

## **Resolving the mineral identity of reactive precipitates formed by clay mineral iron redox reactions**

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Iron-bearing clay minerals are increasingly recognized as important redox-active minerals and redox buffers in natural environments. In the subsurface, microbial respiration can reduce ferric iron in the clay mineral structure to ferrous iron, which, in turn, is capable of reducing a range of organic and inorganic contaminants, elements, and nutrients. Intriguingly, interaction of iron-bearing clay minerals with the microbially produced, abiotic reductant ferrous iron leads not only to clay mineral iron reduction but, more importantly, to the formation of transient, yet highly reactive mineral species capable of degrading recalcitrant contaminants such as chlorinated ethenes. These short-lived reactive mineral intermediates (RMIs) are challenging to characterize, and to date not much is known about their identity, structure, abundance, and life-time or how the environmental conditions of their formation affect their redox reactivity towards contaminants.

Here, we used a range of complementary techniques to characterize the RMIs in the ferrous iron-clay system. We combined the isotope-specificity of Mössbauer spectroscopy to selectively study the Fe-containing RMIs with high-resolution transmission electron microscopic imaging and analysis (HR-TEM, EDS, SAED) and X-ray scattering analyses (XRD, pair distribution functions (PDF)) of the solids. Results to date demonstrate that 10-20 nm-sized RMI nanoparticles – made up of silicon and iron - often occur embedded in the clay mineral matrix, implicating clay minerals as a source of silicon in addition to a sink for electrons. While short reaction times preserve the overall layer structure of the clay minerals, extended exposure (>1 year) to ferrous iron leads to extensive clay mineral alterations, including decreased layer stacking, reduced mineral layer size, and mineral fringe bending, which are typical characteristics of freshly precipitated clay minerals. The absence of nanoparticles in these aged samples confirms the high reactivity and short life-time of these RMIs and suggests their participation in the apparent transformation of the original clay minerals. Ongoing work is exploring a wide range of reference materials to resolve the RMIs' mineral identity and structure, complementing our results from XRD, PDF, and SAED. Our data provide new fundamental process understanding needed to quantify RMIs' contribution to element cycling and contaminant