

Micron-scale imaging of the distribution of bio-available metals (Fe, Zn, Ni, Co) in modern and ancient microbial mats

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Metals are essential micronutrients for all living organisms since they are used as structural elements or as catalytic centers in enzymes. Some, like Fe, are universally used, while others, such as Ni or Co, have a more limited biological function. Yet, they can be associated with enzymes that catalyze specific types of metabolism (e.g. N-assimilation). The evolution of these metalloenzymes likely reflects the variable paleo-geochemistry of metals throughout Earth history. However, in addition to direct uptake for biological use, metals can be incorporated in bacterial exopolymer (EPS) constituting the biofilm matrix in microbial mats. The high chemical reactivity of such surfaces is ideal for metal cation scavenging, and thus leads to metal enrichment during diagenesis. Therefore, in order to use metals as tracers of past biological activity in the ancient rock record, knowledge of the mechanisms of metal uptake in living and diagenetically-modified microbial mats is required.

Here we present a study of the distribution of metals in modern and ancient stromatolites. These structures, ubiquitous in the rock record for the last 3.5Ga, have the potential to preserve biosignatures and are an excellent target for studies of metal tracers. We focused our study on 2.7Ga old stromatolites from the Tumbiana Formation (Western Australia) and on three modern stromatolites from the Bahamas (Storr's Lake, Big Pond and Highborne Cay).

In order to detect metal variation in the laminated organic fraction of stromatolite structures we used synchrotron-based scanning X-ray fluorescence technique. It was applied at the X-ray fluorescence microscopy line of the Australian Synchrotron. We used the Maia detector which consists of 384 detectors-elements. This permitted to perform multielemental imaging of ~cm sample areas with 2µm spatial resolution.

In modern stromatolites organic layers are enriched in metal with a general distribution of Fe, Zn >> Ni and Co. This enrichment becomes higher with increased degree of diagenesis. Indeed, the top of Big Pond's stromatolite contains high organic content linked to a low Fe content whereas the bottom shows lower organic content (diagenetic effect) and higher Fe content. Modern stromatolites, then, show clear evidence of early diagenesis where metals such as Fe, Zn display strong affinity for the organic layers. The ancient stromatolites from the Tumbiana Formation also show a strong metal enrichment in the organic fractions. In organic layers, Fe > Ni, Co > As, V, Ti > Zn are presents. Disseminated organic globules also show this general metal distribution. This could be evidence for pervasive fluid diagenesis in organic layers and of the preservation of the early diagenesis in organic globules. The high metal content in these samples confirms the strong affinity for organic fractions incorporating more and more type of metals with time.

Experimentally Determined Fe Isotope Fractionation between Metal and Silicate

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There has been much work done on quantifying the iron isotopic fractionation of natural samples but the mechanism(s) responsible for the measured fractionations is still largely unknown. Iron is not straightforward to understand because of its differing redox states and compatibility constraints. In this study we aim to understand the mechanism(s) responsible for iron isotope fractionation by performing high pressure and temperature experiments. We have varied the composition, temperature, and duration of the experiments. In particular we have examined the iron isotopic fractionation between metal and silicate with and without the influence of sulfur to represent a possible core formation model for Earth and Mars.

Experiments were conducted in a ½ inch piston cylinder apparatus at temperatures ranging from 1600°C – 1800°C at 1 GPa and for times ranging from 5 to 240 minutes. The run products were characterized, mechanically separated, dissolved and purified by anion exchange before introduction into a Nu Plasma II MC-ICPMS for isotopic analyses. It is crucial in these experiments to prove isotopic equilibrium so microprobe analyses, the three-isotope technique, and textures of run products were all utilized. Of the 50+ experiments conducted so far, fewer than 10% have passed all the requirements for isotopic equilibrium. However, in the experiments in which we are confident that equilibrium was achieved we find that there is a small but resolvable equilibrium iron isotopic fractionation factor between metal and silicate at high temperature, with the metal phase more enriched in ⁵⁷Fe/⁵⁴Fe than coexisting silicate.

Determining whether there is an equilibrium iron isotope fractionation between metal and silicate is central to understanding the Fe isotope signatures found within different meteorites and planetary bodies. The initial set of experiments duplicate the magnitude and direction of data from pallasite meteorites with higher ⁵⁷Fe/⁵⁴Fe in the metal than in coexisting olivine. And extrapolation of our results to the temperature of the Earth during core formation (~3000 K) results in an iron isotopic fractionation of 0.08‰ between the core and mantle. By adding sulfur to the second set of experiments we can test how sensitive the iron isotopic fractionation is to a change in the surrounding ions as well as provide an analog to Mars.