The ^{13}C-^{18}O clumped isotopic quirks of cephalopods: a strong case for vital effects in the clumped isotope composition of biogenic carbonate

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Cephalopods, specifically ammonites and belemnites, have been extensively used in paleo-climate temperature reconstruction using stable isotopes ($\delta^{18}O$ and $\delta^{13}C$).

For this approach to be valid there should be no biogenic fractionation known as "vital effects", ecological factors and ontogenetic changes that affect the lifestyle of the animal.

Carbonate clumped isotope paleothermomety is an innovative temperature proxy based on the thermodynamically dependent relative abundance of ^{13}C-^{18}O bonds within the carbonate crystal lattice, quantified by the metric Δ_{47}. Calculation of Δ_{47} does not require an *a priori* assumption of $\delta^{18}O_{sw}$.

Our measurements of the clumped isotopic composition of modern cephalopods indicate a significant disequilibrium signal that shows intra-shell correlation with $\delta^{18}O$ shell carbonate. We show a decrease in Δ_{47} from juvenile to adult septa that do not correspond with changes in surface seawater temperature or vertical migration through the water column during the lifespan of the organism.

Vital effects in Δ_{47} and correlated intra-shell Δ_{47} and $\delta^{18}O$ have important implications for paleoclimate reconstructions using the stable isotopic composition of cephalopod calcite. Differences in Δ_{47} and $\delta^{18}O$ of fossil specimens with minimal evidence of diagenetic alteration may in part be due to previously un-diagnosed "vital effects".