

## Quantifying electron flow in the sulfidation of lepidocrocite

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The interaction between sulfide and ferric (oxyhydr)oxides exerts control on electron flow and ultimately the sulfur cycle in many anoxic groundwater, soil and marine systems. In most situations it leads to pyrite formation, the pathway still being researched [e.g. 1]. To identify the intermediate products and to quantify the electron flow during the reaction we used Mössbauer spectroscopy, TEM, wet chemistry analyses and a novel technique to determine polysulfides.

We reacted synthetic lepidocrocite enriched in the Mössbauer-sensitive isotope <sup>57</sup>Fe and dissolved sulfide at neutral pH in an anoxic glove box. The solid fraction was extracted at different time steps (15 min, 2hrs, 48 hrs, 72 hrs and one week), frozen and analyzed with Mössbauer spectroscopy. Both iron and sulfur species were measured with wet chemistry analysis methods in parallel runs. Polysulfides were derived with Trifluoromethanesulfonate and measured by HPLC with UV-Detector.

Mössbauer spectra showed the formation of pyrite after 48 hrs. Mackinawite and magnetite were identified as intermediate products and confirmed TEM observations by Hellige *et al.* [1]. The spectra also provided evidence for Fe-deficient FeS phases such as pyrrhotite. Wet chemistry analysis shows polysulfides form in the first few minutes, accompanying with the formation of elemental sulfur. Most of them are surface associated. With the knowledge on the distribution of Fe between its oxidation states, mineral phases and dissolved species and the determination of polysulfides we can quantify the electron flow along the reaction path to pyrite formation.

[1] Hellige *et al.* (2011) *Geochim. Cosmochim. Acta* in review.

## A thermogravimetric study of thermally treated silica nanoparticles

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Silica is the most abundant mineral in the earth's crust. The surface chemistry of silica often plays a critical role in many earth processes, for example weathering of rocks. When the size of silica particles approaches the nanoscale or when they contain nanoscale pores, the surface area of the silica particles increases dramatically and this can fundamentally affect several properties of interest. Using a combination of dehydration (heating 2hrs at 200°C), dehydroxylation (heating 2hrs at 400, 600 or 800°C) and rehydroxylation (boiling overnight in water), we thermally treated three different types of silica particles, *i.e.* AA-05 (spherical, diameter ~ 500 nm) synthesized via the Stöber process, N-2329 (spherical, diameter ~ 75 nm) synthesized through water glass route, and V-258 (irregular, median size ~700 nm) ground glass [1]. Samples were characterized by thermogravimetric analysis (TGA), pycnometry, elemental analysis and scanning electron microscopy (SEM). We found that heating 2hrs at 200°C removed physically absorbed water, while heating at higher temperature incrementally removed surface silanol groups. Boiling overnight in water resulted in partial recovery of silanol groups. However dehydroxylation became irreversible for samples treated at over 400°C inconsistent with the Zhuravlev model [2]. Our results also indicated that AA-05 Stöber silica was nanoporous with a lower density (1.9 g/cm<sup>3</sup>) than that (2.2 g/cm<sup>3</sup>) of the fully condensed N-2329 which was obtained through the water glass route. The considerable carbon content (~ 2wt%) in AA-05 was also consistent with incomplete condensation during Stöber synthesis. Both AA-05 and N-2329 showed better thermal stability than did V-258, which melted at 800°C. The increased density of AA-05 after treatment at 600 and 800°C suggested that the nanopores in Stöber silica begin to collapse at 600°C.

[1] Wan *et al.* (2010) *J Therm Anal Calorim* **99**, 237-243. [2] Zhuravlev (2000) *Colloid Surface A* **173**, 1-38.