High-precision $\Delta_{47}$ and $\Delta_{48}$ acid fractionation factors for aragonite, calcite, dolomite, siderite and witherite

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Dual-clumped isotope thermometry comprises the joint measurement of $\Delta_{47}$ and $\Delta_{48}$ in CO$_2$ evolved from phosphoric acid digestion of carbonates$^1$. The benefit over $\Delta_{47}$-only measurements lies in the capability to identify if $\Delta_{47}$ was affected by rate-limiting kinetics in addition to temperature, and to reconstruct accurate carbonate formation temperatures devoid of kinetic bias$^2$.

Direct measurements of $\Delta_{63}$ and $\Delta_{64}$ in carbonates is not technically feasible. During acid digestion of carbonates, fractionations of clumped isotopes ($\Delta_{63} \rightarrow \Delta_{47}$ and $\Delta_{64} \rightarrow \Delta_{48}$) occur, but the exact magnitude of these acid fractionation factors (AFFs) is uncertain and varies across published estimates.

Theoretical modeling$^3$ indicates cation-dependent differences in AFFs for different carbonate mineralogies. Follow-up empirical studies yielded somewhat inconsistent $\Delta_{47}$ results; some did not observe any differences in AFFs (e.g., for calcite, aragonite, and dolomite$^4$; for calcite and dolomite$^5$), whereas others report differences (e.g., for calcite and dolomite$^6$; for calcite, aragonite, dolomite, and magnesite$^7$).

Recent advances in gas source mass spectrometry led to significant improvements in the external repeatability of clumped isotope measurements, e.g., from $> 20$ ppm to 7-9 ppm for $\Delta_{47}$.$^8$ With this improved analytical set-up, we analyzed a collection of stochastic aragonite, calcite, dolomite, siderite and witherite samples for their $\Delta_{47}$ and $\Delta_{48}$ values to investigate if cation substitution and mineralogy has any effect on AFFs.