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

Jeroen van der Lubbe¹, Cas Nooitgedacht¹, Philip Staudigel², and Martin Ziegler³

¹Department of Earth Sciences, Vrije Universiteit Amsterdam (VU), the Netherlands (h.j.l.vander.lubbe@vu.nl, c.w.nooitgedacht@vu.nl)
²School of Earth and Environmental Sciences, Cardiff University, United Kingdom (staudigelp@cardiff.ac.uk)
³Department of Earth Sciences, Universiteit Utrecht, the Netherlands (m.ziegler@uu.nl)

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 (δ¹⁸O) of calcium carbonates (CaCO₃) assuming the δ¹⁸O of the parental fluid and isotopic equilibrium precipitation conditions. The development of the clumped isotope (Δ⁴⁷) thermometer allows for reconstructing equilibrium calcification temperatures without requiring a priori knowledge of the water δ¹⁸O 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 δ¹⁸O as well as hydrogen isotopic (δ²H) composition. Subsequently, the δ¹⁸O of fluid-inclusion and host carbonate may allow for the determination of paleotemperatures by providing constraint on the δ¹⁸O water value.

Reasonable equilibrium temperatures can be obtained for speleothem calcites from cave systems. On the contrary, anomalously high temperatures are derived from δ¹⁸O fluid-inclusion and calcite pairs in soil carbonates possibly suggesting diffusion of trapped water from host CaCO₃. Deeply-buried and subsequently exhumed (inorganic) calcite veins have yielded discrepant paleotemperature estimates between fluid-inclusion and Δ⁴⁷ 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 CaCO₃ 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 δ¹⁸O of fluid inclusions have been recorded in biogenic aragonites during experimental heating, which coincide with lower carbonate δ¹⁸O values (albeit to a lesser extent due to the overwhelming amount of oxygen in the CaCO₃), indicative of re-equilibration between host carbonate and pore fluids. This effect leads to apparently high equilibrium temperatures. In conjunction, the Δ⁴⁷ derived temperatures do not change significantly after heating of inorganic aragonite, whereas a considerable higher Δ⁴⁷
temperature is derived from aragonitic bivalve samples after heating. The positive shift in both thermometers has interpreted to reflect re-crystallization of \( \text{CaCO}_3 \) 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.