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# Controls of calcium isotope fractionation in biogenic and inorganic calcium carbonate

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Calcium is a widely distributed element on earth and plays an important role in many geological and biological processes. In the marine realm, Ca is of particular interest because the Ca concentration affects the evolution of life in the ocean and due to the precipitation and dissolution of $CaCO_3$, calcium is linked to the oceanic carbon cycle and global climate. Since Ca isotopes are considerably fractionated during biogenic $CaCO_3$ precipitation, the isotopic composition of skeleton elements (bones, shells, test) can be used to reconstruct past climate variability: Calcium isotopes were for instance used to reconstruct the relation of organisms in ancient food chains (Skulan et al., 1997; Clementz et al., 2003), the isotopic composition of seawater, reflecting changes of the oceanic Ca-budget cf. (De La Rocha and DePaolo, 2000; Fantle and DePaolo, 2005; Heuser et al., 2005; Schmitt et al., 2003) and paleotemperatures (Zhu and Macdougall, 1998; Nägler et al., 2000; Gussone et al., 2004; Hippler et al., 2006). One particular feature of Ca isotope fractionation is the establishment of two considerably different temperature sensitivities in different planktonic marine species, which allow the use of Ca isotopes for the reconstruction of temperatures as well as seawater isotopic composition, provided that appropriate species are selected for the respective application.

For the application of Ca isotopes as proxy and their reliable paleoclimatic interpretation it is important to understand what mechanisms influence Ca isotope fractionation and what environmental factors have to be considered. In general, the Ca isotopic composition of biogenic carbonates can be influenced by inorganic and biological fractionation processes, which are characterised by different fractionation behaviour in response to different environmental parameters.

During inorganic $CaCO_3$ precipitation light Ca isotopes are enriched in the solid, relative to the solution. This behaviour differs from the oxygen isotope system, incorporating preferentially the heavy isotopes in the solid. The extent of Ca isotope fractionation depends,

like in other isotope systems, on the crystal structure of the solid phase. For instance calcium isotopes in aragonite are, like in the oxygen isotope system, stronger fractionated than calcite; i.e. lighter Ca isotopes (Gussone et al., 2005) but heavier oxygen isotopes cf. (Böhm et al., 2000) are incorporated into aragonite compared to calcite. Like in the oxygen isotope system, Ca isotope fractionation decreases with increasing temperature, leading to a positive correlation between temperature and Ca isotopy, while $\delta^{18}O$ is inversely correlated to temperature. As well, the observed temperature sensitivity of oxygen and Ca isotope fractionation in inorganic $CaCO_3$ differs significantly. While $\delta^{18}O$ changes with a rate of about -0.2‰/°C, the temperature dependence of Ca isotope fractionation is about 0.02‰/°C cf. (Gussone et al., 2003; Marriott et al., 2004). While the oxygen isotope signal is caused by decreasing equilibrium fractionation with increasing temperature, the temperature dependence of Ca isotope fractionation was recently proposed to be caused by changes in precipitation rate (Lemarchand et al., 2004). In this model, Lemarchand et al. (2004) suggested that the temperature dependence found in inorganic $CaCO_3$ can be explained by the temperature-dependent speciation of the carbonic acid (Millero, 1995), leading to an increase in $[CO_3^{2-}]$ with increasing temperature. The increase in $[CO_3^{2-}]$ then leads to a higher saturation state of calcite/aragonite and to increasing precipitation rates, resulting in reduced Ca isotope fractionation in the calcium carbonate.

In contrast to the inorganic precipitated $CaCO_3$, the calcite skeletons of some marine foraminifers (*O. universa*) and coccolithophores (*E. huxleyi*) show a similar temperature dependence, but no major response to $CO_3^{2-}$-changes. These results indicate a biological control of the fluid chemistry inside the vesicle, in which $CaCO_3$ precipitation takes place (Gussone et al., 2006).

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