

Combined titration, EXAFS and molecular dynamics modeling study of Cu(II) ions sorbed on the model biopolymer xanthane

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Exopolysaccharides are reactive substrates excreted mainly from biofilm-forming bacteria. Most of them bind strongly metals and constitute an a priori important soil reactivity pool. Xanthane, a carboxylic acid containing non-gelling exopolysaccharide of known structure produced by *Xanthomonas campestris* strains was investigated with respect to its site density, acid-base reactivity, folding capacity, Cu bond strength and Cu sorption structures, in the aim to determine its eventual specificity and importance relative to other soil substrates (humic acids for example). Between pH 3 and 5, Cu sorption on Xanthane decreases, which is unusual and contrary to conventional observations. Molecular dynamics calculations (Cerius2 software, universal force field) show that the metal bond strength increases with increasing structural disorder of Xanthane. In the disordered state prevailing at low pH, more inter- and intrachain chelating configurations are formed leading to the thermodynamically observed increase of the Cu (II) bond strength. Inversely at higher pH, the prevailing ordered states lead to rigid chain configurations and a consequently decreased number of Cu (II) chelating structures. The overall Cu bond strength compares to that of small model chelates of intermediate bond strength, and surpasses those of the constituting monocarboxylic acids. The study shows that the folding habit of soil polymers interferes in the metal binding capacity. Moreover, comparison with other soil substrates shows that this – and potentially also other – exopolysaccharides compare in reactivity to other highly reactive substrates such as humic/fulvic acids.

A first principles study of the structure and stability of iron-sulfides and their surfaces

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Iron sulfide minerals are an intrinsic and essential part of the global biogeochemical sulfur cycle [1] and have also been proposed as possible candidates for the catalytic reactions involved in the origins of life [2]. As yet there are very few computational studies which examine the structure and stability of iron-sulfide surfaces that are thought to be important in the iron-sulfur-world.

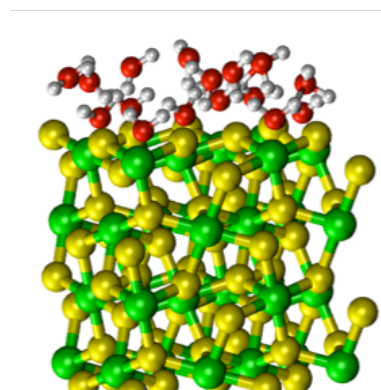


Figure 1: Simulation of water at the pyrite (001) surface

Using first principles quantum mechanical methods we performed a study of the bulk phases of pyrite, marcasite, troilite, and pyrrhotite. Good agreement of the lattice parameters and spin states was found between experimental and simulation data. From these bulk minerals we are able to construct surfaces and begin to explore the structure and stability of solvated iron-sulfide surfaces. Based on this, it is possible to begin to explore both the thermodynamics and activation energies for plausible reaction pathways that control the kinetics for the formation of the precursors of life as catalysed by iron sulfides.

- [1] Rickard & Luther (2007) *Chem. Rev.* **107**, 514–562.
 [2] Wachtershauser, G. (1988) *Microbiological Reviews* **52**, 452–484.