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RESEARCH ARTICLE

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Key Points:

- A cave monitoring study was carried out for ~4 years in Hatchet Bay Cave Eleuthera, Bahamas
- The cave is well ventilated, and prior calcite precipitation and water/rock interactions are drivers of the elemental chemistry
- Differences in ventilation of the cave demonstrate that certain locations precipitate closer to $\delta^{18}\text{O}$ equilibrium than others

Supporting Information:

- Supporting Information S1
- Data Set S1

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Dripwater and Calcite Geochemistry Variations in a Monitored Bahamas Cave

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Abstract A cave-monitoring study in Hatchet Bay Cave on the island of Eleuthera, Bahamas, has examined the origins of variations in oxygen and carbon isotopic and minor element composition in cave calcites. Every 3 to 8 months, between 2012 and 2016, temperature, humidity, cave air ($\delta^{13}\text{C}_{\text{CO}_2}$), dripwaters ($\delta^{18}\text{O}$ and $\delta^2\text{H}$ values, and Ca, Sr, and Mg concentrations), and the chemical composition of precipitating calcite ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values, and Ca, Sr, and Mg concentrations) were analyzed in two rooms in the cave. Results from the elemental analyses show that throughout the cave prior calcite precipitation was a driver of the elemental chemistry of the precipitated calcites. In addition, cave calcites show that $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values were positively correlated with Mg/Ca ratios. The Mg/Ca ratios were also positively correlated with lower calcite precipitation rates. Therefore, water/rock interactions may also influence $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values and Mg/Ca ratios of the calcite. Differences were observed between the two rooms, with the Main Room of the cave exhibiting increased prior calcite precipitation, more ventilation, lower calcite precipitation rates, and $\delta^{18}\text{O}$ values, which were farther from equilibrium when compared to the more isolated portion of the cave. These results also validated previous interpretations from Pleistocene stalagmites collected from a nearby Bahamian cave suggesting that a positive covariation between Mg/Ca and $\delta^{13}\text{C}$ values reflects water/rock interactions.

1. Introduction

Speleothems have proven to be important terrestrial climate archives for unraveling paleoclimate history (Aisawaranunt et al., 2018; Fairchild et al., 2006; Lachniet, 2009). Although speleothem studies typically have utilized geochemistry to determine the relative variations of climate, knowledge of the preservation of geochemical signatures in the stalagmites is critical. One approach to understand such impacts in a given cave system is through the monitoring of a modern cave in which speleothem formation is currently active (Mattey et al., 2008, 2016; Partin et al., 2012; Sherwin & Baldini, 2011). This study examines a currently active cave in the subtropical/tropical Atlantic (Hatchet Bay Cave, Bahamas). The Bahamas was chosen as stalagmites from this region have been used to understand the role of the subtropics in responding to and driving major climate changes throughout the Pleistocene (Clement et al., 2010; Murphy et al., 2014, 2017). Although several studies have presented data on speleothems from the Bahamas (Arienzo et al., 2015, 2017; Beck et al., 2001; Hoffmann et al., 2010; Richards et al., 1994), there have been no studies on the relationship between local climate and modern forming stalagmites. One of the reasons for the absence of such studies is the paucity of caves containing actively forming stalagmites (caves with current calcite precipitation) in the Bahamas, arising from the low-relief and limited catchment area over which fluids can become supersaturated with respect to calcite. Hatchet Bay Cave, located on the island of Eleuthera, is an exception. Its passage is accessible year-round and has more extensive speleothem formation than other caves in Eleuthera possibly because of the 10–15 m of overlying limestone. Study of this cave will add additional information to other caves investigated in the subtropical/tropical Atlantic (Mickler et al., 2004; Ridley et al., 2015; Tremaine et al., 2011; Vieten et al., 2016).

