

Bio-nano-engineering: From clean up to catalysis

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From the study of metal cycling in the environment, a range of microbially-mediated processes have been optimised to produce functional bionanominerals with useful properties including high catalytic, magnetic and light emitting activities. The nature of these processes offers the potential to biogenically 'nano-engineer' the mineral phases for specific applications. Two of these processes will be presented. Firstly, the use of iron (III)-reducing bacteria (e.g. *Geobacter sulfurreducens*) to convert contaminant Fe(III)-oxides present in acid mine drainage into catalytically active Fe(II)-bearing biomineral phases, which can then be used to mediate the transformation of reducible species including metals and organics (Fig. 1) [1]. Secondly, the biotransformation of selenium oxyanions, which accumulate to toxic micromolar concentrations in certain agriculturally significant soils, to produce selenide-containing semiconductor quantum dots [2, 3].

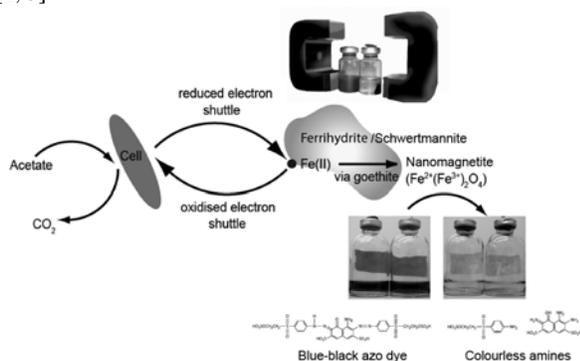


Figure 1: Production of bio-nano-magnetite, using *G. sulfurreducens*, and its use for reduction of organic azo dyes.

[1] Coker *et al.* (2008, accepted) *Am. Mineral.* [2] Pearce *et al.* (2008) *Nanotechnology* **19**, 1556023. [3] Yadav *et al.* (2008) *Biotechnology* **7**, 299-304.

Molybdenum isotope fractionation accompanying weathering, riverine transport and estuarine mixing

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The molybdenum (Mo) isotope system potentially provides a sensitive proxy for determining changes in the redox state of the oceans [1]. The application of this system is predicated on the assumption that the composition of continental input can be characterised from crustal rock types and remains constant. However, relatively little is known about the potential for Mo-isotope fractionation during continental weathering and riverine transport, or during estuarine mixing. Recent work [2] has shown that the $\delta^{98/95}\text{Mo}$ composition of global rivers predominantly varies between 0.1 ‰ and 1.4 ‰, and is consistently heavier than the average composition of the continental crust (~ 0.0 ‰; [3]). This difference is thought to reflect Mo-isotope fractionation caused by the adsorption of Mo onto Fe-Mn oxides during riverine transportation [2].

To understand the processes that control Mo-isotope fractionation during weathering we have determined the $\delta^{98/95}\text{Mo}$ composition for well-characterised rivers in Iceland that drain a mono-lithologic (basaltic) terrain. A systematic change in the dissolved Mo-isotope composition is observed along the river profile, with $\delta^{98/95}\text{Mo}$ values increasing from ~ 0 ‰ in glacial rivers (close to the source) to ~ 1 ‰ further downstream. These changes are directly correlated with the formation of Fe- and Mn-rich secondary mineral phases, and confirm that Mo-isotopes are fractionated during weathering.

Extension of the $\delta^{98/95}\text{Mo}$ profile into the estuarine environment reveals that the $\delta^{98/95}\text{Mo}$ composition of river water is modified in the estuarine mixing zone. $\delta^{98/95}\text{Mo}$ decreases by ~ 0.4 ‰ in the low salinity zone, where the concentrations of dissolved Mo and Fe are lower than predicted by simple mixing.

[1] C. R. Pearce *et al.* (2008) *Geology* **36**, 231-234. [2] C. Archer & D. Vance (2007) *GCA* **71**, A33. [3] C. Siebert *et al.* (2003) *EPSL* **211**, 159-171.