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

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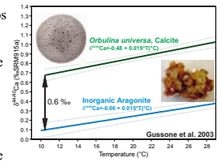
Introduction

It has been shown by Gussone et al. (2003, 2005) that calcium isotope fractionation in inorganic and simple biogenic precipitates depends on mineralogy. Aragonite is depleted by about 0.6‰ 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, 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).

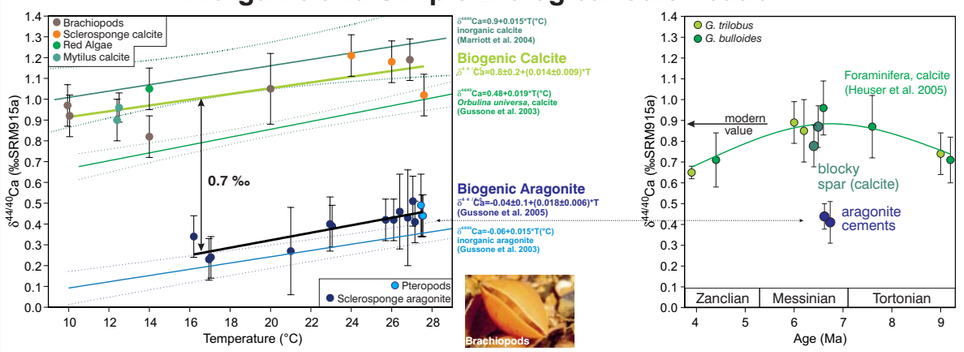


We found several groups of organisms producing carbonates that deviate from this simple isotope fractionation scheme: Several species of scleractinian corals, a benthic gastropod shell and the aragonitic parts of *Mytilus* (bivalvia) are about 0.4‰ enriched in ^{44}Ca with respect to inorganic aragonite. Calcitic spicules of Calcarea (sponges) are 0.2 ‰ depleted in ^{44}Ca compared to "simple" biogenic calcite. Temperature dependencies of these "anomalous" carbonates, however, show the common slope (0.015‰/K).

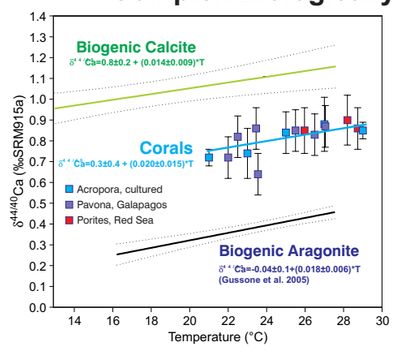
The organisms producing these "anomalous" calcium isotope compositions are characterized by sophisticated calcification mechanisms, designed to produce carbonates at very high precipitation rates and in confined body compartments. We propose that a **biological fractionation** effect (Gussone et al. 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.

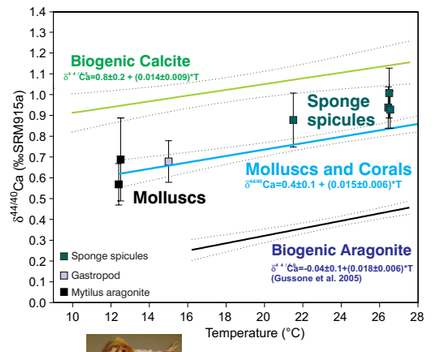
Data

Inorganic and Simple Biological Calcification



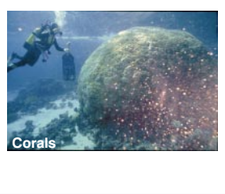
Complex Biologically Controlled Calcification





Calcium isotopes of modern sclerosponges, pteropods, brachiopods, red algae and the outer layer of Mytilus 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.

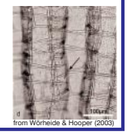
Early Messinian marine aragonite cements from Salento Peninsula (Italy) and from Crete show similar $\delta^{44/40}Ca$ values as modern aragonitic sclerosponges. The foraminiferal $\delta^{44/40}Ca$ reconstruction of Heuser et al. (2005) indicates a calcium isotopic composition of Messinian seawater similar to modern seawater. Calcium isotope fractionation of these cements was therefore similar to that of modern sclerosponge aragonite and inorganic aragonite. Blocky calcite spar (Salento) agrees with calcitic foraminifera.



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) and the aragonite layer of the bivalve *Mytilus* (Baltic Sea) show $\delta^{44/40}Ca$ values that lie on the coral trend line.