2. Stalagmite Geochemistry

Stalagmites form primarily from the precipitation of calcite (CaCO_3) through the degassing of CO_2 from a thin film of saturated dripwater,



with HCO_3^- the dominant dissolved inorganic carbon (DIC) species. Degassing of CO_2 proceeds through the following dehydration mechanism in caves (Guo, 2008; Mickler et al., 2004):



The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of the precipitating mineral are affected by the isotopic composition at the mineral-water and water-air surfaces (Affek & Zaarur, 2014). The mechanism of CO_2 degassing and calcite precipitation is accompanied by kinetic isotope fractionation attributed to the DIC not re-equilibrating with the water (equation (2); Guo, 2008; Affek & Zaarur, 2014). In addition, during the process of degassing, the DIC of the water can undergo isotopic reequilibration with the cave air CO_2 (Dreybrodt & Romanov, 2016). Such impacts may be relatively minor, may complicate the use of isotope ratios to reconstruct cave temperature directly, or may enhance the climate signal preserved in the cave calcite.

Excluding any kinetic fractionation effects, the $\delta^{18}\text{O}$ values of carbonate ($\delta^{18}\text{O}_c$) are dependent on both the temperature and the $\delta^{18}\text{O}$ value of the water ($\delta^{18}\text{O}_w$) at the time of formation (Epstein et al., 1953). Numerous studies have been conducted to determine the temperature dependent fractionation between $\delta^{18}\text{O}_c$ and $\delta^{18}\text{O}_w$ values for carbonates (Craig, 1965; Epstein et al., 1953; Kim & O'Neil, 1997; O'Neil et al., 1969) with a mean fractionation of $\sim -0.2\text{‰}/^\circ\text{C}$. The temperature dependent fractionation equation developed by Kim and O'Neil (1997) used in this study is the modified equation by Kim et al. (2007):

$$1,000\ln(\alpha)_{\text{calcite-H}_2\text{O}} = 18.03(10^3 T^{-1}) - 32.17 \quad (3)$$

With α representing the fractionation factor between two substances (e.g., water and calcite oxygen isotopes) and T in kelvins. A cave monitoring experiment demonstrated a slightly lower fractionation factor for speleothems at $-0.177\text{‰}/^\circ\text{C}$ and this relationship was applicable to cave environments around the globe (Tremaine et al., 2011):

$$1,000\ln(\alpha)_{\text{calcite-H}_2\text{O}} = 16.1(10^3 T^{-1}) - 24.6 \quad (4)$$

The difference between the laboratory and cave findings may be because of disequilibrium isotope effects during the precipitation of cave calcites. Affek and Zaarur (2014) conducted a laboratory experiment in which samples were precipitated under thin film conditions, similar to natural stalagmite precipitation. Affek and Zaarur (2014) found increased $\delta^{18}\text{O}_c$ values when compared to bulk precipitation experiments (such as the Kim & O'Neil, 1997, experiment). This suggests that thin film degassing is mechanistically different from bulk solution processes supporting that calcite geochemistry is in part dependent on precipitation mechanisms (Affek & Zaarur, 2014).

The $\delta^{13}\text{C}$ value of the carbonate ($\delta^{13}\text{C}_c$) can be influenced in the soil zone by biological soil activity and the type and amount of vegetation (Fairchild et al., 2006). In the vadose zone, $\delta^{13}\text{C}_c$ can be influenced by water/rock reactions, ground air, organic carbon within the vadose zone, and/or microbial decomposition of organic matter in the vadose zone (Fairchild et al., 2006; Matthey et al., 2016; Noronha et al., 2015). Within the cave, atmospheric CO_2 ventilation may drive variations in the $\delta^{13}\text{C}$ values of the CO_2 and degassing processes can affect the $\delta^{13}\text{C}$ values of the speleothem calcite similar to oxygen isotopes (Bergel et al., 2017; Meyer et al., 2014). Monitoring studies show that cave ventilation can vary seasonally (Matthey et al., 2008, 2016; Noronha et al., 2017; Vieten et al., 2016).

The minor elemental (Mg and Sr) concentrations are also useful for understanding climatic drivers of the $\delta^{18}\text{O}_c$ and $\delta^{13}\text{C}_c$ values (Arienzo et al., 2017; Fairchild & Treble, 2009; Partin et al., 2012). Various factors can influence the incorporation of minor elements into dripwater including the type of overlying bedrock, water/rock interactions, cave ventilation, and prior calcite precipitation (PCP; Fairchild et al., 2000; Fairchild & Treble, 2009; Wong et al., 2011). PCP can occur through evaporation or CO_2 degassing in the epikarst or within the cave ceiling and usually is associated with periods of reduced rainfall. With increasing PCP, dripwaters become enriched in Mg and Sr as these elements are preferentially excluded from the solid phase and evidence of PCP is suggested by a positively correlated Mg to Sr variation in speleothem calcite

(Fairchild & Treble, 2009). Therefore, dripwaters that have undergone PCP do not reflect the Mg/Ca and Sr/Ca of bedrock (Tremain & Froelich, 2013). The water transit time and/or the routing path of water (Wong & Breecker, 2015) can influence the extent of PCP.

