

Strontium isotope fractionation in scleractinian corals

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Preferentially lighter strontium isotopes ($\delta^{88/86}\text{Sr}_{\text{carbonates}}$ (NBS987) ~ 0.15 to 0.25 ‰) are taken up from seawater ($\delta^{88/86}\text{Sr}_{\text{seawater}}$: ~ 0.39 ‰) by marine calcifiers during calcium carbonate precipitation. A temperature sensitivity of Sr isotope fractionation has been reported [1,2,3]. However the published results are discrepant and enigmatic.

In order to shed light into the temperature dependency of strontium isotope fractionation, we conducted inorganic precipitation experiments of aragonite, and investigated cultured and natural modern corals. The aim of the study is to enhance our understanding of strontium isotope fractionation mechanisms for biocalcification of corals and for the applicability of $\delta^{88/86}\text{Sr}$ as a temperature proxy. Strontium isotope distribution was measured by TIMS using the double spike method [4]. In addition to strontium isotope analyses we determined elemental ratios like Sr/Ca.

Preliminary results indicate seasonal $\delta^{88/86}\text{Sr}$ variations in modern corals which are positively correlated with the Sr/Ca ratios and hence, inversely correlated with temperature. The seasonal amplitude in the Sr/Ca ratios is 0.43 mmol/mol and corresponds to a temperature variation of $\sim 7^\circ\text{C}$. The seasonal variation in $\delta^{88/86}\text{Sr}$ in the same coral is 0.04‰. The positive correlation between $\delta^{88/86}\text{Sr}$ and Sr/Ca is not in accordance with the Rayleigh distillation model for Sr/Ca ratios in corals that was proposed by Gaetani *et al.* [4].

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Modeling glass alteration layers

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Glasses major constituents interact chemically within the amorphous layers resulting from glass alteration in water. These interactions determine the composition, the dissolution kinetic and the apparent solubility of the amorphous layers as well as their potential passivating properties with respect to the underlying glass. The knowledge of these interactions is required to predict concentrations in solution, pH and eventually glass alteration rates. However, these amorphous layers are complex solids resulting both from initial glass structure and recondensation processes, constantly reorganizing as solution composition changes. Identifying the main phenomenologies is required for modeling the amorphous layers with a number of parameters consistent with experimentally accessible data and geochemical modeling tools. These phenomenologies were translated in modeling hypothesis which are part of a model called GRAAL [1,2].

GRAAL model is implemented within a geochemistry and transport code called HYTEC [3]. Therefore, it can account for the thickness and composition of the amorphous layer whatever the time and position in space of a glass under alteration. Chemical description within GRAAL has been recently improved thanks to 24 experiments relative to six simple glasses containing Si, B, Na, Ca, Al and Zr, altered for months at four different neutral to alkaline pH [4]. Ten new modeling hypothesis were done for describing these six elements chemical interactions in the amorphous layer. One example: orthosilicic acid activity in solution is significantly lower than amorphous silica solubility only if enough aluminum is also available. Therefore a silica-aluminum rich end-member is taken into account to model the amorphous layer whereas Ca, Na, B and even Zr interactions with Si can be neglected to account for Si activity in solutions (in our experimental conditions at least).

We aim here at sharing both the success and limits of GRAAL model fundamental hypothesis and we will try to demonstrate the usefulness of the approach.

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