Goldschmidt 2021 Abstract
https://doi.org/10.7185/gold2021.7368

Revisiting Isotopic fractionations Associated with Phosphoric Acid Digestion of Carbonates

MATHIEU DAËRON[1] AND WEIFU GUO[2]

[1]Laboratoire des Sciences du Climat et de l'Environnement
[2]Woods Hole Oceanographic Institution

Presenting Author: daeron@lsce.ipsl.fr

The clumped-isotope signatures of carbonate ion groups involve 16 multiply-substituted isotopologues, but only half as many for carbon dioxide. Phosphoric acid digestion of carbonates, in turn, involves 36 isotopic pathways with different kinetic isotope fractionations, resulting in non-trivial isotopic effects not limited to the widely-used acid-temperature-dependent correction to Δ47 measurements. Here we extend the theoretical model of these kinetic isotope effects first proposed by Guo et al. [1] by considering individual effects on each isotopologue instead of aggregating all offsets relevant to the mass-47 anomaly and reassessing its predictions in light of the methodological advances of the past few years, which include substantially improved precision/accuracy of Δ47 measurements and the emergence of several spectroscopic methods targeting clumped isotopes.

As noted by Guo et al. (2009), the "acid offset" between mass-63 anomaly of a reagent carbonate and the Δ47 value of the evolved CO2 (Δ63→47) is not strictly constant. We show that these small variations vary linearly with various clumped-isotope anomalies, and that most acid offsets (e.g., Δ63→47, Δ64→48, Δ3668→638, Δ2688→828) are primarily affected by only a few carbonate isotopologues. For instance, Δ63→47 varies by up to 15~ppm depending on its 13C16O16O18O, 12C16O18O18O anomalies, and Δ63→47 for carbonates with identical Δ63 values resulting from different processes (e.g., achievement of thermodynamic equilibrium versus mixing of two stochastic carbonates with different bulk compositions) may differ by up to 5~ppm. By contrast, Δ64→48 is virtually constant, as are Δ3668→638, Δ2688→828, implying that spectroscopic measurements of clumped isotopes (Δ638, Δ828) should contend with rather simple acid effects, and allowing us to assess the level of variability to be expected when converting Δ47 to Δ638 values. Finally, this work calls attention to competing, somewhat ambiguous definitions of clumped-isotope anomalies, which will matter increasingly as we start combining observations from mass spectrometry and molecular spectroscopy.

[1] W. Guo, J. L. Mosenfelder, W. A. Goddard III, J. M. Eiler (2009). Isotopic fractionations associated with phosphoric acid digestion of carbonate minerals: Insights from first-principles theoretical modeling and clumped isotope measurements. Geochimica et Cosmochimica Acta 73, 10.1016/j.gca.2009.05.071