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Calcite Farming at Hollow Ridge Cave: Calibrating Net Rainfall and Cave Microclimate to Dripwater and Calcite Chemical Variability

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Stable isotope (δ18O and δ13C) and trace element records in cave speleothems are often interpreted as climate changes in rainfall amount or source, cave air temperature, overlying vegetation and atmospheric pCO_2. However, these records are difficult to verify without in situ calibration of changes in cave microclimate (e.g., net rainfall, interior ventilation changes) to contemporaneous variations in dripwater and speleothem chemistry. In this study at Hollow Ridge Cave (HRC) in Marianna, Florida (USA), cave dripwater, bedrock, and modern calcite (farmed in situ) were collected in conjunction with continuous cave air pCO_2, temperature, barometric pressure, relative humidity, radon-222 activity, airflow velocity and direction, rainfall amount, and drip rate data [1].

We analyzed rain and dripwater δD and δ18O, dripwater Ca2+, pH, δ13C and TCO_2, cave air pCO_2 and δ13C, and farmed calcite δ18O and δ13C to examine the relationships among rainwater isotopic composition, cave air ventilation, cave air temperature, calcite growth rate and seasonal timing, and calcite isotopic composition. Farmed calcite δ13C decreases linearly with distance from the front entrance to the interior of the cave during all seasons, with a maximum entrance-to-interior gradient of $\Delta\delta$13C = -7‰ . A whole-cave "Hendy test" at distributed contemporaneous farming sites reveals that ventilation induces a +1.9 $\pm$ 0.96‰ δ13C offset between calcite precipitated in a ventilation flow path and out of flow paths. Farmed calcite δ18O exhibits a +0.82 $\pm$ 0.24‰ offset from values predicted by both theoretical calcite-water calculations and by laboratory-grown calcite [2]. Unlike calcite δ13C, oxygen isotopes show no ventilation effects and are a function only of temperature. Combining our data with other speleothem studies, we find a new empirical relationship for cave-specific water–calcite oxygen isotope fractionation across a range of temperatures and cave environments:

$1000 \ln \alpha = 16.1(1000/T) - 24.6$

We analyzed anions, cations, and trace elements in dripwater, bedrock, and farmed calcite to examine the relationships between net rainfall, drip rates, drip water chemistry, and calcite chemistry. Dripwater Mg/Ca and Sr/Ca ratios fall on coherent mixing lines between three geochemical endmembers: rainwater, dissolved dolomite, and dissolved limestone. Dripwater Sr/Ca vs. Mg/Ca ratios are also influenced by evaporative enrichment within the epikarst as a function of net rainfall amount [3]. Farmed calcite trace Cation/Ca ratios faithfully track short-term seasonal variations in dripwater chemistry for Na, Mg, Sr, Ba and U. However, speleothem calibrations are unique to each drip site regardless of proximity to one another, suggesting that individual speleothems are unlikely to be useful as a whole-cave hydrologic proxy.

[1] Kowalczk, A. J., Froelich, P. N., 2010. Cave air ventilation and CO_2 outgassing by radon-222 modeling: How fast do caves breathe? Earth & Planet. Sci. Lett. 289, 209-219.

[2] Tremaine, D. M., Froelich, P. N., Wang, Y., 2011. Speleothem calcite farmed in situ: Modern calibration of δ18O and δ13C paleoclimate proxies in a continuously-monitored natural cave system. Geochim. Cosmochim. Acta 75, 4929-4950.

[3] Tremaine, D. M., Froelich, P. N., 2012. Speleothem trace element signatures: A modern hydrologic geochemical study of cave drip waters and farmed calcite. Geochim. Cosmochim. Acta (submitted)