Evidence for the formation of Fe-layered hydroxides using spectroscopic techniques

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Abstract: Iron (oxyhydr)oxides, including layered hydroxides, are important naturally-occurring mineral phases that can significantly influence the stability and mobility of redox-sensitive elements in the environment. In a recent study, Fe(II)/Al(III)-layered double hydroxides (LDH) were shown to form from reactions of Fe(II) with Al-bearing minerals under anoxic conditions during laboratory batch reactions. The implications of other elements commonly present in Al-bearing minerals, such as Si and Fe(III), on LDH phase formation remains unknown. Because silicates are known to alter LDH structure and stability by interlayer substitution, it is important to understand the effects of Si. Likewise, the presence of Fe(III) in the Al-bearing mineral can alter the oxidation state of the aqueous Fe(II) that reacts to form the LDH. This study examines the kinetics of LDH formation from sorption reactions of Fe(II) on pyrophyllite, an Al-bearing phyllosilicate containing structural Fe(III) impurities. Batch reactions were conducted with 3mM Fe(II) (both natural and 57Fe(II)) and 10 g/L pyrophyllite at pH 7.5 under anaerobic conditions (4% H\textsubscript{2} – 96% N\textsubscript{2} atmosphere). Samples were collected at reaction times up to 4 weeks for analysis by X-ray absorption spectroscopy (XAS) and 57Fe Mössbauer spectroscopy. From these analyses, it was determined that an Fe-bearing layered hydroxide phase formed during the 4-week reaction time. This research provides evidence for the formation of Fe layered hydroxide phase during reactions of Fe(II) with Al-, Si-, and Fe-bearing minerals. Better understanding of Fe phase formation in complex laboratory studies will improve models of natural redox systems.