NABIR PI Meeting Breakout Session:

BIOREMEDIATION OF TECHNETIUM

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Technetium

- ^{99}Tc is a fission product
  - Fission yield of 6.1% from ^{235}U and 5.9% from ^{239}Pu
- 21 known isotopes ^{90}Tc – ^{110}Tc
- 3 isotopes have long half-lives
  - ^{97}Tc($t_{1/2}$) = 2.6 x 10^6 y
  - ^{98}Tc($t_{1/2}$) = 4.2 x 10^6 y
  - ^{99}Tc($t_{1/2}$) = 2.14 x 10^5 y *

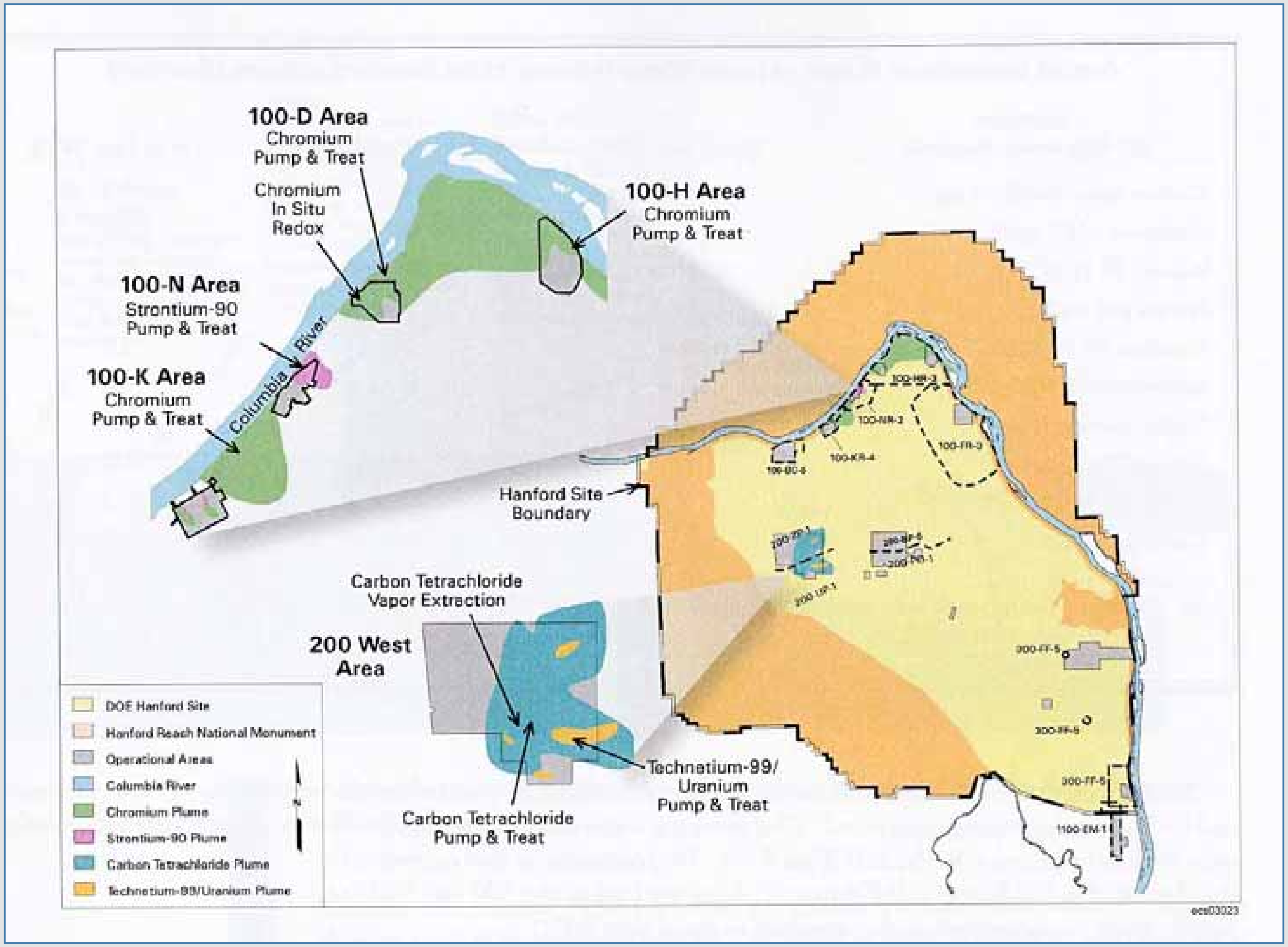
Groundwater Contamination Plumes at Hanford

Area of Contaminant Plumes at Levels Above Drinking Water Standards (square kilometers)

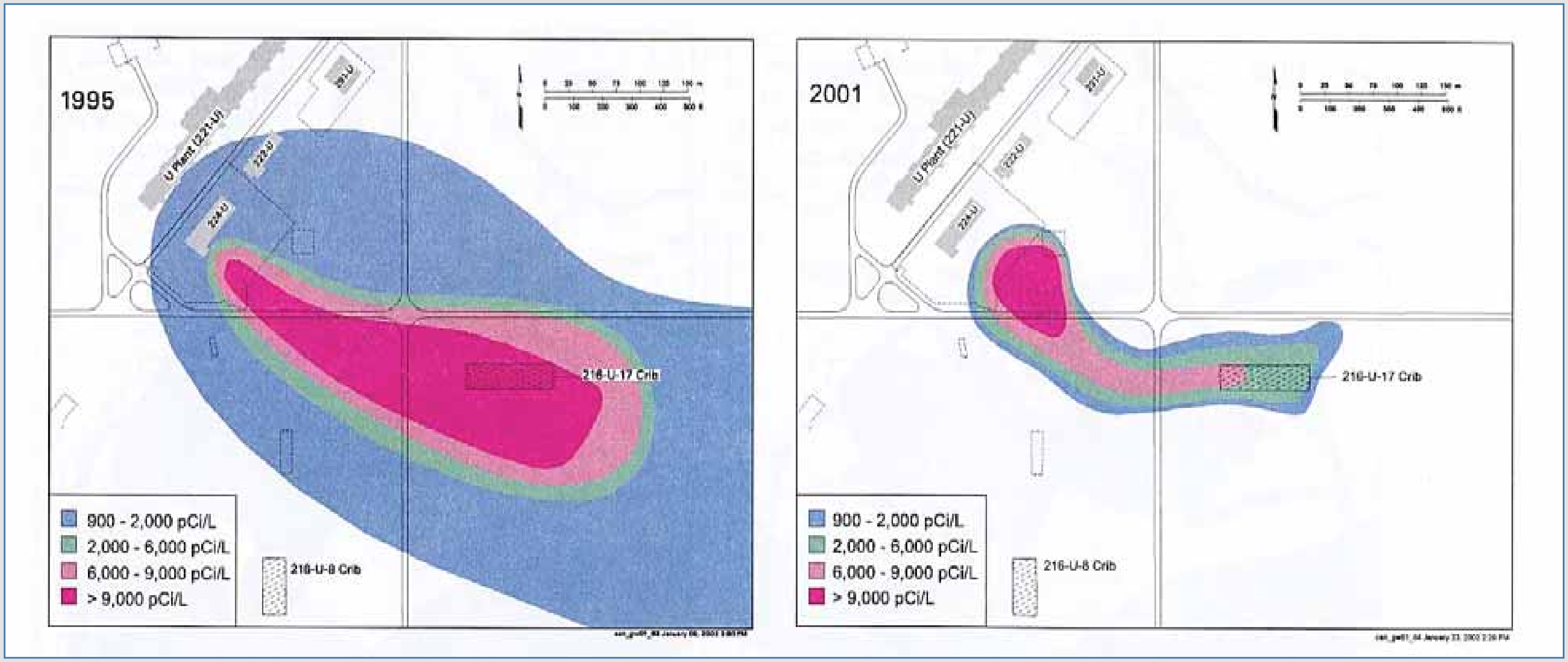
Constituent (drinking water standard)	Fiscal Year 2000	Fiscal Year 2001	Fiscal Year 2002
Carbon tetrachloride (5 µg/L)	9.8	9.8	9.9
Chromium (100 µg/L)	2.8	2.8	2.6
Iodine-129 (1 pCi/L)	89.6	79.5[a]	79.4
Nitrate (45 mg/L)	36.3	38.4	35.7
Strontium-90 (8 pCi/L)	2.8	2.7	2.7
Technetium-99 (900 pCi/L)	2.3	2.4	2.3
Trichloroethene (5 µg/L)	4.2	4.3	3.4[a]
Tritium (20,000 pCi/L)	152	151	142
Uranium (20/30 µg/L)	2.0	1.6	1.5
Combined Plumes	210	208	196

(a) These large changes in estimates of plume area are caused by changing interpretations of the data and changes to the monitoring network. Changes in actual plume size are usually more gradual.

Active Areas of Groundwater Remediation at Hanford



Effects of Pump and Treat on ^{99}Tc at Hanford's 224-U



Oxidation and Reduction

$aA + bB + ne^{-} = cC + dD$

Oxidized state Reduced state

$\Delta G°$, $E°$, $K°$ Reactants and products at standard state

$$E°(\text{volts}) = {}^{-}\Delta G_r° /_{nF}$$

$$Eh(\text{volts}) = E° + \frac{RT}{nF} \ln \frac{(A)^a(B)^b}{(C)^c(D)^d}$$

Tc Redox Chemistry

Tc(VII) and Tc(IV) are most stable valence species

1. $TcO_4^- + 4H^+ + 3e^- = TcO_2 \bullet xH_2O_{(s)} + (2\text{-}x)\ H_2O_{(l)}$

   $E°\ (298.15K) = 0.746 \pm 0.012\ V$

   $\log_{10}K° = 37.8$

   Formulated between reference species of each oxidation

2. $TcO_4^- + 4H^+ + 3e^- = TcO(OH)_{2(aq)} + H_2O_{(l)}$

   $E° = 0.579\ V,\ \log_{10}K° = 29.4$

   $TcO(OH)_2$ is the major aqueous species in non-complexing solutions between pH 2 and 10

