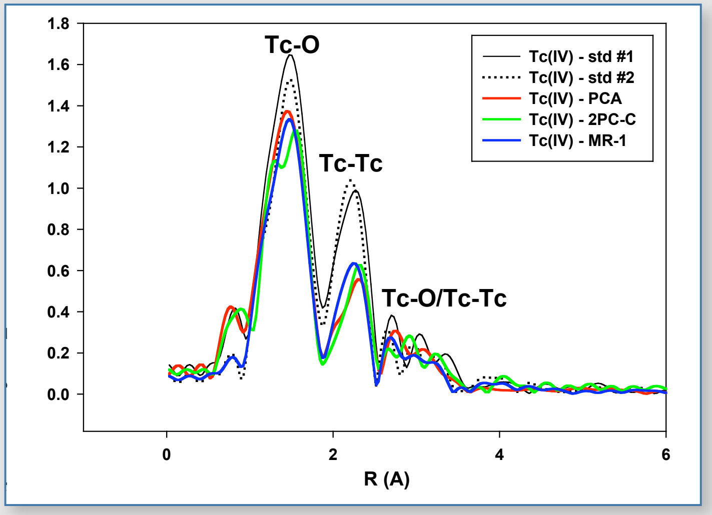


Many Metal-Reducing Bacteria Change the Valence of Pertechnetate [Tc(VII)]



