Molecular Scale Mechanisms of Biogeochemical Electron Transfer Underlying Subsurface U/Tc Valence Transformation and Stability

Kevin M. Rosso

PNNL SFA All-Investigator Meeting
February 2009

PNNL-SA-65035

Project Premise

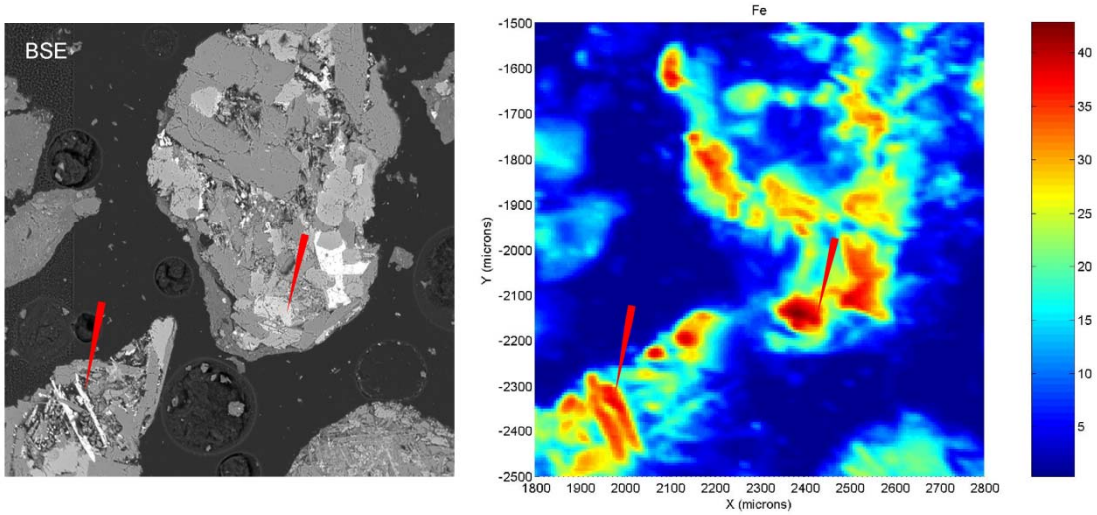
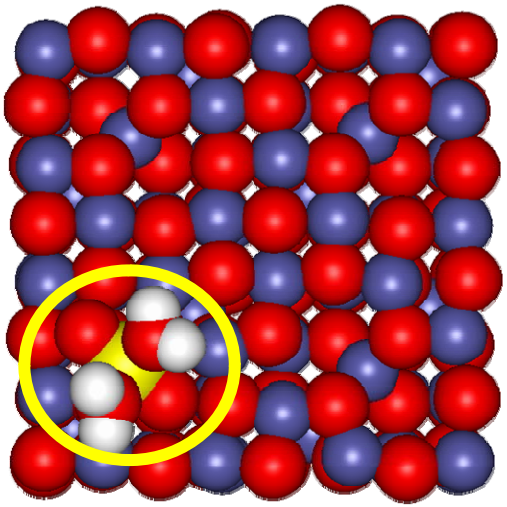


