Biogeochemical Coupling of Fe and Tc Speciation in Subsurface Sediments: Implications to Long-Term Tc Immobilization

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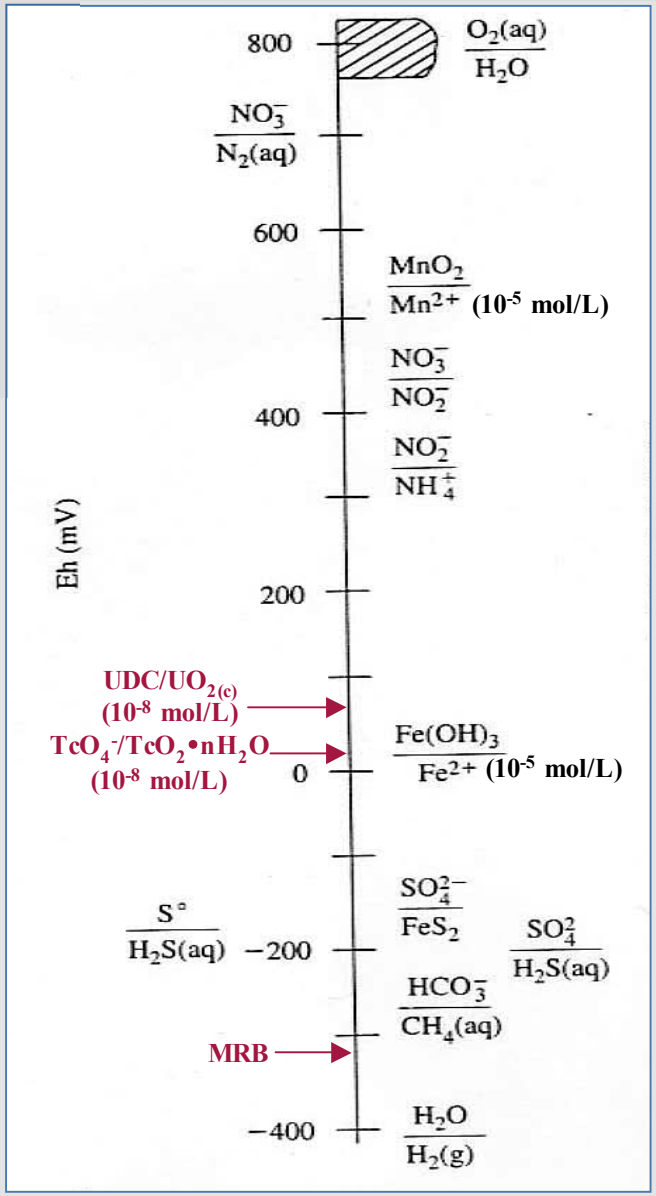
Project Goals

- Characterize coupled redox reactions between biogenic Fe(II) and Tc in Hanford and FRC sediments
  - Reactivity of biogenic Fe(II) for Tc(VII) and O_2
  - Reoxidation rate of Tc(IV)O_2
    - Abiotic
    - Biotic
  - Extra thermodynamic and kinetic factors
- Rigorously characterize reoxidation rates under relevant conditions
  - “In-situ” precipitates
  - Microaerophilic conditions
  - Water advection
  - Other environmental oxidants

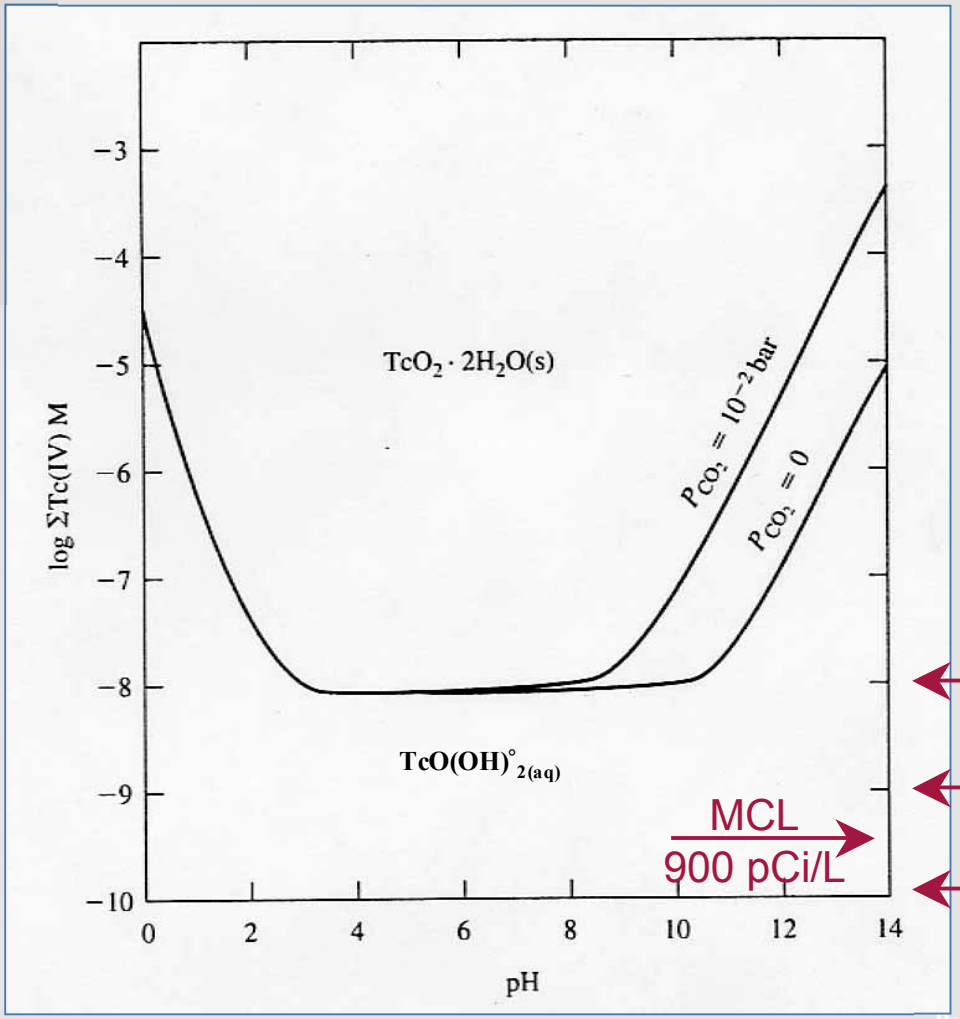
Redox Ladder at pH = 7 and 25° C

[Aqueous species at equimolar concentrations, others as noted]

