Dual Clumped and Triple Oxygen Isotope Measurements of Speleothems from Paraíso Cave, Eastern Amazon Lowlands, and Their Bearing on Interpretations of Existing δ18O Records

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Dual clumped-isotopes (Δ - Δ) and triple oxygen isotopes (Δ ' O) are emerging measurements that can be applied to speleothems to provide information about kinetic isotope effects, formation temperature, and hydrologic processes beyond what is possible from traditional stable isotope records (δ C, δ O). We applied these isotope systems to speleothems from Paraíso Cave, Brazil to better contextualize the δ O record, which shows a large decrease of ≈6 ‰ from the late Glacial (≈25 ka) into the Holocene (<11.8 ka) and was broadly interpreted as the result of an increase Rayleigh distillation and therefore precipitation amount (Wang et al., 2017, Nature 541, 204:207). The new data (n=9) span Marine Isotope Stage 4 (~69 ka) to the late Holocene (~0.8 ka) and support near-equilibrium formation conditions. Dual clumped-isotope data do not resolve negative correlations between Δ and Δ that have been predicted for variable kinetic fractionations. In addition, temperatures inferred from Δ measurements $T(\Delta)$ average 22 °C and most of the values fall within error of each other with no clear temporal patterns. This is 2 to 4 °C cooler than the modern cave temperature of 26 °C (depending on which calibration is used) and this temperature difference is in the opposite direction of that typical for within-cave kinetic effects. Triple oxygen isotopes also support δ O variability being driven by climate. The data show a slight negative correlation between Δ' O and δ O, inconsistent with within-cave kinetic effects being the sole driver but consistent with variable Rayleigh distillation. Collectively, our data show no indication of marked changes in kinetic fractionation across the period, lending support to climate-based interpretations of the Paraíso δ O record (including the initially proposed Rayleigh-distillation mechanism). The $T(\Delta)$ record, taken at face value, shows the cave was not measurably cooler during glacial times compared to the present. Building on the previous δ O interpretation of a significantly lower amount of precipitation during the glacial period (58% of modern), this might be explained by lower plant cover and latent heating and therefore greater sensible heating of the ground surface during the glacial period.

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