

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 Δ_{47} -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 Δ_{47} 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 Δ_{47} values, and the models predict that reordering becomes important at temperatures above ~100-125°C for dwell timescales of 10^8 years.

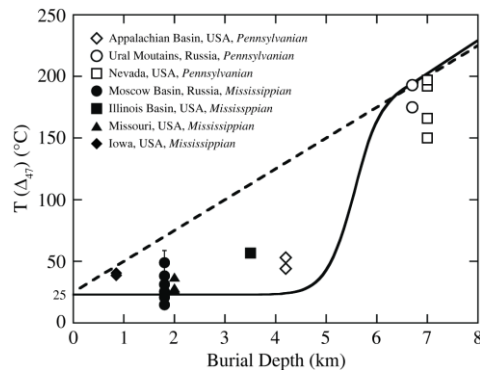


Figure 1: Clumped isotope temperatures and estimated burial depths (based on independent geological information) for pristine Carboniferous brachiopods from several Paleozoic sedimentary basins. The solid line is a modeled solid-state reordering pathway showing the clumped isotope temperature evolution 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.

Monopolar and highly asymmetric nucleation at low temperatures: Insights from tourmaline

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Minerals overcome the nucleation barrier to growth by numerous methods. Epitaxial growth can be found between different minerals that share structural features e.g. kyanite and staurolite. Alternatively, new growth can nucleate on substrates of the same mineral. In low-temperature systems, crystallographically congruent overgrowths are common such as the often observed quartz overgrowths on quartz. Here, composition of the substrate is nearly identical, except for trace element compositions. In contrast, at diagenetic and low grade metamorphic conditions, tourmaline supergroup minerals commonly nucleate on substrates of pre-existing tourmaline, even when their compositions are substantially dissimilar.

In these environments, the substrate, a detrital core, is distinctly different in composition such that it may be classified as a different species that may manifest as a contrasting color (Fig. 1). These interfaces appear sharp with little-to-no diffusion across the interface. In addition, these oriented overgrowths are in optical continuity with the detrital grain and are more pronounced at the +c axis of the crystal providing a crystallographic identifier. Such overgrowths suggest distinct and major differences in surface energy at different poles of the crystal. At diagenetic conditions the tourmaline overgrowth is monopolar – only at the +c axis. At low grades of metamorphism the overgrowths are highly asymmetric along the c axis with significant differences in composition at the opposite poles. With increasing metamorphic grade the asymmetric differences in overgrowth dimensions and compositions diminish and converge at roughly 550°C. Tourmaline is one of the few minerals to exhibit such features at low temperatures and supports the fact that preferred nucleation reduces the nucleation barrier. Because of the temperature dependence of the asymmetric development of tourmaline, it is likely that differential surface energy plays a very significant role in tourmaline nucleation.

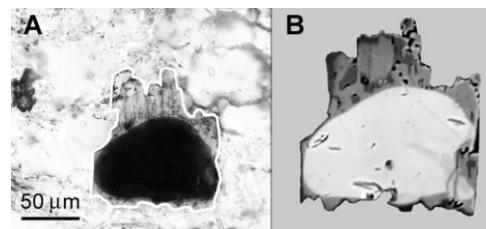


Figure 1: Detrital tourmaline grain with asymmetric overgrowth developed in chlorite zone metawacke. (A) Optical photomicrograph with dark detrital core and lighter overgrowth highlighted by white outline. (B) Backscattered electron image showing some of the textural and chemical variability of the overgrowths. [1]

[1] Henry, D.J., and Dutrow, B.L. (1992) Tourmaline in a low-grade clastic metasedimentary rock - an example of the petrogenetic potential of tourmaline. *Contributions to Mineralogy and Petrology*, **112**, 203-218.