Redox and sorption reactions between magnetite and humic substances

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Humic substances (HS) are ubiquitosly present in natural systems and readily bind to positively charged iron (Fe) mineral surfaces. Furthermore, HS can act as electron shuttles during microbially mediated reduction of Fe(III) minerals like ferrihydrite, goethite and hematite [1]. However, to the best of our knowledge there are no published studies investigating if HS can also reduce the highly crystalline, mixed valent Fe(II), Fe(III) mineral magnetite (Fe_3O_4). Despite the fairly negative standard redox potential of magnetite, -314 mV, magnetite can undergo both oxidation and reduction reactions [2]. The aim of the current study is to investigate whether magnetite can be reduced by HS and/or if HS can be reduced by magnetite.

Previous studies have shown that magnetite reactivity depends on Fe(II)/Fe(III) ratios [3] as well particle size [4]. Therefore, the magnetite synthezised for this study had varying Fe(II)/Fe(III) stoichiometry and particle sizes ranging from a few nm up to hundreds of nm and included biotic or abiotic routes routes of synthesis. The fate of magnetite in the presence of HS was followed using a combination of the spectrophotometric ferrozine analysis, magnetic suceptibility measurements, Mössbauer spectroscopy and XRD. Preliminary results indicate that certain types of magnetite are reduced by reduced HS over a timeperiod of a few days. Hence, HS may play an important role in cycling Fe present as magnetite and thereby influence the biogeochemical cycles of other elements bound to the surface of magnetite.

[1] Bauer & Kappler (2009), *Environmental Science & Technology* **43**, 4902-4908. [2] Byrne, Klugelein, Pearce, Rosso, Appel, Kappler (2015), *Science* **347**, 1473-1476. [3] Gorski, Nurmi, Tratnyek, Hofstetter & Scherer (2010), *Environmental Science & Technology* **44**, 55-60. [4] Swindle, Madden, Cozzarelli & Benamara (2014), *Environmental Science & Technology* **48**, 11413-11420.