

Variations in mineral structure and redox properties of iron-bearing clay minerals during redox cycling

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Redox reactions of iron in clay minerals play an important role during soil development by weathering and diagenesis as well as in carbon cycling and contaminant mitigation. These minerals typically host structural iron in octahedral sheets (substituting for Al) and occasionally also in tetrahedral coordination (substituting for Si). Clay minerals can buffer microbially-catalyzed or abiotic redox reactions over an unusually wide range of reduction potentials due to changes in mineral redox properties arising from re-arrangement of the mineral structure to accommodate additional charge. Whereas such behavior has been reported for iron in octahedral sheets, the contribution of iron in tetrahedral sheets to mineral redox properties and, thus, the behavior of these minerals in the environment, are still unclear.

Here, we studied the redox cycling of synthetic iron-rich nontronites containing octahedral iron (2/2 of octahedral cations) and variable amounts of tetrahedral iron (0 to 1/4 of tetrahedral cations), and characterized mineral structure and redox properties in a comprehensive manner. Using evidence from FTIR, XRD, TEM, and Mössbauer spectroscopy, we found that the 2:1 clay mineral structure was conserved during redox cycling while mineral crystallinity decreased. Further, repeated redox cycling resulted in the convergence of tetrahedral iron content to a low value (0.2/4 tetrahedral cations) independent of the initial tetrahedral iron content. Assessments of the redox properties of the nontronites using mediated electrochemistry showed that despite major structural and morphological changes, the redox buffering capacity of the nontronites was maintained over several redox cycles. As observed with natural iron-rich smectites, the reduced nontronites exhibited standard reduction potentials 520 mV higher than those of oxidized nontronites. The redox properties of the synthetic nontronites were independent of the initial amount of tetrahedral iron but differed between the native and re-oxidized specimens, likely due to variations in mineral crystallinity. Although tetrahedral iron coordination decreased over repeated redox cycles, these changes in iron coordination did not affect the redox properties of the nontronites. Our results indicate that tetrahedral iron plays a critical role in mineral transformation but is of limited relevance for the redox buffering