3. Study Location and Sampling Strategy

The cave monitoring study was conducted in Hatchet Bay Cave (HBC), a cave of active speleothem formation in Eleuthera, Bahamas (Figure 1; 25.3°N, 76.5°W). A schematic sketch of the cave is provided in supporting information Figure S1, and a map of the cave can be found in Mylroie and Mylroie (2009). The entrance of HBC is located 10 to 15 m above sea level and the overburden is primarily composed of limestone. The cave extends linearly west of the main entrance following the Pleistocene aeolian ridge (Mylroie & Mylroie, 2009). The cave consists of three levels. The first level is the shallowest and smallest level with evidence of phreatic dissolution (Mylroie & Mylroie, 2009). The second level is a tubular passage accessed by a ladder from the first level and again contained evidence of phreatic dissolution. The second level is more extensive (~300 m long) with active dripwater and speleothem formation. The second level is thought to follow a thick, terra rossa paleosol, which follows an aeolian ridge (Mylroie & Mylroie, 2009). The second level also contains a shaft entrance to the surface. The third level is the deepest level and was accessed by another ladder from the middle of the second level. The third level is partially filled with seawater, with active stalagmite formation occurring on raised ledges above the water and no evidence of water flooding the rock ledges. The third level consists of two rooms, the Main Room and the West Room. The Main Room is the largest room of the third level. The West Room, located to the west of the Main Room, is much smaller and separated from the Main Room by a small passage. Both rooms consist of active dripping and stalagmite and stalactite formation.

Results from HBC were compared to weather station results from the Leon Levy Native Plant Preserve (LLNPP; Figure 1). LLNPP was located ~40 km southeast from HBC on the Eleuthera. At LLNPP, mean daily air temperature and daily total precipitation were measured from 6 August 2013 to 1 December 2015. In section 7, results from HBC were compared to previously published stalagmite records from Abaco Island, Bahamas located to the north of Eleuthera Island (Figure 1; Arienzo et al., 2015, 2017).

4. Methods

The HBC was visited every 3 to 8 months from 3 June 2012 to 11 March 2016, (Table 1). During each visit, air samples were collected throughout the cave, dripwater samples were collected from the second and third levels, and the experiments involving the precipitation of calcite from dripwater, were performed on the third level (supporting information Figure S1–S3). Calcite precipitates were collected in five locations, three locations in the Main Room and two locations in the West Room.

4.1. Air Temperature

Temperature was measured every two hours using a HOBO U23 Pro v2 Temperature Data Logger from Onset (± 0.21 °C between 0 to 50 °C). The temperature sensor was in the middle of the Main Room (supporting information Figure S1).

4.2. Carbon Isotopic Composition of Cave CO₂

Air samples for carbon isotopes of the CO₂ ($\delta^{13}\text{C}_{\text{CO}_2}$) were collected in 30-ml glass vials at each site throughout the cave. Air samples were also collected outside of the cave in an open field prior to entering the cave. The $\delta^{13}\text{C}$ values of the CO₂ ($\delta^{13}\text{C}_{\text{CO}_2}$) were analyzed using a gas bench coupled to a Thermo-Delta plus Advantage isotope ratio mass spectrometer. The $\delta^{13}\text{C}_{\text{CO}_2}$ measurements were calibrated to four reference pulses of CO₂, two at the start of the sample and two at the end. The $\delta^{13}\text{C}_{\text{CO}_2}$ value of the reference gas was previously calibrated using a dual inlet mass spectrometer (Finnigan MAT 251) and is reported in the standard notation relative to Vienna Pee Dee Belemnite (V-PDB). When possible, duplicate samples were collected, analyzed, and averaged.

