Ca-Isotopes in recent and ancient cements and microbial precipitates

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We analyzed the calcium isotopic composition of recent and fossil marine cements and microbial mats to compare with the published record that is based on brachiopod shells.

The dataset consists of (1) Recent aragonitic cement, aragonitic ooids and Holocene microbialites, and (2) Fossil botryoidal (primarily aragonitic, now calcitic) cements, radiaxial fibrous cements and microbial mats, all precipitated in close contact with seawater. Fossil samples are from the Late Archaean, Devonian, Carboniferous and Cretaceous.

The calcium isotope values of recent aragonite cements and ooids are light and plot close to published values of experimentally precipitated inorganic aragonite. Holocene microbialites – used here as a substitute for calcite cement - are heavier and plot closer to seawater values as expected from experimental results.

Values obtained from calcium isotopic analysis of Late Archaean and Phanerozoic cements and microbial mats plot within the same range. They are systematically heavier and show a smaller scatter than published Phanerozoic values of brachiopod shells.

Secular variations in seawater composition, as formerly suggested based on calcium isotopic composition of Phanerozoic brachiopod shells, are not reflected in our record based on marine cements.

The new dataset from marine cements and microbialites provide intriguing answers that call for more questions on secular variations recorded in organic versus inorganic precipitates.

The history of open ocean seawater stable Fe isotopes from the carbonate record

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We have recently suggested that microbial carbonates, including stromatolites, could potentially serve as an Fe isotope proxy [1] for seawater. Amongst the evidence provided was the observation that modern microbial carbonates contain virtually unfractionated Fe. New data published for dissolved Fe in Atlantic seawater [2] also appear to indicate unfractionated modern seawater Fe. If there is indeed insignificant isotopic fractionation between ambient seawater and Fe incorporated into microbially induced carbonates (both into the lattice and as interstitial hydr-oxides), they may serve as a faithful recorder of seawater Fe. Microbial carbonate offers considerable advantages over more widely used archives to date [3], which record bottom water (BIF, shales) or diagenesis (sulphides). Microbial carbonates are possibly the only widely available archives of truly open ocean water and their major and trace element chemistry as well as Sr-isotope record can be used to screen against diagenetic overprint and to verify precipitation in unrestricted open ocean water.

Our initial survey of microbial carbonates throughout Earth history shows an Fe isotope evolution that mimics that of many other proxies: namely, Neoarchean stromatolitic carbonates from the Hamersley Group, Western Australia, and of the Campbellrand Formation, Kapvaal craton, contain uniquely light Fe (δ^{56}Fe as low as -2.5‰), while older Archean stromatolites and Paleozoic as well as Mesozoic microbial limestones mostly range between 0 and -1‰ δ^{56}Fe.

Unless future studies will identify lighter Fe in older Archean microbial carbonates, the sum of these new records and the chemical sediments published to date [3] provides evidence for the presence of a prominent reservoir of light seawater iron in the ferrous form at the termination of the Archean, time equivalent with the greatest extent of recorded Δ^{33}S MIF [4,5]. In the post 2.4 Ga era, microbial carbonates could be overwhelmed by interstitial ferric Fe from (hydr)oxides.

[1] von Blanckenburg *et al*. (2008), *Chem. Geol*. 249. [2] Lacan *et al.* (2008*) Geophys. Res. Lett.* 35. [3] Johnson *et al*. (2008), *Annual Rev. Earth Planet. Sci* 36,. [4] Ono *et al.* (2003) *EPSL* 213. [5] Kamber & Whitehouse (2007), *Geobiology* 5..