

Calibration of the carbonate clumped isotope thermometer from land snails

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Carbonate clumped-isotope (Δ_{47}) thermometry is based on the temperature dependence of the abundance of $^{13}\text{C}^{18}\text{O}^{16}\text{O}_2^{2-}$ ion groups within the mineral lattice and requires no independent information on the isotopic composition of parent waters, thus being widely investigated in many types of carbonate materials, including some biogenic carbonates such as foraminifera and coral. However, its application in the land snail (an important terrestrial paleoenvironmental archive) is still relatively scarce and whether snail shell carbonate Δ_{47} is impacted by biologically-driven fractionation (the vital effect) remains controversial. We suspect these ambiguities may stem from the lacking of precisely temperature-controlled calibration samples in previously natural-environment-based studies. Also, the standardization scheme (CDES: carbon dioxide equilibrium scale) of carbonate Δ_{47} measurements used in previous studies may lead to additional analytical errors, obstructing the identification for the potential vital effects in the Δ_{47} composition of land snail shells.

Here, we cultured two land snail species with different environmental tolerance (thermos-humidiphilous species: *Achatina fulica* (*A. fulica*); cold-aridiphilous species: *Cathaica fasciola* (*C. fasciola*)) under strictly controlled temperature conditions, covering a growth temperature range of 15–33°C; moreover, we reported the Δ_{47} values of these aragonitic snail shells on a newly developed I-CDES scale using carbonate-based standardization refer to [1]. Results show that the shell Δ_{47} composition both for *A. fulica* and *C. fasciola* correlated significantly with the cultured temperature in their respective optimum temperature ranges (*A. fulica*: 25–33°C; *C. fasciola*: 15–25°C), indicating their reliability of taking as a temperature proxy. However, the shell Δ_{47} values for all cultured *C. fasciola* constantly show a negative deviation from the expected equilibrium values, leading to statistically distinguishable calibration regressions between *A. fulica* and *C. fasciola*. We attribute the lower than equilibrium values to the existence of the vital effect in land snail shells, and more specifically, to the CO_2 degassing associated with dehydration/dehydroxylation during carbonate precipitation in the snail's calcifying fluid.

Key words: Δ_{47} ; land snail shells; culturing experiment; vital effects; terrestrial temperature proxy

[1] Bernasconi et al. (2021) *Geochemistry, Geophysics, Geosystems*, 22, e2020GC009588.
https://doi.org/10.1029/2020G

This work was funded by the National Natural Science