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ABSTRACT TITLE: Redox Behavior of Hanford 300A Fe-Phyllosilicates, Fe-Oxides and Key Biomolecules

ABSTRACT: This research seeks to understand the oxidation/reduction behavior of important mineralogic forms of Fe in the redox transition zone (RTZ) of the Hanford 300A site, associated mechanisms of electron transfer and linkage to carbon and nitrogen cycling across this zone in the subsurface. Select natural Fe minerals from core samples are being isolated, with a focus on Fe-bearing clay, along with analog phases to probe their redox reactivity in nitrification/denitrification in terms of the site structure, occupancy and valence of lattice Fe. Electron transfer kinetics with key microbial outer-membrane cytochromes are also being examined to understand relevant Fe(II)/Fe(III) biotransformation mechanisms. Combined laboratory experimental and computational molecular simulation approaches at user facilities such as the EMSL and the ALS are being used to gain fundamental insight that is prospectively generalizable to other similar subsurface systems.

RTZ sediments are relatively rich in an Fe-bearing 2:1 smectitic clay consistent with Fe-beidellite, a phase that can act as both an Fe(II)-bearing electron source in reduced form below the transition, and an Fe(III)-bearing electron sink in oxidized form above the transition. These minerals can contain Fe in both octahedral and tetrahedral coordination in variable proportion and absolute concentrations, a compositional and structural characteristic expected to impact the net Fe(II)/Fe(III) redox potential. Fe site-occupancy and valence in RTZ Fe-clay along with NAu-1 and NAu-2 Fe-nontronites for comparison were analyzed in oxidized and reduced forms, naturally and chemically reduced, by synchrotron Fe L-edge x-ray absorption (XA) and magnetic circular dichroism spectroscopies (XMCD). XA/XMCD shows that oxidized forms are dominated by magnetically ordered octahedral Fe(III) with no apparent tetrahedral Fe(III), and with increasing extent of reduction an octahedral Fe(II) component becomes apparent with increasing magnetic ordering consistent with more prominent exchange interaction facilitated by an increasing concentration of Fe(II)-O-Fe(III) groups in the octahedral sheet. Computational molecular simulation of the electron transfer exchange rate between such groups indicate an electron mobility from within the lattice towards redox-reactive and accessible edge sites, and vice versa, on the order of 10^5 electrons per second, suggesting rapid electron exchange with adsorbed redox-active species.

Key outer-membrane multi-heme cytochromes from metal reducing and oxidizing bacteria are being examined for their rate of electron transfer interaction with these important Fe-mineral phases. Molecular simulation of hopping electron transport through the deca-heme cytochrome MtrF indicates a sustainable and reversible overall rate of 5×10^4 electrons per second, near that sustainable by 300A Fe-clay minerals. Rates of Fe(II)/Fe(III) oxide nanoparticle oxidation by the deca-heme cytochrome MtoA, and reduction by the deca-heme cytochrome OmcA, are being measured using UV-visible spectroscopy on the protein, and using in situ x-ray diffraction and XA/XMCD on the nanoparticles, to understand biomolecular and mineralogic controls on interfacial electron transfer efficiency; similar studies with the 300A Fe-clay are planned, including measuring redox rates and affects on aqueous N speciation. This research, part of the PNNL Science Focus Area, will improve understanding of the limits of redox reaction kinetics possible between dominant Fe-mineralogy, groundwater species, and microorganisms interacting with these phases in the RTZ.