

Reactivity of structural iron in natural nontronite NAu-1 and synthetic Fe phyllosilicate

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Heterogeneous redox reactions on clay mineral surfaces affect the mobility of redox-sensitive elements in soils. Clay minerals have structural iron (Fe) substituting for aluminum (Al) in the octahedral sheet, which can participate in electron transfer reactions. We compared the redox properties of two substrates: natural nontronite clay NAu-1, and synthetic Fe phyllosilicate, synthesized and characterized in our laboratory (Fig. 1). Their redox behavior was tested in batch experiments with arsenic (As), chromium (Cr), and selenium (Se). Structural Fe in both synthetic Fe phyllosilicate and natural

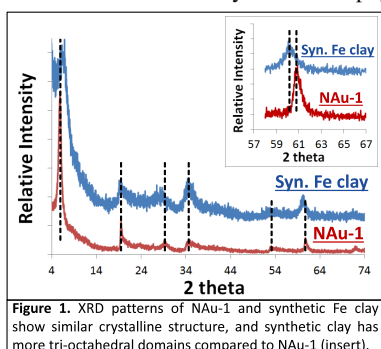


Figure 1. XRD patterns of NAu-1 and synthetic Fe clay show similar crystalline structure, and synthetic clay has more tri-octahedral domains compared to NAu-1 (insert).

NAu-1 clay behaves similarly during As(III) oxidation: if some structural Fe(II) is present, then structural Fe(III) oxidizes As(III) to As(V). We also tested reactivity of NAu-1 towards oxidation of Se(IV). The

analysis of X-ray Absorption Spectroscopy data indicates that Se(IV) is not oxidized to Se(VI) over the 48 hour reaction time. This difference in reactivity between As(III) and Se(IV) correlates to the sorption complex geometry – arsenic forms inner-sphere bi-dentate complexes, and selenium is predominantly adsorbed as an outer-sphere complex. Oxidation experiments with Cr(III) indicate that all examined Fe-rich substrates enhance the rate of Cr(III) oxidation to Cr(VI) under oxic conditions over 24 hours, compared to the homogeneous control system with no clay substrates.

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