

Assessing the redox reactivity of tetrahedral Fe in clay minerals

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Clay minerals are important redox buffers in natural and engineered environments and they determine the fate of nutrients, (trace) elements, and organic and inorganic contaminants. In clay minerals, redox active Fe can be present in both octahedral and tetrahedral sheets of the silicate structure and amount to up to 30 wt% of the mineral. In contrast to other important iron-bearing minerals such as iron (oxyhydr)oxides, reduction of mineral ferric to ferrous iron primarily leads to structural re-arrangements instead of reductive dissolution. This property of iron-bearing clay minerals is thought to be the reason for the observation that these minerals can undergo redox reactions over an unusually large range of reduction potentials (ΔE_H of 600 mV). However, this hypothesis largely ignores the fact that many clay minerals also contain Fe in tetrahedral sheets and that the redox reactivity of tetrahedrally coordinated Fe may be considerably different than that of Fe atoms in the octahedral sheet. In this study, we aim to complement the understanding of the redox buffering by iron-containing minerals in soils and groundwaters by characterizing the role of iron in tetrahedral sheets of clay minerals.

We synthesized five high Fe content clay minerals (nontronites) with a range of tetrahedral Fe content (0-44% of the total mineral Fe bound in tetrahedral sheets) and subjected them to two subsequent cycles of Fe reduction and re-oxidation. The redox properties of these samples were characterized with mediated electrochemistry and linked to structural parameters using a suite of spectroscopic methods. We used FTIR, XMCD, and Mössbauer spectroscopy to determine the extent and reversibility of electron transfer to and from tetrahedral Fe and monitored mineralogical changes with XRD and TEM. Our preliminary results suggest that tetrahedral Fe can reversibly undergo reduction and re-oxidation in nontronites with low tetrahedral Fe content. Conversely, reduction and re-oxidation of clay minerals with high tetrahedral Fe content appear to yield some distinct structural alterations of the clay mineral structure.