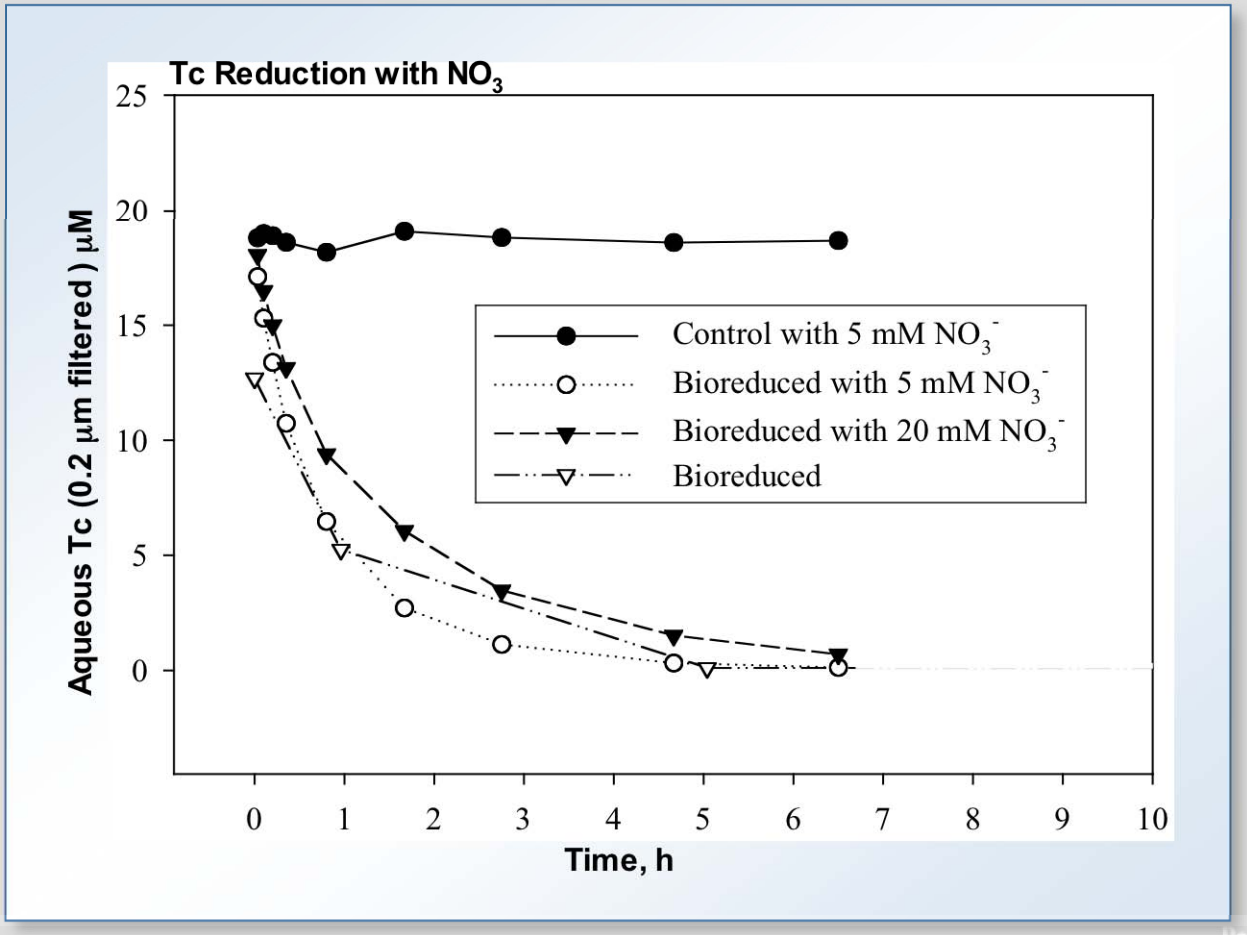


Solubility of $TcO_2 \cdot 2H_2O$

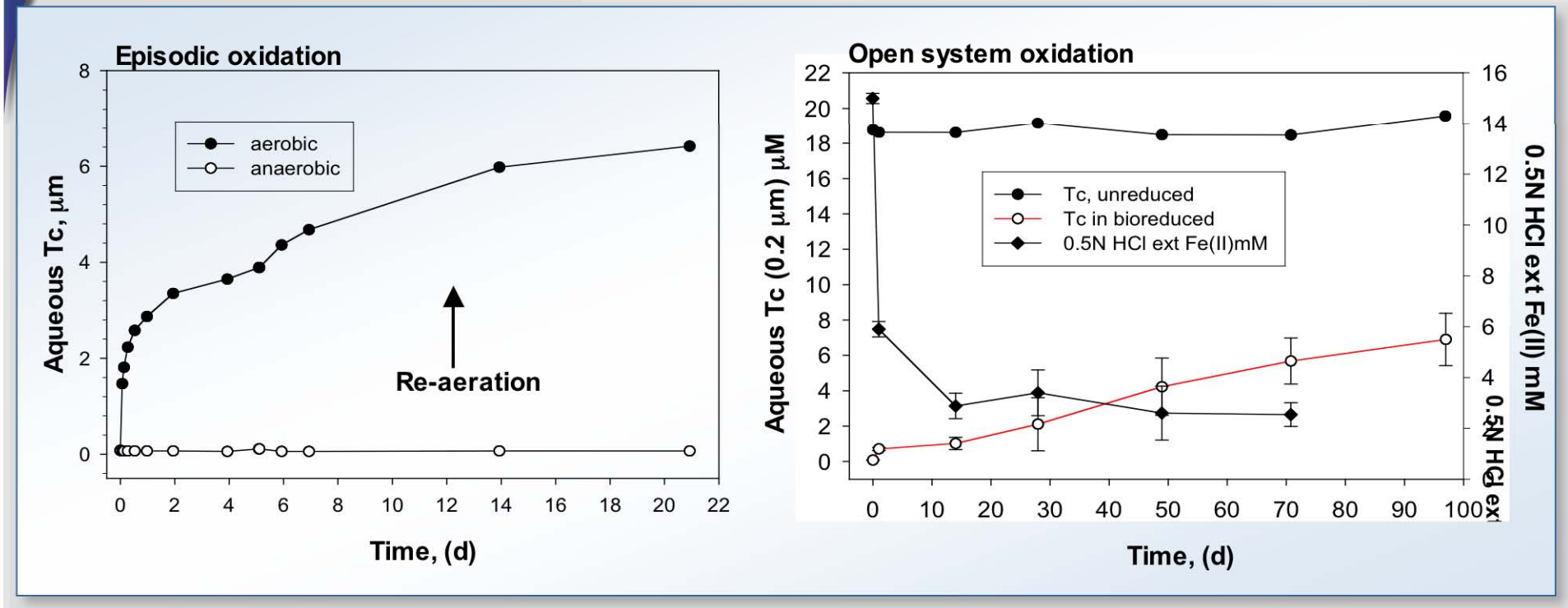
- Concentration of Tc(IV) fixed by solubililty at reduction point
- Downgradient adsorption of Tc(IV) complexes essential to reach MCL (900 pCi/L)
- Adsorption behavior of $TcO(OH)_2^{\circ}{}_{(aq)}$ unknown



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

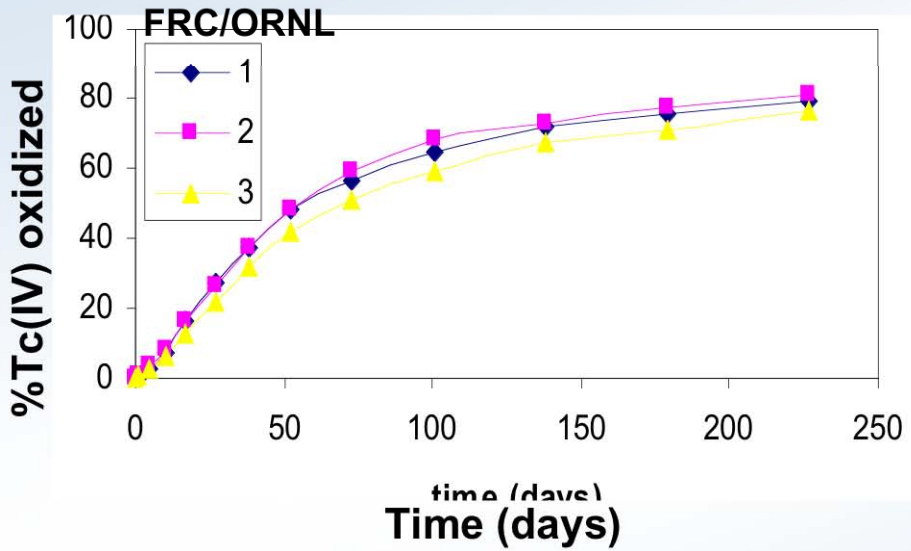


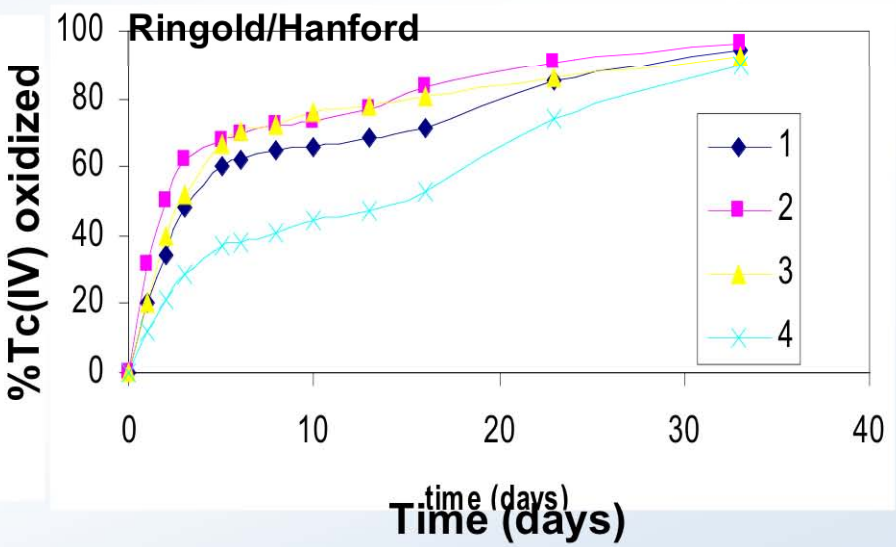
Oxidation of Biogenic $TcO_2 \cdot xH_2O$ in Single Phase Suspensions and in FRC Sediment



