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Calcium Isotope Fractionation of Inorganic and Biogenic Calcium Carbonates

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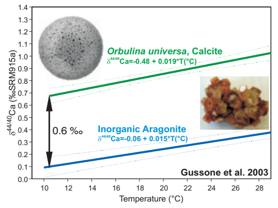
Introduction

It has been shown by Gussone et al. (2003, 2005) that calcium isotope fractionation in inorganic and some biogenic precipitates depends on mineralogy. Aragonite is depleted by about 0.7‰ 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 some biogenic carbonates (e.g. sclerosponges, brachiopods). The temperature dependence of isotope fractionation is similar in calcites and aragonites (0.015‰/K). It can be explained by the temperature-control on the CO_3^{2-} chemistry, which controls $CaCO_3$ precipitation rate (Lemarchand et al. 2004).

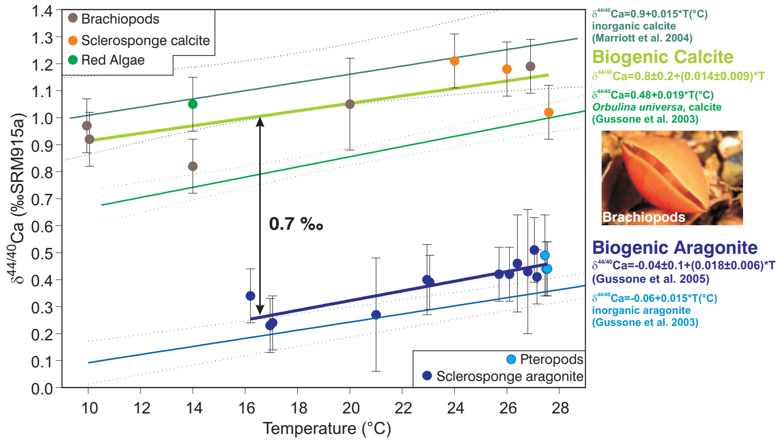


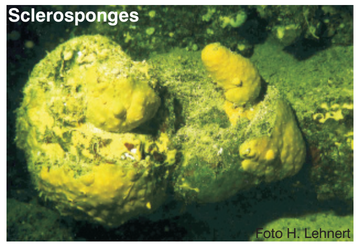
We found several groups of organisms producing carbonates that deviate from this simple isotope fractionation scheme: Scleractinian corals, a benthic gastropod shell and two bivalve species are about 0.4‰ enriched in ^{44}Ca with respect to inorganic aragonite. Temperature dependencies of these "anomalous" carbonates, however, show the common slope (0.015‰/K).

The organisms producing these "anomalous" calcium isotope compositions are characterized by sophisticated calcification mechanisms, designed to produce carbonates at very high precipitation rates and in confined body compartments. We propose that a **biological fractionation** effect (Gussone et al. 2006) controls the $\delta^{44/40}Ca$ of these skeletons. The biological fractionation is independent of the calcification processes and probably occurs during the transcellular transport of calcium.

Calcification in Open Systems

Open System — Fractionation During Mineral Formation

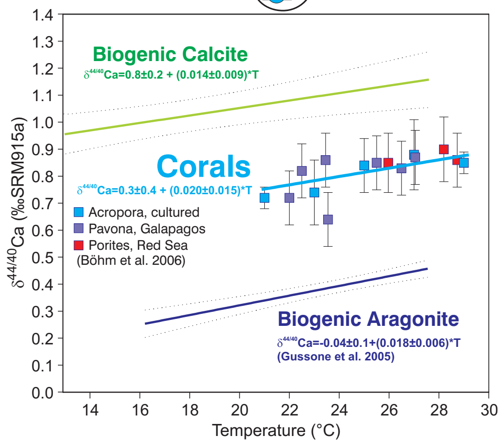


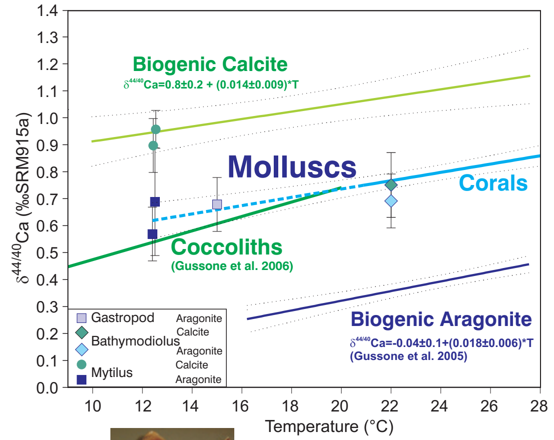


Calcium isotopes of modern sclerosponges, pteropods, brachiopods and red algae from various shallow water environments. Aragonite and calcite values define two separate temperature trend lines that are in good agreement with the fractionation trends described for inorganic aragonite (Gussone et al., 2003) and inorganic calcite (Marriott et al., 2004) (with 95% confidence bands). Aragonite is depleted in $\delta^{44/40}Ca$ by about 0.7‰ with respect to calcite.

