

CO₂ clumped isotope (Δ_{47} , Δ_{48}) and oxygen isotope resetting in a common acid bath is facilitated by certain carbonate samples.

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Exchange between gaseous carbon dioxide and carbonate-bearing mineral phases is a well-documented phenomenon¹⁻². We show that carbonate minerals that precipitated from extremely alkaline solutions facilitate these exchange reactions at room temperature. These reactions occur within autosampler carousels, and thus present a substantial concern for the isotopic analysis of carbonate minerals, making their effect similar to CO₂-water exchange during acid digestion of carbonates³. These exchange reactions may be facilitated by surface-bound water or OH⁻ groups, with near-insignificant mass of oxygen as to minimally affect bulk $\delta^{18}\text{O}$ measurements. These reactions can significantly bias clumped isotope (Δ_{47} , Δ_{48}) measurements. Samples that display this behavior can be easily identified and removed by laboratories that implement both equilibrated CO₂ standardization (that is unaffected by carbonate-CO₂ exchange) and carbonate standards (which are affected), however identification is much more challenging in laboratories that only use one or the other. We further demonstrate that these exchange reactions can be identified experimentally by sealing thermodynamically reset (1000°C) CO₂ with a suspected carbonate powder (Figure 1). We conclude that these reactions can be minimized through careful sample screening, or loading fewer samples into an autosampler carousel.

References

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Figure 1: CO₂-carbonate re-equilibration in sealed vessels. Error bars show $\pm 95\%$ confidence intervals.

