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Clumped isotopes thermometry in *Melanopsis* shells and its paleoclimate implications

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Carbonate clumped isotopes thermometry is based on the relationship of ^{13}C-^{18}O bond abundance (measured as Δ_{47}) in the carbonate lattice with the carbonate formation temperature. Our measurements of synthetic calcite precipitated by bubbling N_2 to remove CO_2 out of saturated $Ca(HCO_3)_2$ solutions, following the original thermometer calibration experiments (Ghosh et al., 2006), are consistent with these original results. On the other hand, calcite precipitated synthetically by passive diffusion of CO_2 out of saturated $Ca(HCO_3)_2$ solutions, at a temperature range of 8˚C to 70˚C, resulted in calcite forming as a surface layer at the water-air interface and a Δ_{47}-T relationship slope that is less steep. These carbonates probably reflect kinetic isotope effects associated with fractionation in CO_2 degassing and slow DIC-water isotope exchange prior to carbonate precipitation; this observed relationship is consistent with the dis-equilibrium observed in speleothems.

Most marine biogenic carbonates are consistent with the original Ghosh et al., (2006) thermometer calibration. We examine Δ_{47} in aquatic fresh water gastropods as a terrestrial analog, focusing on *Melanopsis* snails, sampled in various water bodies along the Jordan Rift Valley (Israel), with $\sim$10˚C temperature range. Clumped isotope results are consistent with measured water temperatures. Oxygen isotope composition of water derived from clumped isotopes based temperatures together with shell oxygen isotope composition broadly agree with the sampled water bodies, suggesting that clumped isotopes in *Melanopsis* shells, like in marine organisms, reflect isotopic equilibrium and fall on the same clumped isotopes thermometer calibration.

We further analyzed a number of fossil *Melanopsis* snails from the early and mid Holocene, LGM, and MIS 3. We observe an increase in water temperature from glacial to Holocene samples. Preliminary data shows an ^{18}O-enriched Holocene by $\sim$2‰ relative to the LGM; opposite of the trend observed in other regional records such as Dead-Sea sediments, Soreq cave speleothems, and Mediterranean Sea foraminifera.

References: [1] Ghosh et. al. (2006) GCA, 70: 1439-1456.