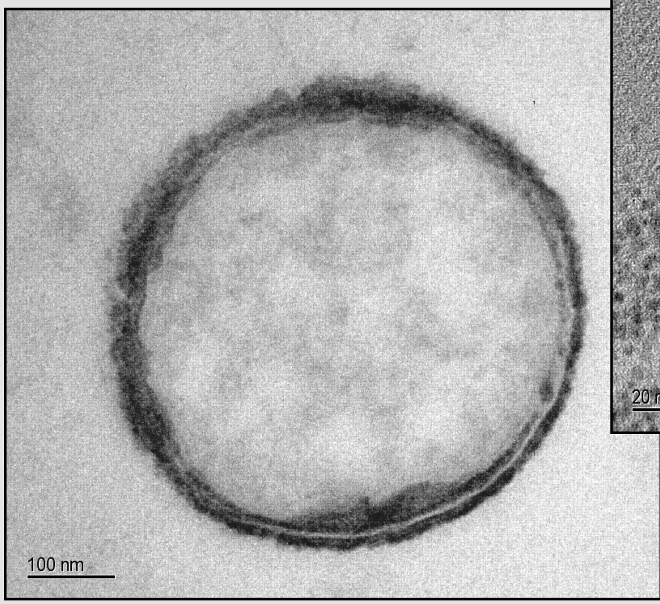


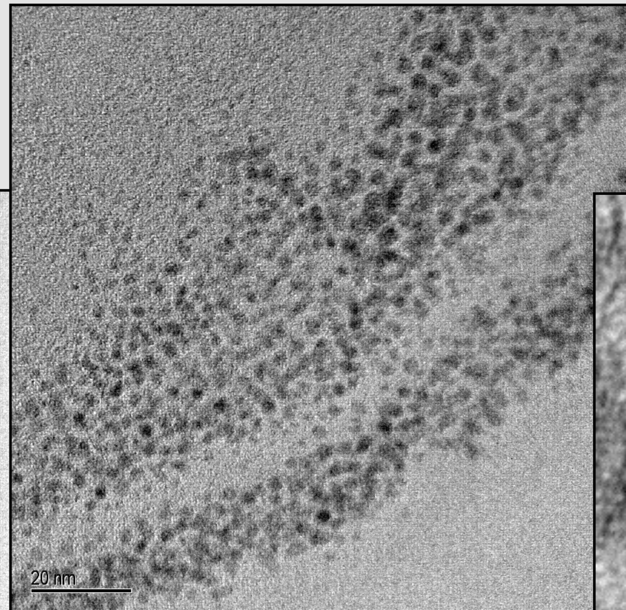
2CP-C

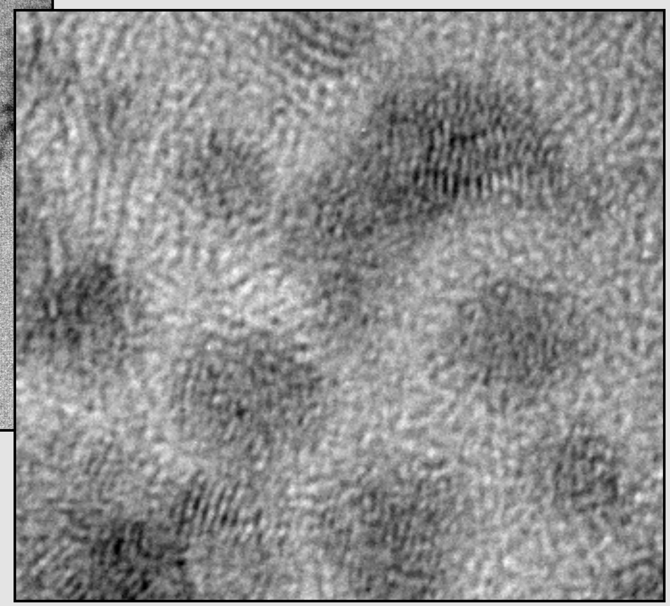


- Biogenic $TcO_2 \cdot nH_2O$ shows less Tc-Tc second neighbors and different long range order
- Consistent with small size (2-3 nm) of biogenic precipitates

HRTEM of $TcO_2 \cdot H_2O$ Precipitates on and within CN32, *S. putrefaciens*







$$\Delta G = 2/3\gamma\ S$$

$$\log K_{so(s)} = \log K_{so(s=o)} + \frac{2/3\gamma}{2.3\ RT} S$$

$$\log K_{so(s)} = \log K_{so(s=o)} + \frac{2/3\gamma}{2.3\ RT} \left(\frac{M\alpha}{\rho d}\right)$$

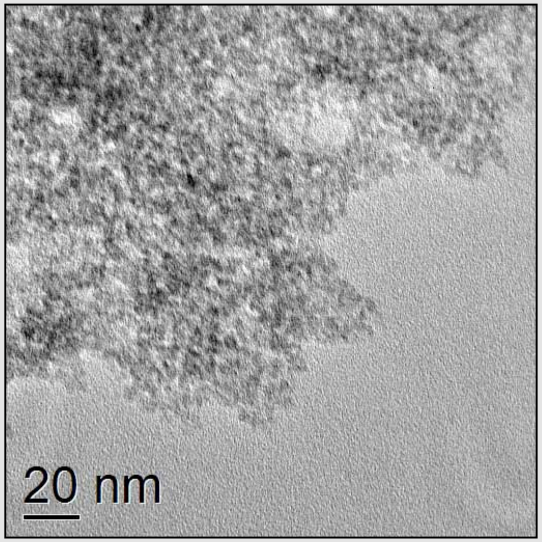
Tc and 2LFH Behavior in Anoxic Suspensions with MR-1 and H_2 or Lactate

ID#	Experiment	Product		$[Tc]_{aq}$	$[Tc(IV)]_{aq}$
			Start	$3.00x10^{-4}$	
3	Tc(IV)-2LFH+Fe(II)	~70% goe; 20% mag.		$<1.5x10^{-9}$	
4	Tc(IV)-2LFH+AH_2DS	nanomagnetite		$1.84x10^{-9}$	
5	bio-Fe_3O_4+Tc(VII)	60 nm magnetite		$1.93x10^{-9}$	
6	Tc(VII)+MR-1+H_2	TcO_2•nH_2O		$1.52x10^{-7}$	
10	2LFH+Tc(VII)+MR-1+H_2	large particle goethite		$3.43x10^{-8}$	
12	2LFH+Tc(VII)+MR-1+lactate	5LFH		$3.78x10^{-6}$	$4.99x10^{-7}$
14	Tc(IV)-2LFH+MR-1+H_2	large particle goethite		$4.11x10^{-8}$	
15	Tc(IV)-2LFH+MR-1+lactate	5LFH		$4.12x10^{-6}$	$2.76x10^{-7}$