4.3. Dripwaters

Unfiltered water samples were collected throughout the second and third levels of the cave by holding a clean, acid washed vial under dripping stalactites. Vials were filled completely (where possible) to avoid

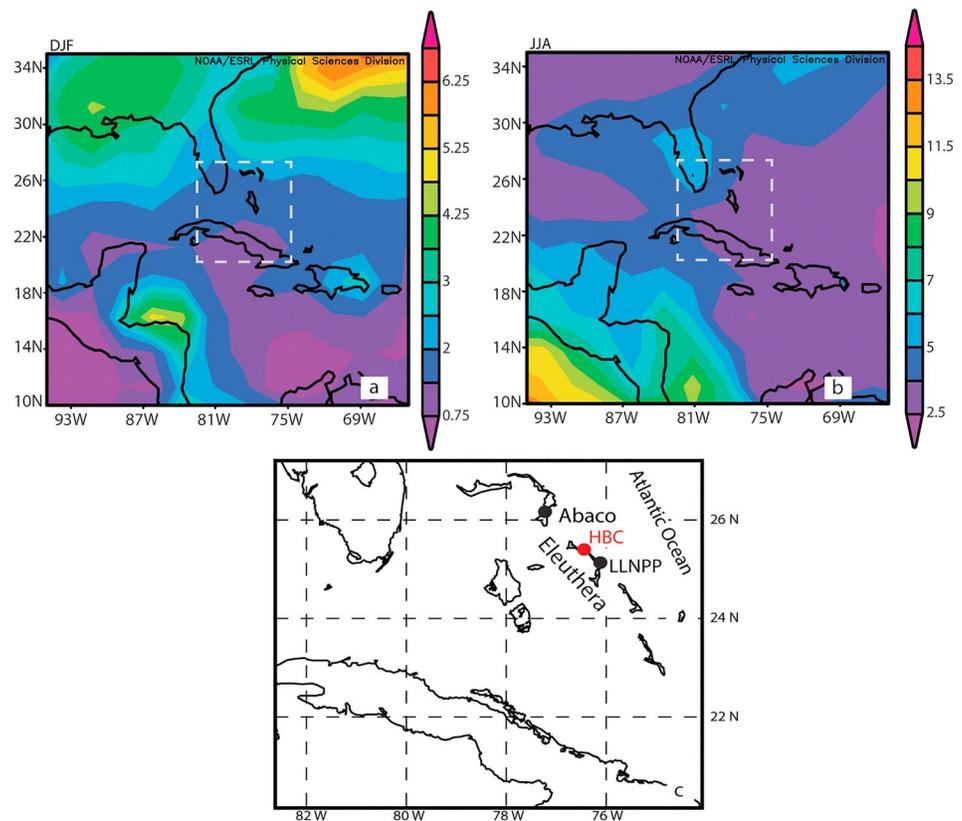


Figure 1. (top row) Mean precipitation rate (mm/day) colored for (a) December-January-February (DJF) and (b) June-July-August (JJA). Data are from the Climate Prediction Center Merged Analysis of Precipitation. Gray dashed box outlines the area shown in (c). (c) Map of the Atlantic showing the Bahamas islands. Hatchet Bay Cave (HBC) shown in red is located on the island of Eleuthera, Bahamas, and LLNPP is located to the south. Previous paleoclimate reconstructions from stalagmites have been conducted from a cave on Abaco Island to the north.

headspace equilibration, then capped and stored until analysis. Samples were filtered using a Whatman 0.2- μm pore filter upon return to the laboratory (within 2–3 days) and subsampled for analysis. For long-term storage, the waters were acidified.

For oxygen and hydrogen isotopes ($\delta^{18}\text{O}_w$ and $\delta^2\text{H}_w$) of the dripwater, samples were measured using a Picarro Cavity Ring-down Spectroscopy (i2140) instrument. Four standard waters were analyzed at the start and end of the analysis of 19 samples. Each sample or standard was injected (0.2 ml per injection) into the Picarro A0211 vaporizer unit (held at 110 °C for the duration of the sample run) 6 times using N_2 as the carrier gas. The water isotopes standards used were previously calibrated to the VSMOW-GISP-SLAP scale and data are reported relative to VSMOW with a mean reproducibility of 0.05 ‰ for $\delta^{18}\text{O}_w$ and 0.1 ‰ for $\delta^2\text{H}_w$. Error was calculated by the repeated analysis of a standard.