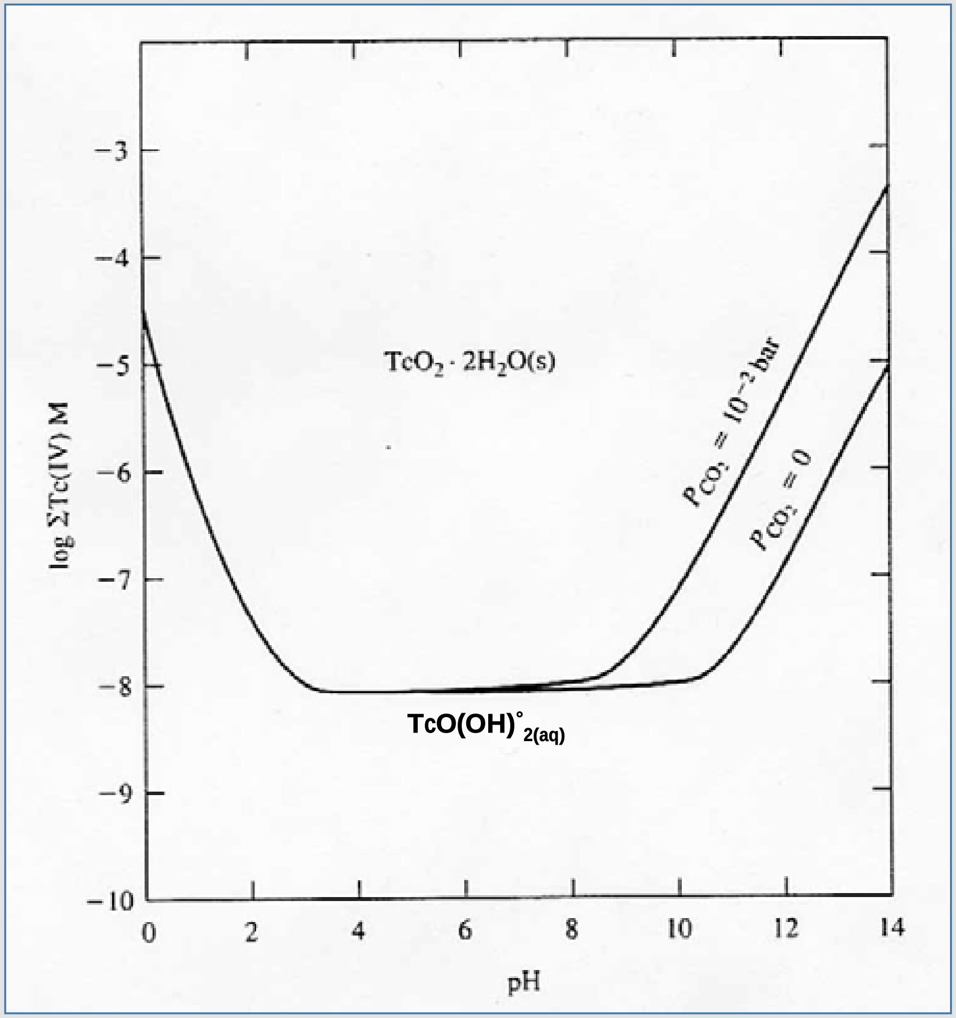
3. $TcO_4^- + 3Fe^{2+}_{(aq)} = TcO(OH)_{2(aq)} + Fe(OH)_{3(s)} + 5H^+$

   $\log_{10}K° = {}^{-}21.8$

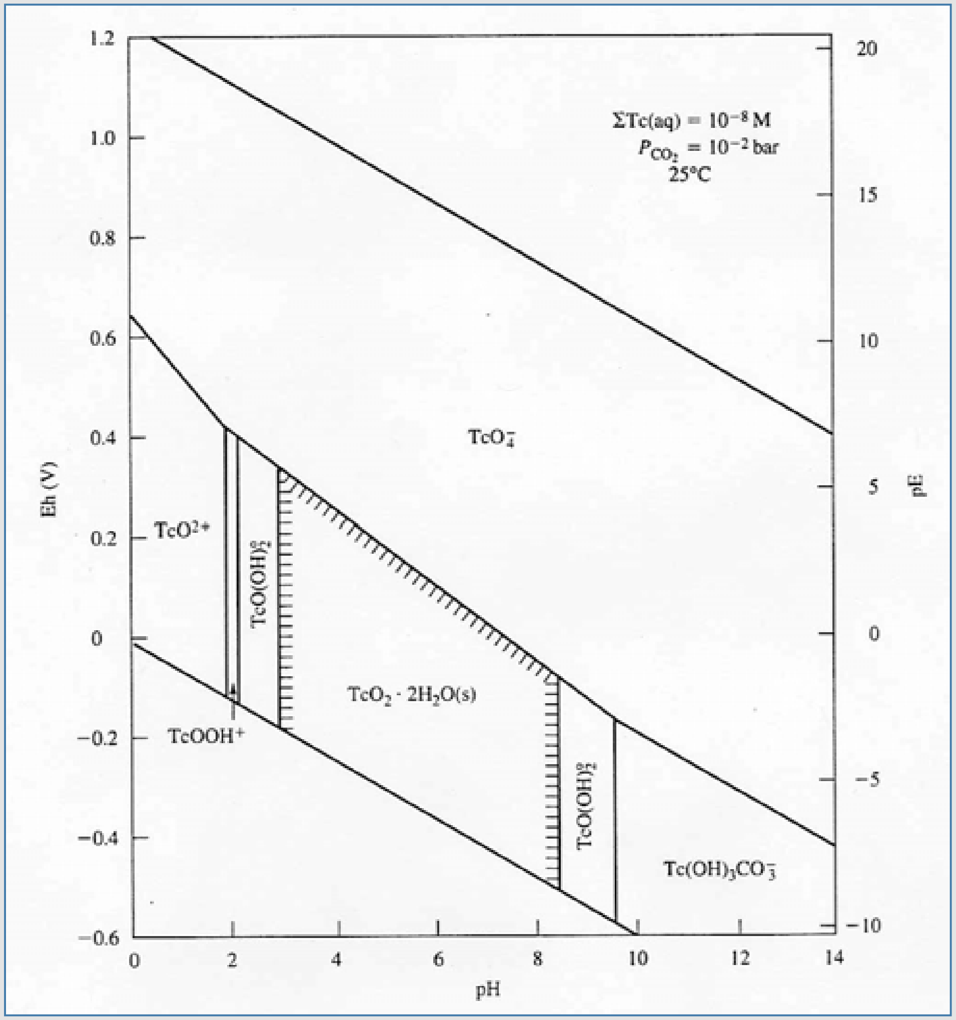
   @ pH 7 — $Fe^{2+} = 10^{-3}$ mol/L, Tc(VII) = $10^{-12.2}$ mol/L

   $Fe^{2+} = 10^{-6}$ mol/L, Tc(VII) = $10^{-3.2}$ mol/L

Solubility of $TcO_2 \cdot nH_2O$



Stability Diagram for TcO_4^-/TcO_2•nH_2O in Presence of $CO_{2(g)}$



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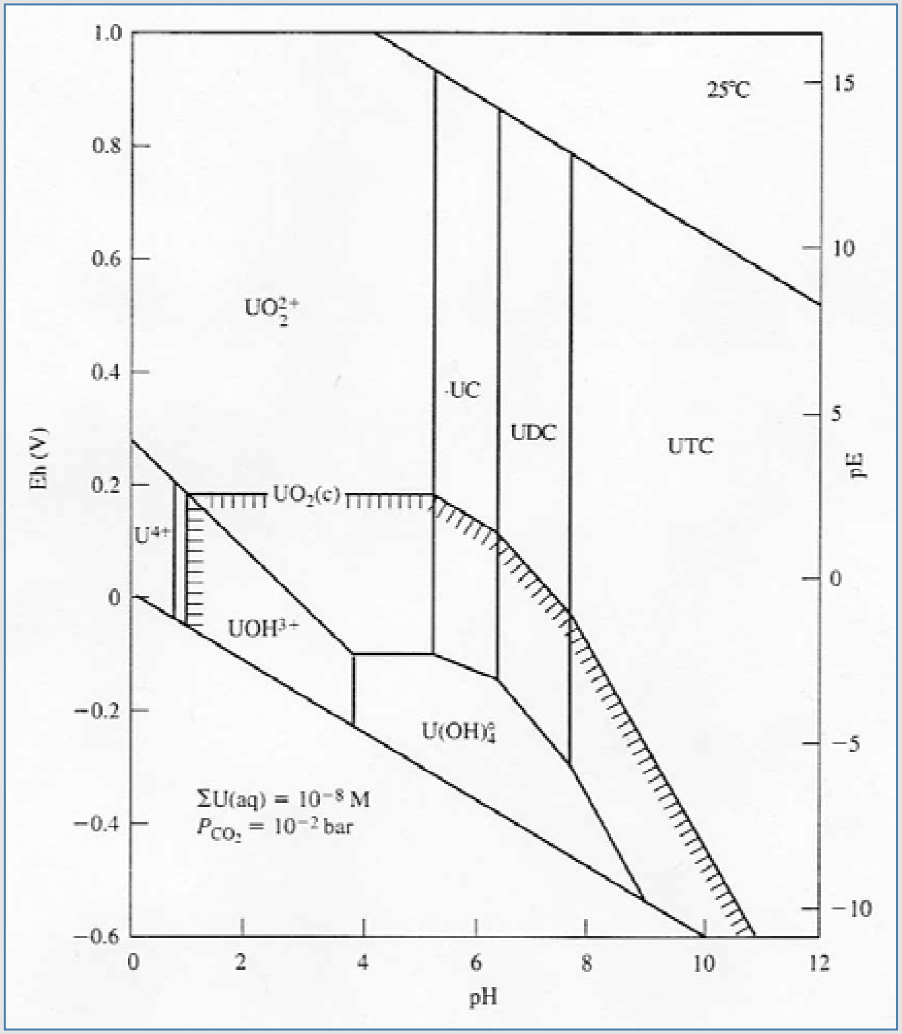
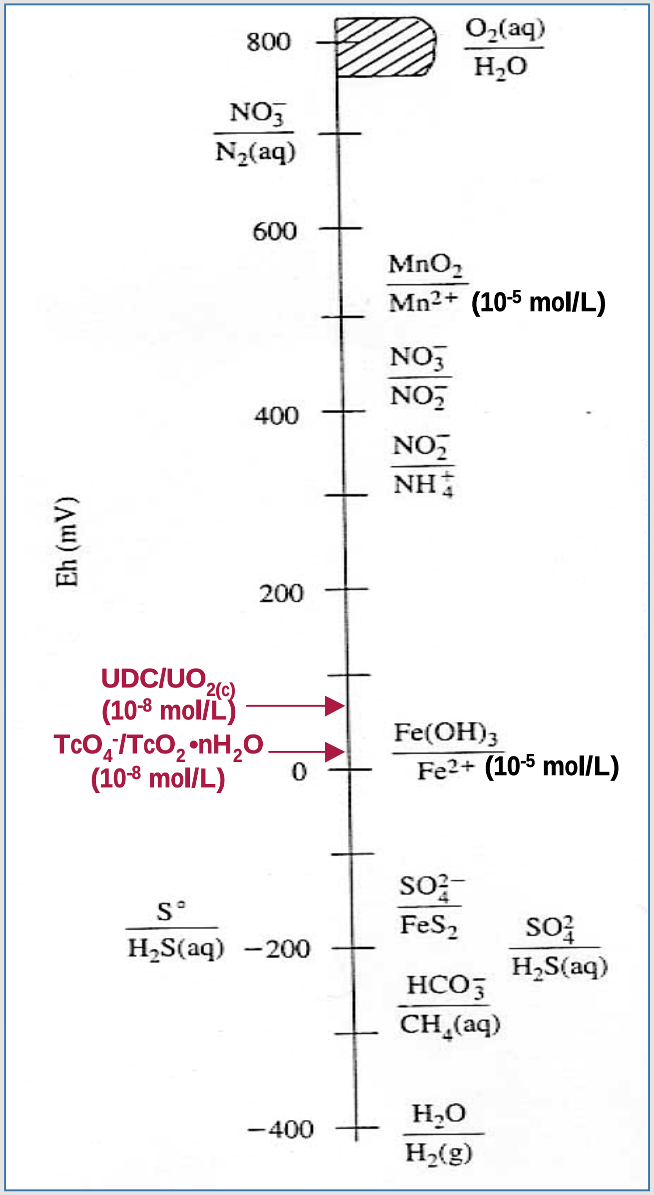
Stability Diagram for $UO_2^{2+}/UO_{2(c)}$ in Presence of $CO_{2(g)}$

