Reactivity of Iron-Bearing Phyllosilicates with Uranium and Chromium Through Redox Transition Zones

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Iron-bearing phyllosilicate minerals help establish the hydrogeological and geochemical conditions of redox transition zones because of their small size, limited hydraulic conductivity and redox buffering capacity. The bioreduction of soluble U(VI) to sparingly soluble U(IV) can promote the reduction of clay-Fe(III) through valence cycling. The reductive precipitation of U(VI) to uraninite was previously reported to occur only after a substantial percentage of clay-Fe(III) had been reduced. Using improved analytical techniques we show that concomitant bioreduction of both U(VI) and clay-Fe(III) by Shewanella putrefaciens CN32 can occur. Soluble electron shuttles were previously shown to enhance both the rate and extent of clay-Fe(III) bioreduction. Using extended incubation periods we show that electron shuttles enhance only the rate of reduction (overcoming a kinetic limitation) and not the final extent of reduction (a thermodynamic limitation).

The first 20% of clay-Fe(III) in nontronite NAu-2 was relatively “easy” (i.e., rapid) to bioreduce while the next 15% of clay-Fe(III) was “harder” (i.e., kinetically-limited) to bioreduce and the remaining 65% of clay-Fe(III) was effectively biologically un-reducible. In abiotic experiments with NAu-2 and biogenic uraninite, 16.4% of clay-Fe(III) was reduced in the presence of excess uraninite. In abiotic experiments with NAu-2 and AH2DS, 18.5 to 19.1% of clay-Fe(III) was reduced in the presence of excess and variable concentrations of AH2DS. A thermodynamic model based on published values of the non-standard state reduction potentials at pH 7.0 ($E^\circ_{\text{U(IV)}}$) showed that the abiotic reactions between NAu-2 and uraninite had attained apparent equilibrium. This model also showed that the abiotic reactions between NAu-2 and AH2DS had attained apparent equilibrium. The final extent of clay-Fe(III) reduction was well correlated to the standard state reduction potential at pH 7.0 ($E^\circ_{\text{U(IV)}}$) of all of the reductants used in these experiments (AH2DS, CN32, dithionite, uraninite).

We also examined the reduction of nitrobenzene by CN32 in the presence of montmorillonite SWy-2 (low Fe(III) content) and nontronite NAu-2 (high Fe(III) content). Nitrobenzene and other nitroaromatic compounds (NACs) have been selected for study because their redox properties are well known and they have previously been used as redox probe molecules to examine the reactivity of clay-Fe(II). We found that the abiotic reduction of nitrobenzene became increasingly important as clay-Fe(II) accumulated in the system.