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Rate controlled fractionation of Ca isotopes in synthetic calcite

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Calcium isotopic variations in carbonates, both marine organisms and inorganic systems, have recently been interpreted as a possible seawater temperature recorder [1,2]. In order to understand the behavior of calcium isotopes during precipitation of Ca-carbonate, synthetic calcite growth experiments were carried out at constant temperature and under various pH and alkalinity conditions.

$CaCl_2$–NH_4Cl solutions were exposed to a CO_2-NH_3 rich atmosphere. This technique permitted the growth of calcite crystals under steady conditions of pH covering a large range of oversaturation states with respect to calcite from $\Omega=3$ to 105 ($\Omega=1$ is equilibrium). Calcite growth experiments were conducted both in unstirred and in stirred solutions at different Ca concentrations.

A systematic enrichment in calcite of ^{40}Ca relative to the mother solution was observed. The magnitude was similar to the range reported by other workers in both natural and synthetic systems. $\Delta^{44/40}Ca$ (permil units of the deviation from the mother solution) shows a clear correlation with the saturation state of the solution. The largest isotopic effect ($\Delta^{44/40}Ca \approx -1.5‰$) was observed at the lowest saturation index ($\Omega=3$). As the saturation state increases, the isotopic effect decreases regularly to zero at $\Omega=105$. Under stirred conditions, exactly the same behavior is observed but with isotopic shiftts much smaller .The largest effect ($\Delta^{44/40}Ca \approx -0.4‰$) was observed at the lowest Ω.

Since the condition $[Ca]>>[CO_3^{2-}]+[HCO_3^-]$ is met in all our experiments, we conclude that the supply of carbon from the bulk solution is the rate controlling mechanism, controlling $\Delta^{44/40}Ca$ of the calcite crystals. Ca diffusion does not appear to play a significant role under these conditions. The largest isotopic shift is interpreted as close to the equilibrium fractionation between solution and calcite. Reduction of the isotopic shift with increasing saturation states is explained by the diffusive inflow of carbon causing Ca from the bulk solution in the neighborhood of the crystal-liquid interface to be increasingly involved in the precipitation. The influence of temperature is then expected to be ~ 0.02 ‰/°C through its influence on the equilibrium constants. These conclusions are in contrast with those previously proposed [2], where $\Delta^{44/40}Ca$ are explained by diffusion of large hydrated Ca complexes. Supported by DOE DE-FG03-88ER13851. Caltech Contribution 8782(1093).

References

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2.7.61

Fractionation of Sr ($\delta^{88}Sr$) and Ca ($\delta^{44}Ca$) during biogenic and inorganic prepicpitation of calcium carbonate

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The knowledge of the influence of temperature and other environmental factors on isotope fraction of divalent cations like Ca^{2+} and Sr^{2+} during inorganic and biogenically controlled precipitation of calcium carbonate is crucial for their interpretation as paleo proxies. In order to extend our earlier studies on Ca-isotope fractionation (e.g. [1]), we determined $\delta^{88}Sr$-isotope ratios on seawater and on corals. We define the stable Sr-isotope ratio $\delta^{88}Sr$ as ($\delta^{88}Sr=(^{88}Sr/^{86}Sr)_{Sample}/(^{88}Sr/^{86}Sr)_{Standard}-1)*1000$; Sr Standard is NBS 987. First measurements of the IAPSO seawater standard result in $\delta^{88}Sr$ of 0.38±0.02 ‰. Coral $CaCO_3$ precipitated from seawater in a temperature range from about 22° C to about 27° C correspond to $\delta^{88}Sr$-values ranging from 0.17‰ to about 0.32‰ indicating that Sr in carbonate precipitated from seawater is isotopically lighter than Sr dissolved in seawater. The slope of 0.027‰ °C for the temperature-$\delta^{88}Sr$ relationship in corals is about a factor of 1.7 larger than the slope of $\delta^{44}Ca$ ratios in inorganically precipitated aragonite. However, the fractionation $\alpha(T)=((^{88}Sr/^{86}Sr)_{CaCO3})/(^{88}Sr/^{86}Sr)_{Seawater})$ at a given temperature is about one order of magnitude less for Sr-isotopes relative to Ca-isotopes. The larger temperature-$\delta^{88}Sr$ gradient in comparison to the Ca-isotopes is interpreted to reflect the smaller ion potential and the correspondingly smaller mass of the associated Sr^{2+}-aquocomplex. The observation that $\delta^{88}Sr$ and $\delta^{44}Ca$ are positively correlated with temperature points to the likelihood that kinetic or equilibrium fractionation effects and the mass of the associated acquocomplex control the degree of divalent cation isotope fractionation during $CaCO_3$-precipitation.

Reference

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