Ca isotope fractionation of inorganic, biologically induced and biologically controlled calcium carbonates

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It has been shown recently (Gussone et al., 2005) that calcium isotope fractionation in inorganic and simple biogenic precipitates depends on mineralogy. Aragonite is depleted by about 0.7 permill with respect to calcite, i.e. fractionation with respect to seawater increases from calcite to aragonite. This fractionation has been observed in experimental inorganic precipitates, in early marine cements and in simple biogenic carbonates (e.g. sclerosponges). The weak temperature dependence of isotope fractionation is similar in calcites and aragonites (0.015 permill/K) and can be explained by the temperature-control on the CO_3^{2-} chemistry (Lemarchand et al. 2004).

The Ca isotope fractionation of calcite (Lemarchand et al., 2004) and aragonite (Gussone et al., 2005) depends on precipitation rates. At higher precipitation rates increasingly more unfractionated Ca is incorporated into the crystal and consequently Ca isotopes are less fractionated. Following theoretical considerations, the Ca isotope fractionation can be modeled as an exponential function of growth rate. Fitting this model to measured data we find an equilibration time of about 100 s and equilibrium fractionation values for aragonite and calcite of -1.1 permill and -1.7 permill, respectively. At high precipitation rates the fractionation between aragonite and calcite decreases and becomes negligible ($<$0.1 permill) above $10^{3.5}$ μmol/m2/h. This is within the typical range of reef coral calcification rates (10^{4} μmol/m2/h). In fact, measured Ca isotope values of reef corals are significantly higher than low-rate aragonite values (e.g. from sclerosponges). On the other hand the coral d44/40Ca values

are still much lower than predicted by the high calcification rates.

We found several other organisms producing carbonates that deviate from the "low-rate" isotope fractionation values: A benthic gastropod shell and the aragonitic part of a Mytilus bivalve are about 0.4 permill enriched in 44Ca with respect to "low-rate" aragonite. Temperature dependencies of these "anomalous" carbonates, however, show the common slope (0.015 permill/K).

In the fast growing skeletons of these organisms the observed fractionation is much stronger than predicted by the precipitation rate model. Therefore, the precipitation rate model cannot explain the "anomalous" fractionation observed in fast growing aragonitic skeletons. We can also exclude closed-system calcification as an expla-nation,because this would only reduce fractionation, which is contrary to our obser-vations. We therefore propose that a biological effect controls the d44/40Ca of fast growing calcifiers like corals and bivalves.

References: Gussone et al. (2005) Geochim. Cosmochim. Acta, 69, 4485-4494; Lemarchand et al. (2004) Geochim. Cosmochim. Acta, 68, 4665-4678.