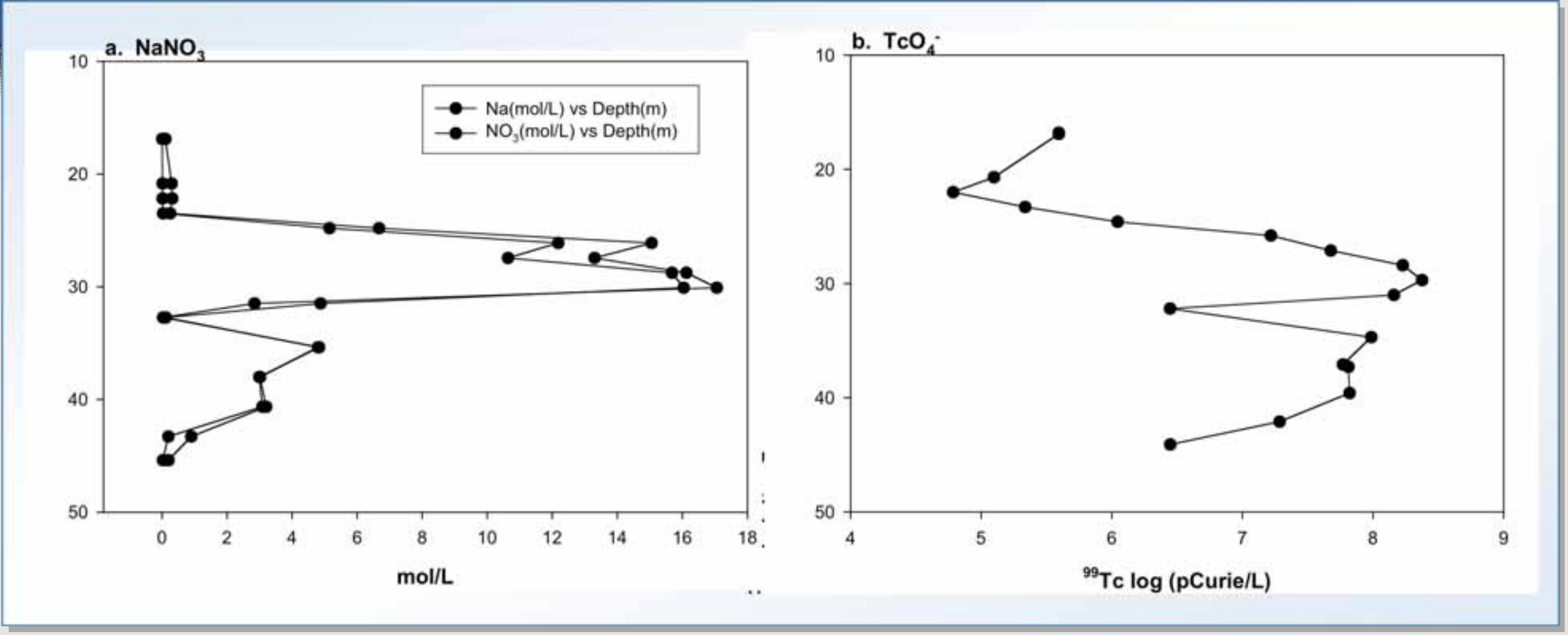


Redox Ladder at pH = 7 and 25° C

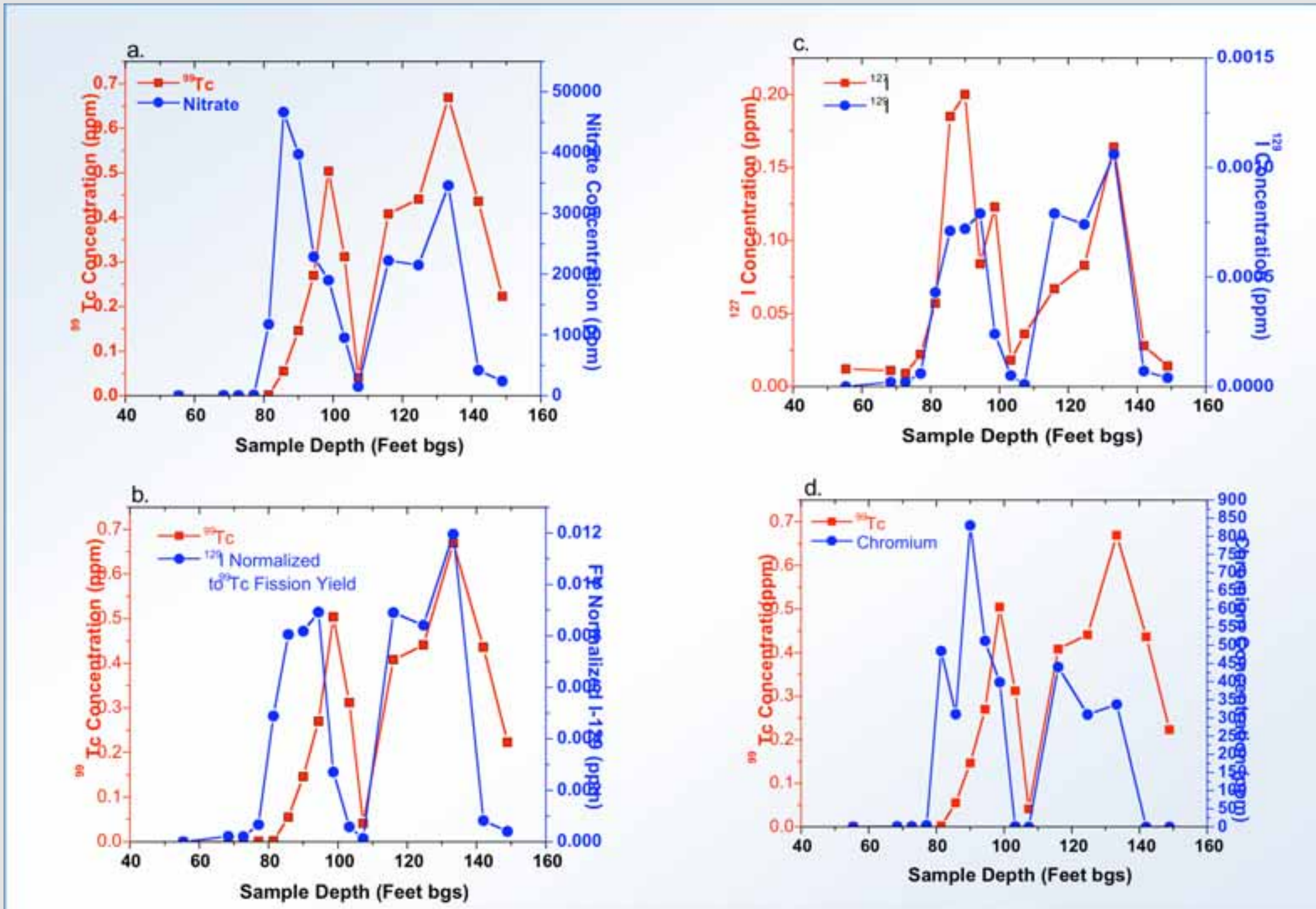
[Aqueous species at equimolar concentrations, others as noted]



TcO_4^- and $NaNO_3$ Beneath Leaked Hanford HLW Tank SX-108



TcO_4^- Co-Contaminants Associated with Hanford REDOX Waste



Laboratory Studies of Tc Reduction and Oxidation

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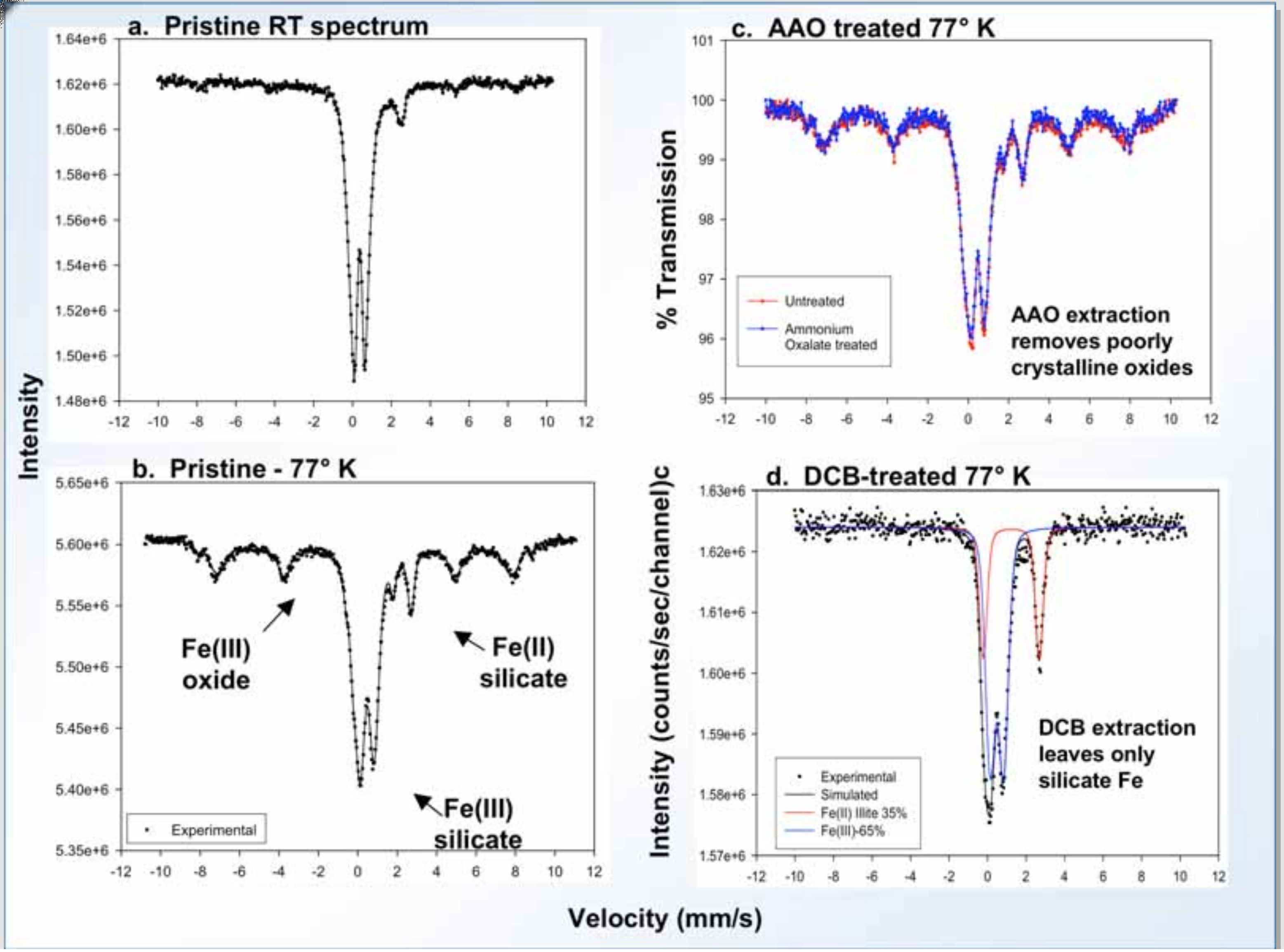
Laboratory Studies of Tc Reduction and Oxidation

