Iron Atom Exchange Kinetics in Iron-rich Organic Freshwater Flocs

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Organic, Fe-rich flocs are common in surface waters of freshwater wetlands and often contain elevated concentrations of trace metal(loid)s. In a previous study, flocs collected from streambeds of the naturally As-enriched peatland *Gola di Lago* (Switzerland) were shown to contain ferrihydrite and nanocrystalline lepidocrocite to which As(V) and As(III) were bound in bidentate surface complexes.[1] These flocs tend to settle under low flow conditions, and thus over time may become buried and subjected to Fe(III)-reducing conditions. Both ferrihydrite and lepidocrocite readily react with Fe(II), recrystallizing into more stable Fe(III) phases, and the nano-crystalline floc-lepidocrocite may enhance floc reactivity. The mechanism for the abiotic reduction of Fe(III)-(oxyhydr)oxides by Fe(II) includes an initial adsorption step, however, in the case of organic, As-rich flocs, this reaction may be hindered due to the presence of surface-adsorbed organic matter (OM) and/or arsenic. To study this, we spiked synthetic ferrihydrite, a ferrihydrite-OM coprecipitate, and flocs from the *Gola di Lago* peatland (31-38 wt.% Fe) with an isotopically enriched ^{57}Fe(II) solution at varying pH and Fe(II) concentrations, and followed Fe atom exchange kinetics and solid phase Fe speciation changes over one week. Using a combination of Mössbauer spectroscopy, X-ray diffraction, and ICP-MS, our results show that ferrihydrite transformed quickly (<7 days) into lepidocrocite and goethite, while the coprecipitated ferrihydrite-OM showed no Fe minerological changes. Flocs showed changes in lepidocrocite and ferrihydrite content and formed solid-phase Fe(II) minerals at higher Fe(II) concentrations, though all phases remained X-ray amorphous. Iron atom exchange kinetics were likewise affected by the presence of OM and arsenic, with flocs and coprecipitates achieving 87-96% fraction of isotopic exchange in one week, while ferrihydrite obtained 96-99%, with slower kinetics observed for ferrihydrite at lower pH. In summary, our results imply the presence of OM and/or arsenic inhibit both Fe mineralological changes and Fe atom exchange, thus potentially stabilizing floc Fe minerals and associated trace metal(loid)s under Fe(III)-reducing conditions.

[1] ThomasArrigo *et al.* (2014) *Environ. Sci. Technol.* **48**, 13218-13228.