

Calibration of the dual clumped isotope thermometer for carbonates

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The Δ_{47} (paleo)thermometer has opened a new avenue to determine carbonate formation temperatures independent of the oxygen isotopic composition of the fluid the carbonate crystallized from. A major limitation of this thermometer is introduced by kinetic effects, i.e. if homogeneous isotopic equilibrium is not attained within the precipitated carbonate. Dual clumped isotope thermometry, i.e. high-precision analysis of Δ_{48} along with Δ_{47} in CO_2 evolved from phosphoric acid digestion of carbonates, has become possible only recently (Fiebig et al., 2019). It provides a new opportunity to identify (bio)mineralization pathways and to determine carbonate formation temperatures devoid of a kinetic bias, just based on isotopic analysis of the single carbonate phase (Guo, 2020; Bajnai et al., 2020).

Identification of the nature and extent of kinetic effects as well as reconstruction of formation temperatures unbiased by kinetics requires knowledge of the position of equilibrium in Δ_{47} vs Δ_{48} space. Here, we present Δ_{47} and Δ_{48} data on carbonates that were previously considered as having crystallized under close-to-equilibrium conditions in a temperature range of 8 to 1100 °C. In addition to these samples, we analyzed the dual clumped isotopic compositions of scale carbonates and experimental precipitates of known precipitation temperatures to test the robustness of our Δ_{47} – Δ_{48} - temperature relationships.

We further demonstrate that carbonates precipitated at high pH can exhibit huge offsets in Δ_{48} from equilibrium that well exceed corresponding Δ_{47} offsets. An anti-clumped Δ_{48} value is obtained for a technical calcite that was precipitated by the injection of CO_2 into $\text{Ca}(\text{OH})_2$. Its negative Δ_{48} value arises from a combinatorial effect (Röckmann et al., 2016), i.e. the carbonate oxygen derives from two sources with different bulk oxygen isotopic compositions. Besides the identification of kinetically controlled (bio)mineralization processes and accurate reconstruction of carbonate formation temperatures, dual clumped isotope analysis, therefore, allows to trace the isotopic heterogeneity of oxygen pools contributing to carbonate and CO_2 formation.

References: Bajnai et al. (2020), Nature Communications 11:4005; Fiebig et al. (2019), Chemical Geology 522, 186-191; Guo (2020), Geochimica et Cosmochimica Acta 268, 230-257; Röckmann et al. (2016), Scientific Reports 6: 31947