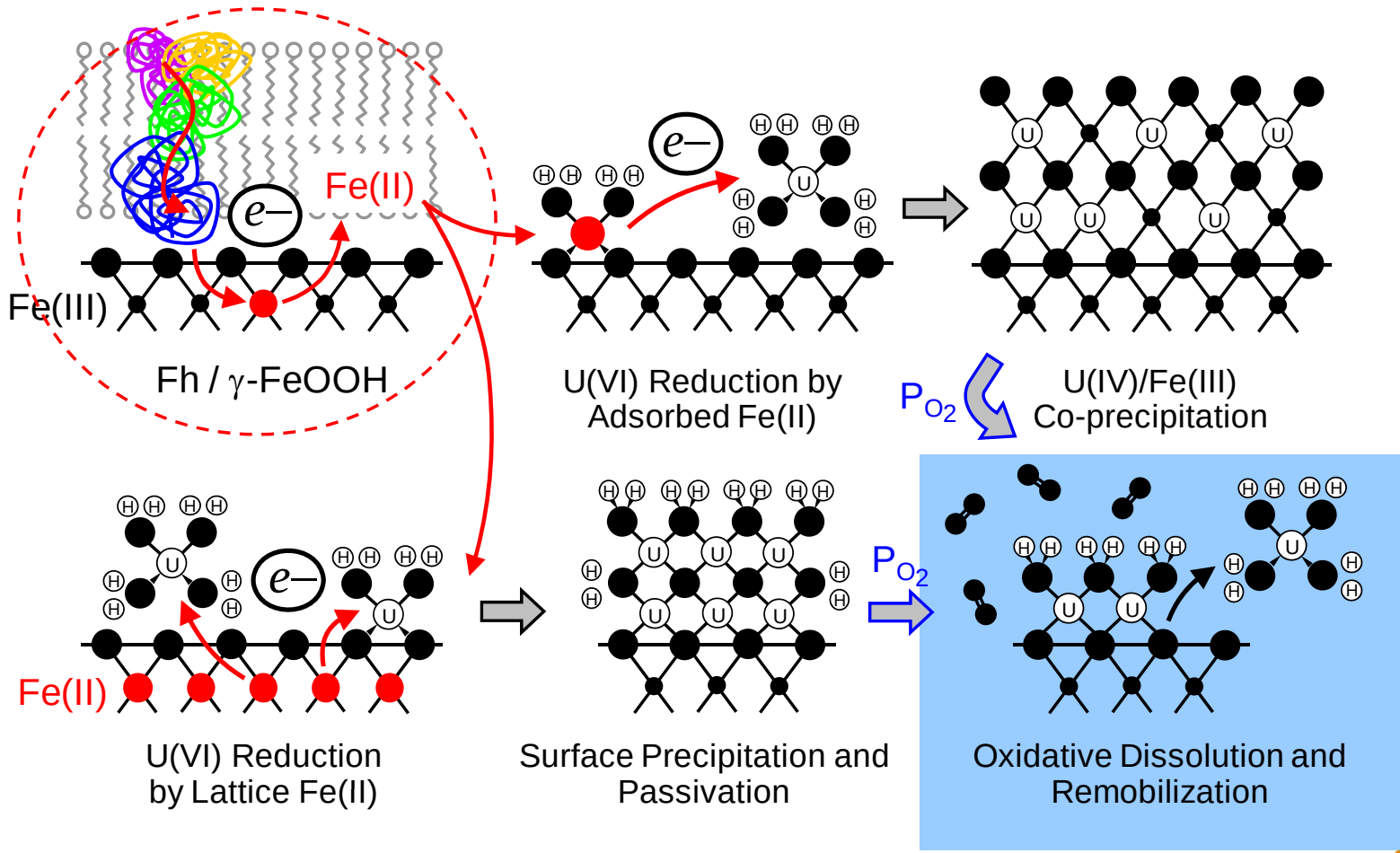
Figure 8. Backscattered electron micrograph of a sediment thin section displaying basaltic lithic fragments (a). X-ray fluorescence microprobe analyses performed at the Advanced Photon Source show regions of Fe localization in the particles (b). The crystallites that contain Fe are primarily magnetite, ilmenite, and pyroxenes, and are speculated to be intra-grain locations of redox reactivity that may consume oxygen or reduce contaminants.



- Redox conditions are central to transformation and stability of U and Tc.
- Reducing microenvironments at Hanford include lithic fragment interiors → O_2 depletion by microbiologic respiration or scavenging by ferrous-containing minerals.
- Parameterizing pore-scale and coupled mass transfer biogeochemical models requires that rates for important nanometer-scale processes have been determined and that reaction mechanisms are well understood.

Scope

Develop quantitative links between molecular scale and pore-scale redox reaction kinetics for biomolecular and abiotic transformation of U(VI) / Tc(VII) and relevant forms of Fe(III).



Objectives

- Characterize molecular mechanisms and kinetics that underlie abiotic and microbiologic valence transformation of U, Tc, and Fe → **link to pore-scale models**.

- Provide molecular-scale reaction kinetics modeling, and microscopic & spectroscopic insight into select abiotic and biologic electron transfer processes for Hanford minerals and microorganisms.

- Adapt focus over time in context of increasing insight into Hanford microorganisms, reactive biomolecules, and mineralogy important to U/Tc disposition.

