**Reactivity of iron-bearing phyllosilicates with uranium and chromium through redox transition zones**

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Operational extractions for the measurement of valence state-specific concentrations of Fe, U and Cr need to minimize secondary reactions that might occur in extract solutions. Because the reduction potentials for Fe and U species are similar, the thermodynamic favorability of one particular redox transformation (e.g., $U(IV)O_2$ oxidation by Fe(III)) may increase during the extraction phase but may not have been important under the geochemical conditions in which the sample was collected. In this scenario, the measured concentrations of U(IV/VI) and Fe(II/III) would not reflect the speciation in the sample but instead the speciation in the extract solution. To avoid these analytical problems when working iron(II/III)-bearing phyllosilicates, U(IV/VI), and Cr(III)/Cr(VI), we have developed a sequential extraction method as an alternative method for the conventional parallel extractions for (e.g., HF-$H_2SO_4$-phenanthroline for clay-Fe(II), and $NaHCO_3$ for U(VI)). We demonstrate that any extraction artifacts can be eliminated by using a sequential extraction procedure where U is first solubilized into $H_3PO_4$ and physically separated from the clay by centrifugation, and then the clay-Fe(II) is measured by HF-$H_2SO_4$-phenanthroline. A similar procedure is developed for Cr measurement. Using this this new procedure, we demonstrate excellent stoichiometric agreement.

Using the new procedure, we have performed Cr reduction experiments using clay-Fe(II). Nontronite (iron-rich smectite), smectite, chlorite, and Hanford site sediments were first bioreduced with *Geobacter sulfurreducens*. After pasteurization and removal of aqueous $Fe^{2+}$, clay-Fe(II) was used to reduce Cr(VI) at $10^o$, $20^o$, and $30^oC$ to mimic natural conditions at DOE contaminant sites and to obtain activation energy of the reaction. The clay reactivity was strongly dependent on temperature. At $10^oC$, nontronite was most reactive and chlorite was not reactive at all, despite a large amount of Fe(II) in its structure. The reactivity of the Hanford site sediments was between these two end members. At the end of Cr(VI) reduction, there were various amounts of Fe(II) remaining in the clays. In order to estimate the capacity of clay-Fe(II), multiple spikes of Cr(VI) were added to the system. The rate of Cr(VI) reduction slowed with each spike. At the end of several spikes, there was still 20% structural Fe(II) in nontronite remaining that was considered not reactive. At $30^oC$, the rates of Cr(VI) reduction by clay-Fe(II) were several times higher than at $10^oC$. Nontronite was still most reactive and its structural Fe(II) was fully consumed upon two spikes of Cr(VI). At this temperature, even chlorite became reactive, but about 50% structural Fe(II) was still remaining after several spikes of Cr(VI).

Scanning and transmission electron microscope (SEM and TEM) observations revealed that reduced Cr was present in micro-structural associations with the clay minerals. Focused ion beam (FIB)-SEM and TEM observations and electron energy loss spectroscopy (EELS) revealed that reduced Cr was likely in the form of $Cr(OH)_3$. The association of reduced Cr with low-permeability clay minerals would minimize any chance of Cr reoxidation and remobilization. The clay minerals are currently undergoing redox cycling to assess any change of clay properties and their reactivity toward Cr under redox-fluctuating conditions.