

Evaluating the removal of contaminants in biogenic carbonates for clumped isotope studies

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Carbonate clumped isotope measurements require careful cleaning of the sample and/or the analyzed CO₂ gas to avoid interferences on mass 47 measurements, which can derive from a number of contaminants including hydro-, halocarbons or sulfuric compounds [1]. This is especially true for studies on biogenic carbonates. Most previous studies employ a simple pH-adjusted hydrogen peroxide oxidation technique, and the effects on $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ are found to be minor in samples with high carbonate content, yet the effects on Δ_{47} are uncertain [2, 3]. In this study, we assessed organic solvent-based cleaning processes as well as those using an oxidizing solution of hydrogen peroxide, neutralized to pH ~8-9, and allowed to react with the sample overnight. The different cleaning techniques were tested on coccolithophores cultured at different temperatures in the laboratory, sediment traps and standards contaminated with organic matter from non-calcifying coccolithophores. Through clumped isotope measurements and scanning electron microscopy, potential dissolution and recrystallization due to the cleaning techniques were measured and visualized. Almost no effects were found on $\delta^{13}\text{C}$, while different cleaning techniques shifted the $\delta^{18}\text{O}$ by up to 0.3‰. Samples without cleaning had systematically higher Δ_{47} values. For some samples, there were appreciable differences in the Δ_{47} values between different cleaning techniques. Visually, more intensive cleaning techniques led to minor dissolution and disaggregation of coccospheres and coccoliths. This study thus highlights the importance of applying and validating cleaning techniques for clumped isotope studies on biogenic carbonates.

[1] Eiler J.M. & E. Schauble. 2004. “ $^{18}\text{O}^{13}\text{C}^{16}\text{O}$ in Earth’s atmosphere.” *Geochimica et Cosmochimica Acta* 68 (23) 4767-4777.

[2] Falster, G., S. Delean, J. Tyler. 2018. “Hydrogen Peroxide Treatment of Natural Lake Sediment Prior to Carbon and Oxygen Stable Isotope Analysis of Calcium Carbonate.” *Geochemistry, Geophysics, Geosystems* 19 (9) 3583-3595.

[3] Katz, Amandine. 2017. “Développement du thermomètre Δ_{47} appliqué sur coccolithes : de la calibration en laboratoire à l’applicabilité au registre sédimentaire.” [Doctoral dissertation, Sorbonne Paris Cité].