



Ca isotope fractionation in modern and fossil bivalve shell carbonate

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Ca isotopes of bivalve carbonate, used in combination with light stable isotopes and metal/Ca ratios may provide a useful archive of annual and seasonal parameters such as temperature, salinity or nutrient level, and therefore for high-resolution palaeoclimate reconstructions, but the reliability of these proxies remains questionable given potential vital/ontogenetic and microenvironmental effects. Furthermore, in order to test the applicability of bivalve-based environmental proxies on geological time-scales, it is of crucial importance to assess the sensitivity of shell geochemistry to early diagenesis.

We investigated these potential effects, first by using field cultured, intertidal and subtidal bivalve species cultured in the Dutch Wadden Sea, and second by using selected fossil bivalve shells from Pleistocene (MIS 5e) uplifted marine terraces located in the SE Gulf of Corinth area, Greece. Cultured individuals offer the chance to compare time series of instrumental environmental data directly to growth rate and shell chemistry, whereas fossil samples, which were exposed to meteoric conditions for an extended period, are perfect for studying potential diagenetic influences on the Ca isotope system.

Ca isotope signatures of both cultured bivalve species are positively correlated with ambient seawater temperature. The slope of the temperature-fractionation relation is similar to inorganic calcite and aragonite precipitates. However, the Ca isotope values are offset from the inorganic curves of about 0.5 permil. The most likely explanation for this offset is a biological induced fractionation, which can be attributed to the active transport of calcium through different cell layers to the site of calcification. In contrast, the studied fossil shells show little variations in Ca isotope composition. We observed that fossil biogenic aragonite from the same chronostratigraphic unit is considerably less fractionated than fossil biogenic calcite, which can be either explained by an implausible temperature effect of approximately 10 degree Celsius or by weak diagenetic overprinting. To summarize, these results provide new insights into biomineralization processes and indicate however a limited use of Ca isotopes in bivalves as temperature proxy.