

## Iron-sulfur biomineralisation and arsenic mobility in acid sulfate wetlands

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Iron sulfide oxidation in drained coastal lowland soils liberates acidity, Fe and SO<sub>4</sub>, and leads to the accumulation of secondary Fe(III) minerals, such as schwertmannite (Fe<sub>8</sub>O<sub>8</sub>(OH)<sub>6</sub>SO<sub>4</sub>). Here we describe new insights on Fe-S biomineralisation and the associated mobility of As following the re-establishment of reducing conditions in reflooded acid sulfate wetlands. Our studies include controlled laboratory-based experiments on model systems as well as field-based observations on acid sulfate wetlands [1–3].

When subjected to prolonged soil waterlogging as a result of wetland re-establishment, the bacterial reduction of schwertmannite-derived Fe(III) releases abundant Fe<sup>2+</sup> (with up to 30 mM in affected groundwater) This process consumes acidity and generates alkalinity thereby driving increases in pH. At near-neutral pH, the presence of mM concentrations of Fe<sup>2+</sup> catalyses the very rapid and complete replacement of schwertmannite by goethite [1]. This replacement triggers a shift from a dominance of bacterial Fe(III)- reduction to a dominance of SO<sub>4</sub>-reduction. This shift can be explained by a partial equilibrium model of the thermodynamic favourability of Fe(III)- versus SO<sub>4</sub>-reduction. The onset of SO<sub>4</sub>-reduction leads to the accumulation of iron sulfide minerals, predominantly in the form of 5 – 30 nm nanoparticles of mackinawite (tetragonal FeS).

Schwertmannite in the initially drained acid-sulfate soil has a large capacity to sorb As(V), through exchange with structural SO<sub>4</sub>. Field-based observations on soil/porewater partitioning and laboratory-based sorption experiments demonstrate that several processes combine to cause significant arsenic desorption and consequent increases in pore-water As concentrations. These desorption processes are driven by increases in the porewater pH, bacterial reduction of As(V) to As(III) and replacement of schwertmannite by goethite via the Fe<sup>2+</sup>-catalysed pathway.

- [1] Burton *et al.* (2008a) *Geochim. Cosmochim. Acta* **72**, 4551-4564. [2] Burton *et al.* (2008b) *Chem Geol.* **253**, 64-73.  
[3] Johnston *et al.* (2009) *Geoderma* **149**, 335-346.

## Osmium isotope constraints on chemical heterogeneities in Indian mid-ocean ridge basalts

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The isotope compositions of many mid-ocean ridge basalts (MORB) from the Indian Ocean have led to the identification of a large scale heterogeneity relative to Pacific and Atlantic ocean MORB [1] (the so-called DUPAL anomaly). A number of studies have proposed that recycling of ancient subcontinental lithospheric mantle (SCLM) or sediment is responsible for this anomalous signature (e.g. [2]). In principle, the <sup>187</sup>Re-<sup>187</sup>Os isotope system should be highly sensitive to the occurrence of recycled SCLM or sediments in the mantle source, but previous work on Indian MORB has been taken to indicate the presence of continental crust rather than SCLM or sediments [3]. However, the low levels of Os in MORB makes these measurements particularly challenging, and also renders such samples prone to seawater contamination (cf. [4]).

This study presents Os isotope data for individual sulphides and host glasses from Indian Ocean MORB (possessing the range of Pb-Sr-Nd compositions associated with the DUPAL anomaly). Previously published data for Indian MORB [3] is shown to have been affected by an analytical artefact, and the radiogenic values observed do not exist. However, a range of Os isotope compositions are still seen in the data presented here. Relatively unradiogenic <sup>187</sup>Os/<sup>188</sup>Os values are associated with unradiogenic Nd and radiogenic Sr and Pb. The Os isotope composition precludes the presence of a significant proportion of continental crust or sediment, but is consistent with the presence of SCLM. Samples with radiogenic Os might be taken to indicate the presence of continental crust, however, covariations with δ<sup>11</sup>B suggest seawater contamination, and individual sulphides in such samples are always less radiogenic than their glass host. Overall, these data are consistent with the presence of subcontinental lithospheric mantle in the Indian MORB source, but as with N-MORB from the Atlantic and Pacific many samples are affected by seawater contamination [4].

- [1] Dupré & Allègre (1983) *Nature* **303**, 142-146.  
[2] Rehkämper & Hofmann (1997) *EPSL* **147**, 93-106.  
[3] Escrig *et al.* (2004) *Nature* **431**, 59-63. [4] Gannoun *et al.* (2007) *EPSL* **259**, 541-556.