Elusive "vital effects" in the clumped isotope thermometer; a focus on Echinoidea

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The carbonate clumped isotope thermometer is a relatively new paleotemperature proxy based on the thermodynamic preference for the formation of heavy-heavy ^{13}C-^{18}O bonds within the carbonate crystal lattice. The success of carbonate clumped isotope thermometry is founded upon the ability to reconstruct carbonate mineral formation temperature independent of the $\delta^{18}O$ of the parent fluid. A further advantage is the percieved lack of "vital effects" in the clumped isotope composition of biogenic carbonate in groups that exhibit strong non-equilibrium signatures in $\delta^{18}O$ and $\delta^{13}C$.

Subtle non-equilibrium fractionation in the clumped isotopic composition of cold water corals, warm water corals, deep sea corals and cephalopods has however recently been reported. Echinoiderms exhibit strong vital effects in $\delta^{18}O$ and $\delta^{13}C$, employing an intracellular strategy of biomineralization, thus afford a good target to explore vital effects in clumped isotope composition.

We present the clumped isotope composition (Δ_{47}) of 24 inter-skeletal elements from 5 echinoid species with growth temperatures varying from 9˚C to 28˚C. Whilst our data shows on average a positive 0.017‰ offset in Δ_{47} from expected values, when considering all statistical errors the Δ_{47} of echinoid calcitie remains within error of inorganic calibration of the clumped isotope thermometer within the 0-250˚C temperature range. This is compared to "vital effects" observed in other groups, and raises the question of the validity of the existence of vital effects in organic calcite.

Our study provides a valuable interface, framing the discussion of "vital effects" in the clumped isotope thermometer within the context of community-wide changes in data processing of Δ_{47} measurement and recently published inorganic calibrations. Improvements in the assessment of uncertainties in the clumped isotope thermometer enhance our ability to characterise carbonate formation temperature based on Δ_{47}.