

The role of Fe(III) (hydr)oxide structure in controlling the kinetics and products of biogenic sulfide oxidation in low sulfate media with *Desulfovibrio* sp.

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Iron (hydr)oxides are a diverse groups of minerals which exist in a spectrum of crystallinities and subsequent bioavailabilities; ranging from ferrihydrite (poorly crystalline) to hematite (well crystalline). While the organisms responsible for the reduction of the poorly crystalline phase ferrihydrite have been well documented (*Geobacter* and *Shewanella*), these model dissimilatory iron-reducing microorganisms (DIRMs) show diminished abilities to reduce the more crystalline Fe(III) (hydr)oxide phases, goethite and hematite. In agreement with this, we have previously shown through enrichment experiments that these model DIRMs are enriched on goethite and hematite yet their presence does not correlate with reduction of these more crystalline phases. Instead, within Fe(III)-reducing enrichments supplemented with lactate, the reduction of goethite and hematite was detected in significant amounts (30–60%) and appeared to be a function of organisms associated with sulfate reduction, *Desulfovibrio putialis* and *Desulfovibrio vulgaris*. Media specific thermodynamic calculations along with enrichment data suggest that sulfate reduction may dominate and control Fe(III) reduction when more recalcitrant Fe(III) phases are provided as the terminal electron acceptor.

Interestingly, sulfate concentrations (200 μ M) and subsequent sulfide oxidation alone could not account for the amount of Fe(III) reduction observed, without the cycling of sulfur. Consequently, the data suggest that either *Desulfovibrio* directly participates in the reduction of goethite and hematite or catalytic amounts of sulfur are being cycled multiple times.

In order to further elucidate the mechanisms of Fe(III) reduction by sulfate-reducing bacteria, pure culture Fe(III)-reducing experiments with *Desulfovibrio* species were conducted using three Fe(III) (hydr)oxides (ferrihydrite, goethite, hematite) and varying freshwater sulfate concentrations (0–800 μ M). In order to track how intermediate Fe and S species varied as a function of Fe(III) (hydr)oxide type and S:Fe ratio, a variety of spectroscopic techniques were coupled with voltammetric microelectrodes. This aqueous data was combined with S and Fe EXAFS to further elucidate the products of sulfide oxidation and Fe(III) reduction. These findings will further illuminate how sulfate reduction kinetics in low-sulfate waters controls Fe(III) reduction of structurally diverse Fe(III) (hydr)oxides. In addition, the role that Fe(III) (hydr)oxide mineralogy and S:Fe ratios play in controlling the stoichiometry of different oxidized S species will be highlighted.

Did life turn the global weathering thermostat back up after turning it down?

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It is now widely accepted that plants (and their associated soil communities) amplify the weathering of silicate rocks, thus accelerating the drawdown of atmospheric CO₂ and ultimately leading to a lower stable state for CO₂ and global temperature. In metaphorical terms, land life has turned down the dial on the global weathering thermostat. Indeed it may have done so several times.

This is a neat way of explaining episodes of global cooling. Most notably, the rise of rooted vascular plants has been linked to the Late Devonian and Permo-Carboniferous glaciations. Recently, we suggested that the earlier rise of the first non-vascular plants could have been responsible for the Late Ordovician glaciations [1]. More speculatively, we have argued that lichen-like land colonisers could explain the episode of extreme glaciations in the Neoproterozoic [2]. Others extend the argument even further back in time [3].

But why were these cold episodes in Earth history transient ones? If the effects of life on weathering persisted each time, one would expect it to have remained cold. One can appeal to a steadily brightening Sun to warm things up again, but that is far too slow a process to explain the rather striking returns to warmer conditions. Often geological mechanisms are invoked to explain recovery from the cold. But it would be rather surprising if every time a biological innovation cooled the planet, some tens of millions of years later a change in geological forcing acted to warm it up again.

Here I suggest that biotic increases in weathering are naturally followed by biotic decreases in weathering. The key mechanism is a transition from weathering-fuelled phases of land colonisation to recycling-based ecosystems. Initially, new colonisers of the land must weather their rocky substrate to extract essential elements for growth, but as that substrate becomes exhausted and soils become established, ecosystems switch to internal recycling of essential elements. Also, by stabilising landscapes and suppressing erosion, vegetation and soils further suppress chemical weathering.

This could provide an intrinsic mechanism by which biotically-driven cooling of the planet would be followed by a relaxation back towards warmer conditions. In other words; perhaps after turning down the weathering thermostat, life turns it back up again.

[1] Lenton *et al.* (2012) *Nature Geoscience* **5**, 86–89.

[2] Lenton & Watson (2004) *GRL* **31**, L05202.

[3] Schwartzman & Volk (1989) *Nature* **340**, 457–460.