Comparative Oxidation of Tc(IV) in Oak Ridge (FRC) and Hanford (Ringold) Sediments

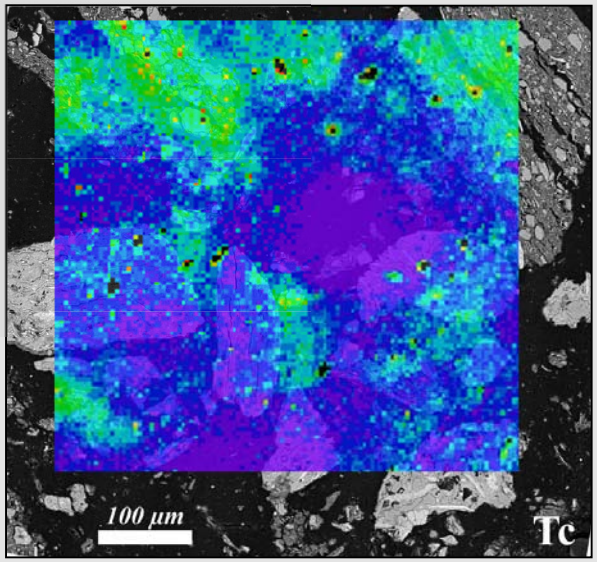
Sediments contain 1 mM of heterogeneously reduced Tc(IV)



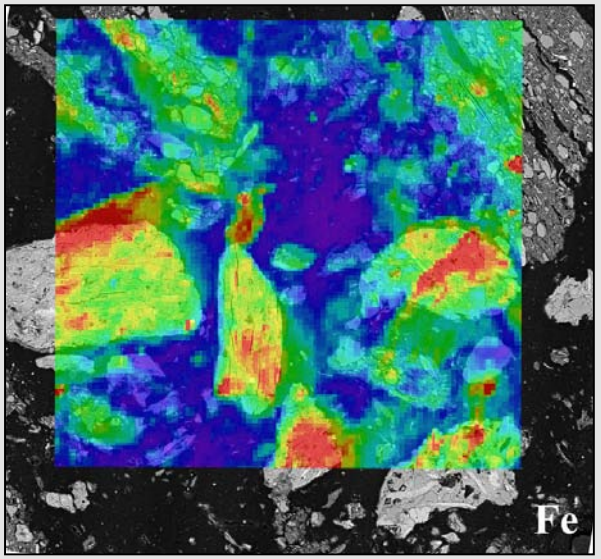


Distribution of Tc and Fe in Bioreduced FRC Sediment (by XRM)

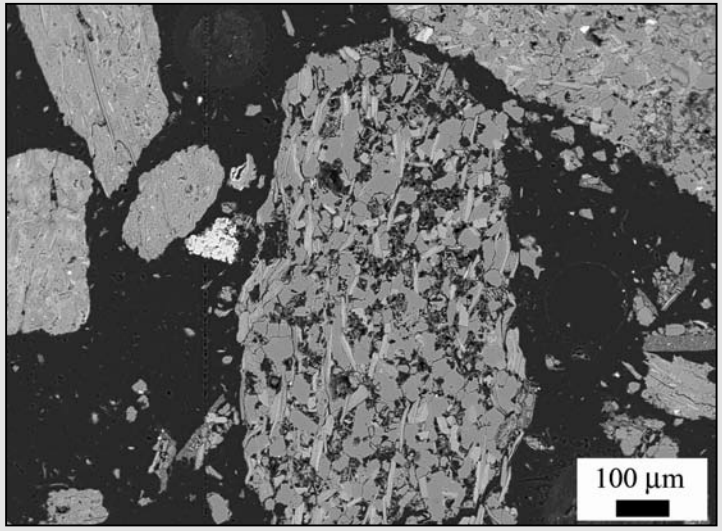
Tc



Fe

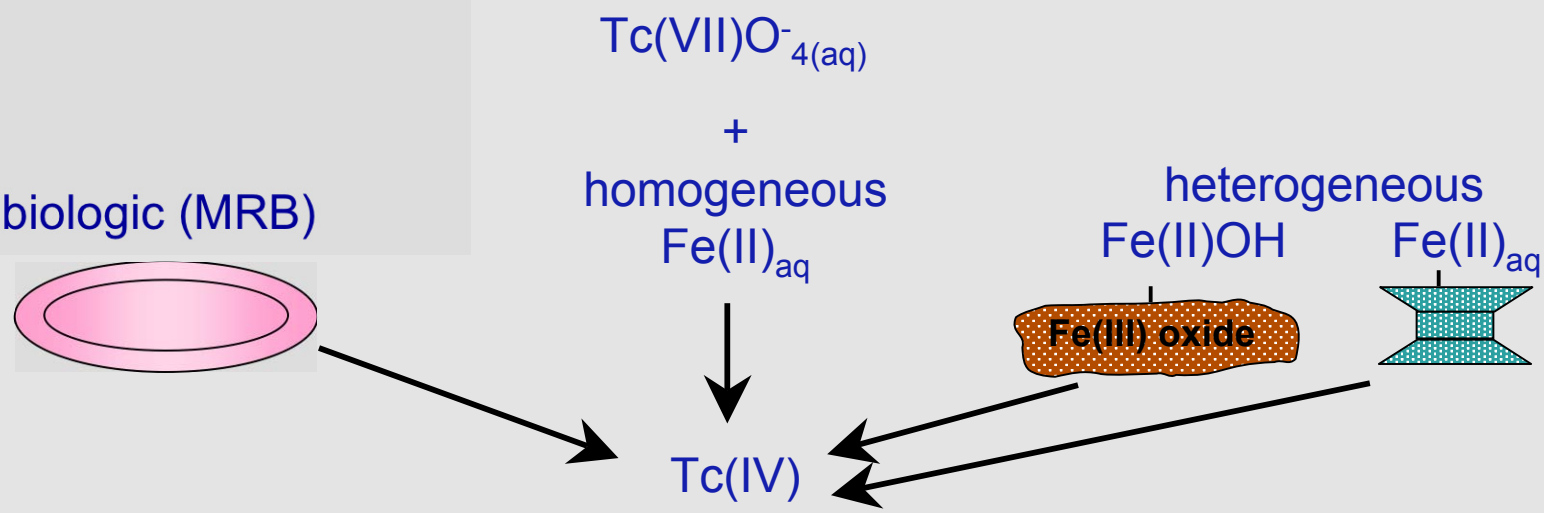


BSE of "weathered" particle



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)