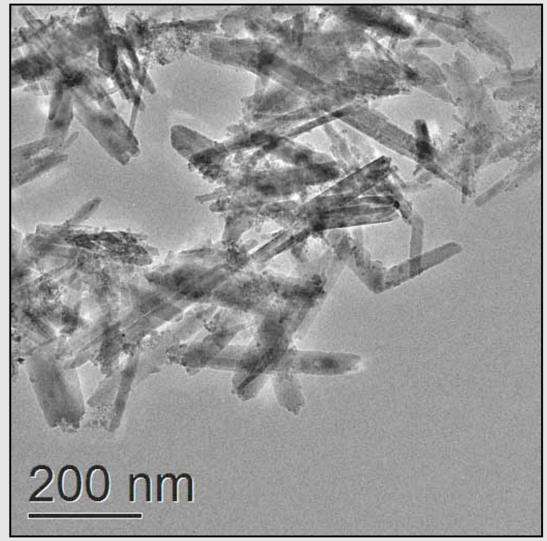
Hypothesis: H_2 would promote microbiologic reduction

What Reductive Process Dominates in Mineral-Microbe Suspension?

$$\text{2-line ferrihydrite} + Tc(VII)_{aq} + \text{MR-1} \xrightarrow[\text{Fe(II)}]{\text{time}} \alpha\text{-FeOOH} + \overline{\text{Fe-O-Fe(II)OH}} + Tc(IV)_{(s)}[?]$$