Research Team

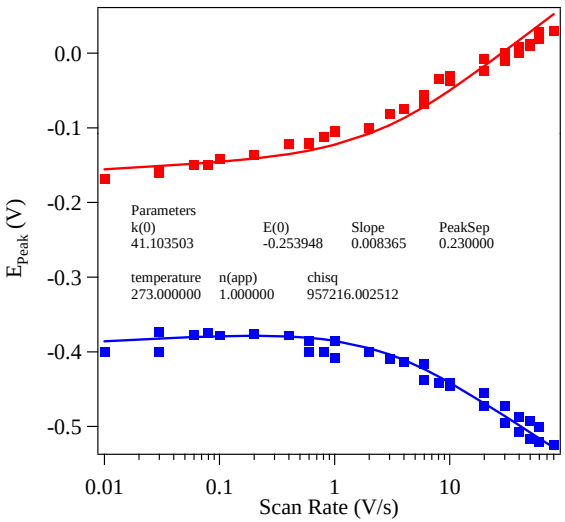
- Rosso
  - Project lead, molecular modeling, surface characterization, electron transfer
- Kerisit
  - Mineral surface and biomolecule molecular dynamics simulations
- J. Liu (Feb 2009)
  - Materials synthesis, reactivity, and characterization
- Pearce (June 2009)
  - Mineralogic transformations and characterization
- Richardson
  - Protein structure and redox characterization
- Key Collaborators:
  - Shi – Biomolecule redox and functional characterization
  - Baer – Particle characterization and metal oxide reactivity
  - C. Liu – Geochemical kinetics
  - Fredrickson – Pore-scale U/Tc biogeochemistry, microbiology
  - Zachara – Mineralogy and U/Tc biogeochemistry

FY09 – Two Lines of Research

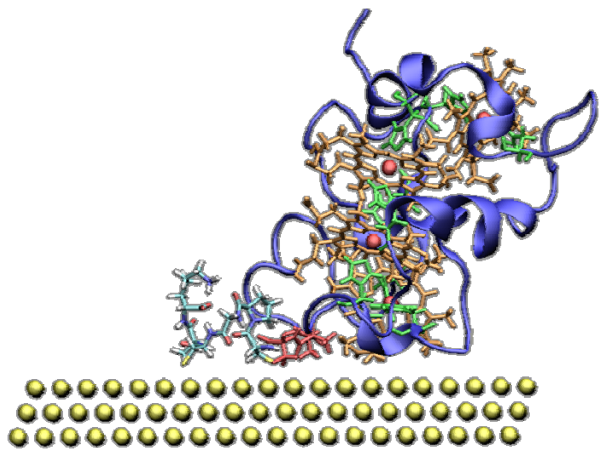
- Biomolecular electron transfer
  - **Objective**: Connect molecular-scale to macroscopic ET kinetics in comprehensive mechanistic studies (collaboration w/ Shi project).
    - **STC/Au(111)** (i.e., the BGC "Integration" paper)
    - **STC/Hematite(001)**
    - **ET modeling support for Shi project MtrC/OmcA/MtrF - flavin studies**
- Hanford-relevant heterogeneous Tc(VII) reduction kinetics
  - **Objective**: Develop a quantitative mechanistic link (via rate expressions) between molecular-scale and "pore-scale" kinetics (collaboration with Baer, Liu, Zachara, Fredrickson).
    - **Heterogeneous Tc(VII) reduction by titanomagnetite ($Fe_{3-x}Ti_xO_4$)**

Biomolecular ET: FY09 Research Plan

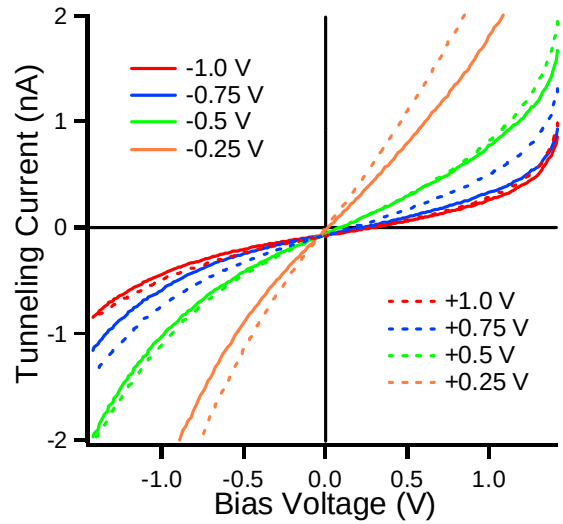
- **<u>STC/Au(111)</u> – Use as a model system to learn how macroscopic ET kinetics relate to molecular-scale ET kinetics for cytochromes.**
  - Take advantage of the data available from the BGC project:



