Clumped isotope thermometry of Carboniferous brachiopods and the effects of burial heating

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Clumped isotope thermometry of well-preserved carbonate fossils holds great promise for detangling the effects of paleotemperature and seawater oxygen isotope composition on the oxygen isotope composition of fossils. Meaningful application of this paleothermometer requires accurate calibration curves, as well as an understanding of the burial temperatures where solid-state reordering of C-O bonds becomes significant. We describe the results of a clumped isotope calibration for modern brachiopods and mollusks, then use this calibration to determine paleotemperatures from a suite of nominally pristine Carboniferous brachiopod fossils. Apparent paleotemperatures of the brachiopods range from 15 to 197 °C. Thus, while the Δ47-derived temperatures of many of the fossils are consistent with formation at Earth’s surface, some shells give paleotemperatures that are clearly inconsistent with biological mineralization. We have conducted laboratory heating experiments on natural calcites to determine Arrhenius parameters for solid-state C-O reordering. These parameters are used in numerical models to predict the Δ47 evolution of the Carboniferous brachiopods, where the T-t paths are constrained by independent geological data. We observe a reasonably close correspondence between predicted and observed Δ47 values, and the models predict that reordering becomes important at temperatures above ~100-125°C for dwell timescales of 10^6 years.

Figure 1: Clumped isotope temperatures and estimated burial depths (based on independent geological information) for pristine Carboniferous brachiopods from several Paleozoic sedimentary basins. The solid line is a modeled solid-state reordering pathway showing the clumped isotope temperature evolution of a shell buried at a rate of 0.25 km/Ma under a geothermal gradient of 25 °C/km (dashed line). Samples undergoing solution-precipitation should plot in the area bounded by the solid and dashed lines.