Calcification in Confined Systems

Confined System — **No** Fractionation at Site of Mineral Formation





The $\delta^{44/40}Ca$ values of different reef-building coral species (cultured *Acropora*, wild *Pavona* from Galapagos and *Porites* from the Red Sea) agree very well. However, the coral calcium isotope ratios are significantly higher than inorganic and sclerosponge aragonite $\delta^{44/40}Ca$. The coral $\delta^{44/40}Ca$- temperature dependence, on the other hand, agrees well with the "simple" aragonites and calcites.

A benthic gastropod (Tasman Sea), the aragonite layer of the bivalve *Mytilus* (Baltic Sea), and calcite as well as aragonite of *Bathymodiolus* (bivalve, Logatchev Field, Atlantic) show $\delta^{44/40}Ca$ values that lie on the coral trend line and close to the trend defined by coccolith calcite (*E. huxleyi*; Gussone et al. 2006). *Mytilus* calcite, however, plots on the biogenic calcite line.

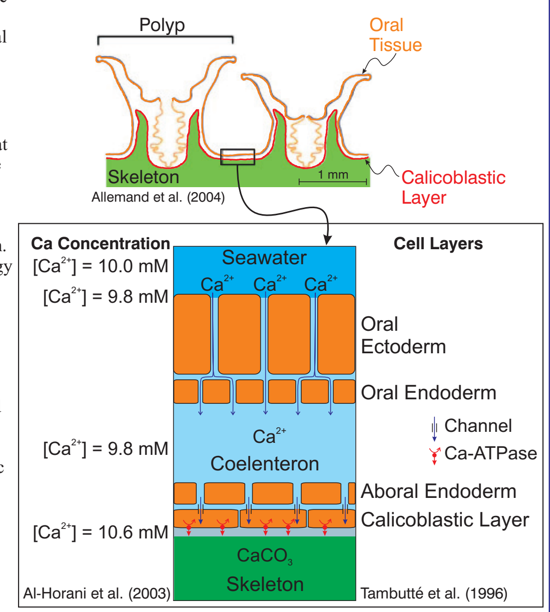
Biological Ca Isotope Fractionation

The coral skeleton is formed in a confined space where the chemistry of the calcifying fluid is under strict biological control. This is also the case for many molluscs and for coccoliths (Gussone et al. 2006).

In this setting all calcium that enters the calcification space will be incorporated into the crystal. Therefore, no fractionation is possible during the mineral formation. This explains why mineralogy has no influence on the calcium isotope ratios, i.e. coral aragonite plots in the same range as coccolith and *Bathymodiolus* calcite.

Calcium ions are transported through the tissue layers of the coral to the calcification site between the calicoblastic layer and the skeleton. This calcification space is sealed from diffusional Ca fluxes from seawater (^{45}Ca experiments, Tambutté et al. 1996; higher calcium concentration than seawater, Al-Horani et al. 2003). The volume of this space is sufficient to maintain typical precipitation rates for only a few seconds. Therefore all

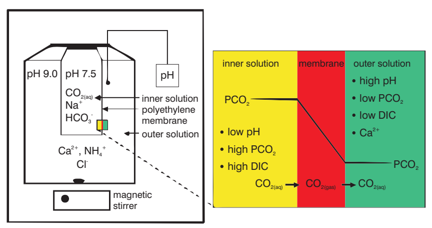
Ca^{2+} Transport Through a Coral

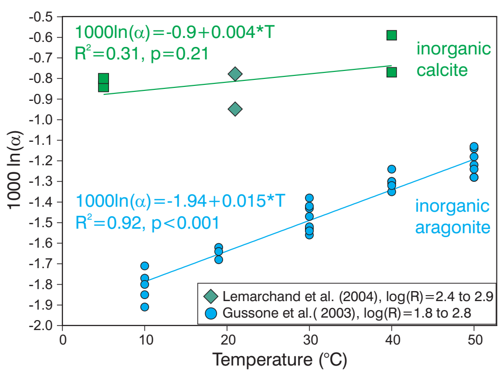


calcium used for skeleton formation has to be transported through the coral tissue with a high flux rate.
Ca isotope fractionation most likely occurs during the passage through cell membranes (Gussone et al. 2006) with a value of
$1000\ln(\alpha_{biol}) = -1.1$‰ at 25°C.

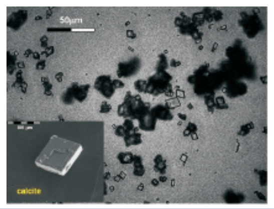
Is Fractionation Controlled by Temperature or Rate?

Precipitation Experiments





Calcite was precipitated in CO_2 diffusion experiments (Dietzel et al. 2004) at two different temperatures (5°C, 40°C). Precipitation rates ranged from $10^{2.3}$ to $10^{3.5}$ µmol/m²/h. The precipitation rates were calculated from the total surface area of the precipitated crystals, taking into account the measured crystal size distributions for each experiment.



Aragonite precipitation experiments using a similar setup (Gussone et al. 2003) showed a clear temperature dependence of calcium isotope fractionation. This was later explained by a temperature control of precipitation rate via the carbonate ion concentration. Kinetic isotope effects depending on precipitation rate then lead to the observed fractionation trend (Lemarchand et al. 2004, Gussone et al. 2005).

