High-precision analysis of Δ_{48} and Δ_{47}: Resolving temperature from the kinetic information recorded in carbonates

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High-precision analysis of the excess abundance (relative to the stochastic distribution) of m/z 48 isotopologues in CO_2 evolved from acid digestion of carbonates (Δ_{48}) has recently not been possible due to the relatively low natural abundance of ^{18}O. Here we show that the 253 Plus™ gas source mass spectrometer equipped with Faraday cups and 10^{13} Ω resistors can perform combined Δ_{47} and Δ_{48} analyses on carbonates with external reproducibilities (1SD) of 0.010‰ and 0.030‰, respectively.

~10 mg aliquots of carbonates are digested with phosphoric acid at 90 °C using a common acid bath. The evolved CO_2 is purified using an automated gas preparation system (including cryotraps and GC) and analyzed for its Δ_{47} and Δ_{48} compositions using the dual inlet system of a 253 Plus™ gas source mass spectrometer. Raw Δ_{47} and Δ_{48} values are finally normalized to the Carbon Dioxide Equilibrium Scale (CDES).

Δ_{48} values for carbonate reference materials Carrara and ETH 1 - 4 increase with Δ_{47} as is predicted if temperature was the major parameter controlling bond-ordering in these carbonates. However, rate-limiting kinetics involved in carbonate precipitation can significantly drag carbonate Δ_{47} and Δ_{48} away from corresponding equilibrium values [1]. Combined analysis of m/z 47 and 48 isotopologue abundances in CO_2 evolved from acid digestion of natural carbonates has an excellent potential for the determination of accurate carbonate formation temperatures *and* the identification of rate-limiting biomineralization reactions. As a consequence, paired (Δ_{47} and Δ_{48}) clumped isotope analysis of fossil carbonates may allow to reconstruct paleotemperatures independent of a kinetic bias.

[1] Guo, W. & Zhou, C. (2019). *7th International Clumped Isotope Workshop*, Queen Mary, Long Beach, CA, USA.