Iron mineral transformations induced by ferrous iron and sulfide in NOM-Fe-rich peatland flocs

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Natural organic matter (NOM) and iron (Fe) rich flocs in surface waters from the minerotrophic peatland *Gola di Lago* in southern Switzerland are strongly enriched in arsenic (As), with reported concentrations up to 2620 mg kg^{-1} [1]. Such NOM-Fe-rich flocs can be exported from the wetland with streams, or settle as part of the peat sediment, exposing them to reducing conditions. Iron in the flocs was found to be 51-59% ferrihydrite and 34-46% nano-crystalline lepidocrocite [1]. To better understand the role of NOM-Fe-rich flocs in As-cycling, we studied Fe mineral transformations and the resulting release of dissolved As induced by ferrous iron (Fe^{2+}; 0.1 or 1 mM; pH 5.5 or 7) or sulfide (S^{2-}; 5.2 mM; pH 7) under anoxic conditions. Quantitative Fe mineral analysis was achieved by Fe K-edge EXAFS and ^{57}Fe Mössbauer spectroscopies. Reacting floc suspensions with isotopically enriched $^{57}Fe^{2+}$ for 7 days did not result in the formation of new Fe phases, in stark contrast to pure ferrihydrite, which rapidly transformed into more crystalline goethite and lepidocrocite. Following the $^{56}Fe/^{57}Fe$ isotope ratios in solution and solid phases, we found that Fe atom exchange was also much slower in flocs than in pure ferrihydrite suspensions. Release of dissolved As was not observed. Spiking floc suspensions with dissolved S^{2-} resulted in rapid formation of elemental S^0 and polysulfides, release of dissolved As (with up to 33% of thioarsenates) and Fe^{2+}, and precipitation of mackinawite (FeS). Floc ferrihydrite appeared to be more reactive with S^{2-} than the nano-crystalline lepidocrocite phase [2]. Overall, our results suggest that Fe mineral phases in NOM-Fe-rich flocs are chemically highly reactive, but NOM hinders formation of crystalline Fe(III) oxyhydroxides in the presence of Fe^{2+}.

[1] ThomasArrigo et al. (2014), *ES&T* **48**, 13218−13228.
[2] ThomasArrigo et al. (2016), *ES&T* **50**, 3607−3616.