To test whether precipitation rate or temperature exerts the dominant fractionation control we use calcite precipitated at similar rates ($10^{2.4}$ to $10^{2.9}$ µmol/m²/h), and different temperatures (5°C to 40°C, including data from Lemarchand et al. 2004). The preliminary results, based on two samples for each temperature, show no significant direct influence of temperature on fractionation (p=0.24).

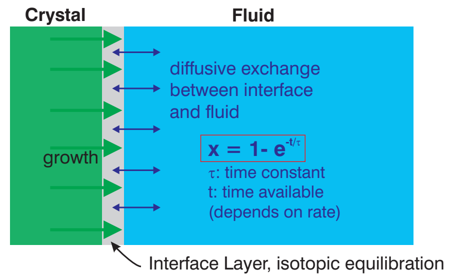
Quantitative Model for Inorganic Ca Isotope Fractionation

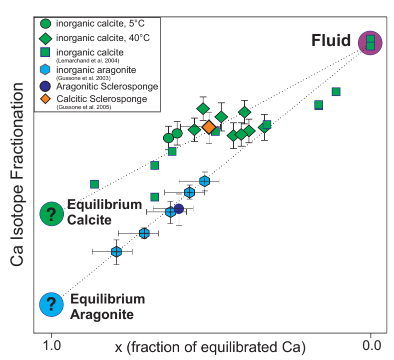
Rate Dependent Fractionation

Rate Dependent End Member Mixing
(Lemarchand et al. 2004, Gussone et al. 2005)

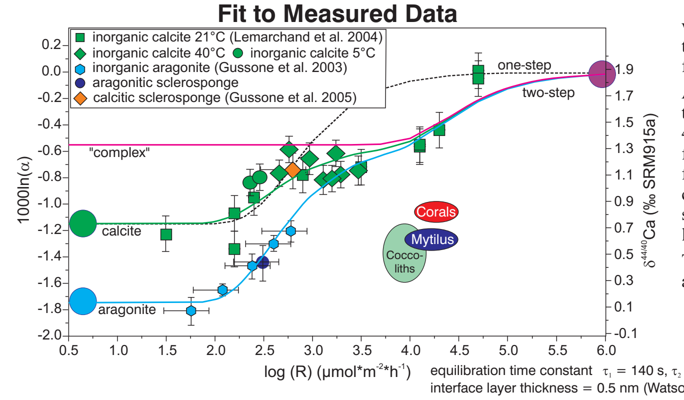
$$\delta^{44/40}Ca_{crystal} = x * \delta^{44/40}Ca_{eq} + (1-x) * \delta^{44/40}Ca_{fl}$$

x = fraction of equilibrated Ca
$\delta^{44/40}Ca_{crystal}$ = Ca isotope composition of crystal
$\delta^{44/40}Ca_{eq}$ = equilibrium Ca isotope composition
$\delta^{44/40}Ca_{fl}$ = Fluid Ca isotope composition





Fit to Measured Data



It has been shown by Lemarchand et al. (2004) and Gussone et al. (2005) that Ca isotope fractionation during precipitation of $CaCO_3$ is rate dependent. Isotopically equilibrated calcium mixes with unequilibrated calcium in an interface layer between fluid and crystal. The faster the precipitation, the less time is available for equilibration. With increasing crystal growth rates the fraction of equilibrated calcium incorporated into the crystal decreases. An apparent fractionation factor arises from the mixing of equilibrated and unequilibrated Ca as a function of precipitation rate.

The fraction of equilibrated Ca (x) depends on the time available for equilibration (t)

$$x = 1 - e^{-t/\tau},$$

which is limited by the advancing crystal growth surface and the diffusional exchange of Ca between interface layer and fluid.

A fit of this relationship to the measured data shows stronger than expected fractionation for log(R) values between 3 and 4.5 (dashed line for calcite). The fit improves if a two-step fractionation process is assumed. Dissolved Ca is first fractionated by forming an intermediate phase (e.g. a surface complex) with a very short equilibration time (about 2 s). The second fractionation step during incorporation into the crystal lattice is much slower (equilibration time constant 2.3 min.)

The equilibrium fractionation values estimated from this fit are -1.2 ‰ for calcite and -1.7 ‰ for aragonite.

fluid (seawater)	$\delta^{44/40}Ca$ = 1.88 ‰ (SRM915a)
equilibrium calcite	$\delta^{44/40}Ca$ = 0.7 ‰ (SRM915a)
equilibrium aragonite	$\delta^{44/40}Ca$ = 0.1 ‰ (SRM915a)

Conclusions

* Ca isotope fractionation of inorganic and biological $CaCO_3$ precipitation in open systems is well explained by a rate dependent equilibration mechanism (Lemarchand et al. 2004) and mineralogy (Gussone et al. 2005).
* Carbonate precipitation in the confined calcification compartments of corals and some molluscs fractionates calcium isotopes by a different mechanism. Fractionation in $^{44}Ca/^{40}Ca$ 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 $CaCO_3$ precipitation rates.

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