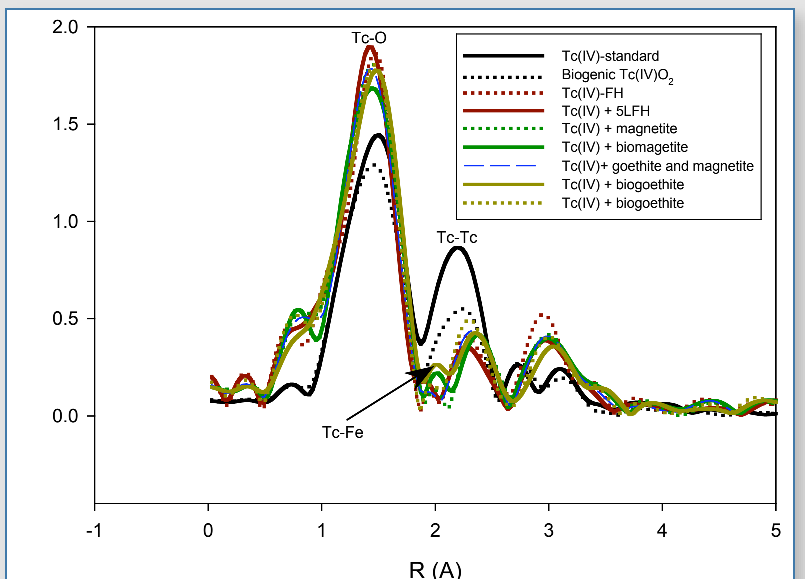


MR-1 → H_2



Products display different EXAFS spectra from abiotic and biotic TcO_2

Aqueous concentration tracks speciation and mineralogy



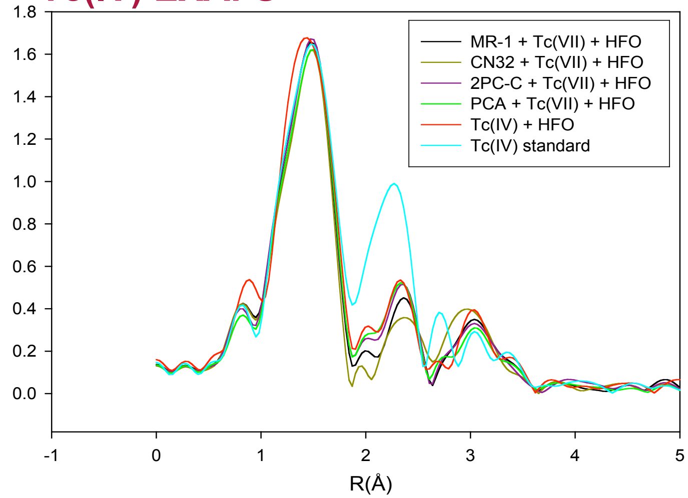
Biomineralization Products and Tc Concentrations with *Shewanella*, *Anaeromyxobacter*, and *Geobacter*

Reactants		Product	[Tc]	[Fe(II)]-0.5NHCl
			(mol L^{-1})	
2LFH + Tc(VII) + MR-1 + H_2	→	goethite	$4.9x10^{-9}$	$1.69x10^{-3}$
2LFH + Tc(VII) + CN-32 + H_2	→	goethite ≥ magnetite	$8.1x10^{-9}$	$3.36\text{-}x10^{-3}$
2LFH + Tc(VII) + 2CP-C + H_2	→	poorly crystalline goethite	$1.17x10^{-8}$	$2.64x10^{-3}$
2LFH + Tc(VII) + PCA + H_2	→	well crystalline goethite & magnetite	$8.49x10^{-9}$	$3.12x10^{-3}$
Tc(VII) + PCA + H_2	→	TcO_2•nH_2O	$1.79x10^{-7}$	

