Electron transfer and atom exchange between aqueous Fe(II) and structural Fe(III) in clays: Role in U and Hg(II) Transformations

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Recent advances in spectroscopic and microscopic techniques, stable Fe isotope measurements, and theoretical calculations of mineral electronic structures have lead to a new conceptual framework for the reaction of aqueous Fe(II) with Fe oxides. Fundamental processes in the reaction of aqueous Fe(II) at the Fe(III) oxide-water interface include electron transfer between aqueous Fe(II) and structural Fe(III), bulk electron conduction, and Fe(II)-Fe(III) atom exchange.

In contrast, reactions of aqueous Fe(II) with clay minerals have received much less attention and descriptions of these reactions have been limited to surface or interlayer reactions such as ion exchange, surface complexation, and/or surface precipitation. Recently, however, we showed that interfacial electron transfer between aqueous Fe(II) and structural Fe(III) occurs in a clay mineral. Whether this observation can be generalized to all iron-bearing clay minerals and whether similar Fe atom exchange processes occur in clays as observed for the heterogeneous redox reaction in Fe(III) oxides is unclear.

Studies on chemical reduction of structural Fe in smectites have showed that the type of reductant as well as smectite structural properties determine the extent of Fe reduction, as well as the speciation of the resulting structural Fe(II). Here, we investigated the reaction of well-characterized smectites differing in structural Fe content, location of structural Fe (octahedral vs. tetrahedral), and location of excess layer charge (octahedral vs. tetrahedral) with aqueous Fe(II), a reductant abundant in natural anaerobic environments.

More specifically, we used stable isotope specific Mössbauer spectroscopy to determine the extent of reduction of structural Fe in smectites after exposure to aqueous ^{56}Fe(II), which is transparent in Mössbauer spectra. Experiments with aqueous Fe(II) enriched in ^{57}Fe were also carried out to determine the exchange of stable Fe isotopes between aqueous Fe(II) and structural Fe(III) in smectites. Different pools of Fe(II) and Fe(III) were investigated by sequential extraction procedures and solid reaction products were characterized with X-ray diffraction and electron-based microscopic methods.