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Dual clumped isotopes in speleothem carbonate

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Speleothem carbonates are important archives for the reconstruction of terrestrial paleo-environmental conditions, but it is challenging to resolve between the temperature, hydrological and kinetic information that is recorded in their stable isotopic composition. Recently, it has been demonstrated that dual clumped isotope thermometry, i.e., analysis of Δ_{48} alongside Δ_{47} in CO_2 evolved from phosphoric acid digestion of carbonate [1], holds the potential to identify, quantify and correct for kinetic bias in carbonate formation temperatures without having to know the oxygen isotope composition of the water from which the carbonate precipitated [2].

We performed paired Δ_{47}-Δ_{48} measurements on speleothems to investigate to which extent isotopic disequilibrium is recorded in these archives. No significant disequilibrium bias is recorded in slowly grown pool carbonates and cryogenic carbonates, and Δ_{47} derived temperatures agree with expected formation temperatures. Stalagmites sampled at the top to represent present-day conditions and close to their growth axis where disequilibrium should be least pronounced also plot indistinguishably from dual clumped isotope equilibrium. However, most stalagmites record a slight, but still significant -Δ_{47} disequilibrium bias with respect to known formation temperatures. The observed bias originates from rapid dehydration/dehydroxylation of bicarbonate occurring dissolved in the drip water. Due to mass spectrometric shot noise limit constraints on Δ_{48}, disequilibrium bias is challenging to be identified through paired Δ_{47}/Δ_{48} analyses alone. Unless kinetic bias can be ruled out independently, Δ_{47} values of stalagmites should, therefore, only be considered as upper estimates of cave temperature.

Correction of kinetic bias in measured Δ_{47}-Δ_{48} pairs and, hence, accurate cave temperature reconstruction seems possible, but is at the expense of precision relative to kinetically unbiased archives such as bivalve mollusks [3].

[1[Fiebig et al. (2019), Chem. Geol. 522, 186-191

[2] Bajnai et al. (2020), Nat. Commun. 11:4005

[3] Schlidt et al. (2025), Geochim. Cosmochim. Acta 410, 174-187.