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Application of combined fluid-inclusion and clumped isotope thermometry to biogenic and inorganic carbonates

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Biogenic and inorganic carbonates are widely used to reconstruct past temperatures and fluid compositions. For decades, calcification temperatures have been inferred from oxygen isotope composition ($\delta^{18}\text{O}$) of calcium carbonates (CaCO_3) assuming the $\delta^{18}\text{O}$ of the parental fluid and isotopic equilibrium precipitation conditions. The development of the clumped isotope (Δ_{47}) thermometer allows for reconstructing equilibrium calcification temperatures without requiring a priori knowledge of the water $\delta^{18}\text{O}$ values.

Carbonate minerals can also contain several weight percentages of water, which are typically trapped within microscopic pores. These fluid-inclusions may preserve remnants of the parental fluid, which can be analyzed for the $\delta^{18}\text{O}$ as well as hydrogen isotopic ($\delta^2\text{H}$) composition. Subsequently, the $\delta^{18}\text{O}$ of fluid-inclusion and host carbonate may allow for the determination of paleotemperatures by providing constraint on the $\delta^{18}\text{O}$ water value.

Reasonable equilibrium temperatures can be obtained for speleothem calcites from cave systems. On the contrary, anomalously high temperatures are derived from $\delta^{18}\text{O}$ fluid-inclusion and calcite pairs in soil carbonates possibly suggesting diffusion of trapped water from host CaCO_3 . Deeply-buried and subsequently exhumed (inorganic) calcite veins have yielded discrepant paleotemperature estimates between fluid-inclusion and Δ_{47} thermometers. The distinctly lower fluid-inclusion derived temperatures might be attributed to kinetic fraction during initial vein cementation and/or isotopic re-equilibration between fluid-inclusions and CaCO_3 at lower temperatures during uplift.

Heating experiments demonstrate that the oxygen isotope exchange between fluid inclusions and host carbonate is limited for inorganic calcite and aragonite at high temperatures (175°C) for short timescales (90 minutes). In contrast, considerable positive shifts in the $\delta^{18}\text{O}$ of fluid inclusions have been recorded in biogenic aragonites during experimental heating, which coincide with lower carbonate $\delta^{18}\text{O}$ values (albeit to a lesser extent due to the overwhelming amount of oxygen in the CaCO_3), indicative of re-equilibration between host carbonate and pore fluids. This effect leads to apparently high equilibrium temperatures. In conjunction, the Δ_{47} derived temperatures do not change significantly after heating of inorganic aragonite, whereas a considerable higher Δ_{47}

temperature is derived from aragonitic bivalve samples after heating. The positive shift in both thermometers has interpreted to reflect re-crystallization of CaCO_3 and isotopic re-equilibration between the host carbonate and fluid-inclusions. This exchange might be facilitated by extremely small fluid-inclusions present in biogenic carbonates and/or water associated with organic substances.

Importantly, these isotopic exchange processes in biogenic aragonites took place in the absence of an external fluid and below the temperature thresholds for solid-state-reordering and the aragonite-to-calcite transition. The novel application of combined fluid-inclusion and clumped isotope thermometry has a proven utility in determining equilibrium precipitation temperatures, monitoring preservation of the primary fluid-inclusions and re-crystallization processes during diagenesis. However, additional experiments and analytical improvements are needed to further constrain the diagenetic behavior of this proxy.