

**ENVIRONMENTAL FACTORS IMPACTING THE FORMATION AND
KINETICS OF FE(II) LAYERED HYDROXIDES ON MINERALS AND SOILS**

by

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ABSTRACT

Fe(II)-Al(III)-layered double hydroxide (LDH) phases have been shown to form from reactions of aqueous Fe(II) with Fe-free Al-bearing minerals (phyllosilicate/clays and Al-oxides); however, these phases have not been observed in the natural environment due to limited data and technical limitations on Fe(II) solid phase speciation in anoxic environments. Potential locations of Fe(II)-Al-LDH phases in nature include areas with suboxic and anoxic conditions. Because these areas can be environments of significant contaminant and nutrient accumulation, it is important to understand the possible interactions and impacts of redox-sensitive and contaminant elements on LDH phase formation. One such contaminant, Zn, can also form as an LDH and has been found to form as a mixed divalent layered hydroxide phase. The effect of small amounts of structural Fe(III) impurities in natural clays and the effect of the environmental contaminant Zn on Fe(II)-Al-LDH phase formation were examined. The potential for Fe(II)-Al-LDH phase formation from the reductive dissolution of soil Fe(II)-oxides was also examined to better understand if and how these phases may exist in the natural environment.

Understanding the kinetics and sorption products of other Al-bearing minerals becomes especially important when impurities such as Fe(III) are present in the mineral due to the changes in phase stability and redox processes that may occur. The goal of the first study was to examine the kinetics and characterize sorption products of Fe(II) sorption to an Al-bearing phyllosilicate with Fe(III) impurities in anoxic conditions. To understand the role of structural Fe(III) impurity in clay, laboratory

batch studies with pyrophyllite (10 g/L), an Al-bearing phyllosilicate, containing small amounts of structural Fe(III) impurities and 0.8 mM and 3 mM Fe(II) (both natural and enriched in ^{57}Fe) were carried out at pH 7.5 under anaerobic conditions (4% H_2 – 96% N_2 atmosphere). Samples were taken up to 4 weeks for analysis by Fe-X-ray absorption spectroscopy (XAS) and ^{57}Fe Mössbauer spectroscopy. In addition to the precipitation of Fe(II)-Al(III)-LDH phases as observed in earlier studies with pure minerals (no Fe(III) impurities in the minerals), the ^{57}Fe Mössbauer analysis indicated the formation of small amounts of Fe(III) containing solids, most probably a hybrid Fe(II)-Al(III)/Fe(III)-LDH phase. The mechanism of Fe(II) oxidation was not apparent but most likely was due to interfacial electron transfer from the sorbed Fe(II) to the structural Fe(III) and/or surface-sorption-induced electron-transfer from the sorbed Fe(II) to the clay lattice. Increase in the Fe(II)/Al ratio of the LDH with reaction time further indicated the complex nature of the samples. This research provides evidence for the formation of both Fe(II)-Al(III)-LDH and Fe(II)-Fe(III)/Al(III)-LDH-like phases during reactions of Fe(II) in systems that mimic the natural environments.

Previous studies demonstrated the formation of single divalent metal (Co-, Ni-, and Zn-Al) and mixed divalent metal (Ni-Zn-Al) layered double hydroxide (LDH) phases from reactions of the divalent metal with Al-bearing substrates and soils in both laboratory experiments and in the natural environment. Because Fe(II) ions are of similar size to the other divalent metal ions that form LDH phases, it is important to understand if and how these ions are incorporated into the LDH structure together. The objective of the second study was to examine Fe(II) and Zn co-sorption to an Al-bearing oxide and phyllosilicate to determine the effects of Zn on sorption products

and kinetics, and ultimately determine if formation of a mixed divalent metal (Fe(II)-Zn-Al-LDH) phase will form from these reactions. By understanding how Zn may interact with Fe-sorption, we can better understand natural environments in which Fe(II)-Al(III)-LDH phases may occur. To understand how Zn impacts the formation of Fe(II)-Al-LDH phase formation and kinetics, 3 mM or 0.8 mM Fe(II) and 0.8 mM Zn were batch reacted with either 10 g/L pyrophyllite or 7.5 g/L γ -Al₂O₃ for up to three months under anoxic conditions. Aqueous samples were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) and solid samples were analyzed with XAS. Shell-by-shell fits of Fe(II) and co-sorption samples with pyrophyllite show the formation of a mixed divalent metal (Fe(II)-Zn-Al) layered hydroxide phase, while Fe(II) and Zn co-sorption samples with γ -Al₂O₃ produce Fe(II)-Al-LDH phases and Zn in inner-sphere complexation with the γ -Al₂O₃. This study demonstrates the formation of a mixed divalent metal layered hydroxide and further iterates the importance of sorbent reactivity on LDH phase formation.

Because of the technical limitations associated with analyzing bulk soils for LDH phases, the potential for Fe(II)-Al-LDH phases to form from the reductive dissolution of soil Fe was examined through a laboratory batch reaction system. Soil solutions of 50 g/L <2 mm size fraction of soil from the Great Cypress Swamp in Delaware (GCS) and the Stroud Water Research Center (SWRC) in Pennsylvania were induced into reductive dissolution inside a glovebox with inert conditions (4% H₂ – 96% N₂ atmosphere) for 21 days or more. During this time, 1 kDa MWCO dialysis tubes with 7.5 g/L γ -Al₂O₃ were submerged in the soil solution. Following the reactions, the γ -Al₂O₃ sorption samples were analyzed with X-ray diffraction (XRD), X-ray fluorescence spectrometry (XRF), XAS, and by acid digestion. The

GCS- γ -Al₂O₃ sorption samples had insufficient Fe sorption to produce usable XAS data. The low concentration of Fe released to the soil solution during reductive dissolution and low soil solution pH were not ideal conditions for LDH phase formation, as seen in other LDH work. Fe(II)-Al-LDH phases were not observed in the EXAFS spectra of SWRC- γ -Al₂O₃ sorption samples; instead, a mononuclear surface species with multiple coordination environments is the most likely sorption product formed. Other elements that complex Fe and Al or that inhibit the dissolution of γ -Al₂O₃ were also included in the sorption products, as observed by acid digestion and XRF. Because EXAFS is a bulk technique, an average of all species of the element of interest (in this case Fe) is taken. Although a mononuclear surface species is likely the dominant sorption form, other Fe phases may have formed with the complexing elements in this system, such as carbonates, P, S, Si, and organic matter. Further systematic research is required to better understand the conditions in the natural environment that are ideal for LDH phase formation.