Making the Case for Reconciled Δ_{47} Calibrations Using Omnivariant Generalized Least-Squares Regression

MATHIEU DAËRON

Laboratoire des Sciences du Climat et de l'Environnement
Presenting Author: daeron@lsce.ipsl.fr

For fundamental thermodynamic reasons, ^{13}C-^{18}O bonds in carbonate minerals formed under isotopic equilibrium conditions are more abundant than predicted for a random distribution of isotopes, yielding positive Δ_{47} clumped-isotope signatures decreasing as a function of formation temperature [1]. Although most Earth-surface carbonates are unlikely to achieve complete isotopic equilibrium, Δ_{47} values of many biogenic/abiotic calcites formed under very different crystallization conditions, with irreconcilable water-calcite oxygen-18 fractionation laws, seemingly follow indistinguishable temperature calibrations, as documented by various groups [e.g., 2-4]. That is not to say that all groups agree on a single calibration linking Δ_{47} and temperature: a recent comparison of 14 reprocessed studies still found evidence for significant inter-laboratory discrepancies [3]. Rigorous statistical tests aiming to prove/disprove consistency between Δ_{47} calibrations are particularly challenging because of potentially large, correlated analytical errors associated with standardization procedures [5], and in some cases because of strong correlations in the uncertainties of formation temperature estimates, making classical least-squares regression ill-suited to model these data.

I propose a new formulation for least-squares regression of data with arbitrarily complex covariances between all predictor and response observations, generally applicable to many sorts of geochemical data. I use this "Omnivariant Generalized Least-Squares" (OGLS) approach to compare 7 published Δ_{47} calibration datasets, (re)processed following the newly established I-CDES scale, purportedly allowing robust comparisons between measurements across laboratories [6]. None of these reprocessed calibration data sets are found to deviate significantly from a single, unified regression line, with an overall reduced chi-squared statistic (adjusted for data covariance according to OGLS) of 0.8, consistent with slightly overestimated uncertainties on temperature constraints. This finding further strengthens the interpretation that "well-behaved" carbonates (to a rough but convenient approximation, those precipitated from an isotopically equilibrated DIC pool) follow a unified Δ_{47} calibration despite obvious oxygen-18 differences. Δ_{47} thermometry has now solved most of the methodological challenges standing in the way of its widespread application to many scientific issues.

[1] Schauble et al. (2006) https://doi.org/10.1016/j.gca.2006.02.011
[2] Kele et al. (2015) https://doi.org/10.1016/j.gca.2015.06.032
[3] Petersen et al. (2019) https://doi.org/10.1029/2018GC008127
[4] Anderson et al. (2021) https://doi.org/10.1029/2020GL092069
[5] Daëron (2021) https://doi.org/10.1029/2020GC009592
[6] Bernasconi et al. (2021) https://doi.org/10.1029/2020GC009588