$[Tc_{ToT}] = 3.02x10^{-4}$ $[Fe_{ToT}] = 3.02x10^{-2}$

XAS of Ferrihydrite Incubated with H_2 and Various MRB

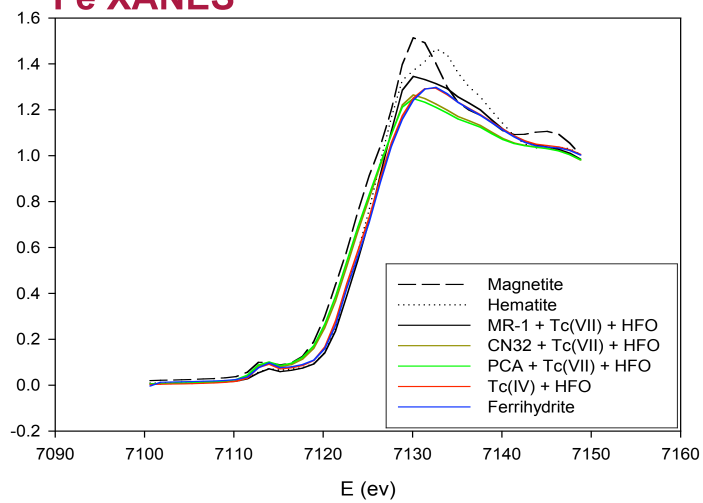
Tc(IV) EXAFS



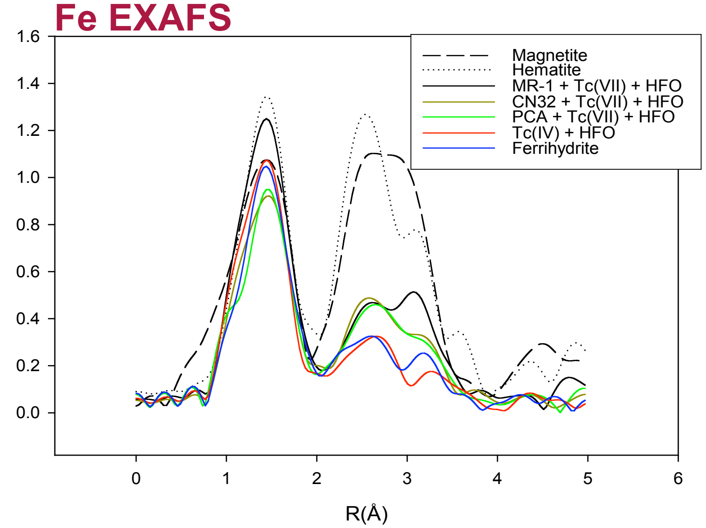
Organisms and Standards

Shewanella oneidensis MR-1
Shewanella putrefaciens CN32
Anaeromyxobacter 2CP-C
Geobacter sulfurreducens (PCA)
Biogenic $TcO_2 \bullet nH_2O$ (PCA)
Tc(IV) + 6LFH
Magnetite
Hematite
Ferrihydrite

Fe XANES



Fe EXAFS



EXAFS Interpretation Involves Various $Tc(IV)O_2$ Models

Tc-Tc

Long chains: Abiotic and biotic $TcO_2 \bullet nH_2O$

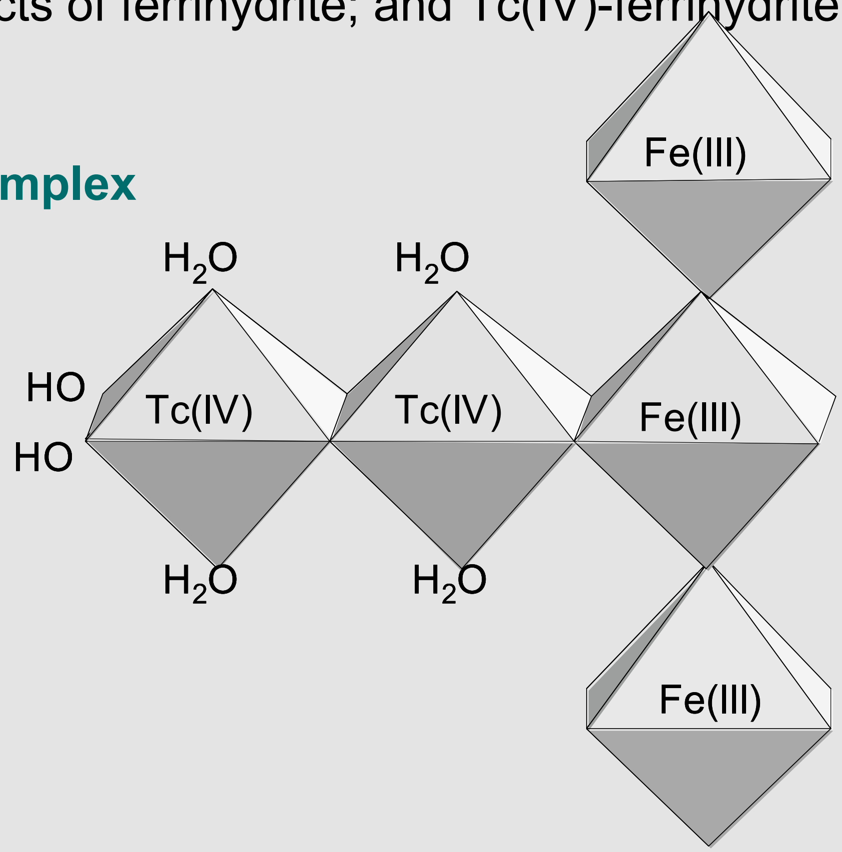
Dimers and trimers coordinated to Fe-O with diffuse Fe scattering: Sorbed Fe(II) on phyllosilicates (FRC)

