The quantitative contribution of oxygenic photosynthesis to Fe(II) oxidation in Precambrian oceans

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Evidence for oxidation of Fe(II) and deposition of Fe(III)-bearing minerals in anoxic or stratified Precambrian oceans has received support from decades of sedimentological and geochemical investigation of Banded Iron Formations (BIF). However, the exact mechanisms by which Fe(II) was oxidized and stabilized in anoxic sediments remain equivocal. The oxidation of Fe(II) by abiotic reaction with O_2 produced by oxygenic photosynthetic cyanobacteria is consistent with evidence for an iron chemocline in some Precambrian BIF basins. However, if oxygenic photosynthesis oxidized Fe in the Archean, O_2 release to the atmosphere must have been minimal, consistent with geochemical evidence for an anoxic atmosphere prior to 2.3 Ga.

We evaluate the hypothesis that Fe(II) oxidation and deposition was mediated by O_2 with laboratory experiments using *Synechococcus* PCC 7002 to represent an early marine cyanobacterium [1]. Our initial results confirm that this strain can grow in Fe(II) concentrations up to 5 mM. The kinetics of Fe(II) oxidation are consistent with an abiotic reaction between Fe(II) and O_2 and not via direct use of electrons from Fe(II) in photosynthesis. We also measured the isotopic fractionation factor between aqueous Fe(II) and precipitated Fe(III) during growth of *Synechococcus* PCC 7002 with Fe(II), which is similar to fractionation factors in abiotic experiments. Microscopic and spectroscopic analysis of the cell-mineral aggregates also inform the location of Fe(II) oxidation and the speciation, mineralogy and spatial relationship of iron to carbon in the resulting precipitates. Our efforts are now focused on quantifying the rates of O_2 production and Fe deposition in a laboratory-scale model of a ferruginous water column where Fe(II) upwells into an engineered photic zone. Our intent is that these results will provide a mechanistic and quantitative framework for evaluating the geochemical consequences of perhaps life's greatest metabolic innovation.

[1]Blank and Sánchez-Baracaldo (2010) *Geobiology*, **8**, 1-23.

Size-dependent reactivity of magnetite nanoparticles: A bridge between lab and field investigations

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Research on nanoparticles has exploded in recent years as we have begun to understand the extensive role these materials play in natural systems as well as their potential benefits and risks to human society. However, the very nature of nanoparticles makes them challenging to study, particularly in a field setting. As a result, many questions remain to be to answered concerning how nanoparticles behave in a natural environment and how accurately laboratory results reflect reactions that occur in the field.

In this investigation magnetite nanoparticles with average diameters of 6 nm, 44 nm and 90 nm were synthesized and throughly characterized. The nanoparticles were emplaced in the anoxic groundwater zone of the leachate plume in the subsurface of the USGS Norman Landfill Site with custom-built TEM grid-holders. Laboratory analog experiments were also conducted using nanoparticles and synthetic groundwater modeled on the chemistry of the groundwater from the landfill site, but omitted DOC. Finally, a series of magnetite-chromate adsorption experiments was conducted with varying amounts of DOC added to investigate the impact of organics on the surface reactivity of the magnetite nanoparticles.

The field investigation revealed that a thin coating of organics developed on the particles surfaces that occluded the particles from the groundwater and inhibited dissolution. This is supported by geochemical models indicating that magnetite is not thermodynamically stable under the given chemical conditions and by the laboratory analogs which provided evidence of magnetite dissolution in the absence of organics. The chromate adsorption experiments showed that DOC concentrations as low as 1 mg/L can impact the surface reactivity of magnetite even when an excess of mineral surface area is present.

The results of this investigation revealed that under the field conditions, magnetite dissolution decreased as particle size decreased, while this trend was reversed in the laboratory experiments. Adsorption experiments indicate that this reversal is likely due to dissolved and particulate organics. Together, these experiments show that organics play a significant role in the surface reactivity of nanoscale minerals and remain integrally important to understanding the environmental fate of nanomaterials.

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