Protein film voltammetry



Molecular dynamics



Scanning tunneling spectroscopy

  - <u>FY09 Deliverable: Draft and submit the "Integration" effort manuscript.</u>

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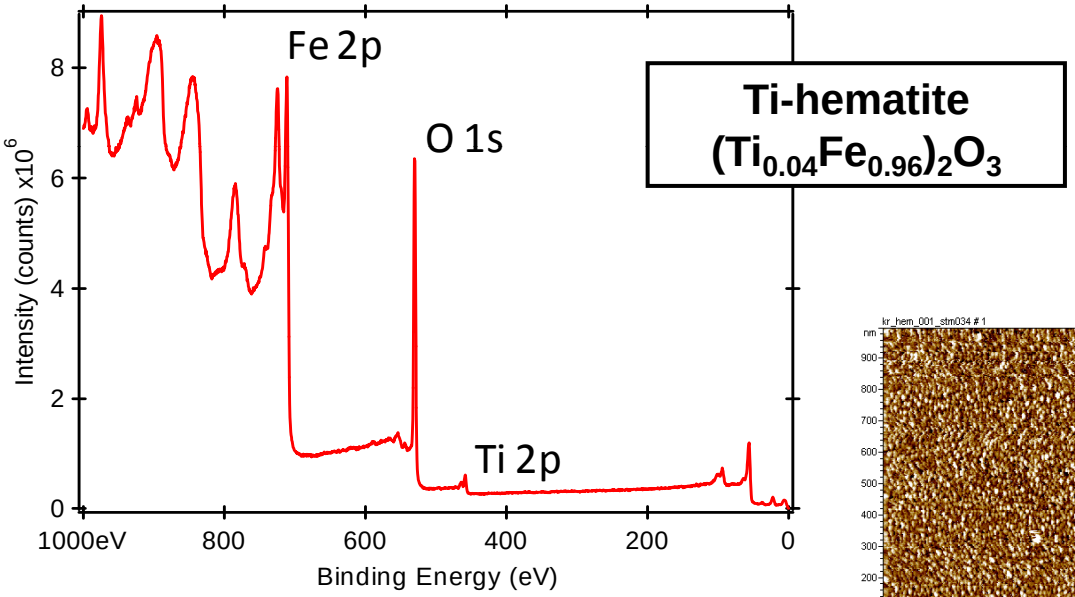
Environmental Remediation Sciences