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

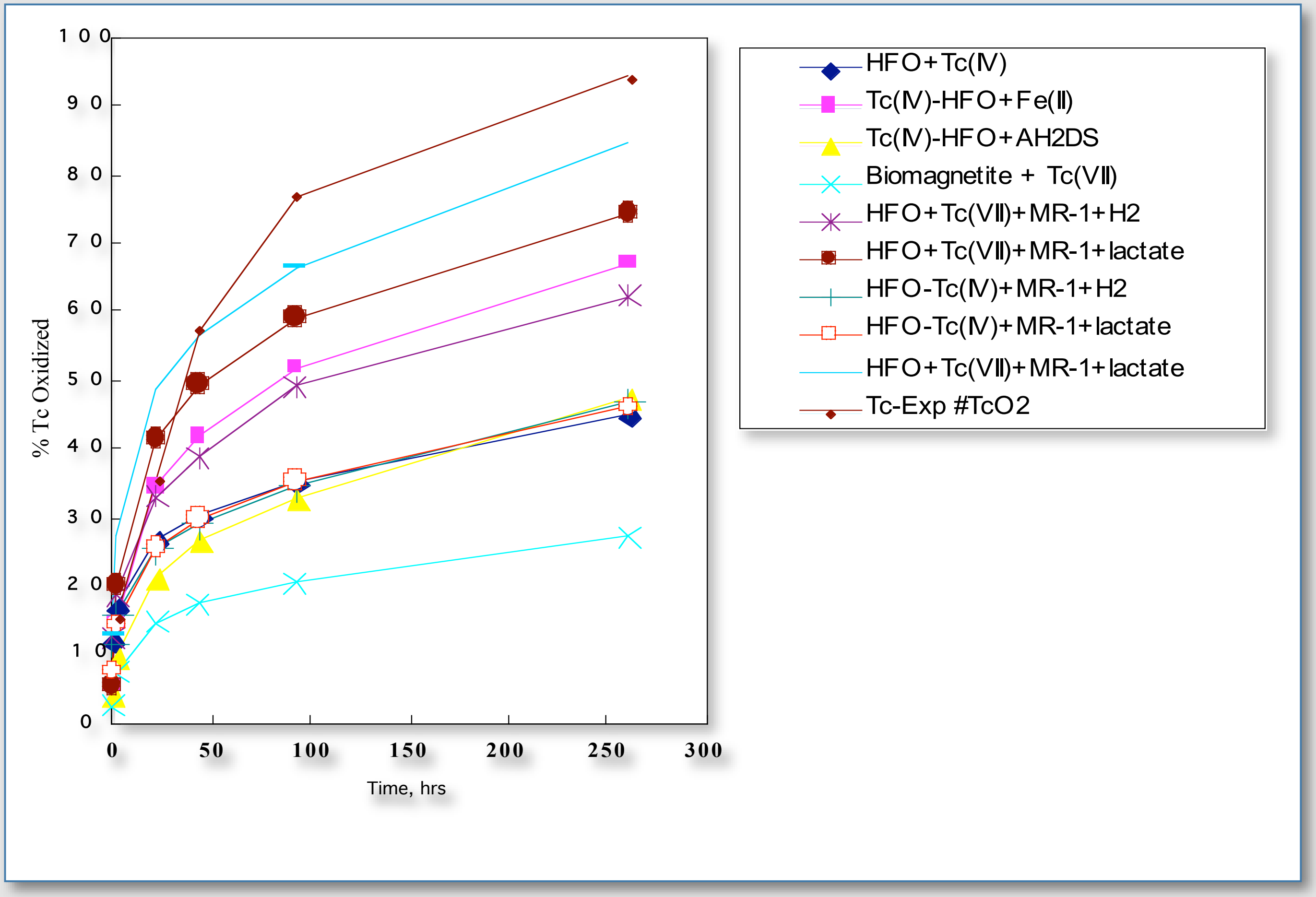
Tc-Fe

$[Tc]_{aq}$

Dimeric surface complex



Interfacial Speciation of both Tc and Fe Influence Oxidation Rate



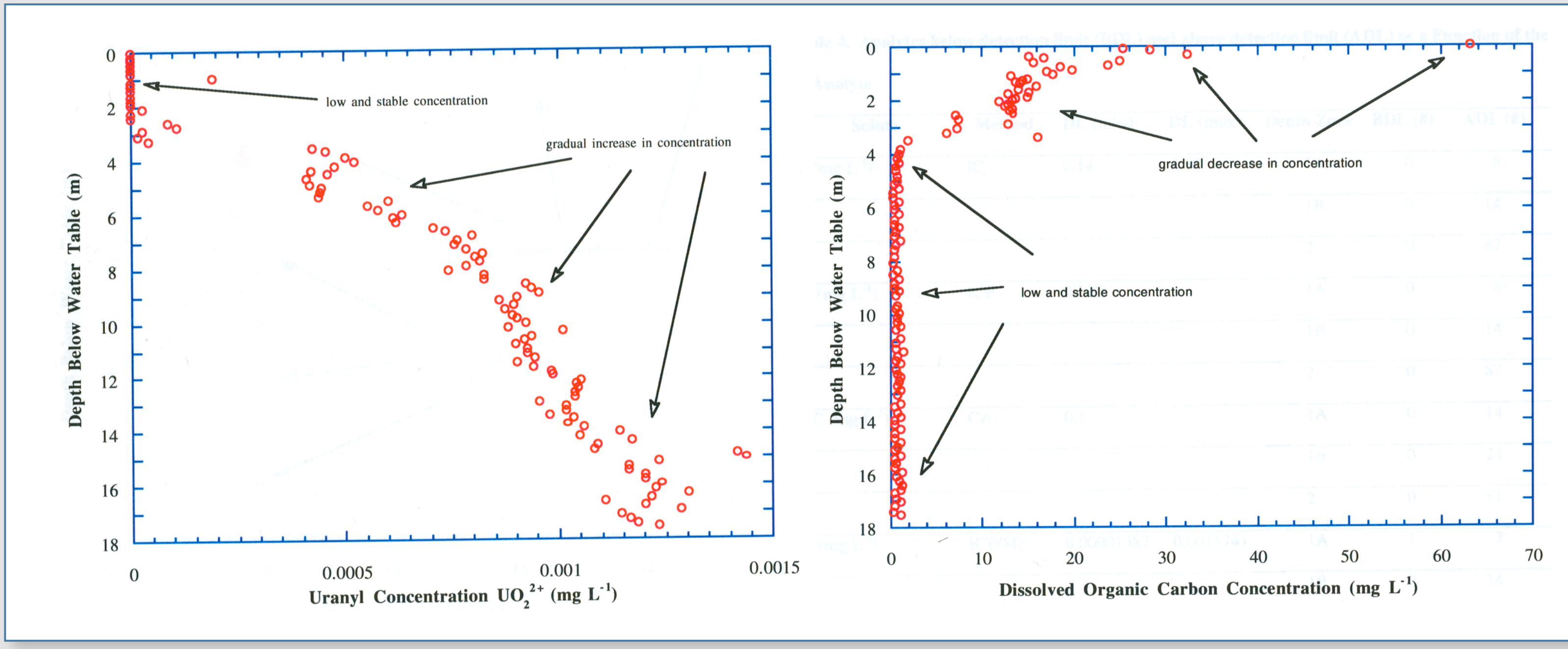
Conclusions

- Electron donor has a major role because of effects on enzymology and Tc/Fe
  - Lactate-enhances Fe(III) reduction, slows Tc(VII) reduction, and complexes Tc(IV)
  - H_2 – stimulates Tc(VII) reduction and slows Fe(III) reduction
- Heterogeneous Tc(VII) reduction predominates in Fe(III) oxide-microbe systems
- Slower rates of heterogeneous reduction in phyllosilicate dominated systems may allow microbiologic reduction to predominate
- Tc(VII) speciation varies in octahedra chain length
  - Relatively insensitive to biogenic mineral phase
  - Sensitive to apparent respiration rate and Fe(II) location
- Tc(IV) oxidation rates slowed by mineral association, difficult to interpret

