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Assessing kinetic fractionation in brachiopod calcite using clumped isotopes

DAVID BAJNAI¹, JENS FIEBIG¹, JACEK RADDATZ¹, ADAM TOMAŠOVÝCH², UWE BRAND³

¹ Institut für Geowissenschaften, J. W. Goethe-Universität, Altenhöferallee 1, 60438, Frankfurt am Main, Germany (david.bajnai@em.uni-frankfurt.de)

² Earth Science Institute, Slovak Academy of Sciences, Dubravska cesta 9, 84005, Bratislava, Slovakia

³ Department of Earth Sciences, Brock University, 1812 Sir Isaac Brock Way, L2S 3A1, St. Catharines, Ontario, Canada

Brachiopods serve as an important archive for the marine record of Phanerozoic climate. Their low-magnesium calcite shell is widely used to reconstruct palaeoclimatic variations based on its $\delta^{18}\text{O}$ value. Conventional $\delta^{18}\text{O}$ palaeothermometer equations include two unknowns: the oxygen isotopic composition of the calcite and of the seawater. The assumption that the present-day seawater $\delta^{18}\text{O}$ value of 0 ‰ SMOW is constant in deep-time could lead to intolerably high temperature estimates for ancient oceans. The clumped isotope palaeothermometer has the potential to resolve this challenge, since the clumped isotope value of a carbonate is independent of the oxygen isotope composition of the seawater. Despite the growing number of studies on the clumped isotopic composition of brachiopod calcite, the question remains if these marine invertebrates secrete their shell in clumped isotopic equilibrium.

Here, we investigated 20 modern brachiopod shells belonging to 15 species and collected from various temperature habitats for their Δ_{47} composition and Mg content. The Δ_{47} -T calibration line based on these samples describe a significantly steeper slope compared to previous calibrations made at $\geq 70^\circ\text{C}$. Oxygen isotope equilibrium offset values were calculated for the $\delta^{18}\text{O}$ measurements, based on the equations of (1) and (2), and for the Δ_{47} values, based on the equation of (3).

A significant negative correlation between the $\delta^{18}\text{O}$ and the Δ_{47} offset values is visible. Isotopic mixing, pH-effect, and mineralogical effect were ruled out as possible explanations but both the $\delta^{18}\text{O}$ and the Δ_{47} offset values correlate with the growth rate. Therefore, kinetic effect, related to growth rate, is suggested to be the main contributing factor to cause $\delta^{18}\text{O}$ and Δ_{47} disequilibrium during calcite precipitation in brachiopods.

(1) Kim & O'Neil, 1997, GCA; (2) Brand et al., 2013, ChemGeol; (3) Wacker et al., 2014, GCA