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

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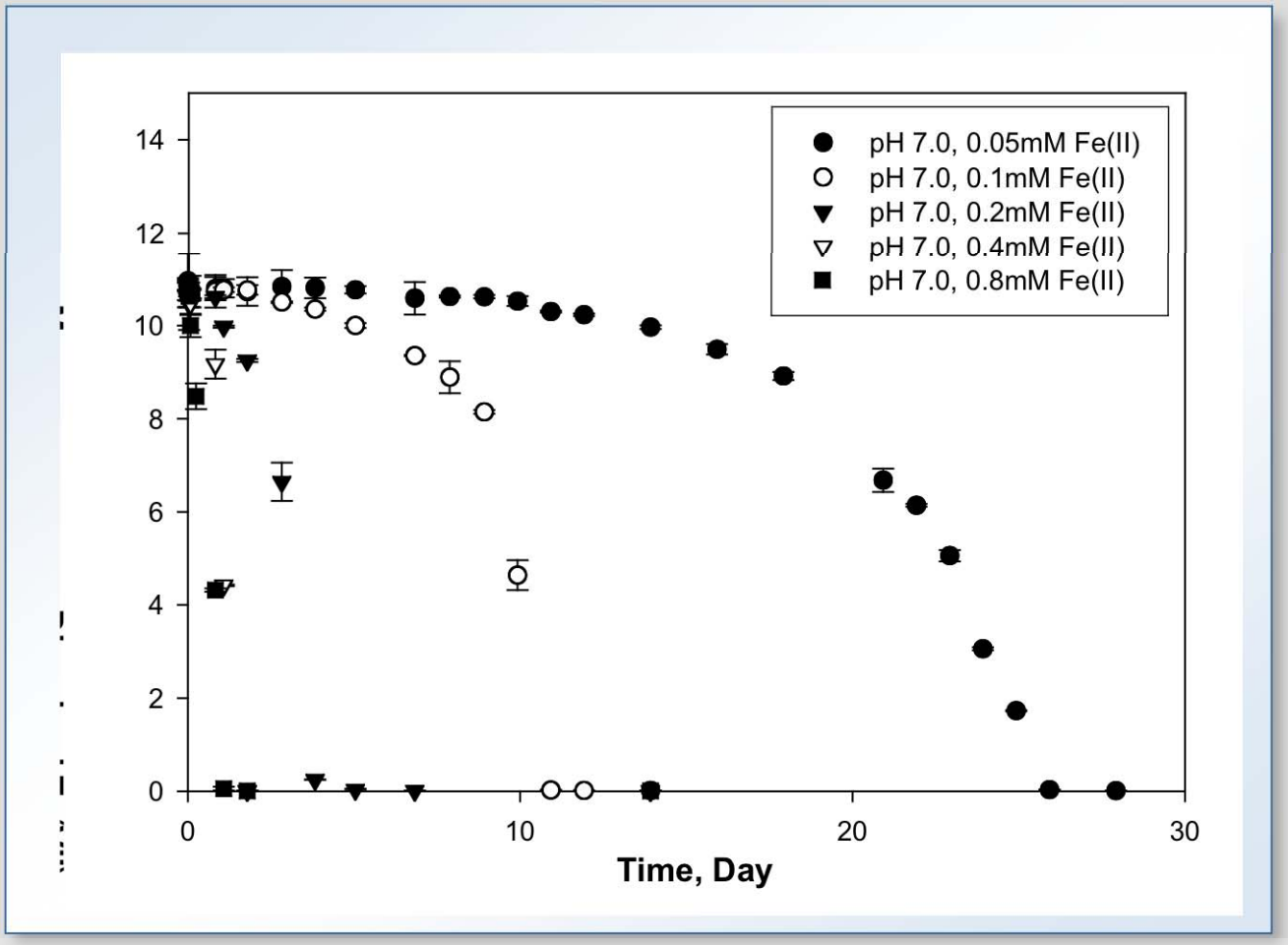
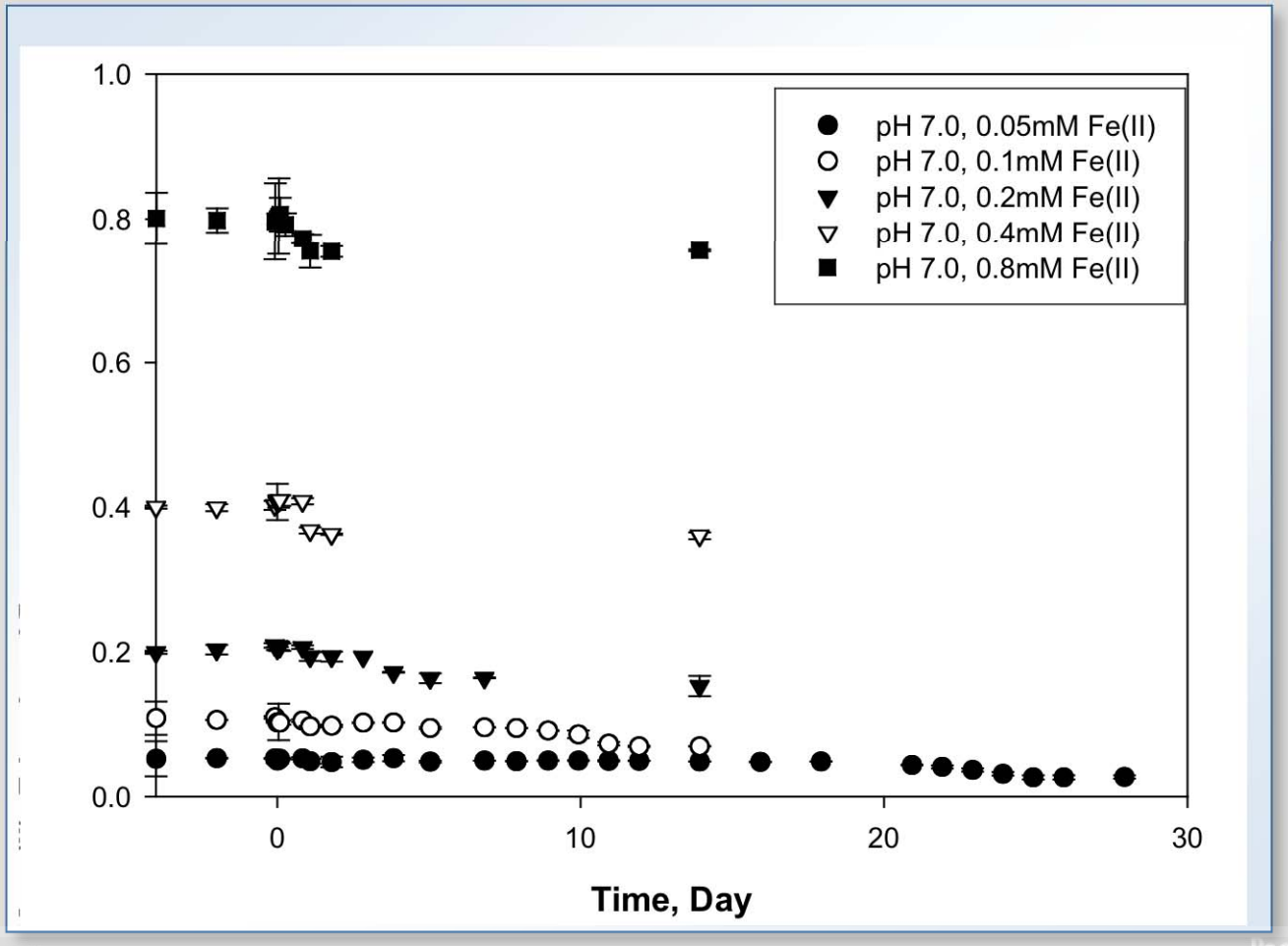
Homogeneous Reduction of $Tc(VII)O_4^-$ by $Fe(II)_{aq}$ (Tc)

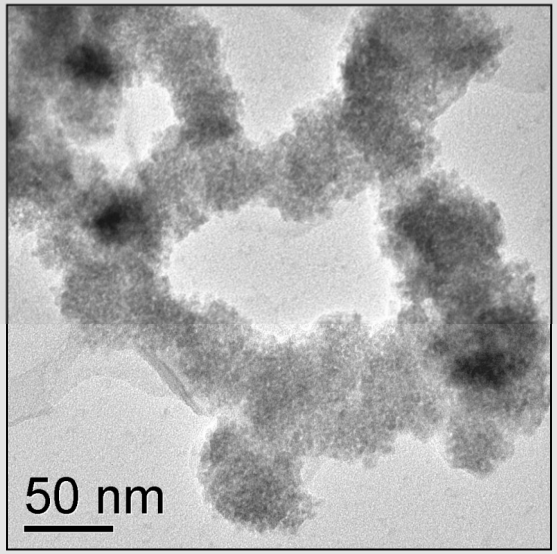


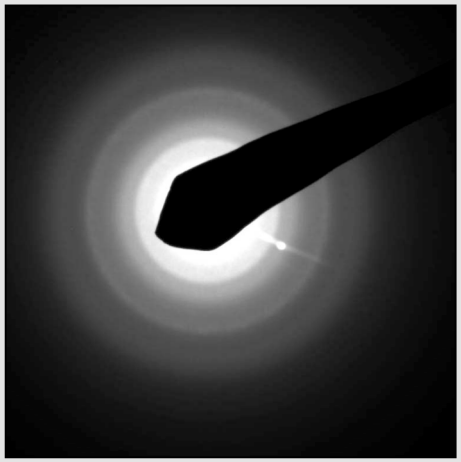
Homogeneous Reduction of $Tc(VII)O_4^-$ by $Fe(II)_{aq}$ (Fe)

