Electron Transfer and Atom Exchange Between Fe(II) and Structural Fe(III) in Clays

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Fe-bearing clay minerals serve as an important source and sink for electrons in redox reactions in various subsurface geochemical environments. Heterogeneous reactions between aqueous Fe(II) and Fe(III) oxides have been extensively studied, leading to a new conceptual framework which includes electron transfer between Fe(II) and structural Fe(III), bulk electron conduction, and Fe(II)-Fe(III)oxide atom exchange. Reactions of aqueous Fe(II) with clay minerals have received much less attention and are often described in terms of surface reactions including ion exchange, surface complexation, and/or surface precipitation. Our objectives here are to:

1. Determine if electron transfer occurs between sorbed Fe(II) and structural Fe(III) in clays over a range of conditions and clay structures.

2. Evaluate whether Fe atom exchange occurs between aqueous Fe(II) and structural Fe(III) in clays, and natural, clay-rich sediments.

We have investigated Fe electron transfer and atom exchange in clay minerals via selective chemical extractions, Fe isotope experiments and computational molecular modeling. Our findings indicate that structural Fe(III) in two nontronite clay minerals (NAu-1 and NAu-2), as well as a montmorillonite clay mineral (SWy-2) is reduced by aqueous Fe(II) and that electron transfer occurs when Fe(II) is sorbed to either basal planes and edge OH-groups of clay mineral NAu-1. Significant electron transfer occurred from edge OH-group bound Fe(II) at pH 7.5. At pH 4.0 and 6.0, where Fe(II) is sorbed primarily to the basal planes, electron transfer still occurred but to a much lower extent than from edge-bound Fe(II). Interestingly, the greatest extent of reduction was observed in the SWy-2 montmorillonite which contains the lowest % by weight Fe (2.8%). Findings from highly enriched isotope experiments suggest that between 5 and 20% Fe atom exchange is occurring between aqueous Fe(II) and structural Fe in a clay mineral. Experiments with higher precision isotope measurements using the multi-collector ICP-MS at Wisconsin confirm these findings. First principles calculations using a small polaron hopping approach suggest surprisingly fast electron mobility at room temperature in nontronite consistent with temperature dependent MÃ¶ssbauer data. Electron conductivity of bulk nontronite is predicted to be highest through the octahedral sheet, as opposed to the tetrahedral sheet or from the tetrahedral to the octahedral sheet.