

Microbial and geochemical controls on bacteriogenic iron oxide formation and fate

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Bacteriogenic iron oxides (BIOS), composed of a mixture of poorly ordered hydrous ferric oxides and intact and partially decomposed bacterial cells, are thought to play an important part in regulating aqueous trace element concentrations. The geochemistry, mineralogy and microbiology of bacteriogenic iron oxides (BIOS) deposited in abundance at a circumneutral groundwater seep were examined in order to evaluate the biogeochemical controls on the redox cycle of iron in such environments. XRD and Fe K-edge EXAFS analysis indicated that the BIOS was composed primarily of 2-line ferrihydrite (60-70%) with minor amounts of lepidocrocite and goethite. Subsurface porewater profiles displayed an increase in dissolved equilibrium concentrations of Fe(II) at depth, also reflected in peaks in HCl-extractable sedimentary Fe(II), indicative of microbial Fe(III)-reduction. Interestingly, sediments collected from such depths revealed little mineralogical change from the surficial BIOS.

SEM images of the surface BIOS exhibited a proliferation of sheath structures characteristic of Fe(II)-oxidizing *Leptothrix* spp., while 16S rRNA profiling of the BIOS microbial community detected microorganisms closely associated to known Fe(II)-oxidizing (*Gallionella* spp., *Sideroxydans* spp.) and Fe(III)-reducing (*Rhodospirillum rubrum*, *Geothrix fermentans*) bacteria. Similar analysis of subsurface sediment collected from a Fe(III)-reducing horizon found a drop in the proportion of β -Proteobacteria, the phylum that hosts numerous Fe(II)-oxidizing genera, and a rise in the δ -Proteobacteria, home to many anaerobic metal-reducing prokaryotes. The presence of clones with close identity to bacteria intimately involved in complementary iron redox transformations in the same surficial BIOS sediment suggests that microbial redox cycling of iron may be tightly coupled in this, and other, shallow sedimentary environments.

Cadmium isotopic compositions and nutrient cycling in the Southern Ocean

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Cadmium (Cd) in conjunction with phosphate (PO₄) has been used as a paleoproxy for understanding nutrient cycling in historic oceans. However, our limited knowledge of Cd biogeochemical cycling in the oceans has led to many assumptions being used in the application of the Cd/PO₄ proxy. Cd isotopes offer the potential to provide new insights into the distribution and cycling of marine Cd than can be obtained through Cd concentration measurements alone, and may, in itself, prove to be a reliable proxy for past and present nutrient cycling.

New techniques for Cd isotopic measurement, utilizing double-spiking protocols combined with multiple-collector inductively coupled plasma mass spectrometry (MC-ICPMS) [1], have increased our ability to measure Cd isotopic fractionation. The simultaneous collection of multiple Cd isotopes results in high precision measurements with uncertainties at the 0.01%-level, allowing the resolution of very small isotopic fractionations that could not be previously explored. Research using these techniques has already shown a strong 0.1%-level biological fractionation of Cd in seawater, thought to be caused by phytoplankton uptake [2]. Using a Nu Instruments Nu Plasma MC-ICPMS at the University of Otago, we are applying Cd isotopic measurement to a diverse selection of seawater and marine biota samples from the Southern Ocean, in particular, samples from the Otago transect, found off the southeast coast of New Zealand. This transect passes through both subtropical (iron replete) and subantarctic (HNLC) water bodies. The differing chemistries of these two water masses allows us to examine changes in both the concentration and isotopic composition of surface water Cd and how these parameters are related spatially and seasonally. This information will have a direct bearing on the mechanisms controlling Cd uptake in the Southern Ocean and will help to determine and improve the effectiveness of the current Cd/PO₄ paleoproxy.

[1] Ripperger & Rehkamper (2007) *GCA* **71**, 631-642.

[2] Ripperger *et al.* (2007) *EPSL* **261**, 670-684.