

Coupled cycling of iron and bioessential trace-metals

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In oxic soils and sediments ferrous iron is usually oxidised and precipitated as nanoparticulate and poorly crystalline iron(III) (hydr)oxides. In natural environments these secondary minerals are often found spatially associated with bacteria. This spatial association is the result of both microbial metabolic activity (e.g., the microbially mediated oxidation of Fe(II)) and the precipitation of iron (hydr)oxides in the presence of non-Fe metabolizing bacteria. These processes give rise to bacterially associated iron (hydr)oxides that are composite solids, consisting of iron (hydr)oxide intermixed with intact and partially degraded bacterial cells. By analogy with isolated iron (hydr)oxides and bacteria, these composite phases are highly reactive towards dissolved metal ions, and their formation and cycling is thus tightly coupled to the biogeochemistry of a number of essential trace-metals. Importantly, the intermixing of iron (hydr)oxides with bacterial cells can considerably alter the surface properties of the composite particles, compared to the isolated end-member phases. This means that in environments where bacterially associated iron (hydr)oxides make up a significant proportion of the reactive iron, trace-metal concentrations and isotopic compositions are often difficult to predict and explain.

Here we present new results from an on-going study to determine the role of iron minerals in the biogeochemical cycling of essential trace-metals, in both modern and ancient environments. We will focus on the molecular mechanisms of metal sorption to bacterially associated ferrihydrite, and how these can be used to predict and explain metal behaviours in simple composite - electrolyte solutions. Specifically we will show that, compared to abiotic ferrihydrite, the presence of carboxyl groups on the bacterial fraction of the composites significantly modifies Cu and Ni sorption behaviour and thus the mobility and cycling of these bioessential metals in both freshwater and marine environments.