William R. Wiley EMSL

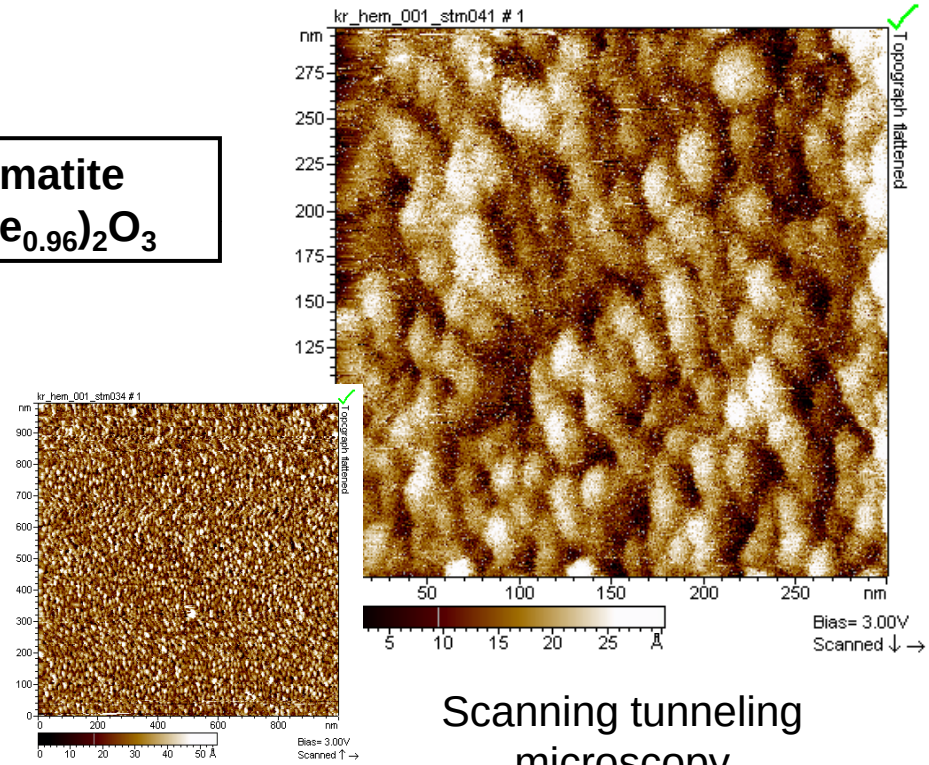
Pacific Northwest NATIONAL LABORATORY

Biomolecular ET: FY09 Research Plan

- **<u>STC/Hematite(001)</u> – With Shi project, compare measured PFV kinetics to molecular modeling predictions to establish cytochrome mediated reduction rates for an Fe(III)-oxide.**