For minor element analyses of the dripwaters, samples were acidified using trace grade HNO_3 and analyzed using the Varian Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES). Results from procedural blanks were below detection limits.

4.4. Calcite Precipitates

For the collection of recently precipitated calcite, standard glass microscope slides (2.5 cm \times 7.6 cm) were placed on top of currently forming stalagmites, directly under the stalactite drip. Microscope slides were held in place by a wire and tied down at a slight ($\sim 5\text{--}10^\circ$) angle, similar to the methods of Banner et al. (2007) and Tremaine et al. (2011; supporting information Figure S2). Prior to installing the slides in the cave, the slides were weighed in the laboratory. Initially, four-calcite precipitation sites were installed, three in the Main Room and one in the West Room. A fifth station was added to the West Room in November 2013.

Table 1
Details of Each of the 29 Slides Deployed in the Cave

Slide #	Location	Date deployed	Date removed	# of days in cave	Calcite Precipitated (mg)
1	Main Room	06/03/2012	08/21/2012	79	140.3
3	Main Room	06/03/2012	08/21/2012	79	228.7
4	Main Room	06/03/2012	08/21/2012	79	118.3
8	Main Room	08/23/2012	12/11/2012	110	80
9	Main Room	08/23/2012	05/1/2013	250	333.5
10	Main Room	08/23/2012	12/11/2012	110	314.6
12	Main Room	12/12/2012	05/01/2013	140	40.2
13	Main Room	12/12/2012	05/01/2013	140	245.3
15	Main Room	05/03/2013	08/06/2013	95	165.6
16	Main Room	05/03/2013	08/06/2013	95	—
17	Main Room	05/03/2013	08/06/2013	95	214.5
19	Main Room	08/08/2013	11/21/2013	105	366.4
20	Main Room	08/08/2013	11/21/2013	105	262.5
21	Main Room	08/08/2013	11/21/2013	105	160.3
S-25	Main Room	11/21/2013	04/17/2014	147	334.7
S-32	Main Room	09/03/2014	02/07/2015	157	6
S-36	Main Room	02/07/2015	08/04/2015	178	91.9
S-A	Main Room	08/04/2015	03/11/2016	220	447
S-D	Main Room	08/04/2015	03/11/2016	220	923
6	West Room	06/03/2012	08/21/2012	79	470.6
11	West Room	08/23/2012	12/11/2012	110	345.8
14	West Room	12/12/2012	05/1/2013	140	790.7
18	West Room	05/03/2013	08/06/2013	95	491.2
22	West Room	08/08/2013	11/21/2013	105	609
S-26	West Room	11/21/2013	04/17/2014	147	670.9
S-29	West Room	04/17/2014	09/03/2014	139	258
S-7	West Room	04/17/2014	09/03/2014	139	892
S-30	West Room	02/07/2015	08/04/2015	178	52.1
S-B	West Room	08/04/2015	03/11/2016	220	1993

Note. Slides 2 and 7 were destroyed in transport to the cave and therefore were not deployed. Slide 16 was broken after collection and therefore calcite precipitation rate was not calculated. Dates are formatted as MM/DD/YYYY.

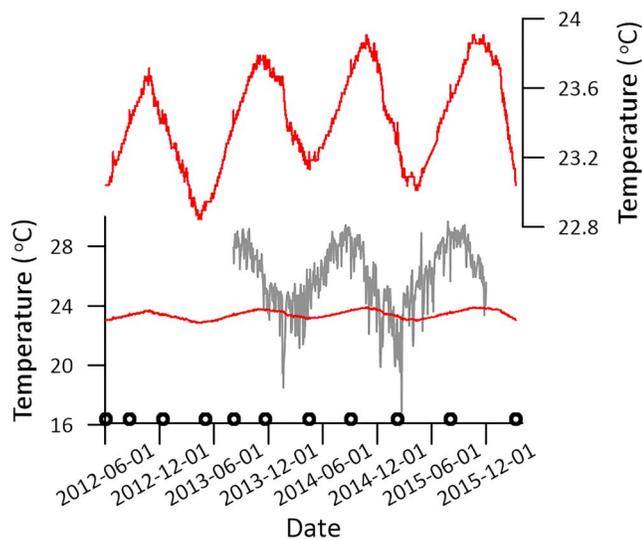


Figure 2. Cave temperature from June 2012 to March 2016 in red measured every two hours. Leon Levy Native Plant Preserve mean daily temperature shown in gray (bottom). Open circles indicate the dates when the cave was visited.

