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

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Objective

This project is focused on developing a molecular-scale understanding of biogeochemical electron transfer reactions affecting the stability of U and Tc in Hanford-specific microenvironments towards long-term resolution of SFA Global Hypothesis #2.

Two lines of Research

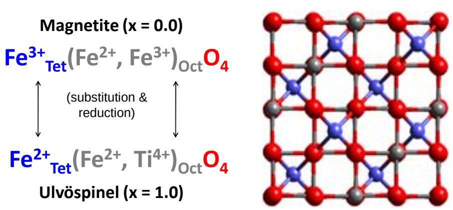
- Develop mechanistic rate expressions useful for pore-scale reactive transport models of heterogeneous Tc(VII) and U(VI) reduction by dominant Fe(II)-bearing mineral phases in Hanford sediments, focusing on the roles of impurities, surface oxidation and passivation.
- Establish a fundamental understanding of biomolecular electron transfer processes and kinetics in the reduction of Tc(VII), U(VI), and relevant forms of Fe(III) that contribute to Hanford-relevant microbial behavior at the pore-scale.

FY09 Results and Accomplishments

- Successfully developed a set of model Hanford-relevant Fe(II)-bearing oxides in the form of nanoparticulate, thin film, and bulk titanomagnetites ($Fe_{3-x}Ti_xO_4$). The materials are of controllable Ti^{4+} and consequently Fe^{2+} content, used for exploring Tc(VII) and U(VI) reduction kinetics with and without surface pre-oxidation.
- Completed a detailed structural and compositional characterization activity using acid digestion / ICP-MS / ferrozine, XRD, XANES, EXAFS, XMCD, TEM/EDS, Mossbauer, XPS, and RHEED.
- Initiated successful reactivity studies of heterogeneous Tc(VII) reduction on titanomagnetite nanoparticles and thin films as a function of Ti^{4+} content, pH, and particle size (NPs).
- Completed or contributed to BGC follow-on manuscripts on biomolecular electron transfer involving DMRB OMCs.
- Developed a coupled atomistic-continuum modeling tool for simulating the interplay of diffusion, electron transfer, adsorption/desorption, and precipitation/dissolution processes for heterogeneous reduction.

Example: $Fe_{3-x}Ti_xO_4$ Nanoparticles

Magnetite and titanomagnetite are model Hanford metal oxides. Ti-doping provides the opportunity for a 'tunable' Fe(II/III) redox potential.



Hypothesis: The sorption of TcO_4^- on the magnetite surface by a ligand-exchange mechanism is the initial rate-determining step for TcO_4^- reduction. Over the long term, Fe(II) access is rate-limiting.

$Fe_{3-x}Ti_xO_4$ Nanoparticle Synthesis

- "Soft chemistry approach": Stoichiometric solutions of $FeCl_3$, $FeCl_2$ and $TiCl_4$ mixed in 0.3M HCl under N_2 atmosphere.
- Solutions added dropwise to NH_4OH solution (20%) with vigorous stirring.
- Black precipitate collected using magnetic field and washed 3 times in de-gassed DI-H_2O.

Millot et al. (1998) J. Solid State Chem., 139, 66

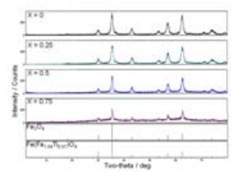
Nanoparticle Composition

Theoretical values			Measured values (5M HCl digestion)			Calculated
			Ferrozine	ICP-MS		
Fe(II)	Total Fe	Ti	Fe(II)	Total Fe	Ti	$Fe^{II}Fe^{III}TiO$
mM/g			mM/g			*Empirical formula*
4.286	12.860	0.000	4.422	12.730	0.015	$Fe_{1.11}Fe_{2.08}O_4$
5.429	11.950	1.090	4.928	11.009	1.019	$Fe_{1.23}Fe_{1.52}Ti_{0.26}O_4$
6.571	10.960	2.190	5.920	10.103	2.082	$Fe_{1.48}Fe_{1.05}Ti_{0.52}O_4$
7.750	9.960	3.320	6.461	8.044	2.686	$Fe_{1.62}Fe_{0.4}Ti_{0.67}O_4$

Characterization

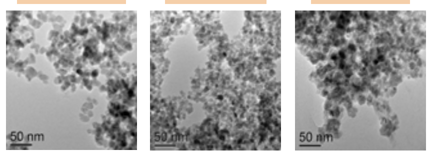
XRD of $Fe_{3-x}Ti_xO_4$ Nanoparticles

- Nanoparticle suspension was freeze-dried for preparing XRD sample preparation .
- Broad peaks indicate small particle size.
- No oxidation or Ti-containing phases observed.



