Redox Transition Zone Phyllosilicate Reactivity: Thermodynamics and Microscopic Processes

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This research, part of the PNNL SFA, seeks to identify and understand active biogeochemical processes across the redox transition zone (RTZ) of the Hanford 300A site, a regionally expansive subsurface aquitard of fine-grained sediments that displays a dramatic redox transition. These sediments are dominated by Fe-bearing phyllosilicates capable of redox reactions coupled to diffusive biogeochemical fluxes across the RTZ, including C and N. The objective is that through laboratory and simulation of RTZ sediment redox reactivity we can develop a mechanistic understanding of reactions that regulate these climate change gases, as well as contaminant species such as technetium, which can be incorporated into process-based field-scale reactive transport models.

RTZ core samples of oxidized (59-60' depth) and reduced (62-63' depth) material were collected. The clay-sized fraction was isolated from each while preserving native redox conditions and characterized for mineralogy, composition, Fe valence and site occupancy, cation exchange capacity, and redox potential by equilibrating with the AH2DS/AQDS couple. The ferruginous smectite SWa-1 was selected for comparative redox properties characterization and thermodynamic modeling including charge neutralization effects. Molecular simulations were performed using EMSL supercomputing.

Quantitative x-ray diffraction, elemental composition, and cation exchange capacity measurements showed that RTZ oxidized and reduced clay-sized fractions were dominated by Fe-rich montmorillonite (90% and 83%, respectively), a dioctahedral smectite, as the only crystalline Fe-bearing (1.45 and 1.38 mmol/g, respectively) mineral present. The ferrous content was found to be 4.6% and 22.4% of the total Fe, respectively. Synchrotron Fe L-edge x-ray absorption and magnetic circular dichroism spectroscopies showed that the oxidized form is dominated by magnetically ordered octahedral Fe(III) with no apparent tetrahedral Fe(III); an octahedral Fe(II) component is observed in the reduced form. The reduced clay fraction, studied in batch reactors at groundwater pH for Tc(VII) reduction kinetics as a probe of in-ground reduction capacity below the RTZ, in the absence and presence of added aqueous Fe(II), showed that 10% of 10 UM Tc(VII) was reduced in 15 weeks (9 g/L loading) and that this extent doubles after a 58 UM Fe(II) spike. A concomitant loss of octahedral Fe(II) was spectroscopically observed. Molecular simulation shows electron mobility within the octahedral sublattice is 105 s 1, consistent with sufficiently rapid electron transfer to adsorbed redox-active species. A thermodynamic model was developed that links Fe-smectite redox properties to biogeochemical parameters such as electrolyte type, concentration, and pH. Plans to incorporate the findings into process-based reactive transport models will be discussed.