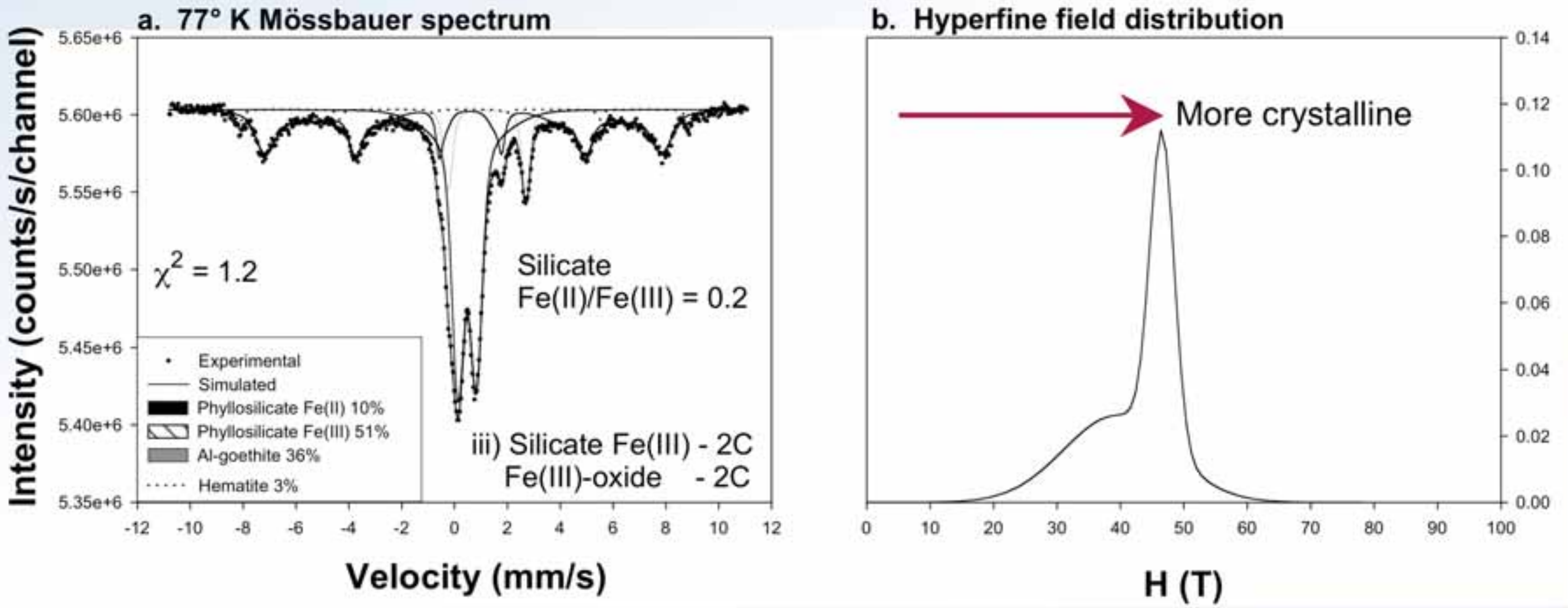
Experimental Issues

- Reactivity of biogenic Fe(II) for Tc(VII) reduction
  - Reactive forms and their properties and concentration terms
  - Kinetic parameters and empirical correlations
  - Nature of reduction products
  - Biogeochemical context and microbiologic relationships
- Factors controlling oxidation rate
  - Intrinsic oxidation kinetics
  - Mineral residence, spatial location, and mass transfer effects
  - In-situ features controlling reaction rate
  - Bacterial oxidation

Effects of Chemical Treatments on the Distribution of Fe in the FRC Background Sediment



Distribution of Fe in the FRC Background Sediment



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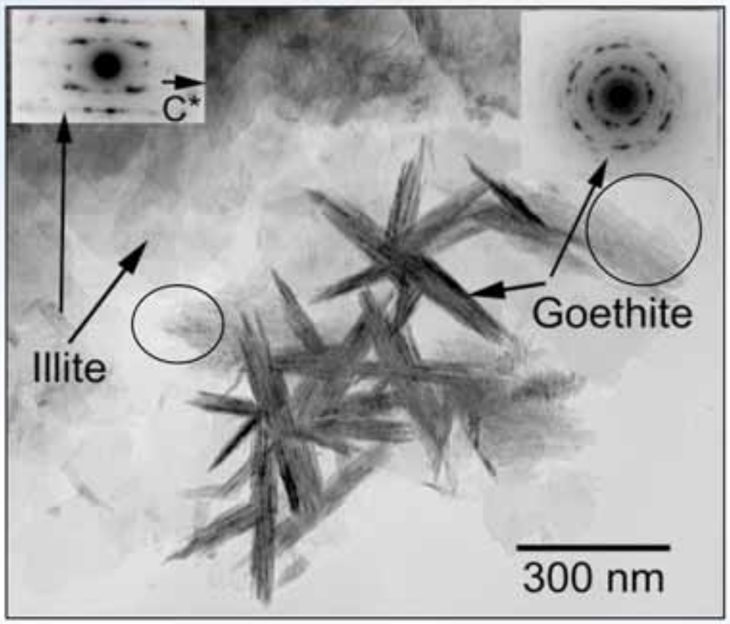
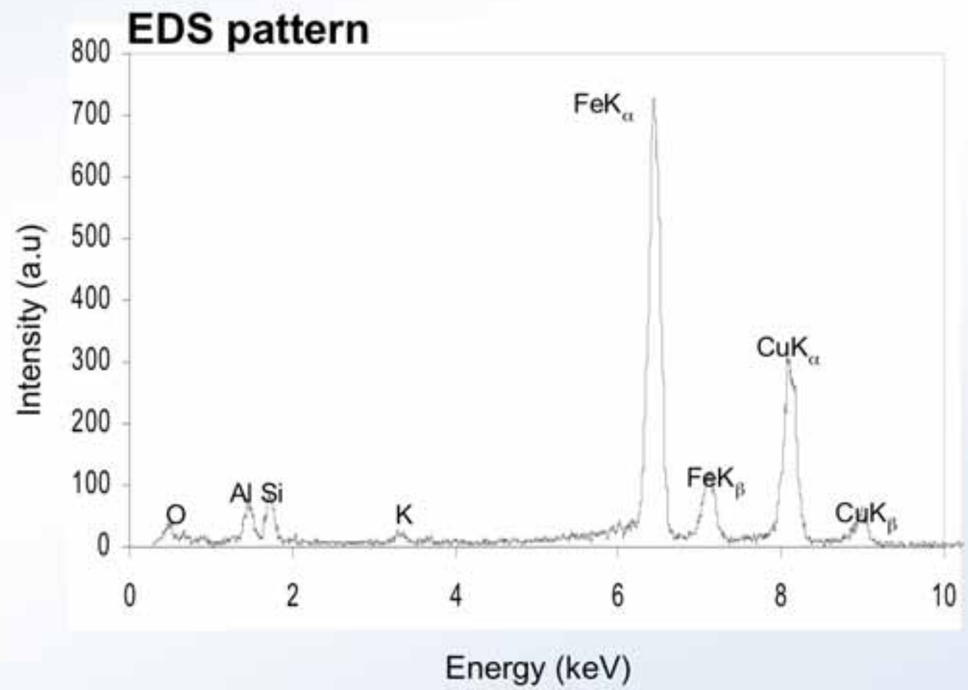
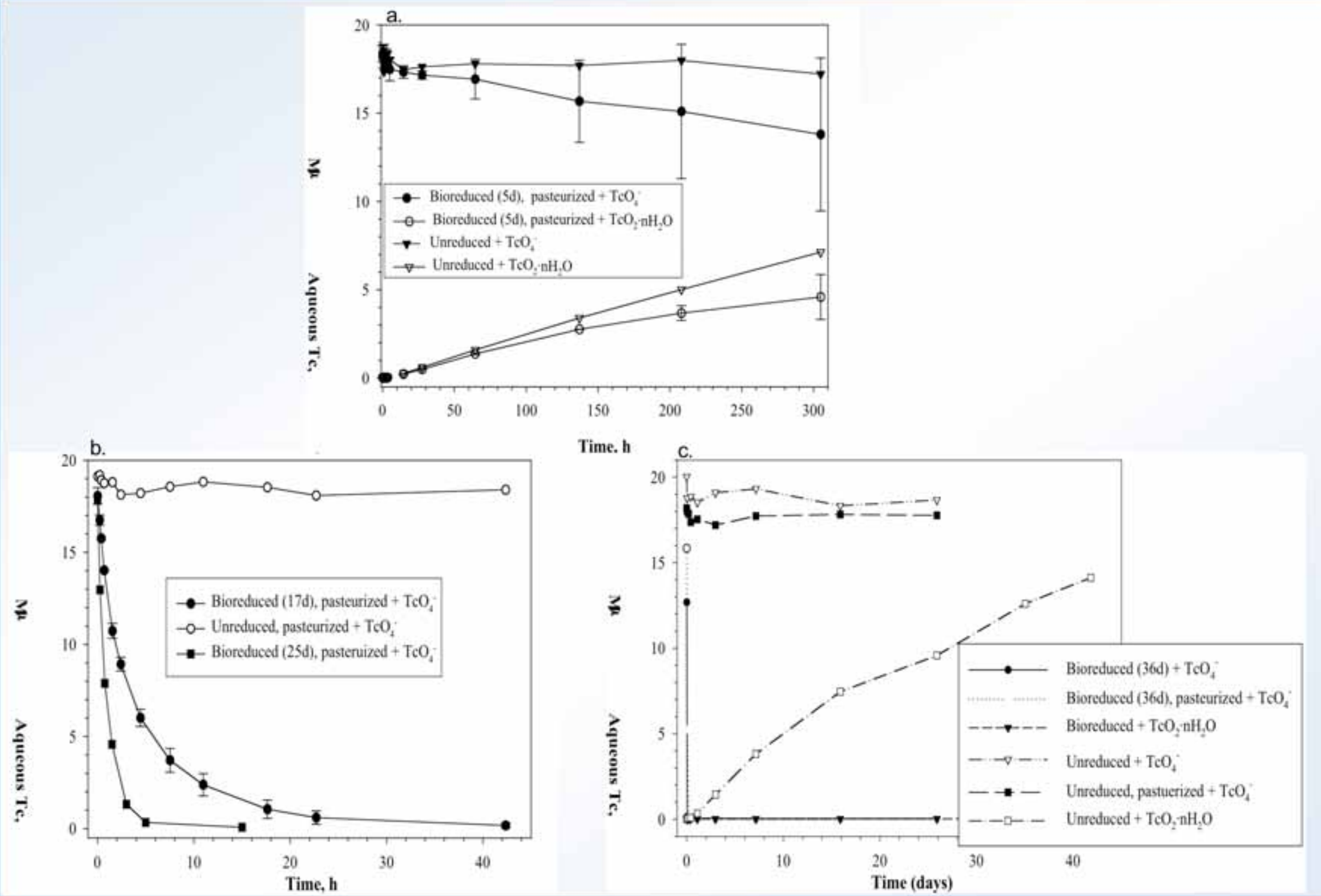
Goethite in the Background FRC Sediment