X-ray photoelectron spectroscopy



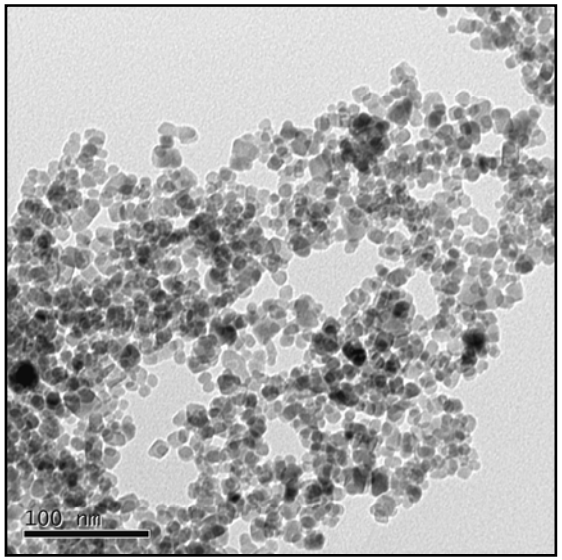
Scanning tunneling microscopy

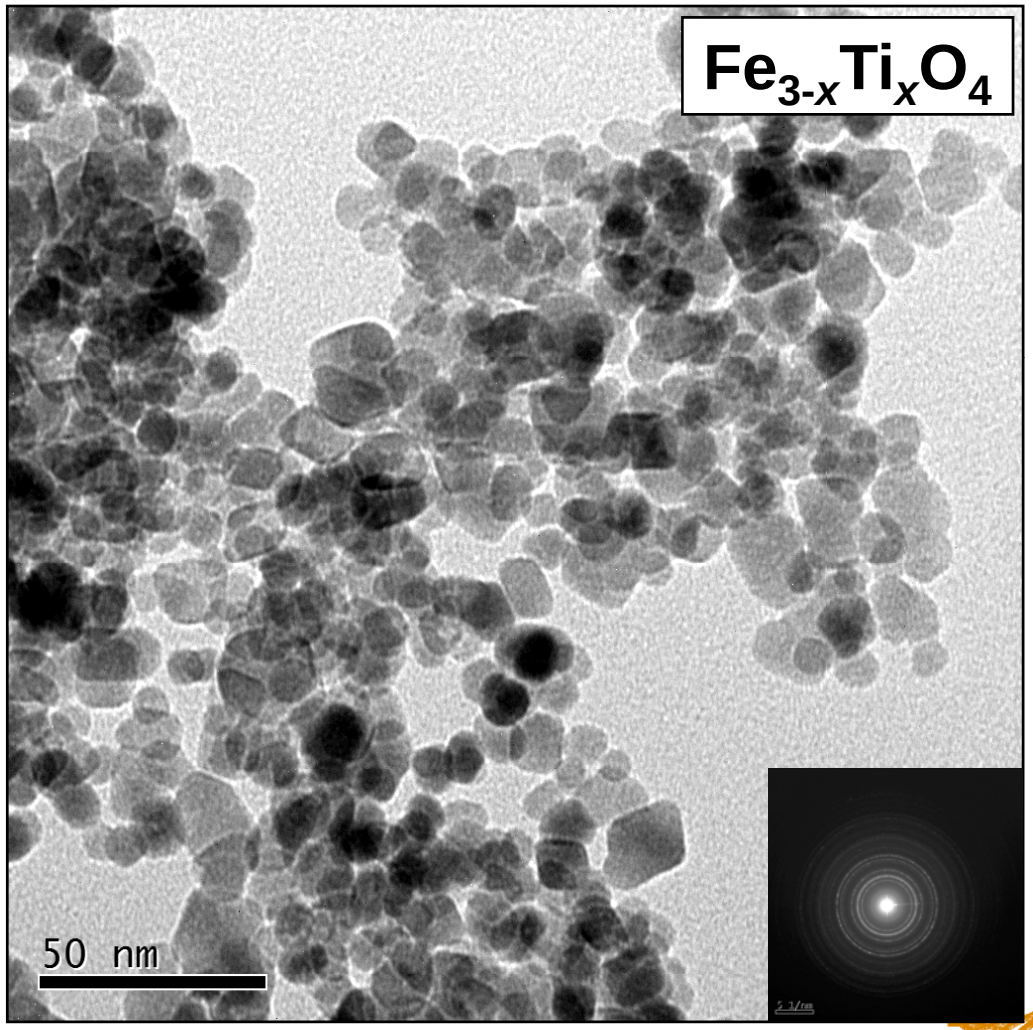
- <u>FY09 Deliverables:</u>
  - Appropriately doped hematite film synthesis and characterization.
  - Comprehensive model of STC/Fe(III)-oxide ET.

