

Examining the nature of siderophore-montmorillonite interactions

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Whereas microbial siderophores have been shown to affect clay mineral dissolution and metal adsorption to clays, our understanding of the mechanisms of interactions between siderophores and the clay structure itself, including adsorption, are more limited.

To better understand the nature of the interaction between siderophores and montmorillonite clay, we measured sorption of two hydroxamate desferrioxamine siderophores, DFO-B and DFO-D₁, to Na-saturated montmorillonite in 0.1 M NaClO₄ at 22°C. These two siderophores have the same fundamental structures, but different terminal groups lead to DFO-B being monovalently charged to pH ~8 (pK_a of deprotonation reaction is 8.4), whereas DFO-D₁ is uncharged. Sorption of DFO-B was significant at pH between 4 and 6 (195 μmol/g), decreased to 170 μmol/g at pH 8, and to < 20 μmol/g at pH 10. DFO-D₁ followed the same sorption trend with pH as DFO-B, but was sorbed to a lesser extent. DFO-B sorption densities were approximately 85 μmol/g, 45 μmol/g, and 5 μmol/g at pH 4-6, 8 and 10, respectively. The observed adsorption of the neutral molecule DFO-D₁ to montmorillonite over a wide pH range suggests that electrostatic interactions are at most only partly responsible for the sorption of trihydroxamate siderophores to montmorillonite. Additional research on sorption kinetics and mechanisms, including application of spectroscopic and diffraction techniques, is ongoing.

Abiotic Tc(VII) reduction by Fe(II)

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The subsurface behavior of ⁹⁹Tc, a contaminant resulting from nuclear fuels reprocessing, is strongly dependent on its valence (e.g., IV or VII). We investigated the abiotic reduction of soluble Tc(VII) by Fe(II) in pH 6-8 solutions under strictly anoxic conditions using an oxygen trap ($<7.5 \times 10^{-9}$ atm O₂). Complete and rapid reduction of Tc(VII) to precipitated Tc(IV) [Tc(IV)O₂·nH₂O_(s)] was observed when 11 μM of Tc(VII) was reacted with 0.4 mM Fe(II) at pH 7.0 and 8.0, while no significant reduction was observed over 1 month at pH 6.0. The reduction kinetics were strongly pH dependent. Experiments conducted at pH 7.0 with Fe(II) = 0.05-0.8 mM further revealed that Tc(VII) reduction was a combination of homogeneous and heterogeneous reaction (Figure 1). The kinetics of homogeneous reduction correlated with the concentration of Fe(OH)⁺. Fe(II) loss from solution was higher than the stoichiometric demand for complete reduction to Tc(IV) indicating Fe(II) sorption or precipitation. Preliminary TEM and Mössbauer spectroscopy measurements indicated that the reaction product was a magnetite/Tc(IV) coprecipitate.

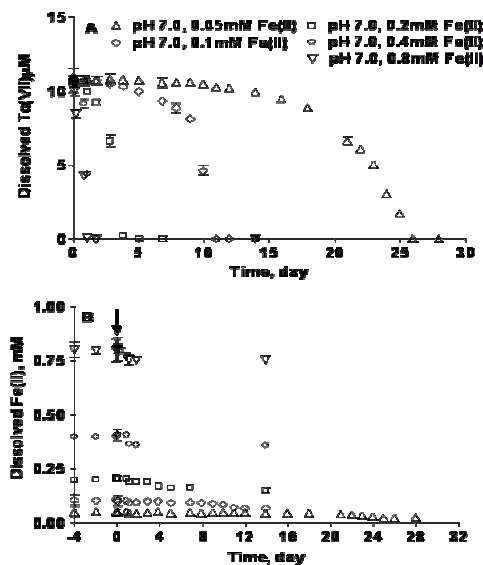


Figure 1. Abiotic reduction of Tc(VII) by Fe(II) (A) and recovery of added Fe(II) (B) from the 10 mM PIPES buffer solutions for different added Fe(II) concentrations at pH 7.0. [Tc(VII)]_{added} = 11 μM, and [Fe(II)]_{added} = 0.05-0.8 mM.