# Consumption-regeneration cycle of micronutrients and their isotopes in seawater

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The vertical cycling of micronutrients in seawater is well understood qualitatively, following early work by Boyle, Bruland and others. However, more quantitative models of the consumption-regeneration process are sorely needed in order to evaluate concentration profiles, and relate these to stable isotope fractionation of essential micronutrients, such as Cd, Zn, Fe and Ni, during biological utilization. Here, we have derived a mathematical formulation of micronutrient-limited cycling in the water column, where nutrients are consumed by a single phytoplankton species in the mixed layer (photic zone), and are regenerated/remineralized at depth by oxidation of sinking organic matter. This has been done within the framework of a simple 1-D advection-diffusion model of the water column, parameterized in terms of the upwelling velocity $w$ and diapycnal mixing (eddy diffusion) coefficient $\kappa$. Simple expressions are derived for the micronutrient profiles at steady state, along with the corresponding stable isotope effects. It is shown how the depth profiles are related to those of conservative tracers (S, T) as well as AOU.

The rate of biological uptake of micronutrient in the mixed layer is assumed to follow Michaelis-Menten (Monod) kinetics. At steady state, the micronutrient consumption rate by the phytoplankton crop is balanced by the regeneration rate due to crop mortality. Interestingly, the micronutrient concentration in the mixed layer is governed by this kinetic balance and, paradoxically, not by the rate of supply of micronutrient from below. The biomass size in the mixed layer and the absolute primary production does depend on the micronutrient influx, however. This simple conceptual model suggests that there exists a self-regulating limiting micronutrient concentration for a given phytoplankton species. In reality, external factors will play a role too; these include light, which influences growth rates, and zooplankton grazing and removal from the photic zone by eddy diffusion which adversely affect mortality, as well as the mixed layer depth. Such effects, along with nutrient co-limitation and aeolian input, can easily be incorporated to yield a more realistic micronutrient cycling model.

# Evaluating the role of microscopic pyrite for budgets of vital metals in Precambrian Carbonate

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The measurement of redox sensitive trace metal abundances and their stable isotope compositions is a popular tool for reconstructing the Precambrian environment. Of all Precambrian sediments, carbonates hold the best promise for reconstruction because their sedimentological origin can be inferred relative to modern analogues (e.g. microbial carbonates, abiotic carbonates, dolomites, etc.). The redox state of ancient seawater can be reconstructed from the REE pattern in Precambrian carbonates as can be connectivity to the open ocean via Sr isotopes. It is thus tempting to apply transition metal tools to well studied Precambrian carbonates.

Here we report on trace metal distribution in previously characterised carbonates of Precambrian age. Specifically our study investigates the role of microscopic to sub-microscopic sulphides (mainly pyrite) that are often encount-ered in microbial carbonates. A first-order mass balance was carried out to establish how much of the metal found in the bulk rock is actually hosted in pyrite vs. carbonate. Pyrite is a dominant host of Cu but insignificant in its V and Zn content.

Apart from mass balance, a key question is whether the pyrite incorporates its metal inventory from the microbial mats, genetically older carbonates or diagenetic fluids. This was investiagted with metal profiling across spheroid pyrite of sulphate reducing bacterial origin (SRBO). For the ele-ments V, Co, Ni, As, Mo, Pb and Bi, the profiles showed concentric zonations. In the case of V, the bell-shape profile indicates uptake from surrounding rock matrix but for Co, Ni, As, Mo, Pb and Bi, the W-shaped profiles suggest that metal was likely sourced from pore water (as was S). In this latter case, it is likely that the geochemistry of the carbonate itself reflects the marine ambient condition whereas the sulphide chemistry might reflect the diagenetic environment and erro-neous conclusions could be drawn from combining the two sources of information when performing bulk rock analysis.

Finally, previous sulphur isotope studies have highlighted a variety of possible origins for the ubiquitous if minute sul-phides. Our study also aimed to investigate whether one can distinguish pyrites of different origins (i.e. biogenic vs. late diagenetic forms) based on their trace metal abundances. Preliminary anlysis of the dataset suggests that small grained matrix pyrite is characterised by enrichment in Mn, Co, Ni and As wheras pyrite of SRBO is depleted in these metals.