Calcitic sponge spicules (Calcarea, E Australia) are slightly depleted in $\delta^{44/40}Ca$ compared to "simple" biogenic calcite. These spicules are formed inside the sponge tissue.



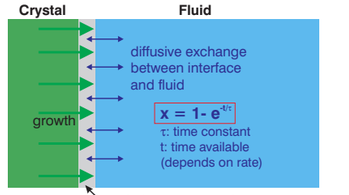
Model for Inorganic Ca Isotope Fractionation

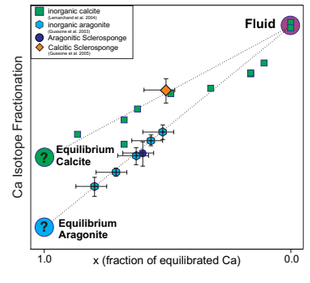
Rate Dependent Fractionation

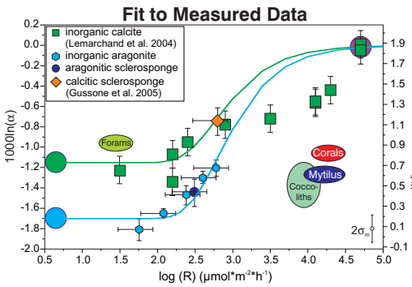
Rate Dependent End Member Mixing
(Lemarchand et al. 2004, Gussone et al. 2005)

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

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







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. The fraction of equilibrated Ca (x) 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 measured data allows to estimate the equilibrium fractionation values of calcite (-1.2 ‰) and aragonite (-1.7 ‰) and the equilibration time constant (63% equilibration during 1.5 min.).

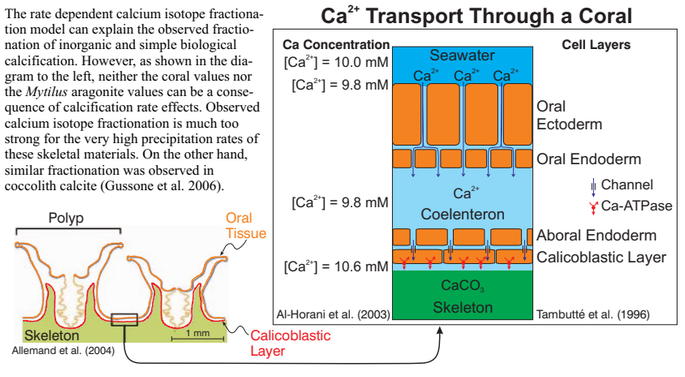
interface layer thickness = 0.5 nm (Watson 2004)
equilibration time constant τ = 80 s

fluid (seawater)	$\delta^{44/40}Ca$ = 1.88 ‰ (SRM915a)
equilibrium calcite	$\delta^{44/40}Ca$ = 0.7 ‰ (SRM915a)
equilibrium aragonite	$\delta^{44/40}Ca$ = 0.2 ‰ (SRM915a)

Biological Ca Isotope Fractionation

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 coral values nor the *Mytilus* aragonite values can be a consequence of calcification rate effects. Observed calcium isotope fractionation is much too strong for the very high precipitation rates of these skeletal materials. On the other hand, similar fractionation was observed in coccolith calcite (Gussone et al. 2006).

Ca^{2+} Transport Through a Coral



The sketch above shows how Ca ions are transported through the tissue layers of a coral to the site of calcification in a thin layer of fluid between the calicoblastic layer and the skeleton (the subcalicoblastic layer). The subcalicoblastic layer is sealed from diffusional Ca fluxes from seawater (^{45}Ca experiments, Tambutté et al. 1996; higher Ca concentration than seawater, Al-Horani et al. 2003). The volume of the subcalicoblastic layer is sufficient to maintain typical precipitation rates for only a few seconds. Therefore all Ca used for skeleton formation has to be transported through the coral tissue with very high flux rates.
Ca isotope fractionation most likely occurs during the passage through cell membranes as recently observed in coccolithophorids by Gussone et al. (in press) with a value of **$1000\ln(\alpha_{tissue})$ = -1.1‰ at 25°C**.

Conclusions

- Ca isotope fractionation of inorganic $CaCO_3$ precipitation and "simple" biological calcification is well explained by a rate dependent equilibration mechanism (Lemarchand et al. 2004) and mineralogy (Gussone et al. 2005).
- Biologically controlled carbonate precipitation of corals, some molluscs and sponge spicules 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., in press).
- This biological fractionation mechanism may be widespread among marine carbonate producers, especially among organisms with high $CaCO_3$ precipitation rates.

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