Ca Isotope Fractionation in Inorganic, Biologically Induced and Biologically Controlled Calcium Carbonates

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Introduction

It has been shown by Gussone et al. (2004, 2005) that calcium isotope fractionation in inorganic and simple biological calcification systems is characterized by a rate-dependent fractionation that varies by about 0.8‰ with respect to calcium, i.e., fluorite values, with respect to water decreases from calcite to aragonite. This fractionation has been observed in experimental inorganic precipitates in seawater, marine calcans and in “simple” biological calcite. Temperature dependences of isotope fractionation is similar to calcium carbonate (0.017‰/°C). It can be explained by the temperature control on the CΔ, chemistry, which controls Ca/Ca precipitation rate (Lemarchand et al. 2004). We found several groups of organisms producing calcification that deviate from this simple isotope fractionation scheme. Several species of echinoderms, shellfish, mollusks, and the aragonitic parts of brachiopods are about 4‰ enriched in 44Ca with respect to inorganic aragonite. Calcareous species of Cretaceous corals are 1.2‰ depleted in 44Ca compared to “simple” biological calcite. Temperature dependences of these “anomalous” carbonate isotope compositions are characterized by a temperature independent fractionation (Gussone et al. 2006) and temperature dependent fractionation rates and in confined organism compartments. We propose that these biological fractionations are characteristic of calcification processes that occur in the growth rates and even in body compartments. We propose that these biological fractionations are characteristic of calcification processes that occur in the growth rates and even in body compartments. We propose that these biological fractionations are characteristic of calcification processes that occur in the growth rates and even in body compartments.

Model for Inorganic Ca Isotope Fractionation

Rate Dependent Fractionation

\[ \frac{\delta^{44}Ca_{\text{crystal}}}{\delta^{44}Ca_{\text{fluid}}} = \frac{x}{1-x} \frac{\delta^{44}Ca_{\text{crystal}}}{\delta^{44}Ca_{\text{fluid}}} \]

where \( x = \text{fraction of equilibrated Ca} \)

\[ \delta^{44}Ca_{\text{crystal}} = \text{Ca isotope composition of crystal} \]

\[ \delta^{44}Ca_{\text{fluid}} = \text{Ca isotope composition of fluid} \]

\[ \delta^{44}Ca_{\text{crystal}} = \text{Fluid Ca isotope composition} \]

Fitting to Measured Data

The rate dependent calcium isotope fractionation model can explain the observed fractionation of inorganic and simple biological calcification. However, as shown in the diagram to the left, neither the curve values nor the Mollusca calcium values can be a consequence of a fractionation effects. Observed calcium isotope fractionation is much too strong for the very high fractionation rates that were observed in simple calcification systems (Böhm et al. 2006). Similar fractionation was observed in mollusc calcite (Gussone et al. 2006) and in coccolith aragonite and inorganic aragonite (Gussone et al. 2005). The rate dependent calcium isotope fractionation model can explain the observed fractionation of inorganic and simple biological calcification. However, as shown in the diagram to the left, neither the curve values nor the Mollusca calcium values can be a consequence of a fractionation effects. Observed calcium isotope fractionation is much too strong for the very high fractionation rates that were observed in simple calcification systems (Böhm et al. 2006). Similar fractionation was observed in mollusc calcite (Gussone et al. 2006) and in coccolith aragonite and inorganic aragonite (Gussone et al. 2005).

References

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