Calcite farming in Florida caves: Calibrating modern calcite $\delta^{18}O$ and $\delta^{13}C$ to ventilation and *in situ* air temperature

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Stable isotope records ($\delta^{18}O$ and $\delta^{13}C$) in cave speleothems are typically interpreted as climate changes in rainfall amount and source, cave air temperature, atmospheric CO_2, and overlying vegetation. But these records are difficult to interpret without *in situ* calibrations between cave microclimate (e.g., ventilation) and contemporaneous calcite isotopic composition. In this study at Hollow Ridge Cave (HRC) in Marianna, Florida (USA), cave dripwater 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, 2]. We analyzed rain and dripwater isotopes, dripwater [Ca^{2+}], pH, $\delta^{13}C$ and TCO_2, cave air pCO_2 and $\delta^{13}C$, and farmed calcite $\delta^{18}O$ and $\delta^{13}C$ to examine the relationships among rainwater isotopic composition, cave air ventilation, cave air temperature, seasonal calcite growth rate and timing, and calcite isotopic composition. Farmed calcite $\delta^{13}C$ decreases linearly with distance from the front entrance to the interior of the cave during all seasons, with a maximum ventilation-induced entrance-to-interior gradient of $\Delta\delta^{13}C$ = -7‰. Farmed calcite $\delta^{18}O$ exhibits a +0.82 ± 0.24‰ offset from values predicted by both theoretical calcite-water calculations and by laboratory-grown calcite (Figure). Unlike calcite $\delta^{13}C$, oxygen isotopes show no ventilation or evaporation 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: $\mathbf{1000 \ln \alpha = 16.1(10^3\ T^{-1}) - 24.6}$ (light blue dashed line in the Figure).

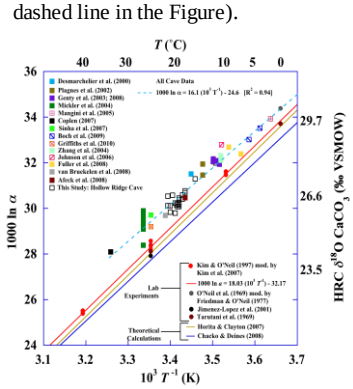

Figure: 1000 ln α vs. $10^3\ T^{-1}$ for HRC calcite (black open squares) plotted with other modern cave studies (solid & crossed squares), laboratory inorganic precipitation values (circles), and theoretical calc-ulations (solid lines). The red line is the best-fit line from [3] as modified by [4]: 1000 ln α = 18.03 ($10^3\ T^{-1}$) - 32.17.

[1] Kowalczk & Froelich (2010) *Earth Planet. Sci. Lett.* **289**, 209-291. [2] Tremaine et al. (2011) *Geochim. Cosmochim. Acta* **75**, 4929-4950. [3] Kim & O'Neil (1997) *Geochim. Cosmochim. Acta* **61**, 3461-3475. [4] Kim et al. (2007) *Chem. Geol.* **246**, 135-146.