Reduction and Oxidation Behavior of TcO_4^- and Biogenic $TcO_2 \cdot nH_2O$ in FRC Sediment



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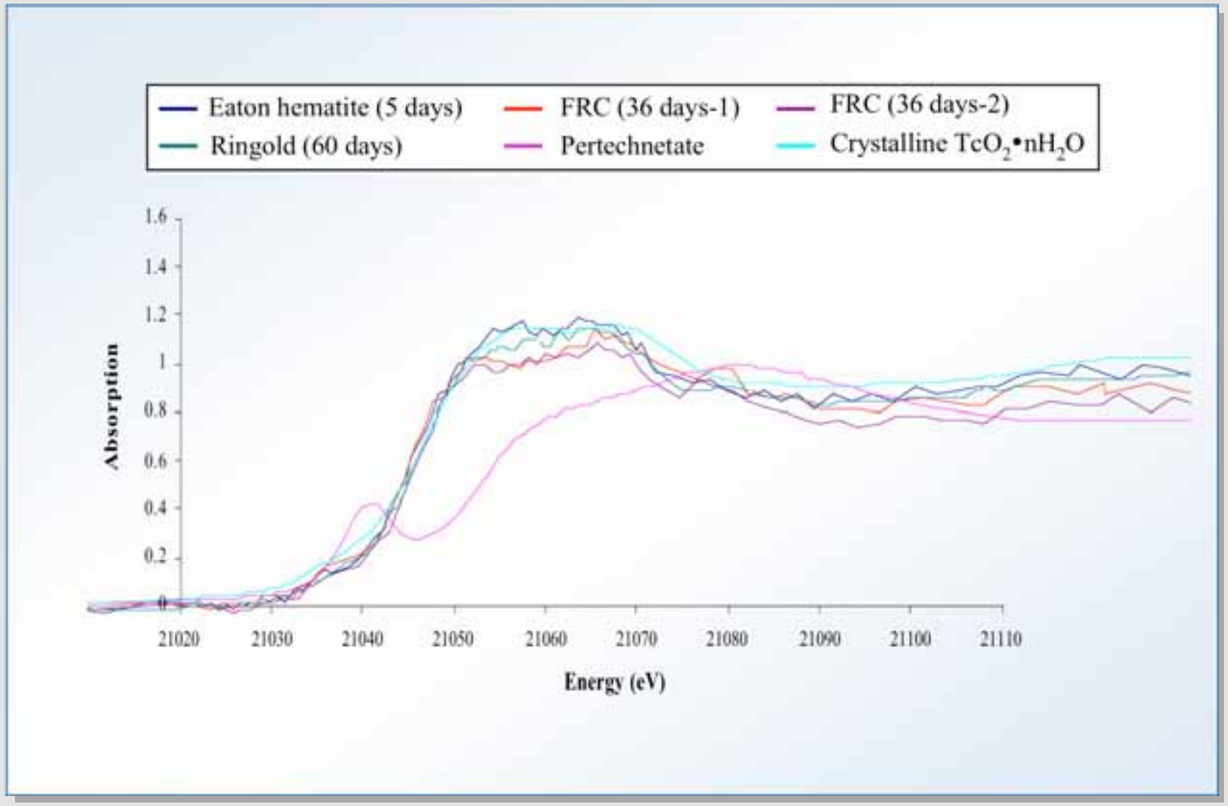
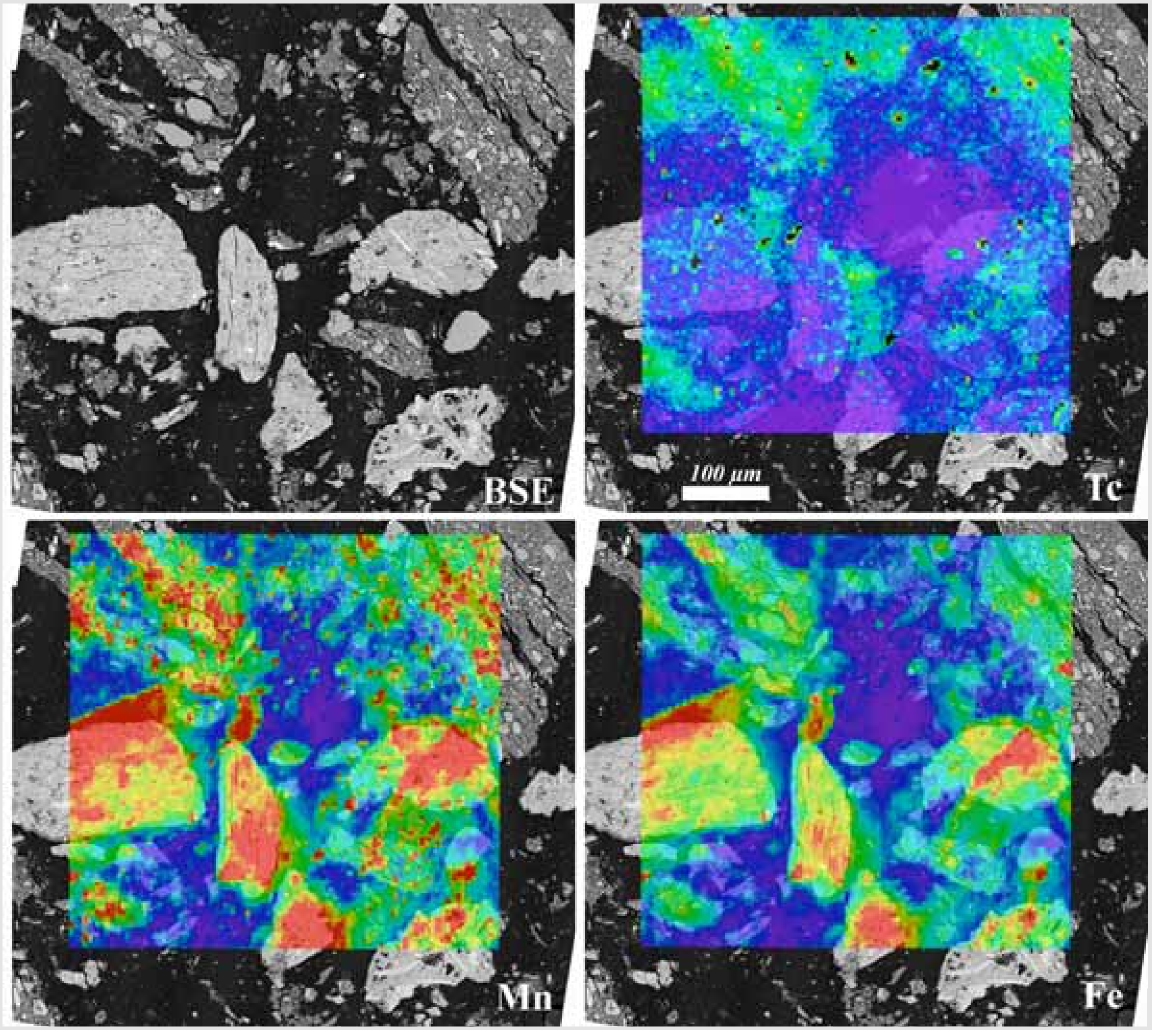
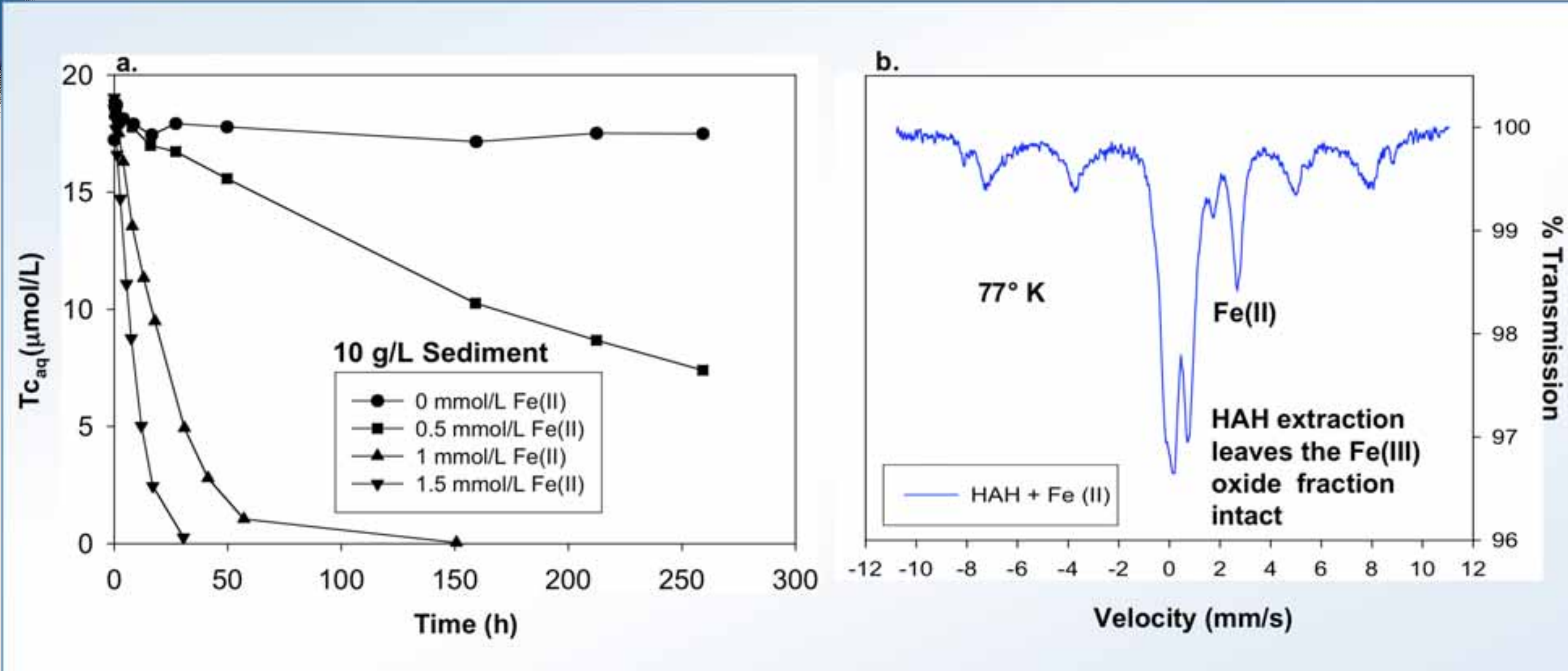
X-ray Absorption, XANES Spectra for Tc(VII) and Tc(IV) Compounds and Bioreduced Sediments Reacted with TcO_4^-



