Clumped Isotope Methodology

Carbonate samples were drilled with a small dental drill using a 0.5 mm carbide bit to avoid fracturing and veining, unless specifically targeted. Depending on the size of the phase of interest, 2-10 mg of powder was drilled. Clumped isotope analyses were performed on carbonate powders using a Nu Perspective IRMS at the MIT Carbonate Research Laboratory, following the procedures outlined in Anderson et al. (2021). Samples were acidified with a NuCarb automated sample preparation unit held at 70°C. Carbonate samples (including dolomite) weighing 400–600 μg reacted for 25 minutes in individual glass vials with 150 μl orthophosphoric acid (ρ = 1.93 g/cm³). Evolved CO₂ gas was purified cryogenically and by passive passage through a Porapak trap (1/4" ID; 0.4 g 50/80 mesh Porapak Q) held at −30°C. Purified sample gas and reference gas of known composition were alternately measured on six Faraday collectors (m/z 44–49) in 3 acquisitions of 20 cycles, each with 30 seconds integration time (30 minutes total integration time). Initial voltage was 8–20 V on the m/z 44 beams with 2 × 10⁸ Ω resistors, depleted by approximately 50% throughout an analysis. Sample and standard gases depleted at equivalent rates from microvolumes over the integration time. Each run of approximately 50 individual analyses began with each of ETH-1–ETH-4 in random order, then alternated between blocks of three unknowns and two ETH anchors or IAEA-C2. Additionally, IAEA-C1 was measured once or twice per run as an internal consistency check. The unknown-to-anchor ratio was planned at 1:1 for each run, although gas preparation or mass spectrometer error occasionally modified this ratio. The reference side of the dual-inlet was refilled with reference gas every 10 analyses. No pressure baseline correction was applied.

Raw mass spectrometer data were first processed by removing cycles (i.e., single integration cycles of mass spectrometer measurement) with raw Δ47 values more than 5 "long-term" standard deviations (0.50‰; the mean of the respective cycle-level SD for ETH-1–4 over a 3-month period was 0.10‰) away from the median Δ47 measurement for the analysis (0.2% of cycles removed). Analyses were removed if more than 10 cycles (out of 60 total cycles) fell outside the 5 long-term SD threshold. Analyses with transducer pressure below 15 mbar, typically corresponding to sample collection issues or incomplete digestion, and analyses that ran misbalanced by > 1% were also removed. After cycle-level outlier removal, data were processed using the “D47crunch” Python package (Daëron, 2023) with IUPAC 17O parameters, a 70°C 18O acid fractionation factor of 1.00871 for calcite (Kim et al., 2007) and 1.009926 for dolomite (Rosenbaum and Shepard, 1986), and projected to the I-CDES with values for ETH-1–4 and IAEA-C2 from the InterCarb exercise (Bernasconi et al., 2021; Daëron, 2021). Raw Δ47 measurements were converted to the I-CDES using a pooled regression approach that accounts for the relative mapping of all samples in δ47-Δ47 space (Daëron, 2021). The long-term external repeatability (1SD) of Δ47 for all analyses (after data processing described above) is <<BLIMP VALUE>>‰. IAEA-C1 was treated as an unknown and used as an internal consistency check for Δ47 (n = <<BLIMP VALUE>>, mean = <<BLIMP VALUE>>‰ versus nominal value of 0.302‰, 1SEexternal = <<BLIMP VALUE>>‰, 1SD = <<BLIMP VALUE>>‰). The dataset contains <<BLIMP VALUE>> analyses of <<BLIMP VALUE>> unique samples and anchors conducted over <<BLIMP VALUE>> sessions.