Heterogeneous Tc(VII) Reduction: FY09 Research Plan

- **<u>Develop mechanistic rate expressions for heterogeneous Tc(VII) reduction by titanomagnetite, focusing on the roles of surface oxidation and passivation.</u>**
  - Hanford relevant Fe(II)-bearing phase (**$Fe_{3-x}Ti_xO_4$**)
  - 'Tunable' redox potential via Ti-doping and partial oxidation to maghemite.
  - Model materials and natural samples available
    - Nanoparticles of specific size, shape, and surface expression.
    - MBE/PLD films of specific surface expression.
    - Natural samples from the Baer project.
  - Nanoparticles provide high surface area for solution phase measurements of Tc(VII) concentration → Solution kinetic modeling
  - Films and nanoparticles amenable to microscopic and spectroscopic characterization → μ-XRD, XANES/EXAFS, XPS, SAM, TEM, XMCD.
  - A model system for developing rate laws robust enough to describe heterogeneous Tc(VII) reduction kinetics and to guide molecular modeling of key steps.

Heterogeneous Tc(VII) Reduction: Model Materials

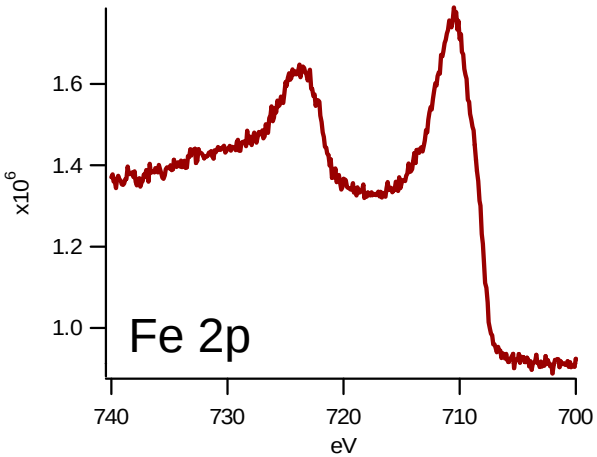


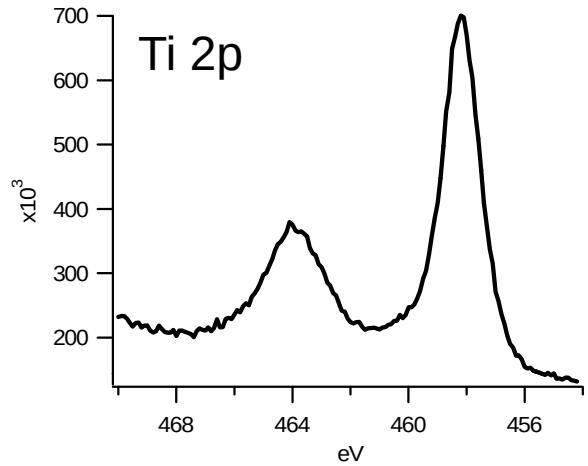


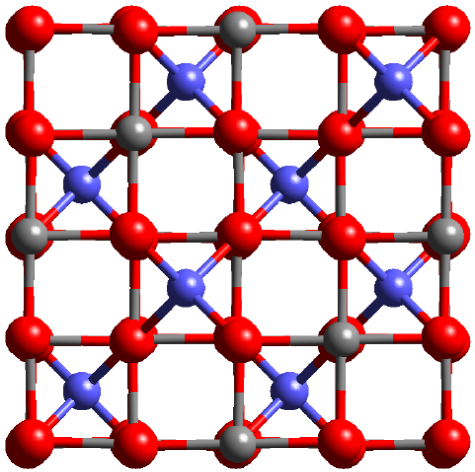
O. Qafoku, C. Wang

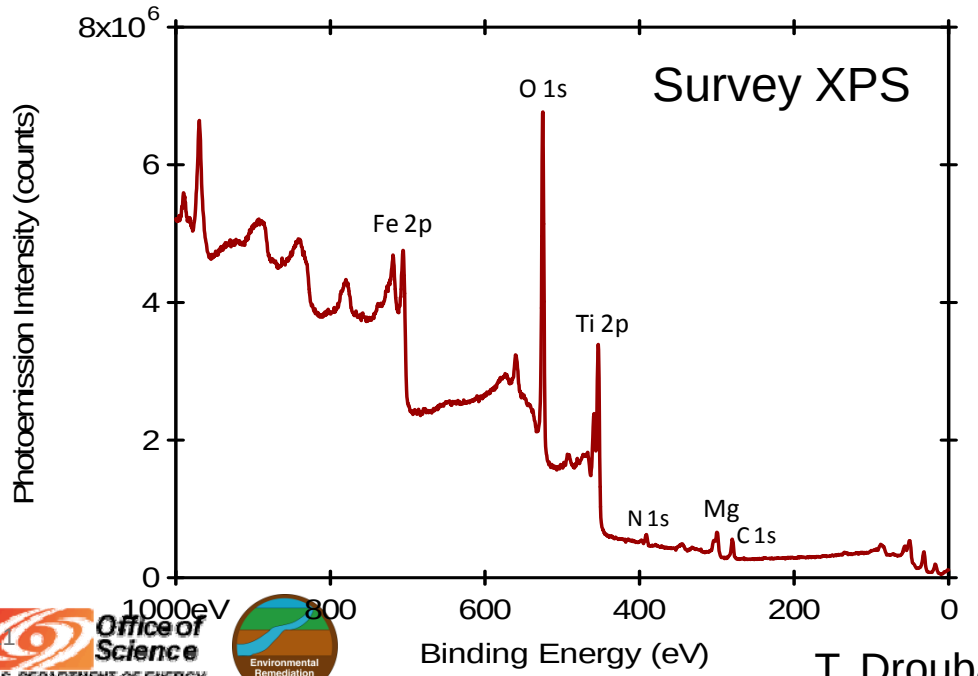
Heterogeneous Tc(VII) Reduction: Model Materials

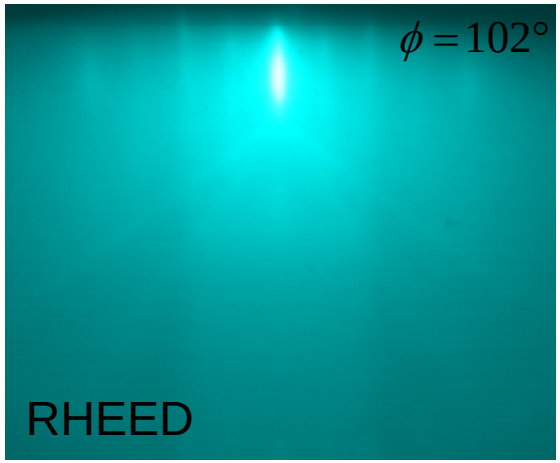
$Fe_{3-x}Ti_xO_4$ thin films by pulsed laser deposition











