

Evaluation of clumped isotope thermometer using aragonitic bivalve shells reared at different temperatures and pH conditions

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Clumped isotope (Δ_{47}) thermometry is a novel temperature proxy based on analyzing the ^{13}C – ^{18}O -bond enrichment in carbonates and can independently constrain the formation temperatures of carbonates. To achieve more accurate paleotemperature reconstruction, we conducted culture experiments on the marine bivalve *Scapharca broughtonii* under precisely controlled temperature and pH conditions. Using our experimental specimens, we evaluated the clumped isotope thermometer of aragonitic bivalve shells and discussed the bivalve calcification process based on the vital effect observed in the shell isotopic compositions.

Δ_{47} analysis was performed using MAT 253 and MAT 253 Plus isotopic ratio mass spectrometers with a Kiel IV carbonate device (Thermo Fisher Scientific, Bremen, Germany) as described by Müller et al. [1]. The Δ_{47} analytical system at ETH Zurich allows for high-precision Δ_{47} analysis from small carbonate samples, as low as 1–2 mg, with multiple replicate analyses. Each experimental sample and standard was weighed for 6–10 replicate analyses of 95–120 μg aliquots. In the Kiel IV, carbonate samples were automatically reacted with 104% phosphoric acid at 70 °C under vacuum. Standardization of analytical values was performed according to Bernasconi et al. [2] using carbonate standards (ETH1–4) for inter-laboratory absolute standardization.

Shell Δ_{47} values showed a significant negative correlation with temperature except for fast-growing specimens. In fast-growing specimens, Δ_{47} values decreased with increasing growth rate. Previous studies (e.g., [3]) have reported a growth-rate dependency on Δ_{47} in corals and molluscs, highlighting the importance of evaluating the relationship between Δ_{47} and growth rate for precise temperature reconstruction. In addition, the shell Δ_{47} showed no significant relationship with pH, and thus the Δ_{47} of this species is a useful thermometer unaffected by pH. The Δ_{47} of bivalve shells may reflect changes in the kinetics of calcification fluid, and the calcification process in bivalves can be understood by interpreting the carbon and oxygen isotope and Δ_{47} compositions together.

References

- [1] Müller, I.A., Fernandez, A., Radke, J., van Dijk, J., Bowen, D., Schwieters, J., and Bernasconi, S.M. (2017) Carbonate clumped isotope analyses with the long-integration dual-inlet (LIDI) workflow: scratching at the lower sample weight boundaries. *Rapid Communications in Mass Spectrometry* 31, 1057–1066.
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