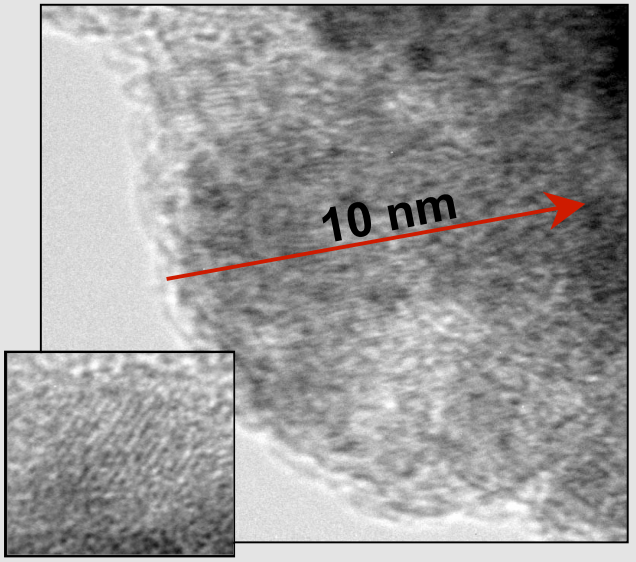
$$TcO_4^- + 3^{57}Fe^{2+} + [9 + (2\text{-}X)H_2O] = TcO_2 \cdot xH_2O + Fe(OH)_3 + 5H^+$$

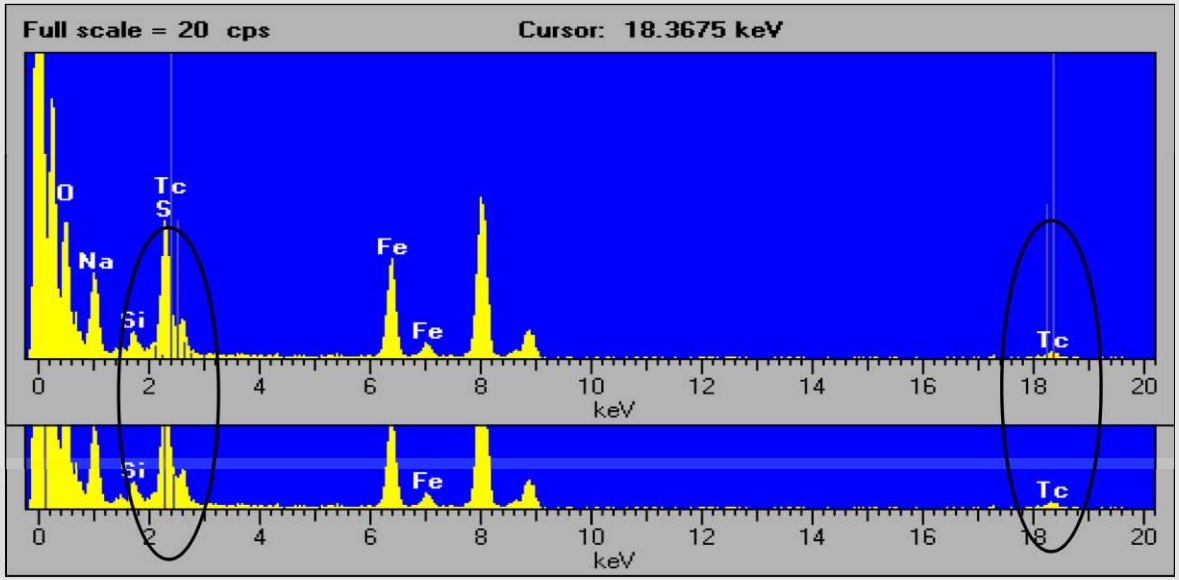


Transmission Electron Microscopy of Homogeneous Fe/Tc Precipitates (pH = 7.0)









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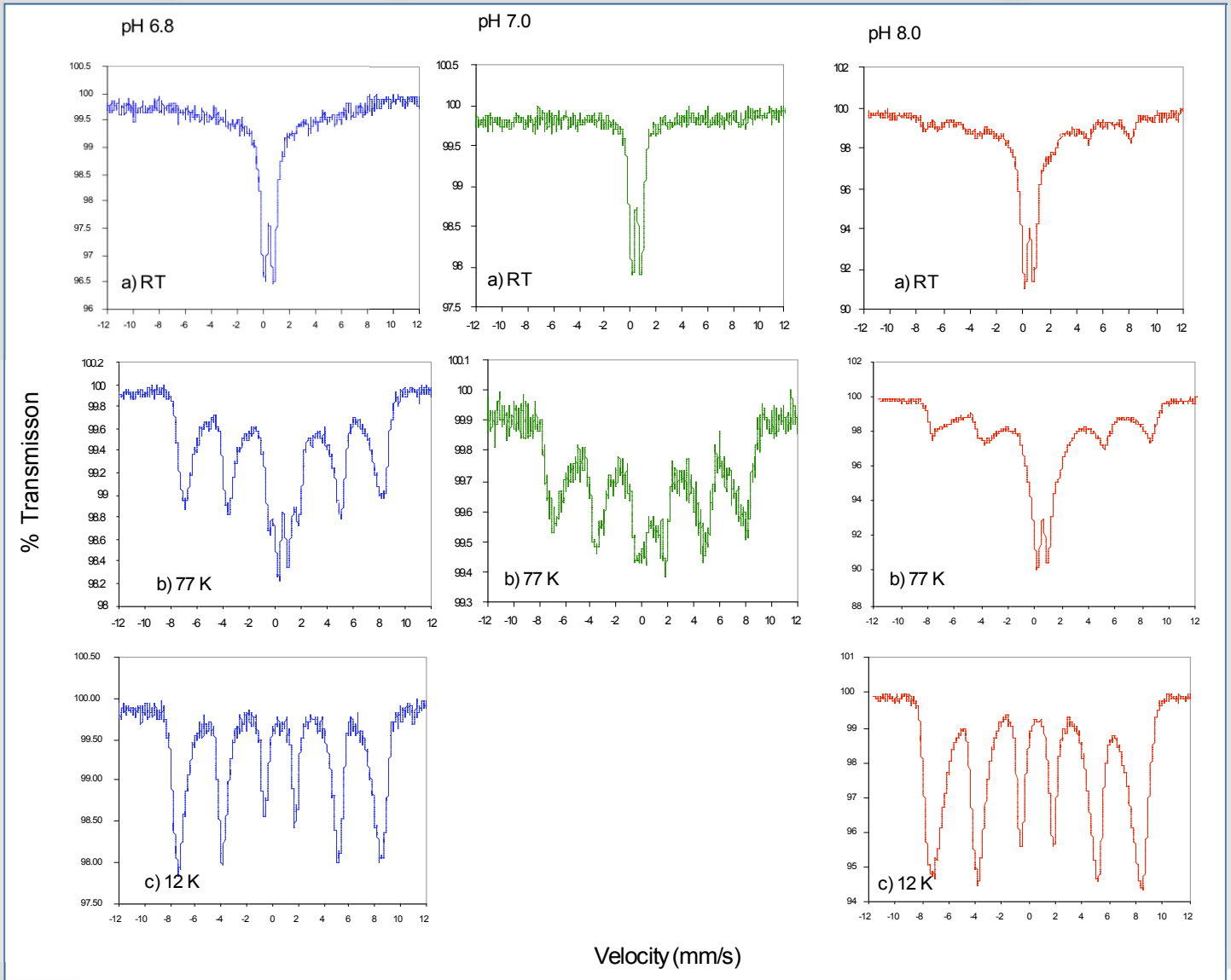
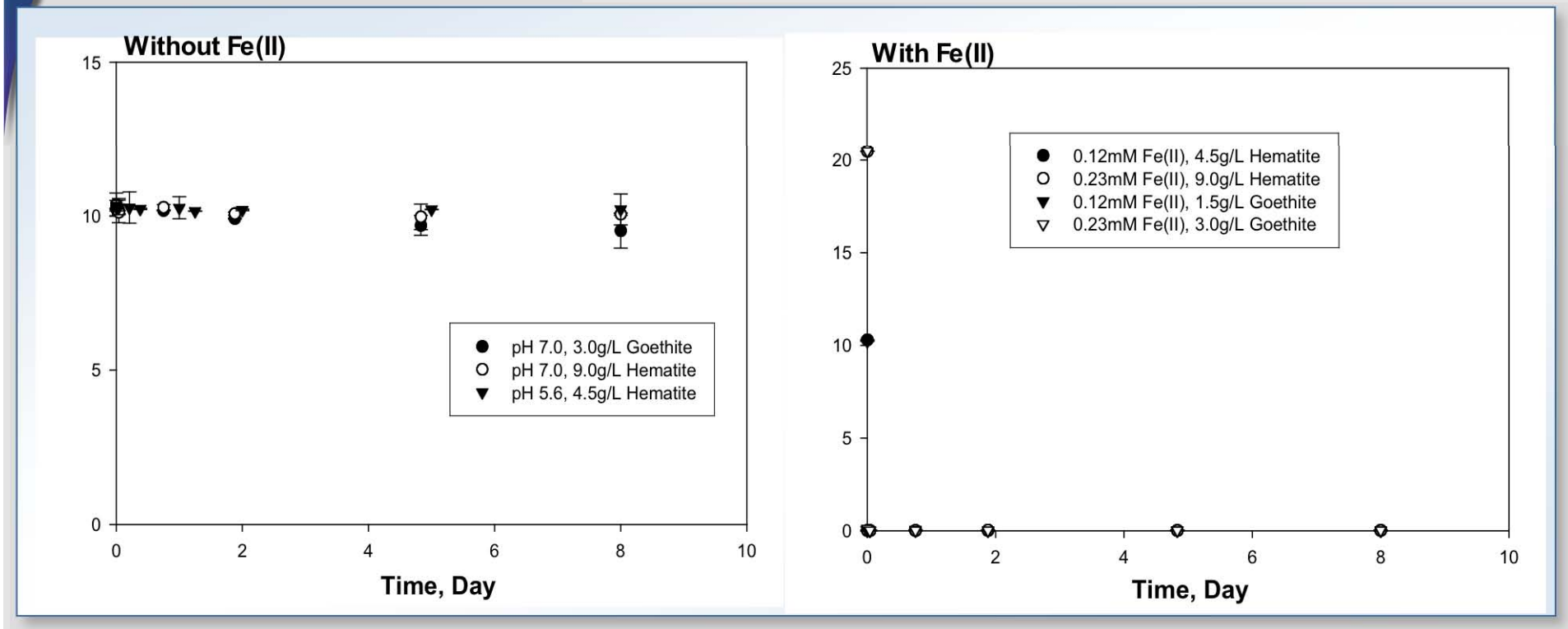
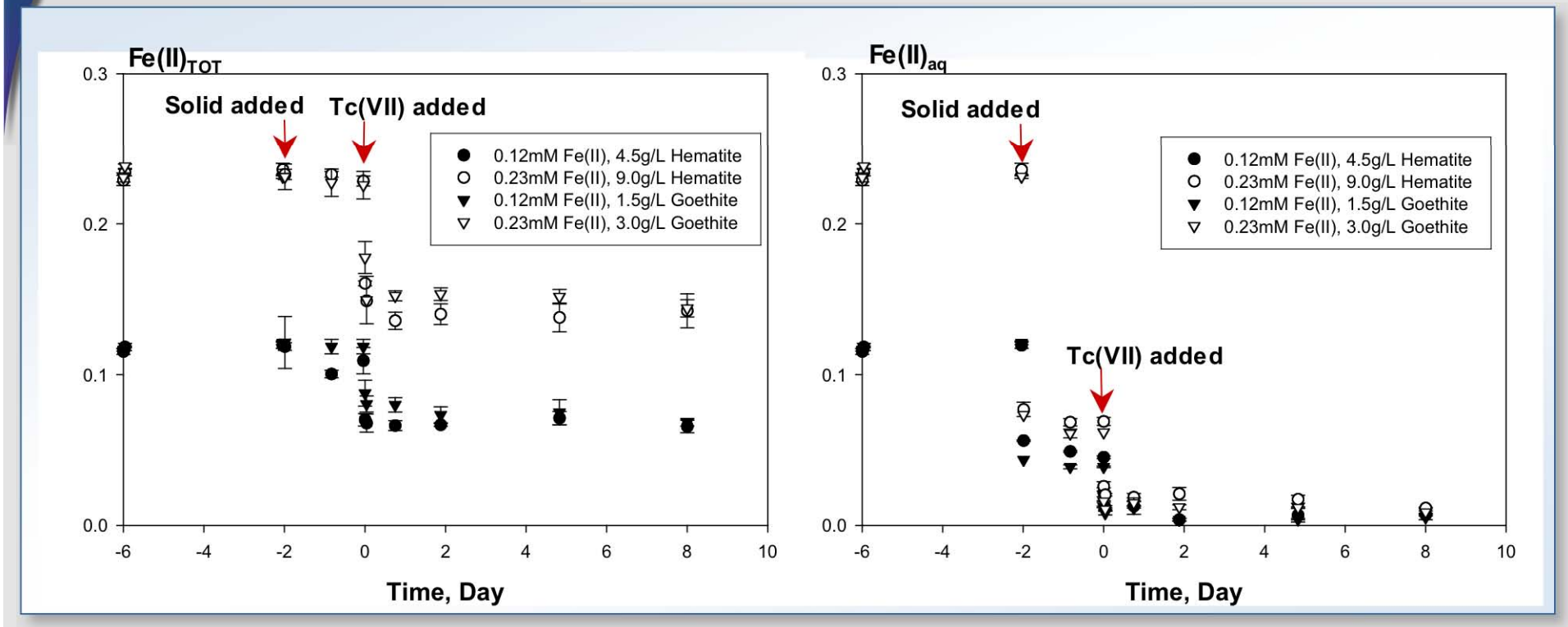
^{57}Fe Mössbauer Spectra of Homogeneous Fe/Tc Precipitates (Tc^{4+} substituted Magnetite?)



