



## Calcium isotope fractionation in the calcium carbonate polymorphs calcite and aragonite

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Calcium isotope fractionation was measured on skeletal aragonite and calcite from different marine biota and on inorganic calcite. Precipitation temperatures ranged from 0 to 28°C. Calcium isotope fractionation shows a temperature dependence in accordance with previous observations:  $1000\ln(\alpha_{cc}) = -1.4 + 0.021 \cdot T$  (°C) for calcite and  $1000\ln(\alpha_{ar}) = -1.9 + 0.017 \cdot T$  (°C) for aragonite. Within uncertainty the temperature slopes are identical for the two polymorphs. However, at all temperatures calcium isotopes are more fractionated in aragonite than in calcite. The offset in  $\delta^{44/40}\text{Ca}$  is about 0.6 permill. The underlying mechanism for this offset may be related to the different coordination numbers and bond strengths of the calcium ions in calcite and aragonite crystals, or to different Ca reaction behaviour at the solid-liquid interface.

Recently, the observed temperature dependence of the Ca isotope fractionation (Gussone et al., 2003) was explained quantitatively with the temperature control on precipitation rates of calcium carbonates in an experimental setting (Lemarchand et al., 2004). We show that this mechanism can in principle also be applied to  $\text{CaCO}_3$  precipitation in natural environments in normal marine settings. Following this model, Ca isotope fractionation in marine Ca carbonates is primarily controlled by precipitation rates. On the other hand, the rate control mechanism does not explain the larger Ca isotope fractionation of aragonite compared to calcite. This can be shown by com-

paring data from biogenic and inorganic calcites and aragonites that precipitated at known rates.

*References:*

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Lemarchand D., Wasserburg G. J., and Papanastassiou D. A. (2004) Rate-controlled Calcium Isotope Fractionation in Synthetic Calcite. *Geochim. Cosmochim. Acta* 68(22), 4665-4678.