Redox reactions between humic substances and magnetite

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Humic substances (HS) are highly abundant in natural systems and readily bind to mineral surfaces. Furthermore, HS can act as electron shuttles during microbial Fe(III) reduction [1] and abiotically reduce Fe(III) compounds [2]. The electron transfer capacity of HS to Fe(III) has been shown to decrease with decreasing redox potential of the Fe(III) mineral (ferrihydrite > goethite > hematite). Therefore it is unclear if HS can reduce minerals with even lower redox potential than hematite, like the crystalline, Fe(II)-Fe(III) mineral magnetite. Magnetite can undergo cycles of alternating microbial oxidation and reduction, i.e. act as a biogeobattery [3] and the aim of the current study was to investigate if four different types of magnetite with varying size and Fe(II)/Fe(III) ratio can undergo similar, abiotic, redox reactions with HS.

Native and chemically reduced humic acids (HA) were incubated with magnetite and the concentrations of Fe(II) and Fe(III) were followed in order to quantify the electron transfer over time. Changes in magnetite redox state and properties were followed using magnetic susceptibility measurements, μXRD, ^{57}Fe Mössbauer spectroscopy and transmission electron microcopy. The direction and extent of electron transfer between magnetite and the native or chemically reduced HA varied among the four types of magnetite. Magnetite reactivity is influenced by particle size [4], but our study suggests that the route of magnetite synthesis also plays a major role in determining the electron accepting and/or donating capacity of magnetite. We clearly show that HS play an important role for Fe cycling in organic rich environments. Furthermore, HS redox reactions with magnetite may influence the use of magnetite for remediation of contaminants like Cr(VI) as the Fe(II)/Fe(III) ratio in magnetite is strongly linked to its reduction capacity [5].

[1] Nevin & Lovely (2000), *Environ. Sci. Technol.* **34**, 2472-2478. [2] Bauer & Kappler (2009), *Environ. Sci. Technol.* **43**, 4902-4908. [3] Byrne *et al.* (2015), *Science* **347**, 1473-1476**.** [4] Swindle *et al.* (2014), *Environ. Sci. Technol.* **48**, 11413-11420. [5] Gorski *et al.* (2009) *Environ. Sci. Technol.* **43**, 3675-3680