Calcium Isotope Fractionation of Inorganic and Biogenic Calcium Carbonates

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Introduction

It has been shown by Gussone et al. (2013, 2005) that calcium isotope fractionation in inorganic and biogenic carbonate precipitates depends on mineralogy. Aragonite is depleted by about 0.7‰ with respect to inorganic calcium in aragonitic skeletons of brachio pods, which is in agreement with the temperature control of the Ca isotopic composition. However, the fractionation of these "anomalous" calcium isotopes in inorganic aragonite is relatively small and does not show a slope with temperature (Gussone et al. 2005).

Calcification in Open Systems

Calcification in Confined Systems

Biological Ca Isotope Fractionation

Calcium isotope ratios of biogenic carbonate precipitates are controlled by a variety of factors, including the chemistry of the calcifying fluid, which is influenced by the temperature, salinity, and pH of the seawater. The temperature dependence of the Ca isotope ratio in biological calcification is typically smaller than that in inorganic calcification, and is often positive (0.015‰/°C).

Quantitative Model for Inorganic Ca Isotope Fractionation

Rate Dependent Fractionation

Crystal Fluid

Fit to Measured Data

It has been shown that Lemairechand et al. (2004) and Gussone et al. (2005) that Ca isotopic fractionation during precipitation in CaCO3 is rate dependent. Isotopically fractionated calcium with unshifted calcium is an interface layer between fluid and crystal. The faster the precipitation, the less is available for equilibrium. With increasing crystal growth rate, the interface layer becomes thinner and more calcium is taken into the crystal. An accurate fractionation factor between the mixing of unshifted and isotopically fractionated Ca in a function of precipitation rate. The fraction of fractionated Ca is dependent on the time available for equilibrium (t).

Conclusions

Calcium isotope fractionation of inorganic and biogenic CaCO3 precipitation in open systems is well explained by a rate-dependent equilibrium mechanism (Lemairechand et al. 2004) and Gussone et al. (2005). Carbonate precipitation in the confined calcification compartments of corals and sponges fractionates calcium isotopes by a different mechanism. Fractionation in CaCO3 is -1.1‰ at 25°C and is probably independent of mineralogy and precipitation rate. Temperature dependence is similar as for inorganic precipitation.

The latter fractionation most likely occurs during the passage of Ca ions through biological membranes (Gussone et al. 2006). This biological fractionation mechanism may be widespread among marine carbonate producers, especially among organisms with high CaCO3 precipitation rates.

References


References


