Arsenate forms monodenate complexes at the surface of goethite

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The overwhelming consensus in the geochemical literature is that arsenate forms predominantly bidentate-bridging surface complexes on iron-(hydr)oxides, including goethite. Of course, any challenge to this belief is controversial and must be motivated by strong evidence. Its primary basis is that Fe-As distances fall into two ranges: 2.70 Å to 3.45 Å, indicating bi- or tridentate, and 3.50 Å to 3.60 Å, indicating monodentate coordination. We begin by presenting XRD evidence that demonstrates this is an over-simplification; in fact, monodentate coordinated arsenate complexes can have metal-As distances as small as 3.25 Å.

We collected As-EXAFS spectra for nine arsenate-goethite samples at total arsenate concentrations between 0.6 and 1.8 ▯mol/m^2, and in the pH range 3.3 to 10. We used a modeling strategy that focuses on a determination of the coordination number of Fe in the second shell. For all nine samples, we find that arsenic is coordinated to 4.0 oxygens in the first shell, and the second shell Fe coordination number is between 0.8 and 1.0. Although the errors in the Fe coordination number are large, they allow for a value no greater than 1.8, in the worst case. We also obtain As-Fe distances spanning 3.29-3.31 Å, and we find no statistically significant contribution from a longer As-Fe distance.

We compliment our EXAFS data with results from simultaneous potentiometric and infrared spectroscopic titrations, and we show for the first time the As-O stretching bands of arsenate adsorbed on goethite. These bands indicate that there are at least two general classes of arsenate-goethite surface complexes depending on pH, and both have C_{2v} symmetry or less. The OH stretching and As-O-H bending modes reveal that the difference between these complexes is due to protonation of the arsenato moiety, and the ligand is doubly protonated at low pH.

An unbiased interpretation of these results is that arsenate is coordinated in a monodentate fashion to just one Fe, and its coordination geometry is not significantly changing as a function of pH and surface coverage. At low pH, this monodentate complex is doubly protonated, and at moderate to high pH, it is singly protonated. There is no doubt that hydrogen-bonding contributes strongly to the stabilities of these complexes, and we show graphical models indicating their most likely structures at the goethite surface.

Sulphide isotope stratigraphy through the Scottish Neoproterozoic: links to global glaciations and changing ocean sulphate content

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Pyrite and pyrrhotite are common accessory minerals in many Neoproterozoic sequences. Sulphate is rare, often only occurring at low concentrations in carbonate, resulting in low resolution and highly variable seawater curves for this period. Neoproterozoic pyrite δ^{34}S profiles for Australia and Namibia [1] can be closely correlated. These records provide information about ocean sulphate contents and distinguish post-Sturtian from post-Marinoan sedimentation.

A new stratigraphic record for pyrite δ^{34}S from the Neoproterozoic Dalradian Supergroup of western Scotland matches the trends seen for Australia and Namibia. Pyrite δ^{34}S values of +40 to +50‰ are found throughout 150m of stromatolite-dominated sediments stratigraphically overlying glacial diamictites. These have recently been proposed as a Sturtian event by correlation with Ireland [2] and the δ^{34}S results confirm this.

Some 4-5 km higher in the sequence is a shift from +30 to -12‰ over 35 m of stratigraphy, the lowest shift to a ^{34}S-depleted tenor in the Dalradian sequence and it is maintained through the overlying 2 km of stratigraphy. Global correlation suggests that this negative excursion post-dates Marinoan glacial events. Correlation with the carbonate δ^{13}C record, the very low organic matter content and low continental input to this part of the section, suggest a cold climate period, but so far without evidence of a glacial deposit in Scotland.

Large stratiform barite deposits in the middle Dalradian indicate seawater sulphate δ^{34}S of +40‰. This suggests that Δ^{34}S between sulphate and sulphide in the proposed post-Marinoan section increased over a short interval from 10-15‰ to 40-45‰, the latter normally occurring in a system where sulphate reservoir recharge is in excess of sulphate removal. This is likely to be a post-Marinoan response to increasing oceanic sulphate content [1], possibly as a result of increasing levels of atmospheric oxygen. The Scottish section further re-inforces this event as a global phenomena.

[1] Hurtgen *et al.* (2005) *Geology* **33,** 41-44. [2] McCay *et al.* (2006) *Geology* **34,** 909-912.