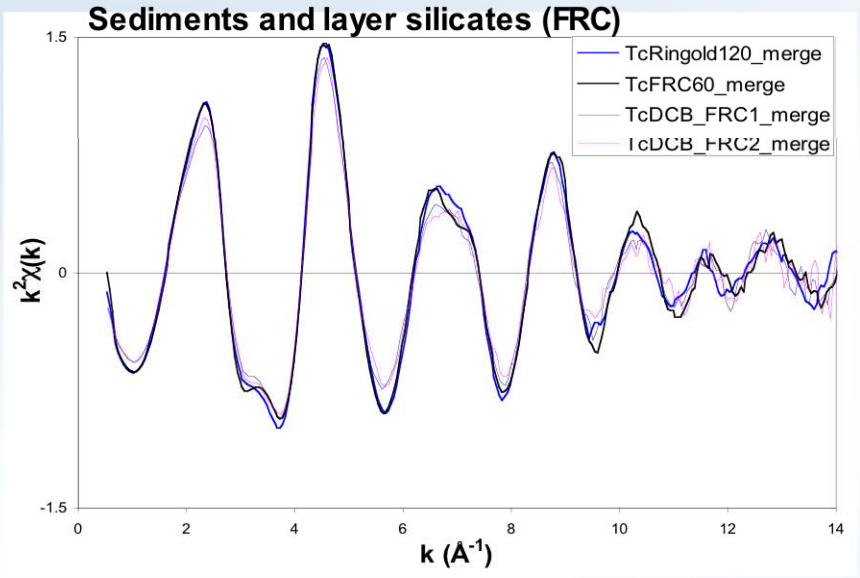
Heterogeneous Tc Reduction by Fe(III) Oxides (Tc)

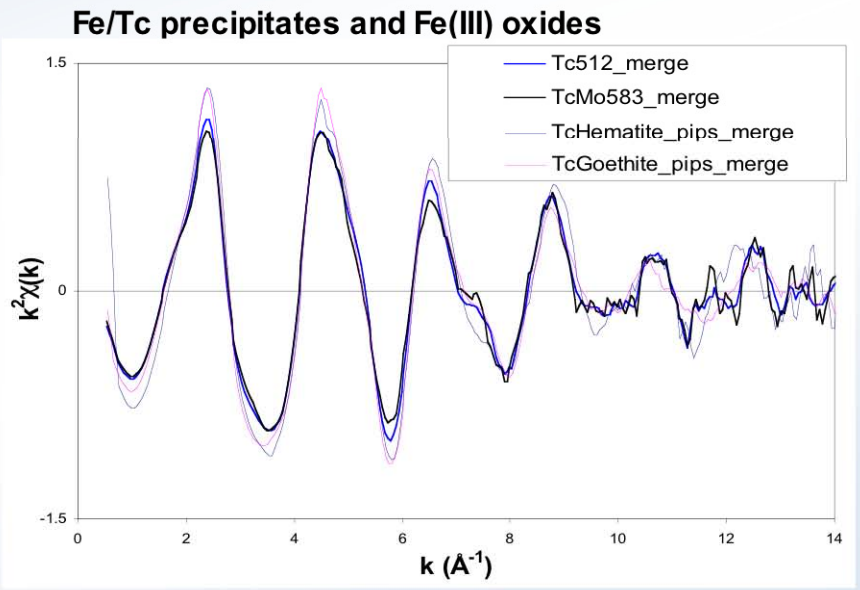


Heterogeneous Tc Reduction by Fe(III) Oxides (Fe)