The microscope slides were left in the cave for 3 to 8 months at which point they were replaced with new slides (Table 1). Slides were returned to the laboratory, dried, and weighed. Using a dental pick, the calcite was removed, homogenized with a mortar and pestle, and analyzed for carbonate isotopes and elemental concentrations. The $\delta^{13}\text{C}_c$ and $\delta^{18}\text{O}_c$ measurements were made using a Kiel III interfaced with a Thermo-Finnigan Delta Plus isotope ratio mass spectrometer at the University of Miami. All data have been corrected for isobaric inferences at mass 45 and 46 and are reported relative to V-PDB. The precision of the $\delta^{13}\text{C}_c$ and $\delta^{18}\text{O}_c$ measurement is better than $\pm 0.1\%$. For minor element analysis of the calcite, samples were dissolved in trace grade HNO_3 to yield a concentration of approximately 4 ppm Ca and analyzed using the Varian ICP-OES as described above.

5. Results

5.1. HBC Environment

The temperature on the third level of the cave varied from 22.8 to 23.9 °C for the sampling period, with a mean temperature of 23.4 ± 0.3 °C (Figure 2). Typically, the warmest month in HBC third level was November, while the coolest month was April. The $\delta^{13}\text{C}_{\text{CO}_2}$ values demonstrated a progressive trend toward more negative values from outside the

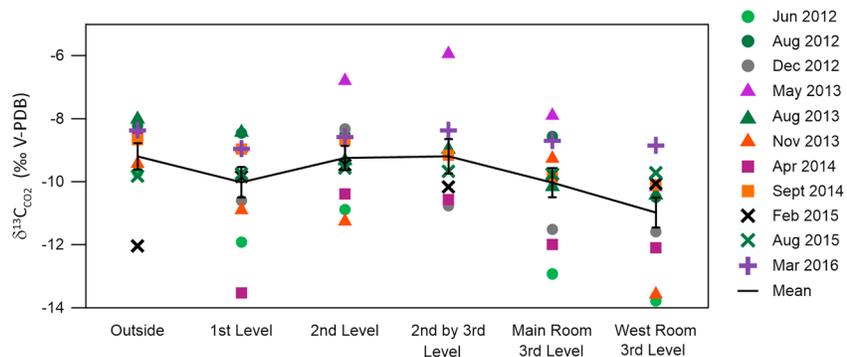


Figure 3. Carbon isotopic values of cave air CO₂ ($\delta^{13}\text{C}_{\text{CO}_2}$) from the outside and inside the cave between June 2012 to March 2016. “Outside” air sample was taken outside of the cave in an open field. Error bars are the standard error of the mean for the specified location.

cave to the most isolated room, the third level West Room (Figure 3). On average, the difference between outside (-9.2‰ V-PDB) and third level West Room (-11‰ V-PDB) was 1.8‰ for the sampling period.

5.2. Dripwaters

The $\delta^{18}\text{O}_w$ and $\delta^2\text{H}_w$ values of dripwaters from HBC second and third levels plot on the Global Meteoric Water Line (GMWL; Figure 4). The mean $\delta^{18}\text{O}_w$ value from the second level was $-3.3 \pm 0.9\text{‰}$ VSMOW and there was no difference between the $\delta^{18}\text{O}_w$ values of the dripwaters in the third level Main Room and the West Room (Table 2). The $\delta^{18}\text{O}_w$ values of the dripwater were relatively stable between June 2012 and November 2013 on the second and third levels (Figure 5a). Although data from April 2014 to August 2015 are sparse, an increase in the $\delta^{18}\text{O}_w$ value was observed, particularly for the third level Main Room (Figure 5a).

