Re-evaluation of electron transfer budgets for oxidation and incorporation of bisulfide by dissolved organic matter under anaerobic conditions

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While it is known that functional groups of organic matter, such as quinones, can reversibly transfer electrons, there is little known about electron transfer (e-transfer) processes in redox reactions of reactive species, such as sulfide, with organic matter.

We investigated the chemical oxidation of H_2S with a reduced (as control) and non-reduced dissolved humic acid (HA), in batch experiments at pH 6 under anoxic conditions. Thereafter, electron transfer budgets were calculated from sulfide consumption and production of oxidized sulfur species formed.

Sulfide reacted rapidly with DOM and thereby regenerated more oxidized forms of sulfur, either inorganic sulfur species (S^0 and $S_2O_3^{2-}$) or organic products (e.g. as carbon bonded sulfur). Lower concentrations of HA in solution reacted more effectively towards sulfide (25 ppm C: moles S/moles C = 0.024; 75 ppm C: moles S/moles C = 0.015). The main reaction product was S^0 (making up about 40~50 %), important intermediate was $S_2O_3^{2-}$ (about 13~32 % reaction for 48 hours). Total recovery in the inorganic fraction accounted to 60~78%, while a gap remained in the budget of about 22~40% of sulfur that had presumably added to the HA as organic sulfur. Thus, in all non-reduced HA treatments, 10-30 μmol/L sulfide added to the HA as organic sulfur (22~40%), and X-ray absorption spectroscopy data supported organic sulfur to be approximate zerovalent sulfur. E-transfer capacities of non-reduced HA towards sulfide based on formation of organic sulfur was therefore about 0.8~1.24 μeq/mg C. The amount of electrons transferred to reduced HA was comparable to the difference of e-transferred to oxidized HA minus e-transferred to HA pre-reduced with H_2/Pd.

In conclusion, the results showed that HA chemically reoxidized sulfide under anoxic condition at significant rates, and formed reduced organic sulfur compounds that provided a sink for sulfur and reduces the amount to be recycled.

Uranium reduction on magnetite: An electrochemistry approach

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Electrochemical methods provide a unique approach that allows one to measure or control the redox environments close to the surface of semiconducting minerals. Cyclic voltammetry and potential step voltammetry have been applied in order to investigate the redox reactions of aqueous uranyl on the electrodes made of bulk and nano-powder of crystalline magnetite. *In-situ* Atomic Force Microscopy and Raman spectroscopy were used to probe the surface morphology and phase change as a function of the redox potential.

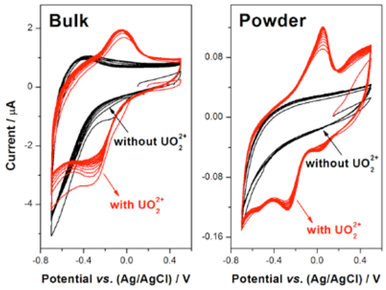

Figure1: Cylcic voltammetry of the bulk and the powder magnetite electrode in solution with and without uranyl and the AFM height image of the bulk electrode surface after the reaction (220×220nm).

Two sets of redox peaks were found on the cyclic voltammogram of magnetite nano-powder in blank solution, showing its high reactivity, but none was detected on the bulk crystalline electrode. The one-electron reduction from U^{6+} to U^{5+} was verified by fitting the potential step voltammetry of the crystalline electrode. The U^{6+} to U^{5+} reduction peak was evident at a more negative potential (-0.33 V *vs*. Ag/AgCl) on the cyclic voltammetry of the bulk electrode as compared with that of powder electrode (-0.27 V *vs*. Ag/AgCl). This reflects the slower kinetics of the electron transfer on the bulk magnetite surface. After immersion in a uranyl sulfate solution, the surface roughness of the magnetite increased as the redox potential decreased from -0.22V to -0.30V within one hour. Island-like features of about 20 nm height were found on the magnetite surface, which could be iron hydroxides resulting from the oxidation of magnetite.