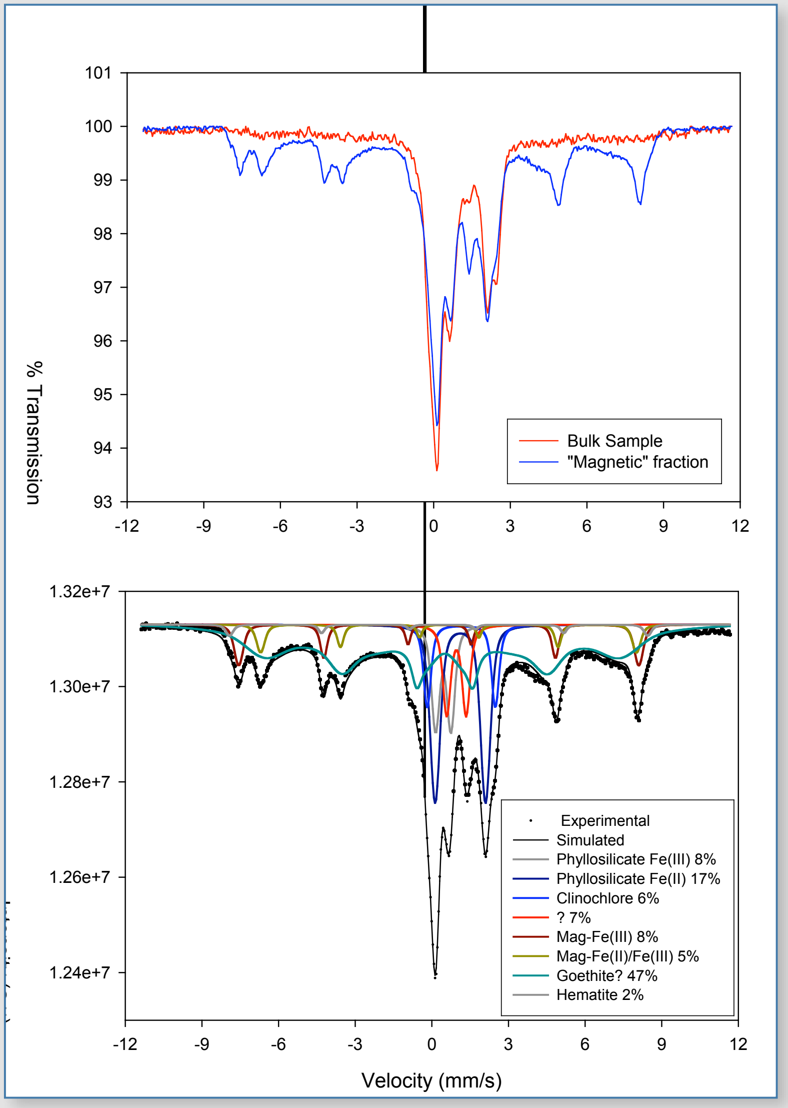
Future Research Directions

- Focused on Tc-biogeochemistry in Hanford subsurface sediments and effects of the globally falling water table (lower O_2 and slower flow rates).
- Based on the observation that sorbed Fe(II) on certain surfaces is a strong reductant for Tc(VII), even when aqueous Fe(II) is near DL.
- Emphasizes effects of O_2 consumption by indigenous microbes and ferrous-containing mineral solids on Fe(II) solubility, surface complexed Fe(II), and in-situ heterogeneous Tc(VII) reduction.
- Will incorporate aquifer sediments along a flow-path from 200 A plateau to Columbia River.
- Involves laboratory studies with Hanford aquifer sediments (microbial ecology, mineralogy, biogeochemistry) and field experiments in pristine and Tc(VII)-contaminated groundwater plumes.

Historic Releases of Processes Waters at Hanford Have Strongly Influenced Groundwater Composition
These will change in the future



^{57}Fe Mössbauer Spectroscopy of Hanford Sediments



Secondary Fe(II)-Rich Saponite Results as a Weathering Product of Ferrous-Silicate Glass in Basaltic Lithic Fragments