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

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Clay minerals are ubiquitous in soils, sediments, and aquatic environments, and contain a significant proportion of the iron present in these environments. Fe-bearing clay minerals serve as an important source and sink for electrons in redox reactions in various subsurface geochemical environments. The 2:1 tetrahedral-to-octahedral smectite clay minerals contain a wide range of Fe contents from trace (e.g. montmorillonites) to 30% of their mass (e.g. nontronites). Here we focus on the redox reaction between aqueous $Fe(II)_{aq}$ and structural $Fe(III)_{clay}$ in smectites. We isolate the reduction of $Fe(III)_{clay}$ by $Fe(II)_{aq}$ using the isotope specificity of ^{57}Fe-Mössbauer spectroscopy. In experiments with Mössbauer-inactive $^{56}Fe(II)$, we observe more relative reduction of $Fe(III)_{clay}$ by $Fe(II)_{aq}$ for the low-Fe clay mineral SWy-2 (67% reduction) than for high-Fe containing nontronites NAu-1 and NAu-2 (10-20% reduction). Mössbauer spectra suggest that electrons are localized in SWy-2 as distinct $Fe(II)_{clay}$ species, which contrasts with the observed hopping of electrons between $Fe(II)_{clay}$ and $Fe(III)_{clay}$ for the nontronites. Our observations are consistent with clustering of Fe atoms in the nontronites but not SWy-2.

We also use enriched isotope tracers to track movement of Fe atoms between solution and the structure of the clay minerals. Our results indicate up to nearly 20% exchange between $Fe(II)_{aq}$ and NAu-2 over 6 months in pH 7.5 suspension, with less, but still significant amounts of exchange at pH 6.0. The clay minerals SWy-2 and NAu-1 exchange approximately 7 to 10% of their Fe with solution. Our calculations indicate that these levels of exchange require mixing of at least 2-3 unit cells deep, and suggest that a significant amount of Fe in the clay mineral structure is susceptible to reduction and atom exchange.