

Exploring the impact of temperature and fluid chemistry on Ca and Sr isotope composition of *Arctica islandica* shells via experimental alteration

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Carbonate shells of marine organisms record by their chemical and isotopic composition environmental conditions like temperature, salinity and pH during their formation. However, primary signals can be overprinted by diagenesis, which has to be considered for the interpretation of environmental proxy data and on the other side may provide additional information about distinct reaction pathways throughout diagenesis (e.g. Allison et al, 2007).

Aragonitic *Arctica islandica* shells widely used as proxy archives (e.g. Schöne et al, 2005) were chosen for hydrothermal alteration experiments in order to get a more detailed insight into diagenetic effects.

Here we present results of experiments in which *Arctica islandica* shell fragments were exposed to North Sea seawater at temperatures of 100°C and 175°C at distinct reaction times. Strontium isotope composition of the experimental medium was adjusted from an original composition of $\delta^{88/86}\text{Sr}_{\text{SRM987}} = 0.391(1)\text{‰}$ and $^{87}\text{Sr}/^{86}\text{Sr} = 0.70921(1)$ to $\delta^{88/86}\text{Sr}_{\text{SRM987}} = 0.179(1)\text{‰}$ and $^{87}\text{Sr}/^{86}\text{Sr} = 0.70789(1)$ by sulfate extraction and Sr replacement procedures. The artificially altered shell material (six sub-samples of six shell fragments) and the corresponding solutions were prepared and analyzed.

Results show that at 100°C aragonite is still the predominant phase, but show lower peak intensities with Raman and XRD near the surface of the shell fragments. At 175°C the aragonitic shell material recrystallized almost completely to calcite. In addition a rim of weakly ordered dolomite (10 μm) was found around these samples.

Analysis of element concentrations of initial and final solutions show that at 175°C Sr and Ca concentrations increase (Sr: 79 to 183 $\mu\text{mol/l}$; Ca: 8 to 30 mmol/l), while Mg concentration decreases (Mg: 42 to 22 mmol/l). A corresponding Sr and Ca depletion along with an increase of Mg occurred in the samples, especially in the dolomite rim. At 100°C only minor increase of Sr, Ca and Mg concentrations were observed in the experimental solutions.

Changes of Sr isotopic composition are observed in the solutions. At 175°C $\delta^{88/86}\text{Sr}$ increased by up to 0.04‰ and $^{87}\text{Sr}/^{86}\text{Sr}$ increased by 7.5×10^{-4} . At 100°C $\delta^{88/86}\text{Sr}$ increased by up to 0.31‰ and $^{87}\text{Sr}/^{86}\text{Sr}$ increased by 1.6×10^{-4} . On the other hand shell analyses show no significant changes in isotopic composition ($\delta^{88/86}\text{Sr}_{\text{SRM987}}$ 0.25 to 0.3‰ $^{87}\text{Sr}/^{86}\text{Sr} = 0.70915$ before and after experiments). This indicates that Sr is primarily released by dissolution of shell material without isotopic fractionation.

Ca isotopes show no significant changes in the solutions for 100°C experiments ($\delta^{44/40}\text{Ca}_{\text{SRM915a}} = 1.7$ to $1.9 \pm 0.1\text{‰}$). However, for experiments at 175°C Ca isotopic composition of the fluids decreases by around 1‰. In the shell fragments no significant changes of the Ca isotopic composition were detected. Similar to Sr isotopes results this indicates dissolution of Ca without fractionation.

Under these experimental conditions Sr and Ca isotopes are relatively stable proxies, while changes in elemental composition and strong changes in mineralogy were observed.

Allison, N., et al. (2007). "Palaeoenvironmental records from fossil corals: The effects of submarine diagenesis on temperature and climate estimates." *GCA* 71: 4693-4703.

Schöne, B. R., et al. (2005). "Climate records from a bivalved Methuselah (*Arctica islandica*, Mollusca; Iceland)." *Palaeo* 3 228: 130-148