

## The redox reactivity of Fe-bearing clay minerals and formation of reactive precipitates: A field study

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Fe-bearing clay minerals are important redox buffers, which may cycle electron equivalents for microbial respiration, contaminant transformation, and nutrient cycling. Clay mineral Fe(III) may be reduced microbially or by a variety of chemical reducing agents. Intriguingly, the mechanism of Fe reduction governs the characteristics and reactivity of the reduced mineral. Furthermore, interactions of natural reductants such as aqueous Fe(II), Mn(II), and sulfide with clay minerals may result in the formation of redox-active precipitates such as Fe/Mn (oxyhydr)oxides, Fe sulfides, and amorphous Fe-bearing silicates. Although these processes have been well documented in the lab, few studies have investigated clay mineral reduction and reactivity *in-situ* and it is unknown whether these precipitates form in the complex biogeochemical conditions found in soils and sediments.

Here, we incubated two nontronites (NAu-1, NAu-2, ~20 wt.% Fe) and a montmorillonite (SWy-2, ~3 wt.% Fe) under periodically reducing conditions in three coastal field sites with varying biogeochemical characteristics including sites with higher porewater Fe(II) (~0.7 mM), high porewater sulfide (~1 mM), and low aqueous Fe(II)/sulfide (~0.1 mM and <4 μM respectively). We aimed to (i) determine the extent of clay mineral Fe reduction, (ii) assess the electron donating capacity (EDC) and therefore reactivity of clay minerals reduced *in-situ*, and (iii) identify the formation of precipitates and their contributions to the measured EDC. We used a combination of Mössbauer and X-ray absorption spectroscopies to determine mineral reduction extent and composition with mediated electrochemical analyses (MEA) to determine EDC. We show that clay mineral reduction occurred in periodically reducing field conditions (up to 69 % Fe(II)/Fe(tot) in SWy-2 and up to 17 % Fe(II)/Fe(tot) in nontronite) and in the presence of porewater Fe(II) we observed the formation of Fe (oxyhydr)oxide/green rust-like phases. Our electrochemical analyses show that under sulfidic and low Fe conditions, clay mineral Fe(II) dominates the EDC whereas with higher porewater Fe(II) the EDC stems from a combination of clay mineral and precipitate/surface-associated Fe(II)). Our results highlight the importance of considering both clay mineral and precipitates when assessing mineral reactivity.