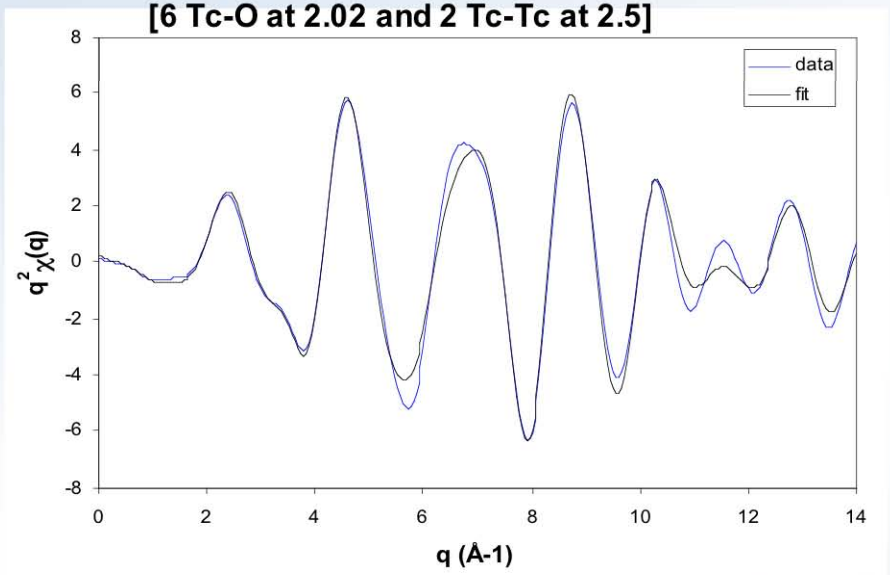
Tc-XAFS of Homogeneous and Heterogeneous Precipitated Tc(IV)



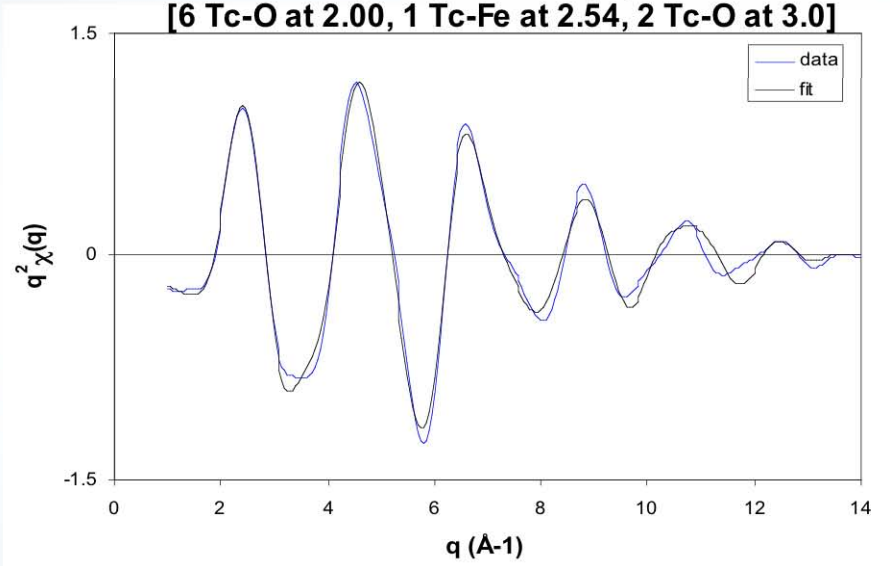


XAFS Modeling of Homogeneous and Heterogeneous Precipitated Tc(IV)

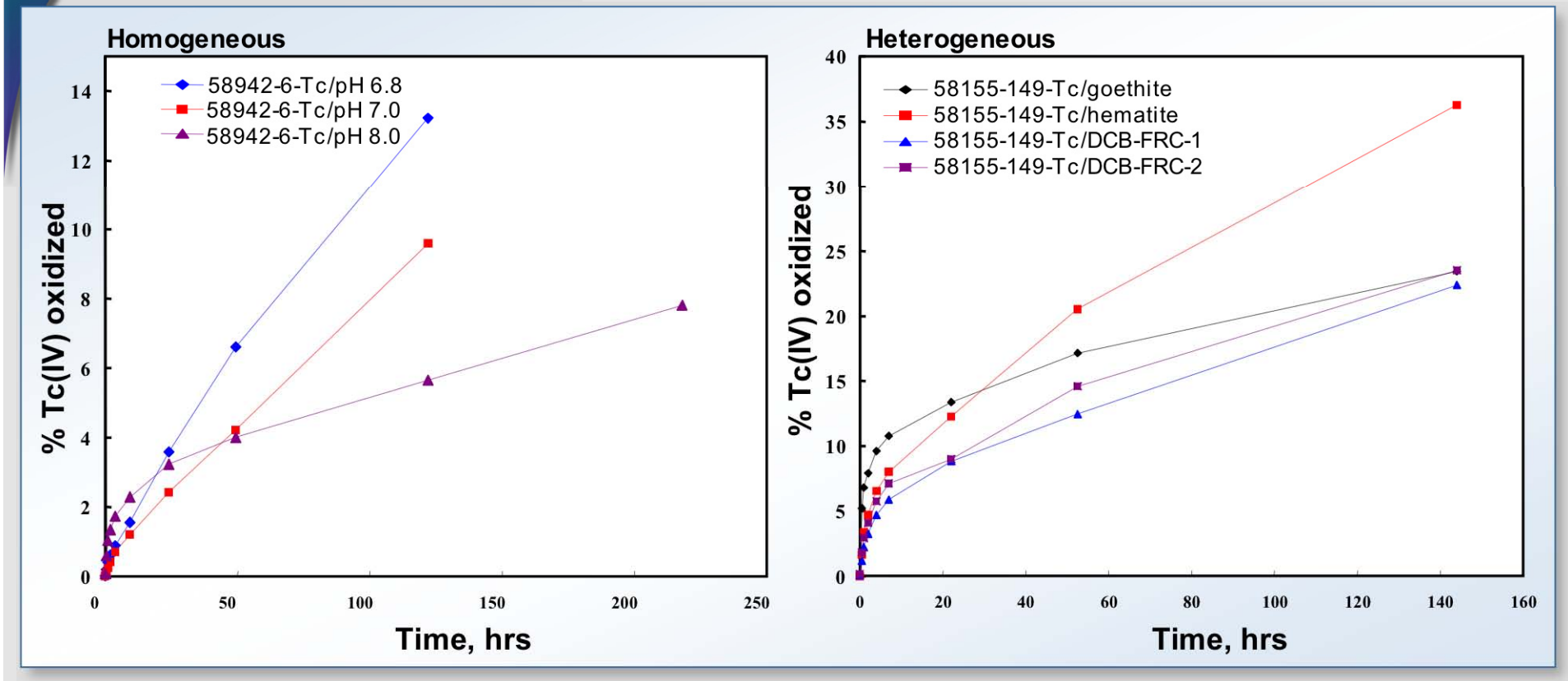
Heterogeneous LLS
$TcO_2 \cdot H_2O$ chains
[6 Tc-O at 2.02 and 2 Tc-Tc at 2.5]



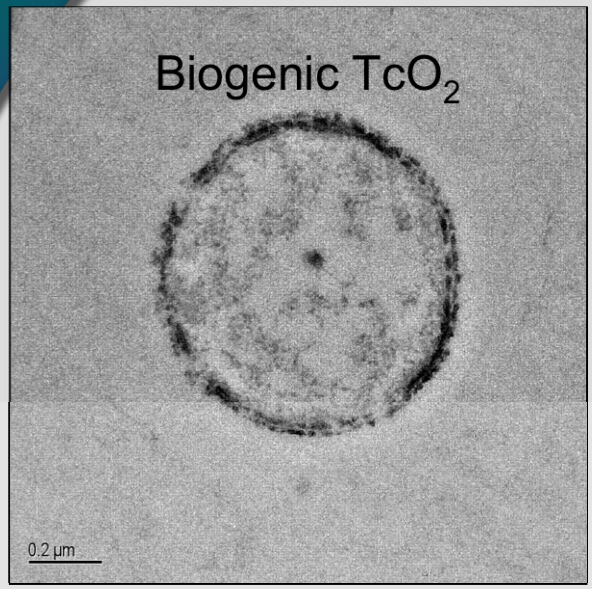
Heterogeneous oxide
Adsorbed/coprecipitated Tc(IV)
[6 Tc-O at 2.00, 1 Tc-Fe at 2.54, 2 Tc-O at 3.0]

