



## Getting Better All the Time: How Well Do Recent Carbonate Clumped Isotope Calibrations Agree With Each Other?

Mathieu Daëron (1), Dominique Blamart (1), Marion Peral (1), Russell Drysdale (2), Tyler Coplen (3), Damien Huyghe (4), and Giovanni Zanchetta (5)

(1) Laboratoire des Sciences du Climat et de l'Environnement LSCE / IPSL, CEA-CNRS-UVSQ, Université Paris-Saclay, France, (2) University of Melbourne, Australia, (3) U.S. Geological Survey, Reston, Virginia, USA, (4) Laboratoire d'Ecogéochimie des Environnements Benthiques, CNRS - Université Pierre et Marie Curie, France, (5) University of Pisa, Italy

Carbonate clumped isotope thermometry provides a method to constrain the crystallization temperature of carbonate minerals based on statistical anomalies in the internal distribution of carbon and oxygen isotopes among  $(\text{CO}_3)^{2-}$  isotopologues, without requiring prior knowledge of parent water  $\delta^{18}\text{O}$  values. Precisely calibrating this isotopic thermometer has been the focus of a large body of work over the past 12 years, with somewhat contrasted results. Although calibrations studies originating from the same laboratory generally appear self-consistent, inter-laboratory discrepancies are larger than expected for purely analytical uncertainties, and they remain an important factor limiting carbonate clumped isotope applications. The situation is further complicated by the rapid pace of technical and analytical advances over the past decade, which hinders direct comparisons between early calibration data and more recent measurements. Nevertheless, studies of the past few years based on a large number of observations appear to yield very similar thermal sensitivities ("calibration slope"), although large differences persist among results from different laboratories. A number of observations suggest that the remaining discrepancies are primarily caused by the use of "thermodynamic"  $\text{CO}_2$  standards (as opposed to carbonate standards), and to a lesser extent by uncertainties in the isotopic fractionations associated with the phosphoric acid reaction used to convert samples to  $\text{CO}_2$ . To test this hypothesis, we describe a simple way to compare measurements from different laboratories with two or more carbonate standards in common, and we find excellent agreement among inorganic calibration regressions obtained using very different analytical protocols. Moreover, the improvement in long-term reproducibility that we obtained using carbonate standards makes it possible to detect small but resolvable differences between rapidly calcified biogenic carbonates and very slow-growing inorganic calcites, which argues against the use of a single calibration relationship for all types of carbonates.