Metastable sulphur species at iron mineral surfaces –missing links in the sulphur cycle?

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The reaction between dissolved H_2S and ferric (hydr)oxides leads to the formation of significant amounts of **ME**tastable Sulphur species at the Surface of Iron (hydr)oxides (MESSIs), such as FeS, surface polysulphides presumably bound to Fe(II), or S8-sulphur [1-3].

Such species appear to be intermediates for the formation of pyrite. Their formation rate and formation pathways depend on the reactivity of the ferric (hydr)oxide and the Fe/S ratio. Once this ratio is > 1 (e. g. ground waters, non-marine aquatic systems with a limited formation rate of dissolved H_2S) the formation rate of MESSIs can be very high in the range of hours and their half life of the order of weeks.

Such time scales are characteristic to aquatic systems exposed to frequent fluctuations of redox conditions, which makes MESSIs potential participants in the biogeochemical cycles occurring during such fluctuations. Surprisingly, inspite of their quantitative importance, there occurrence has been overlooked to date let alone that their ecological role in biogeochemistry has been considered.

MESSIs are energy-rich sulphur compounds that may exert a variety of biogeochemical functions: i) involvement in the sulphur cycle i) through disproportionation of elemental sulphur (either from polysulphides or S8 sulphur) and ii) as electron donors for chemolithotrophic metabolic acitivities (e. g. denitrification), ii) working as an electron shuttle taking up electrons as well as releasing electrons and mediating electron transfer e. g. for microbial iron reduction

[1] Wan, Shchukarev, Lohmayer, Planer-Friedrich & Peiffer (2014) *Environ. Sci. Technol.*, **48**, 5076–5084. [2] Peiffer, Berends, Hellige, Larese-Casanova, Wan, & Pollok (2015), *Chemical Geology*, **400**, 44-55. [3] Wan & Peiffer, Goldschmidt Conference, Session 25k