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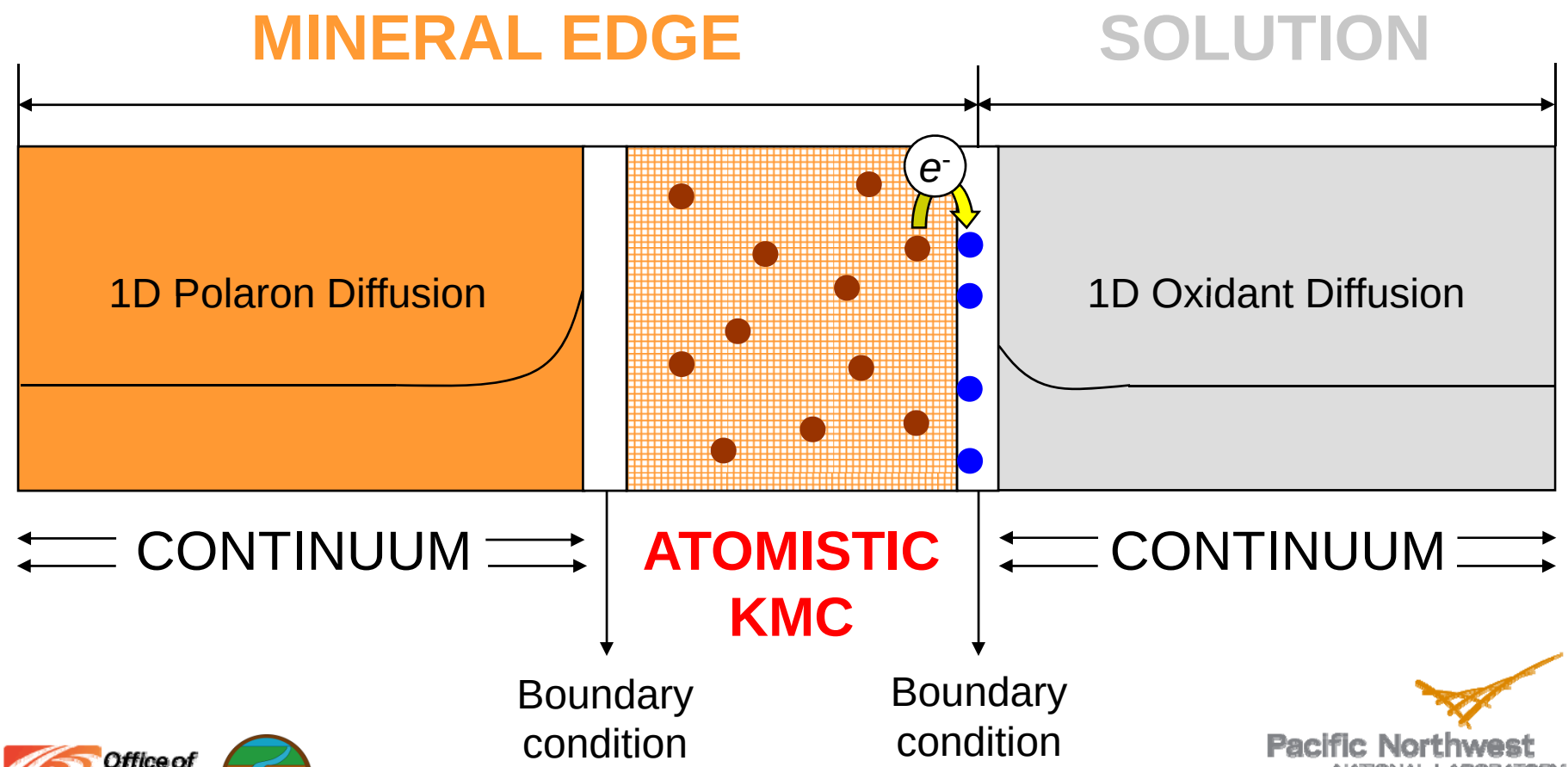
T. Droubay

Heterogeneous Tc(VII) Reduction: Computational Model Development

Development of a coupled atomistic-continuum model for simulating the interplay between diffusion, electron transfer, adsorption/desorption, and precipitation/dissolution processes during contaminant reduction at Fe(II)-bearing mineral/solution interfaces.



S. Kerisit

Science Milestones for the Next Two Years

- Molecular-scale insights into initial stages of heterogeneous reduction of Tc(VII) by lattice Fe(II) from one or more Hanford-relevant mineral phases.
- Molecular-scale insights into fundamental mechanisms and rates of heterogeneous reduction of an Fe(III) oxide by key biomolecules.
- Demonstrable utility of molecular-scale insights and kinetic data for informing one or more research projects in the SFA.