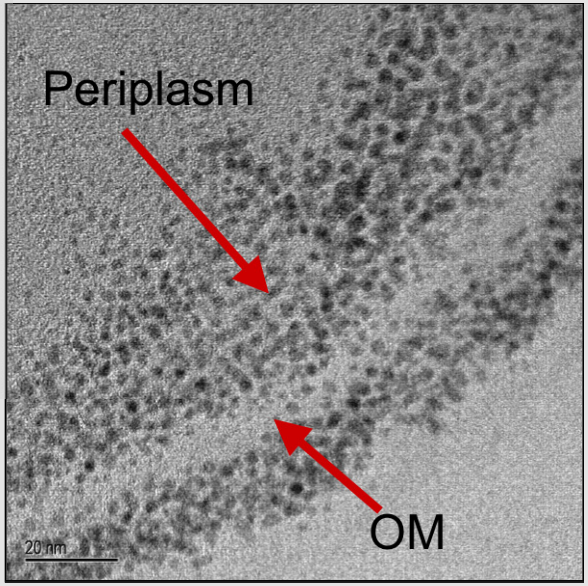


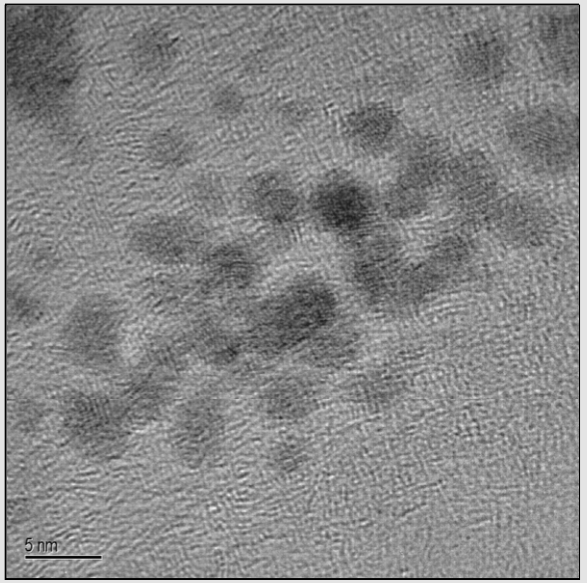
Oxidation of Homogeneous and Heterogeneous Precipitated Tc(IV)

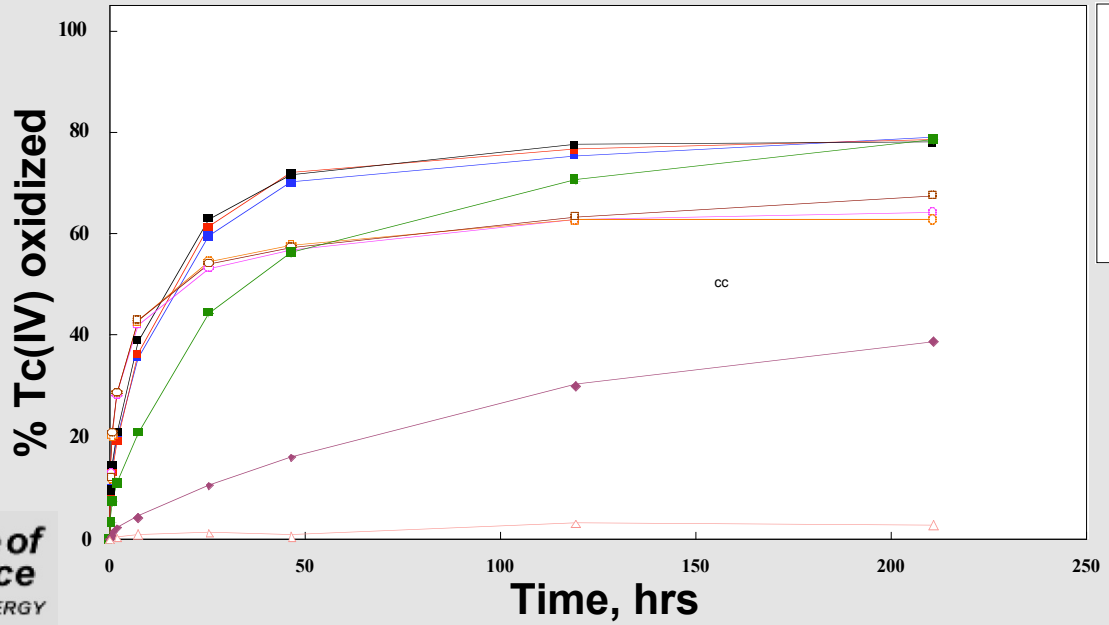


Oxidation of Biogenic $TcO_2 \cdot xH_2O$









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Conclusions

Reduction

Rate: hetero (oxide) >> hetero (LLS) >> homo

biotic

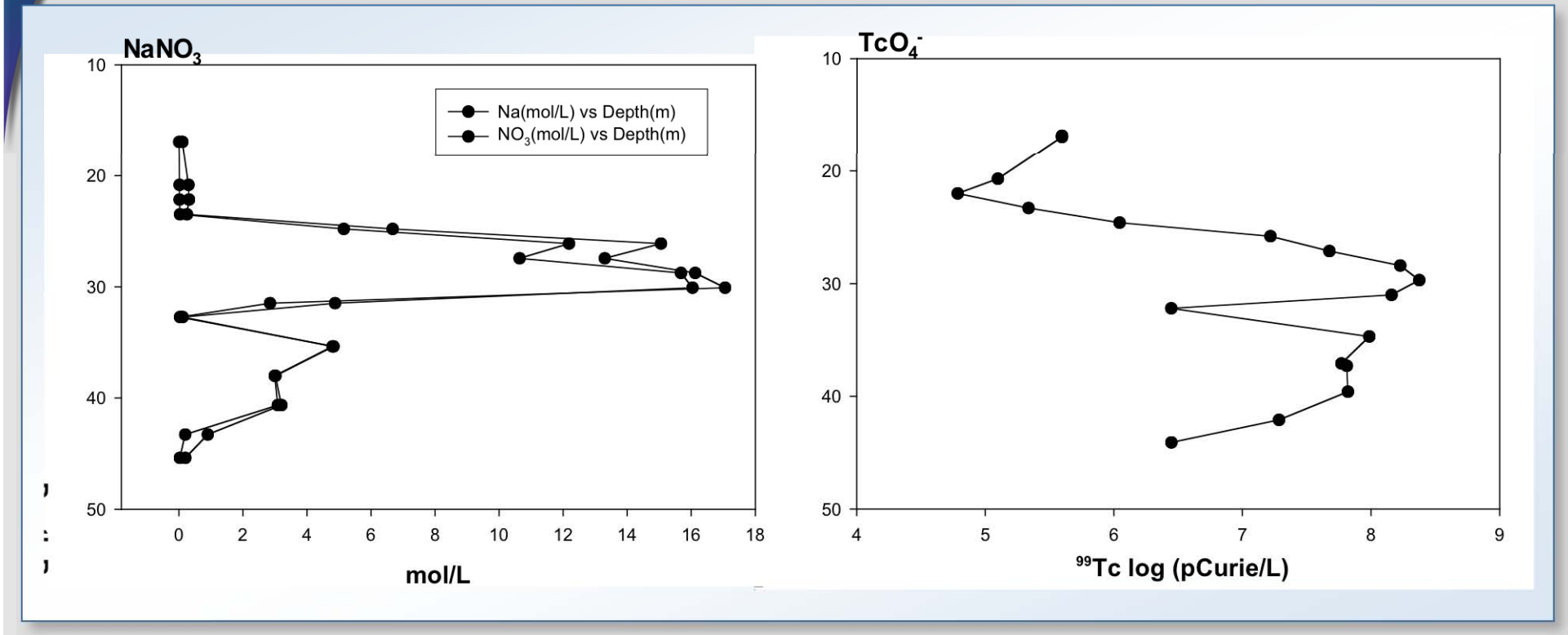
- Rate increases with pH and Fe(II)
- Three speciation forms observed
- Outer sphere Fe(II) on LLS not reactive

Oxidation

Rate: cell associated > hetero (oxide) ≈ hetero (LLS) > homo

- Highly variable rates and extent
  - Tc reduction mechanism/speciation
  - pH
  - Fe(II) concentration/speciation
  - O_2 concentration and flux
  - Aging effect
  - Physiologic effects unexplored

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



Miscible Displacement of $^{99}Tc(VII)O_4^-$ From Contaminated Hanford Sediment