Linking mackinawite (FeS) structure to redox activity

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The nanoparticulate tetragonal iron sulfide mineral mackinawite (FeS) is thought to be ubiquitous in wetlands, estuaries and groundwater where bacterially produced sulfide and ferrous iron mix. FeS has the potential to be used as a bioremediation tool because of its ability to reduce a range of contaminants including chlorinated organics, metals and metalloids.

The goal of our research is to link the molecular-scale structure of FeS to its reactivity towards environmental contaminants, in this case, the biomagnifying toxicant mercury. To this end, we have integrated X-ray spectroscopic, X-ray scattering, computational and wet chemical techniques to investigate FeS size and structure, and to identify which FeS moieties participate in reduction as well as what oxidized products result as a function of time, pH, and [Hg(II)] in batch reactors.

Using Hg L_{III}-edge extended X-ray absorption fine structure (EXAFS) spectroscopy we have found that Hg(II) forms a discrete Hg(0) phase after reaction with FeS. Density functional theory (DFT) computations show that surface Fe(II) in FeS preferentially binds Hg(II) relative to surface S(-II), suggesting a pathway by which electrons might be transferred to Hg(II) to produce Hg(0) and Fe(III). Using Fe K- and $L_{II,III}$-edge X-ray absorption spectroscopy, we have quantified Fe(III) formation in FeS suspensions. Fe(III) exists in octahedral coordination as a second, amorphous phase, possibly as a mixed Fe(II)-Fe(III) phase, which may be a pre-cursor to the Fe(II)-Fe(III) sulfide, greigite. Lastly, we used X-ray diffraction, electron microscopy and Fe K-edge EXAFS spectroscopy to derive a particle size distribution for FeS, and to determine FeS molecular-nanoscale structure before and after oxidation. We combined this information with thermodynamic modelling of equilibrium aqueous Fe(II) and S(-II) concentrations in order to identify the redox processes that occur in FeS suspensions.

Our research demonstrates that Fe(II) in FeS is key to FeS reactivity, dominating its surface chemistry and redox activity.

Timing the evolution of seawater chemistry during the Neoproterozoic: case study of the Svalbard succession.

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The Neoproterozoic Era (1000-542 Ma) is a key period in the evolution of the Earth system. This period is characterised by the widespread occurrence of glacigenic sediments and by large variations in carbon isotope compositions of seawater [1]. These excursions are among the largest described in the geological record, and together with global periods of glaciation, make the Neoproterozoic one of the most dramatic periods of change in surface processes on Earth. Another major change that occured during this period is a purported increase in oxygen concentration in the atmosphere and associated changes in ocean redox [2]. In order to unravel the global record of evolving Neoproterozoic ocean chemistry, several successions around the world have been studied [e. g. 3]. However, the lack of precise radiometric constraints on suitably preserved samples in most Neoproterozoic sedimentary successions hinders the interpretation and correlation of geochemical signals. The Polarisbreen Group in northeast Svalbard is one of the best preserved Neoproterozoic successions and has great potential to significantly improve the record of Neoproterozoic environmental evolution, but to date has yielded no direct radiometric age constraints

In this study, we investigate the potential of the Svalbard succession to represent a type succession to assess the climate and chemical variations that occured during the Neoproterozoic. The Svalbard succession is characterised by the presence of 2 distinct glaciation episods which have been correlated with the first and second Cryogenian glaciations [3, 4]. Here, we present new constraints on the depositional age of two discrete glacial intervals in the Polarisbreen Group based on U-Pb detrital zircon data from siliciclastic sediments. We also investigate Sr isotopes and REE concentration in well preserved carbonate rocks through the succession in order to correlate the variation in Sr isotopes to the proposed Neoproterozoic seawater Sr curve [3] and assess variation in marine redox conditions during this interval.

These new data will allow a better correlation of the Svalbard succession with other Neoproetrozoic successions and provide a framework to characterise the evolution of seawater during the Neorpoterozoic.

[1] Fairchild and Kennedy (2007) *Journal of the Geological Society.* [2] Holland (2006) *Philosophical Transactions of the royal Society.*[3] Halverson et al. (2010) *Precambrian Research*. [4] Fairchild and Hambrey (*1995) Precambrian Research.*