Size and Specific surface area of $Fe_{3-x}Ti_xO_4$ Nanoparticles

X = 0 | X = 0.25 | X = 0.5



TEM images of $Fe_{3-x}Ti_xO_4$ nanoparticles

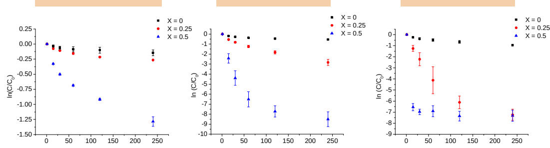
X	BET SA* m²/g	Size nm
0	98.2	12
0.25	153.4	8
0.5	157.0	7

* BET SA: specific surface area measured by BET method

Tc(VII) Reduction by $Fe_{3-x}Ti_xO_4$ Nanoparticles

- Buffer Solution: HEPES, pH = 8;
- Tc(VII): 10 µM spike after 20 h pre-equilibration
- SA: the total surface area of nanoparticles

SA = 0.1 m² | SA = 0.2 m² | SA = 0.3 m²

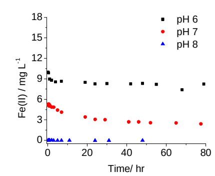


$$TcO_4^- + 3Fe^{2+}_{(aq)} = TcO(OH)_{2(aq)} + Fe(OH)_3 + 5H^+$$

Dissolution Studies of $Fe_{3-x}Ti_xO_4$ Nanoparticles

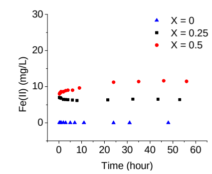
Hypothesis: Tc(VII) reductant is Fe(II) supplied to surfaces and to solution from particle interiors.

pH Dependence of Fe(II) Release



- Systematically increasing Fe(II) release with decreasing pH.
- Fe(II) release reaches steady state after 20 hours at pH 6-8.

Ti-Doping Dependence of Fe(II) Release



- More Ti-doping, more Fe (II) released.
- Fe(II) release reaches steady state after 20 hours at pH 8.

$Fe_{3-x}Ti_xO_4$ Nanoparticles Summary FY09

- $Fe_{3-x}Ti_xO_4$ nanoparticles of controlled composition can be synthesized through a "Soft Chemistry Approach" at room temperature.
- Ti-doping systematically increases Fe(II) content in the solid and Fe(II) release in solution at pH 6-8. The amount of dissolved Fe(II) increases with decreasing pH.
- Titanomagnetite (e.g., x = 0.5) nanoparticles exhibit the systematically higher reactivity than pure magnetite nanoparticles at pH 8 for the reduction of Tc(VII).

Proposed Research for FY10

Heterogeneous Tc(VII) Reduction by Titanomagnetites

- Expand kinetics studies to thin films and bulk powders; combine with nanoparticle behavior. Quantify mass/electron balance for the development of analytic rate expressions compatible with pore-scale reactive transport simulations.
- Examine surface orientation effects (thin films) on the rate and extent of reaction by XPS.
- Oxidation studies to assess effect of dissolved oxygen on thin films/nanoparticles/bulk powders, and assess effects of surface oxidized layer on Tc(VII) reactivity.
- Through comparison, identify structural and compositional differences between model materials and natural samples from the Hanford site.
- Finish developing coupled atomistic-continuum simulation tool for mechanistic interpretation of experimentally observed reaction rates, and their dependence on Ti-doping, pH, surface structure, and surface area.
- Collaborative downhole experiments for surface alteration and microbial activity and identity associated with model materials exposed to key redox horizons in well 399-3-27 at the Hanford IFRC site.

Biomolecular Electron Transfer

- Integrated PFV and/or UV-vis experiments and simulations of interfacial ET kinetics for MtrF-Fe(III) oxide; comparison to whole cell kinetics in laboratory pore-scale experiments.
- Simulations of Tc(VII) reduction processes and rates by NiFe-hydrogenase.
- Completion of the integration manuscript on STC/Au(111) interfacial electron transfer.

Identity and Nature of FY09 and FY10 Collaborations

- FY09: Zachara project: Heterogeneous Tc(VII) reduction by $Fe_{3-x}Ti_xO_4$ via Peretyazhko.
- FY09: Shi project: PFV of STC-hematite (001) for comparison wiith ET simulations.
- FY10: Liu project: Pore-scale-compatible heterogeneous ET rate expression development.
- FY10: Shi project: PFV/theory characterization of MtrF ET; NiFe-hydrogenase-Tc(VII) ET.
- FY10: Fredrickson project: Downhole incubation experiments with model titanomagnetites.

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