



Assessing kinetic fractionation in brachiopod calcite using clumped isotopes

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Brachiopod shells are widely used to reconstruct palaeoclimatic variations based on their oxygen and clumped isotopic compositions. However, it is not conclusive whether brachiopods precipitate their shells in thermodynamic equilibrium. Previous works have postulated that brachiopods secrete their shells in clumped isotopic equilibrium, even though the only brachiopod-based calibration is discrepant from the theoretical and mollusc-based calibrations. No clear explanation has yet been given for this disagreement. In this study, we investigated the significance of kinetic controls on brachiopod shell Δ_{47} and $\delta^{18}\text{O}$ values. For this purpose, we analysed modern brachiopods with independently-known growth temperatures and water $\delta^{18}\text{O}$ values for their bulk and clumped isotopic compositions and magnesium content. For the clumped isotope analyses, homogenised carbonate powder was reacted at 90 °C with >105% phosphoric acid using a fully automated gas extraction and purification line. Most specimens exhibited deviations in measured Δ_{47} and $\delta^{18}\text{O}$ values from predicted equilibrium. These observed departures from equilibrium correlate with each other and with brachiopod growth rates. Thus, we conclude that the oxygen and clumped isotope composition of modern brachiopod shells is affected by growth rate-induced kinetic effects. The most likely source of the kinetic effects is the incomplete hydration and/or hydroxylation of $\text{CO}_2(\text{aq})$ at higher growth rates. Based on our findings, information about taxon-specific growth rate and kinetics involved in calcite precipitation would be essential whenever constraining seawater temperatures from Δ_{47} and $\delta^{18}\text{O}$ values in brachiopods.