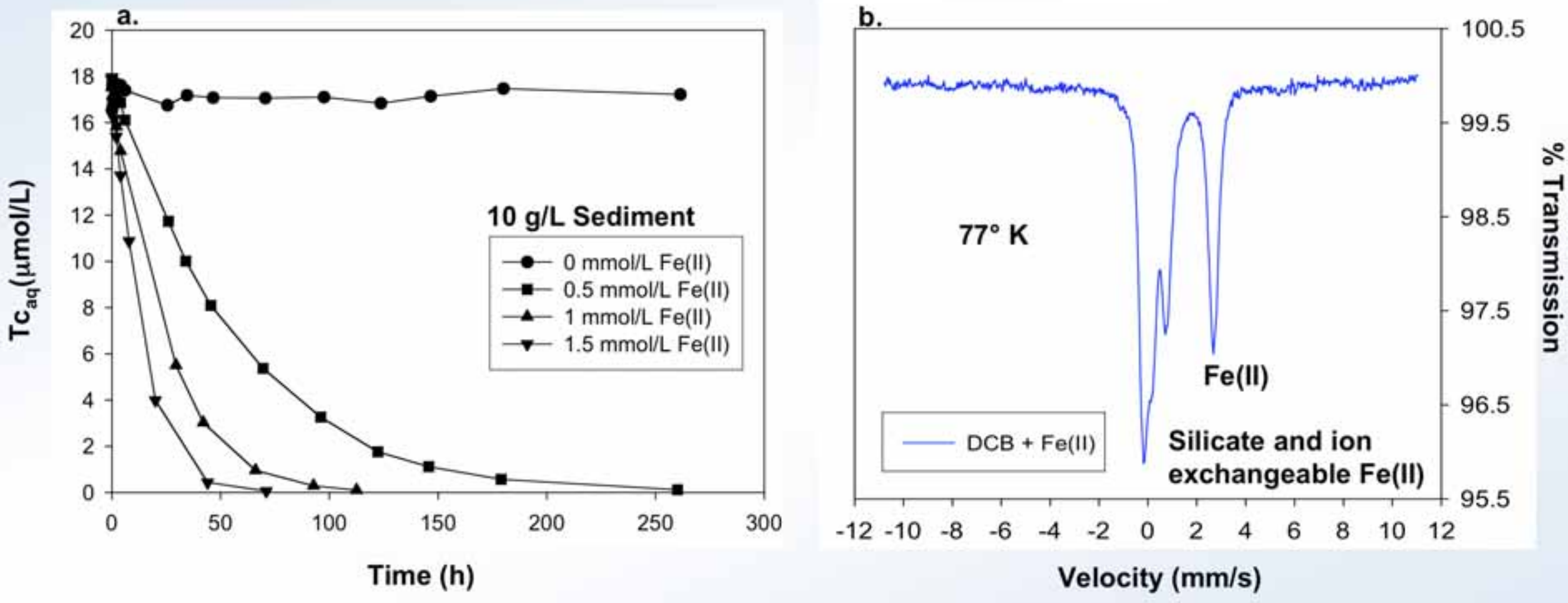
Synchrotron X-ray Microscopy of Bioreduced FRC Sediment that was Spiked with TcO_4^-



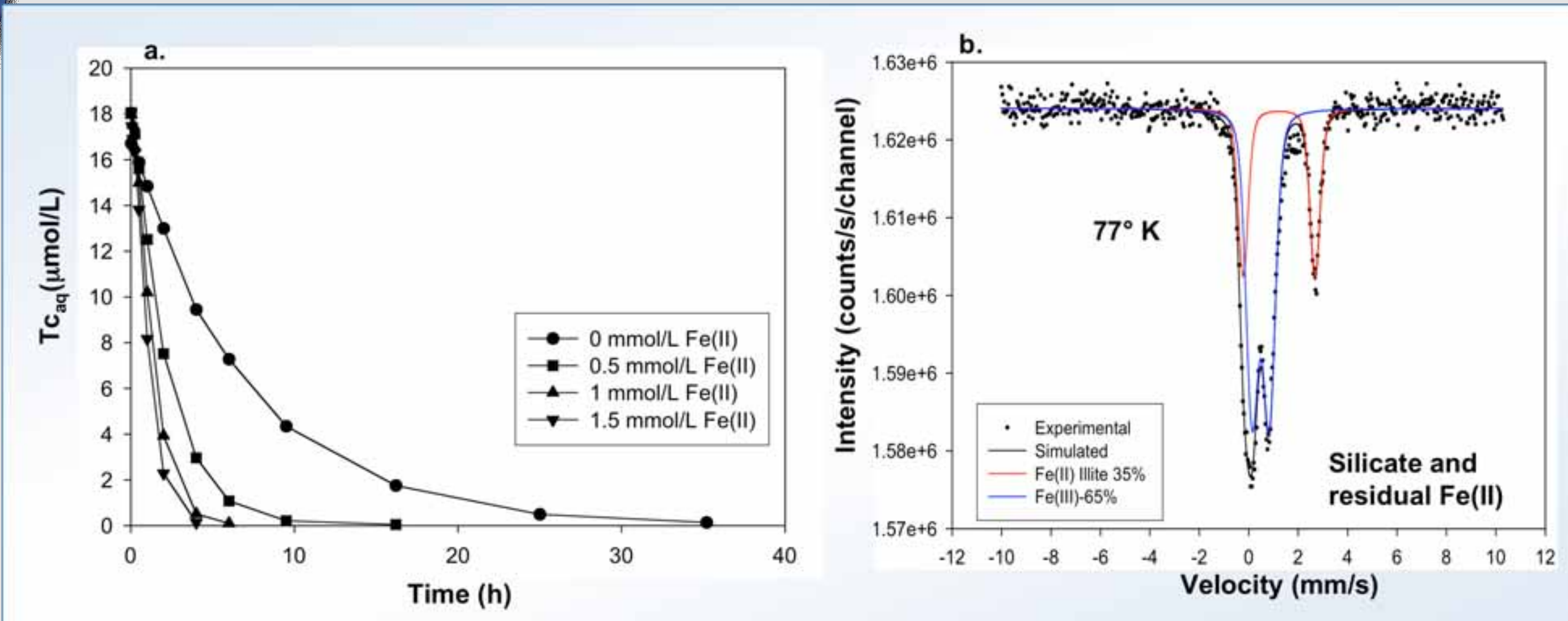
Effect of Fe(II) on TcO_4^- Reduction in HAH Extracted FRC Sediment



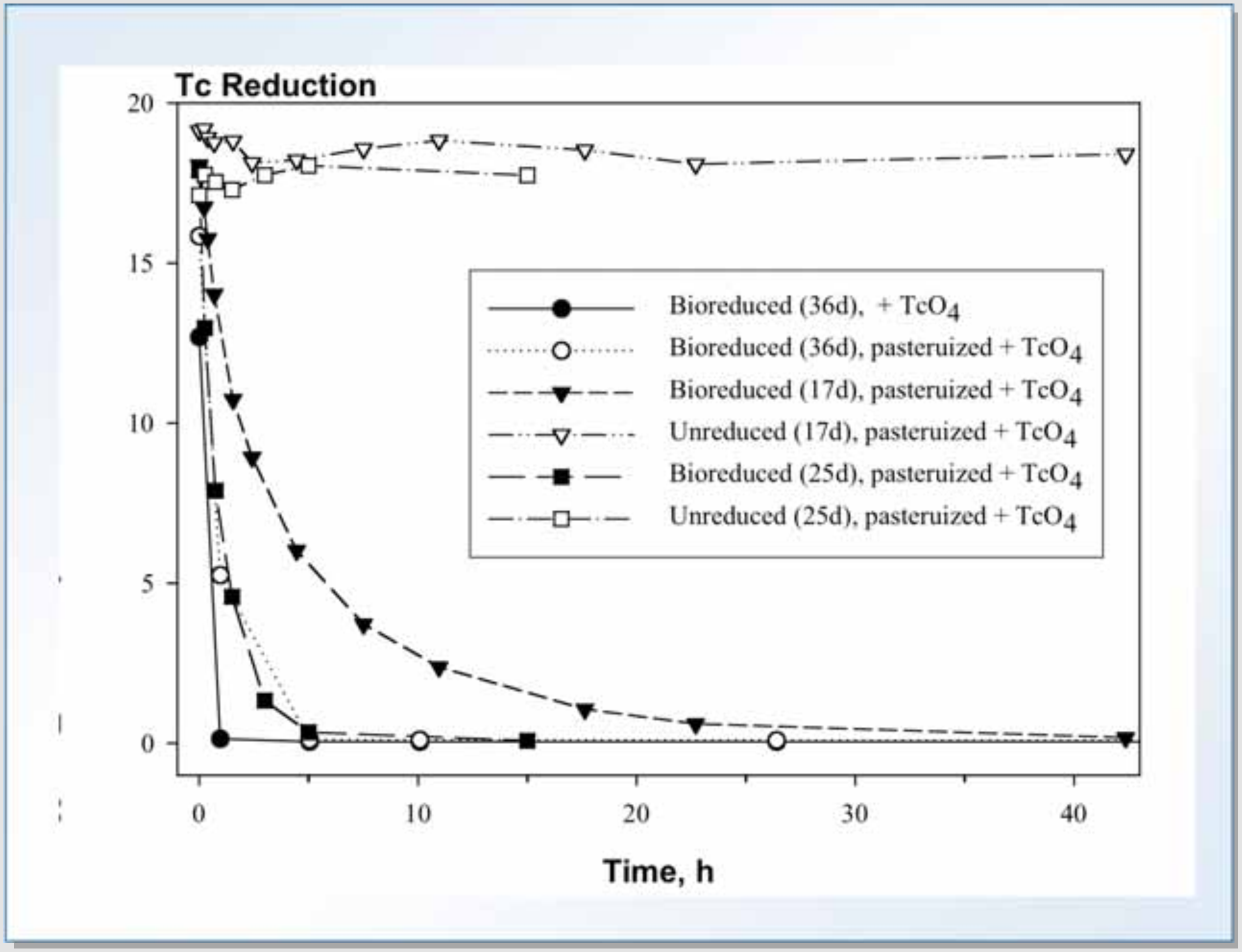
Effect of Fe(II) on TcO_4^- Reduction in DCB/0.5 N HCl Extracted FRC Sediment



