

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

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Dual-clumped isotope thermometry comprises the joint measurement of Δ_{47} and Δ_{48} in CO_2 evolved from phosphoric acid digestion of carbonates^[1]. The benefit over Δ_{47} -only measurements lies in the capability to identify if Δ_{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 Δ_{63} and Δ_{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 Δ_{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 Δ_{47} ^[1,8]. With this improved analytical set-up, we analyzed a collection of stochastic aragonite, calcite, dolomite, siderite and witherite samples for their Δ_{47} and Δ_{48} values to investigate if cation substitution and mineralogy has any effect on AFFs.

[1] Fiebig, J. et al. (2019) *Chem. Geol.* 522, 186–191.

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

[3] Guo, W.F. et al. (2009). *Geochim. Cosmochim. Acta* 73, 7203–7225.

[4] Defliese, W.F. et al. (2015) *Chem. Geol.* 396, 51–60.

[5] Bonifacie M. et al. (2017) *Geochim. Cosmochim. Acta* 200, 255-279.

[6] Murray, S.T. et al. (2016) *Geochim. Cosmochim. Acta* 174, 42–53.

[7] Müller, I.A. et al. (2017) *Chem. Geol.* 449, 1–14.

[8] Fiebig, J. et al. (2021) *Geochim. Cosmochim. Acta* 312, 235–256.