Iron isotope signatures in magnetite formed by marine invertebrates

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Marine organisms can be powerful recorders of past environmental conditions. Fe isotopic signatures in marine organisms might be used to infer paleoenvironmental conditions and/or biological processes. Chitons - a type of marine mollusk - are a remarkable group of marine invertebrates that accumulate significant amounts of Fe. They produce radula (teeth) that are coated in biomineralized magnetite, enabling them to graze on algae living on the surface of rocks [1]. As a result, their Fe isotopic signatures might be expected to provide an efficient tracer of ambient oceanic conditions and biogeochemical cycling.

Here, we examine Fe isotopes in modern marine chitons collected from different locations in the Atlantic and Pacific oceans to assess the range of isotopic values that might be encountered, and whether or not the isotopic signatures reflect seawater values. Furthermore, by comparing two species that have very different feeding habits but collected from the same location, we attempt to isolate the possible impact of diet on isotopic signatures.

The Fe isotopic analyses were performed on a total sample set of 17 individual chitons using a *Neptune* MC-ICP-MS at GFZ Potsdam. δ^{56}Fe values (relative to IRMM-014) cover a range from -1.89 to +0.12 (±0.03‰ external reproducibility in δ^{56}Fe). All analysed teeth show negative δ^{56}Fe values, some even more negative than reported for oceanic Fe(II). Strikingly, two different species from Port Orchard (Washington, USA) have distinct isotopic signatures. The teeth of the species feeding on red algae (*Tonicella lineata*) show a tight range in δ^{56}Fe of -0.58±0.12(1σ), while *Mopalia muscosa*, which feeds primarily on green algae, cover a range in δ^{56}Fe from -1.89 to -0.92.

The results suggest that although chitons do not record the ambient seawater Fe isotope signature, they could provide a potential tracer of Fe biogeochemical cycling. The distinct Fe isotope signatures of the two species from the same locality might be a result of the different ways in which magnetite is biomineralized (presumably Fe is being taken up as Fe(II) in the organisms); alternatively, the chitons may simply be inheriting the signatures from the different algal food sources.

[1] Lowenstam and Weiner (1989) *On Biomineralization. Oxford University Press.*

Mineral reactions in a porous world: calcite dissolution experiments revisited

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The dissolution of calcite influences processes as diverse as the evolution of karst landscapes and the response of carbonate-hosted oil reservoirs to enhanced recovery techniques. Although much research has focused on determining the reaction kinetics of calcite dissolution from individual crystals, it is often assumed that the empirical rate laws derived in such studies can be used in a straightforward manner to describe calcite dissolution in porous and fractured rocks. In this study we challenge this assumption by using atomic force microscopy (AFM) to study the dissolution of natural porous carbonate substrates. We demonstrate how AFM can be used to estimate in situ reaction rates and identify dissolution mechanisms during reactive transport in porous media. Critically, in advective systems we observe a high degree of spatial heterogeneity that can be directly related to the porous structure. The precise mechanism behind pore-scale heterogeneous reaction rates is discussed, and we present a 3D numerical model that accurately reproduces the observed dissolution patterns on a porous surface. We also discuss the implications for current continuum descriptions of reactive transport, and how they might be modified to incorporate pore-scale heterogeneity.