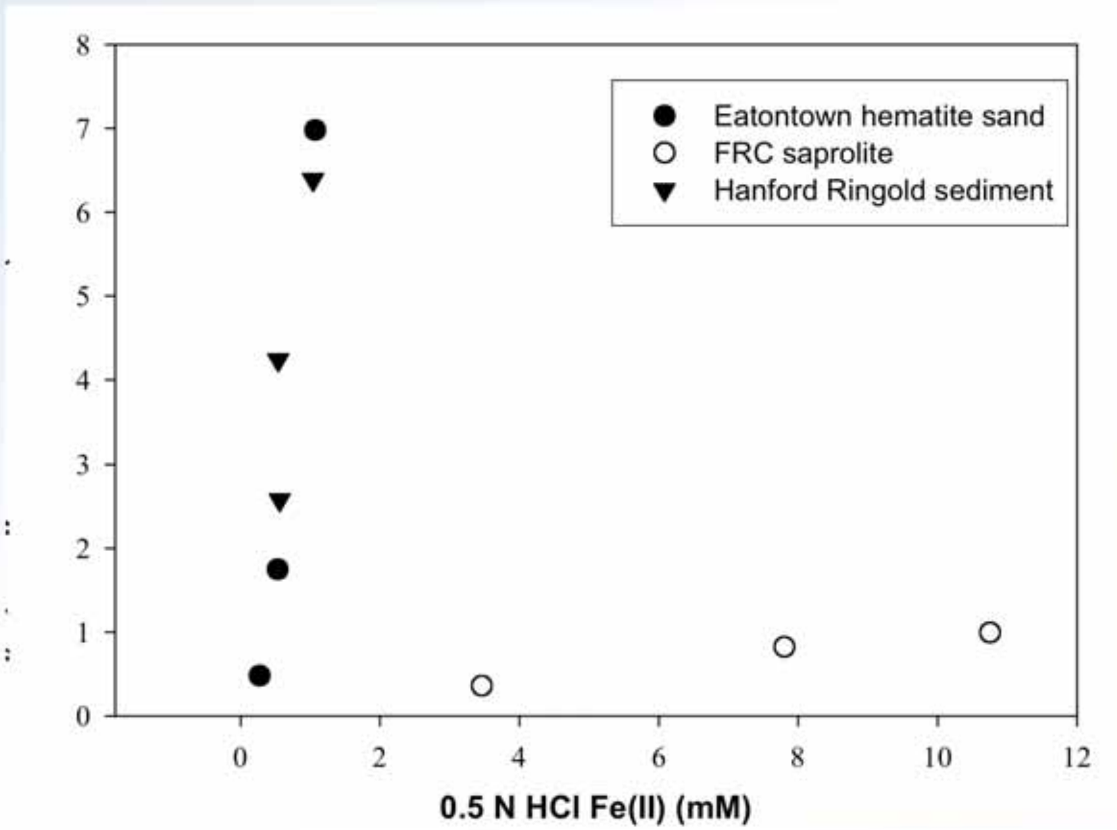
Effect of Fe(II) on TcO_4^- Reduction in the DCB Extracted FRC Sediment



TcO_4^- Reduction by Bioreduced, Pasteurized Eatontown Hematite Sediment

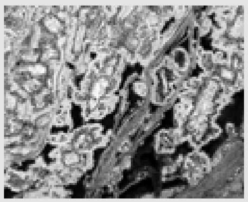


First Order Rate Dependency of TcO_4^- Reduction on Biogenic Fe(II) Concentration

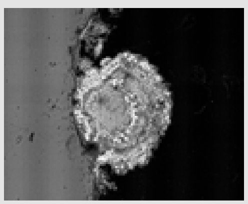


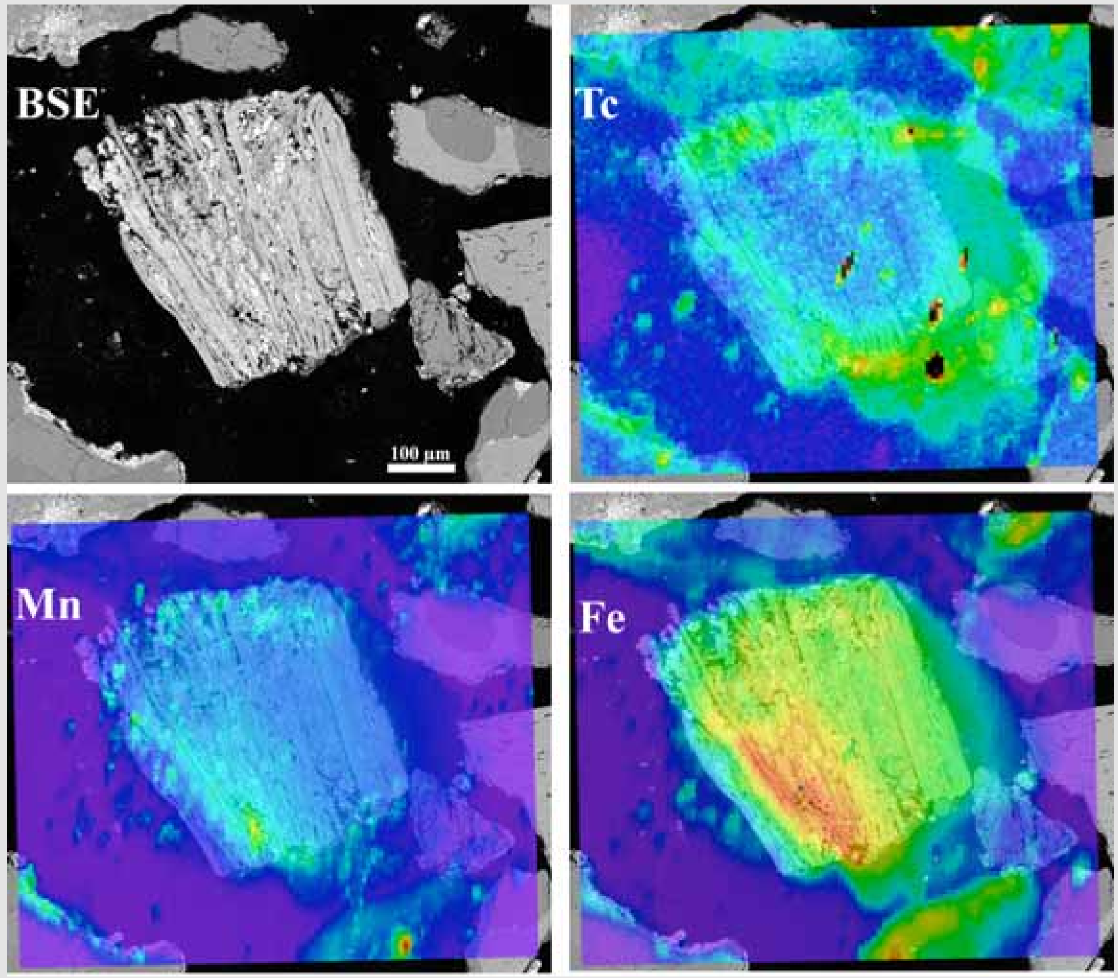
Synchrotron X-ray Microscopy of Bioreduced Hanford/Ringold Sediment that was Spiked with TcO_4^-

