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Calcium Isotopic Fractionation during Precipitation of Calcium Carbonate Polymorphs and ACC at Low Temperatures

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Calcium isotopic fractionation can provide fundamental insights into the growth mechanisms of calcium carbonates. It may be used to reconstruct environmental conditions like precipitation rate, temperatures and solution chemistry during calcium carbonate precipitation by using multiproxy approaches. However significant gaps of knowledge exist for calcium isotopic fractionation in calcium carbonate, especially for vaterite and amorphous calcium carbonate (ACC). In this contribution the calcium isotopic fractionation into calcium carbonate polymorphs and ACC are discussed.

Spontaneous calcium carbonate precipitation experiments without seeds using a CO_2-diffusion technique (TANG et al., 2008) and mixing experiments were carried out. All experiments are conducted (i) at various Mg/Ca ratios (up to 10), and/or (ii) in presence of polyaspartic acid at different temperatures (5 - 50°C). CO_2-uptake rates are varied to adjust different precipitation rates.

In general, calcium isotopes fractionate less for vaterite ($\Delta^{44/40}$Ca$_{CaCO3(s)-Ca(aq)}$= -0.3 to -0.6 ‰ compared to calcite (-0.9 to -2 ‰ and aragonite (-1 to -1.6 ‰). Least fractionation is obtained for ACC ($\approx$ -0.25 ‰). In calcite the $\Delta^{44/40}$Ca$_{CaCO3(s)-Ca(aq)}$values depend on both temperature and precipitation rate, whereas the precipitation rate effect is much smaller for aragonite and vaterite. The $\Delta^{44/40}$Ca$_{CaCO3(s)-Ca(aq)}$values show an inverse correlation with the distribution coefficient of strontium into calcium carbonatefor all polymorphs with distinct characteristic slopes. Notably, slopes and intercepts of individual regression lines are independent of temperature, precipitation rate and Mg incorporation. Our results may be used to decipher biogenic from inorganically induced calcium carbonateformation, polymorph transformation, and alteration processes. Respective processes and proposed models will be discussed.

Reference:

Tang J., Köhler S.J. and Dietzel M. (2008) Sr^{2+}/Ca^{2+} and $^{44}Ca/^{40}Ca$ fractionation during inorganic calcite formation: I. Sr incorporation, *Geochimica et Cosmochimica Acta*, **72**, 3718-3732.