

## Photochemistry of arsenite and chromate on iron oxyhydroxide

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The (photo)chemistry of arsenite [As(III)] and chromate [Cr(VI)] in the presence of ferrihydrite and goethite was investigated. A variety of techniques, including infrared spectroscopy, X-ray absorption near edge structure (XANES) and solution phase analysis were used to characterize the surface bound and aqueous phase species. The exposure of the iron oxyhydroxides to As(III) in the dark resulted in a adsorbed layer of As(III). Irradiation of the As(III)/ferrihydrite or As(III)/goethite system to simulated solar radiation resulted in the conversion of As(III) to adsorbed and aqueous phase As(V). The relative amounts of adsorbed and aqueous phase As(V) product varied whether ferrihydrite or goethite was present in solution due to differences in the rate of the heterogeneous oxidation of surface Fe(II) on the surfaces by dissolved oxygen. This particular reaction resulted in the formation of reactive oxygen species. Redox reactions of mixtures of As(III) and Cr(VI) in the presence of the two iron oxyhydroxides also were investigated. In this circumstance even in the absence of light, As(III) was oxidized to As(V) (~92% conversion) and Cr(VI) was reduced to Cr(III) if one of the small band gap semiconductor iron oxyhydroxide materials was present. As a comparison nanophase aluminum oxyhydroxide (an insulator) was exposed to As(III) and Cr(VI) under dark conditions. Under these experimental conditions far less As(III) oxidation and Cr(VI) reduction occurred (~50% conversion of As(III) to As(V)) compared to when iron oxyhydroxide was present. Furthermore, the exposure of the As(III)/Cr(VI)/ferrihydrite system to simulated solar light led to additional As(III) oxidation and Cr(VI) reduction (compared to dark conditions) while light had no effect on the As(III)/Cr(VI)/aluminum oxyhydroxide system. In general the results suggested that the semiconducting materials were able to drive the redox chemistry more efficiently due to facile surface mediated electron transfer from As(III) to Cr(VI).

## Water mass mixing in the Drake Passage during the last 40 kyrs

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The modern Southern Ocean is a key area for the global ocean circulation as wind-driven mixing, upwelling and redistribution of water masses in the Antarctic Circumpolar Current (ACC) all have a significant impact on the properties and flow patterns of global water masses. It has been suggested that the Southern Ocean plays a central role in oceanographic and climatic changes observed on glacial-interglacial timescales, in particular with respect to carbon sequestration between the deep ocean and the atmosphere.

For the purpose of unravelling Southern Ocean water mass mixing over the past ~40,000 years, the aragonitic skeletons of solitary deep-sea corals collected from two cruises on the Nathaniel B. Palmer to the Drake Passage are used as archives for seawater Nd isotopes. These corals were collected from water depths between 300 and 1750 m and have previously been directly dated by U-Th and analysed for their radiocarbon content.<sup>[1]</sup>

Neodymium was extracted from the wash solution of the U-series anion-exchange chemistry using a two-stage ion chromatography (RE-spec and Ln-spec resins). Subsequent analyses of Nd were performed as NdO<sup>+</sup> on a Triton TIMS using a TaF<sub>5</sub> activator on W filaments. This method yields within run uncertainties around 10 ppm (2σ SE) and external uncertainties around 20 ppm (2σ SD) for sample loads as small as a few ng of Nd.

Preliminary Nd isotope results on *D. dianthus*, *F. curvatum* and *B. malouinensis* specimen growing during the last 40 kyrs show significant variability at intermediate water depths (εNd of ~-5 to -8) and a more stable Nd isotopic composition in the lower water column (>1000m; εNd ~-8).

We will interpret our unique data set in the context of published glacial-interglacial radiocarbon results and inferred Southern Ocean water mass variability and ventilation rates.

[1] Burke & Robinson (2012), *Science* **335**, 557-561.