Interlaminar
Fe & Mn oxides

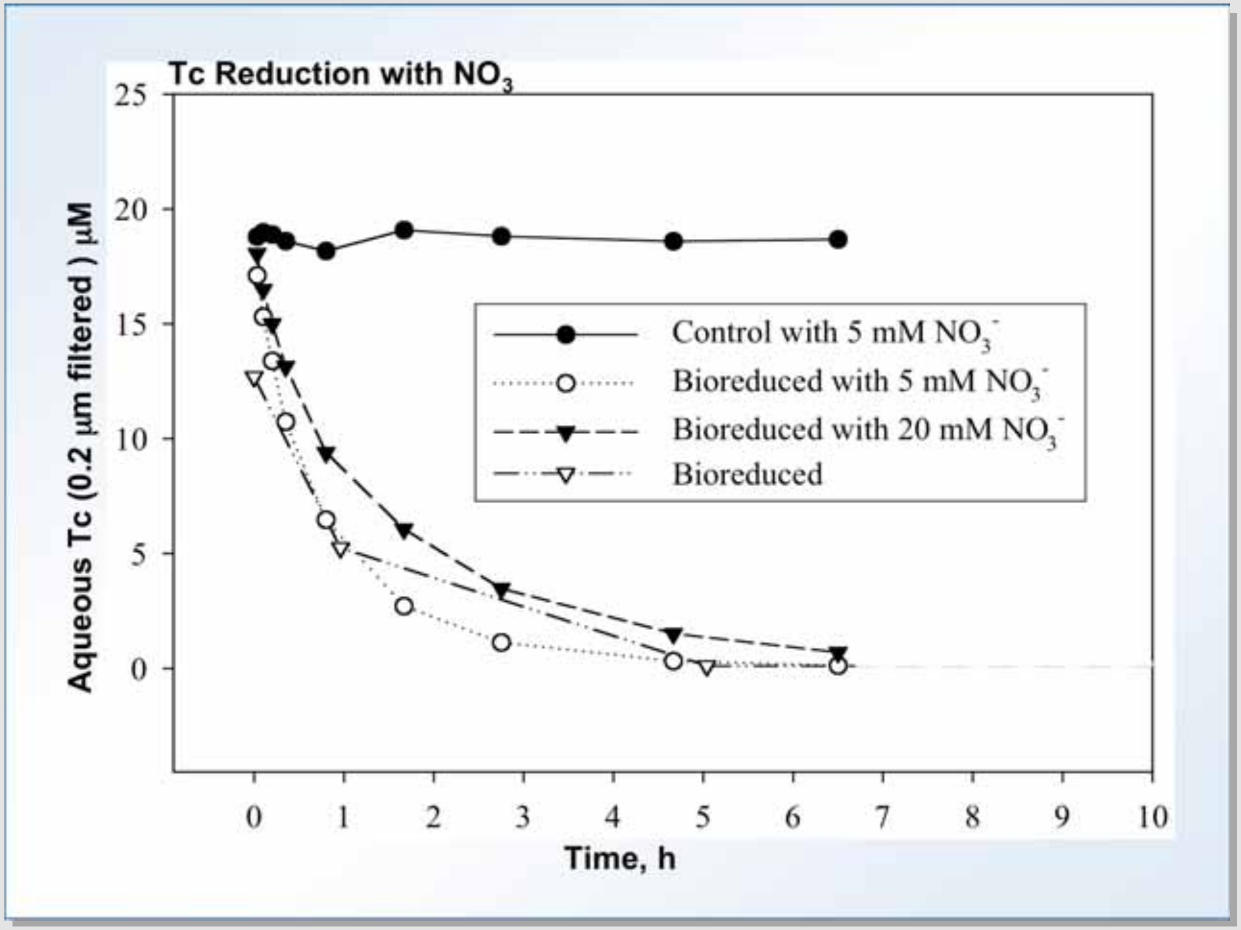


Fe & Mn oxide
grain coatings

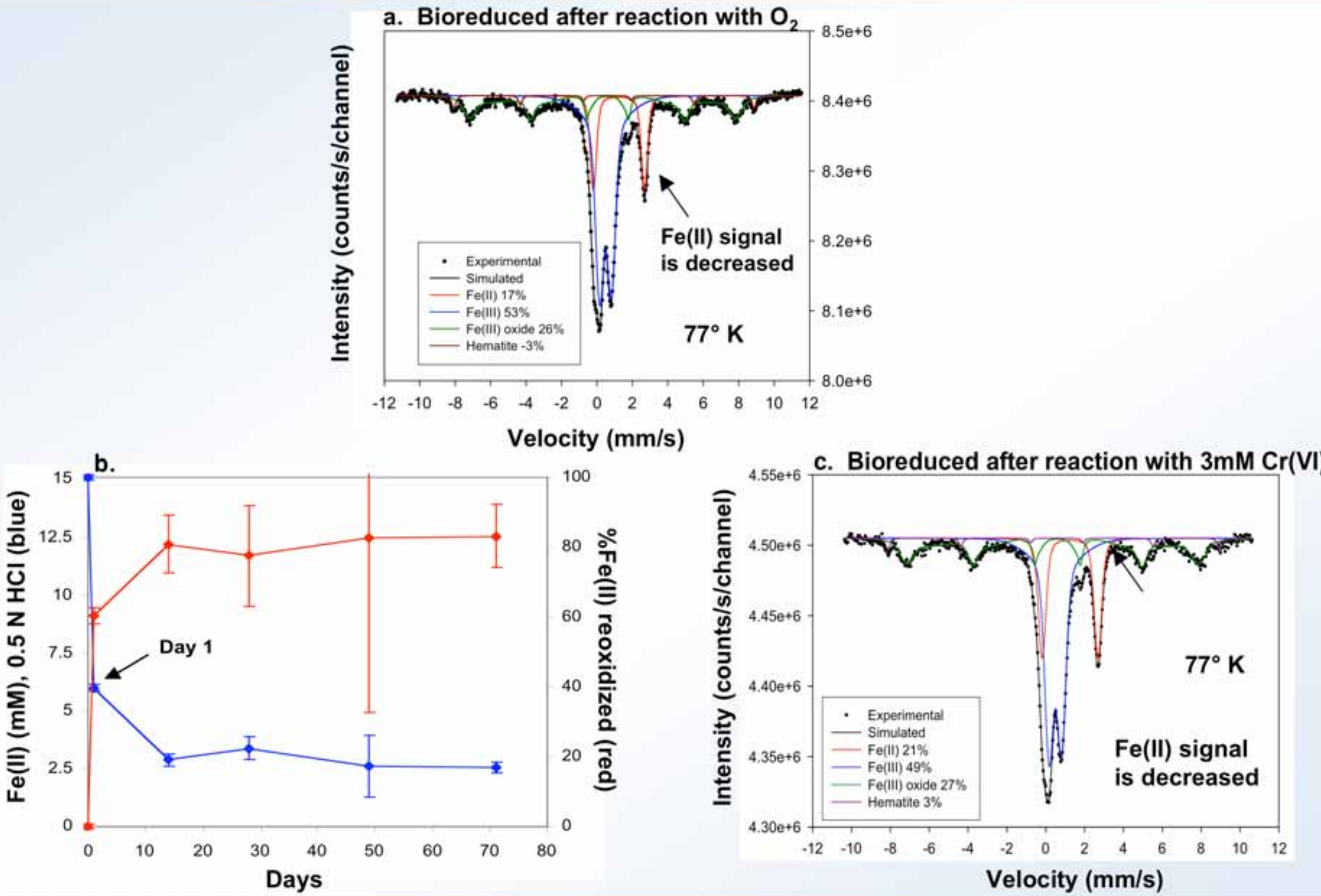




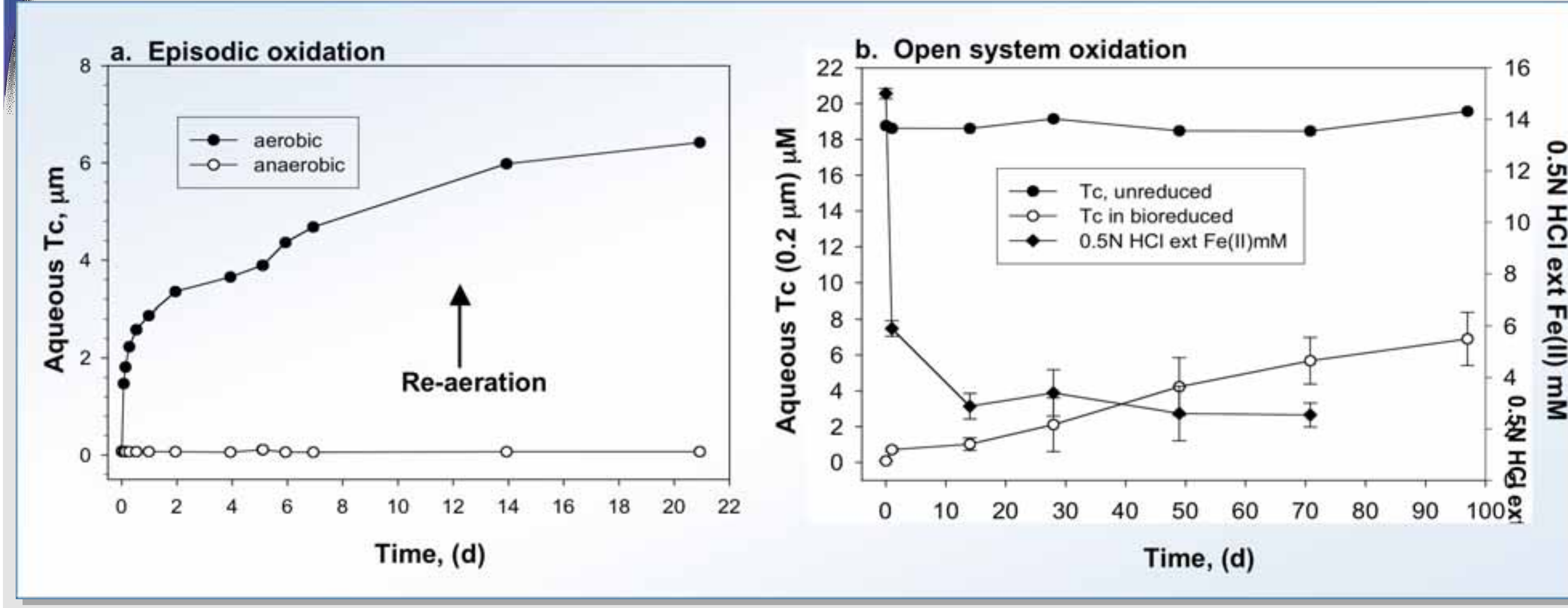
Influence of NO_3^- on TcO_4^- Reduction by Bioreduced, Pasteurized FRC Sediment



Lability of Biogenic Fe(II) in FRC Sediment to Reaction with Environmental Oxidants



Oxidation of Biogenic of $TcO_2 \cdot nH_2O$ in Single Phase Suspensions and in FRC Sediment



Findings to Date – Tc(VII) Reduction

- Biogenic Fe(II) is strongly sorbed by different sediments
- Quantifying Fe(II) speciation is difficult
- Biogenic Fe(II) is a strong reductant for TcO_4^-
- Redox properties of sorbed Fe(II) wrt Tc(VII) reduction are difficult to rigorously define
- Fe(II) surface precipitates appear as the strongest Tc(VII) reductants
- Similarities and differences in the reactivity of sediment Fe(II) for Tc(VII)

Findings to Date – Tc(IV) Oxidation

- The relative rate of $TcO_2 \bullet nH_2O$ oxidation is slower than Tc(VII) reduction

- Presumptive evidence from oxidation behavior that Fe(II) and Tc(IV) are closely associated
  - Chemical/mineralogic
  - Physical

- Fe(II) oxidizes more rapidly than Tc(IV), but oxidation is incomplete

- Fe(III) oxidation products influence Tc(IV) oxidation
  - Intragrain, intrapore mass transfer effects
  - Fixing Fe(II)/Tc(IV) proximity

Areas for Future Research

- Identity of biogenic Fe(II) reductants
- Molecular association of Fe(II) and Tc(IV)
- Thermodynamic and kinetic reaction parameters for biogenic Fe(II)
- Kinetic reaction parameters for “abiotic” $TcO_2 \cdot nH_2O$
- Physical and chemical controls on $TcO_2 \cdot nH_2O$ oxidation
- Linked geochemical, microbiologic, and hydrologic modeling of reductive and oxidative processes

Tentative Discussion Topics

1. Microbiologic uncertainties
   - Presence of suitable organisms
   - Enzymatic reduction and oxidation
   - Reactivity of periplasmic $TcO_2 \bullet nH_2O$
   - In-situ bioreduction rates and influence of co-contaminants

2. Geochemical and hydrologic uncertainties
   - Controlling factors, reaction mechanisms, and rate laws for abiotic reduction and oxidation
   - Identifying and quantifying solid phase reductants and oxidants
   - Mass transfer and advective controls on Tc oxidation and reduction
   - Microbiologic evolution of physical and chemical properties

3. Key areas for future research