

## **EXAFS study of secondary Fe(II) precipitates formed during Fe(II) sorption onto clay and metal-oxide substrates**

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Microbial respiration of Fe(III)-oxides in suboxic and anoxic aqueous geochemical environments leads to release of Fe(II) to solution. The geochemical fate of released Fe(II) is at least partially controlled by Fe(II) sorption reactions with mineral substrates of the soil matrix. Our previous work has shown rapid formation of Fe(II)-Al(III) layered double hydroxides (Fe(II)-Al(III)-LDH) during sorption of aqueous Fe(II) onto  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at the near-neutral pH values typical of anoxic soil environments [1]. The aim of the work presented here was to characterize the secondary Fe(II) phases formed during Fe(II) sorption in anoxic suspensions of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, clay and amorphous silica over a range of reaction conditions and sorption times.

Experiments were performed with varying pH (6.0-8.0) and reaction time (up to 110 days) using a combination of batch experiments and synchrotron X-ray absorption spectroscopy. Formation of secondary Fe(II) precipitates was observed at pH > 7 in all systems, with the rate of precipitation and the types of precipitates formed varying with pH and substrate type. Precipitation of Fe(II)-Al(III)-LDHs was observed pH  $\geq$  7.0 in the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> suspensions and at pH 7.0 and 7.5 in the Fe(II)-clay system, whereas poorly-crystalline Fe(II)-phyllosilicates formed at pH  $\geq$  7.5 in the amorphous SiO<sub>2</sub> suspensions and at pH 8.0 in the clay suspensions. Precipitation rates increased with pH in all systems, and were faster in the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and amorphous SiO<sub>2</sub> suspensions than in the clay suspension at same reaction conditions. Attainment of sorption equilibrium in the Fe(II)- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> sorption experiments permitted calculation of the thermodynamic solubility products of the Fe(II)-Al(III)-LDH phases formed. The findings of this study suggest an important role of soil mineralogy in directing Fe(II) precipitation in anoxic soils, and suggest the potential for considerable variability in the composition and structure of secondary Fe(II) precipitates formed.

[1] Elzinga (2012) *Environ. Sci. Technol.* **67**, 4894-4901