The Sr/Ca ratios of the dripwaters were similar throughout the cave (Table 2 and Figure 5b). The mean Mg/Ca ratio was lowest for the second level dripwaters (mean = 545 ± 97 (1 standard deviation) mmol/mol) and the Mg/Ca ratio of the dripwater from the third level West Room was less variable (mean = 991 ± 47 mmol/mol) than the third level Main Room (mean = 887 ± 300 mmol/mol). Overall, there was a positive correlation between Mg/Ca and Sr/Ca ratios for the third level waters (coefficient of determination, $r^2 = 0.6$, $p < 0.01$, $n = 48$) and the second level waters ($r^2 = 0.6$, $p < 0.01$, $n = 25$; Figure 5d). However, the correlation of the Mg/Ca and Sr/Ca ratios in the third level waters was because of three samples with low Mg/Ca and Sr/Ca ratios (Figure 5d).

5.3. Calcite Precipitates

Calcite precipitation rates were calculated based on the amount of calcite precipitated on the microscope slides. Mean calcite precipitation rates were greater in the West Room than the Main Room (Table 3). We note that from this approach we are only accounting for calcite precipitation on the slide. Lowest calcite precipitation rates were observed from September 2014 to August 2015 in both rooms (Figure 6). Minimal differences were observed between the Main Room and West Room calcite geochemistry, with overall greater variability observed in the Main Room (Table 3). More negative $\delta^{13}\text{C}_c$ and $\delta^{18}\text{O}_c$ values are observed in the West Room; however, the values are within the variability of the Main Room isotopic results. Geochemical cross plots from the carbonate results are shown in Figure 7.

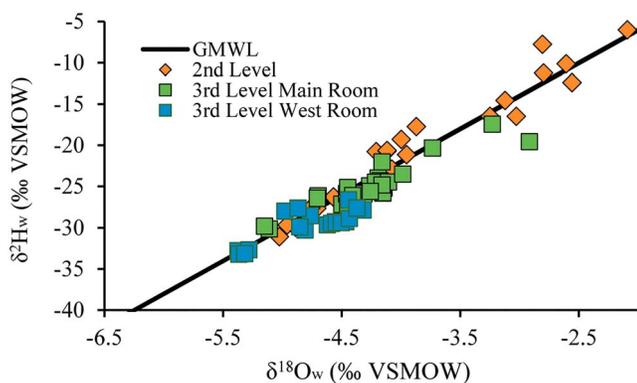


Figure 4. The $\delta^{18}\text{O}_w$ and $\delta^2\text{H}_w$ values for dripwater samples from the second level (orange diamonds), third level Main Room (green squares) and third level West Room (blue squares). Results plot near the Global Meteoric Water Line (GMWL; black).

6. Discussion

6.1. Cave Environment

The HBC temperature variation of $\sim 1^\circ\text{C}$ during the monitoring period contributes an approximate 0.2‰ variability in $\delta^{18}\text{O}_c$ value, less than

Table 2

Isotopic and Minor Element Results and Standard Deviations for Dripwaters for the Second Level, Third Level Main Room and Third Level West Room Locations

Location	$\delta^{18}\text{O}_w$ (‰ VSMOW)	stdev	$\delta^2\text{H}_w$ (‰ VSMOW)	stdev	Sr/Ca (mmol/mol)	stdev	Mg/Ca (mmol/mol)	stdev
2nd Level	-3.28	0.85	-16.73	6.82	2.26	0.33	545.49	97.83
3rd level Main	-3.39	1.49	-18.55	11.42	2.16	0.59	887.50	300.90
3rd level West	-4.84	0.24	-29.58	1.47	2.14	0.15	991.52	47.28

Note. Since multiple water samples were collected during each visit, values were averaged by visit.

the overall $\delta^{18}\text{O}_c$ variability observed (3.3‰ and 2.5‰ Main and West Rooms, respectively). When comparing the HBC third level temperature record to the LLNPP air temperature record, on average the LLNPP temperatures were much warmer than the cave, with an annual mean temperature of $\sim 26 \pm 2$ °C (Figure 2) compared to 23.4 ± 0.3 °C in the cave. An approximate 70-day temperature lag from above ground to third level of the cave was observed. This lag results in periods when the cave remains warmer than the outside air.

The cave air $\delta^{13}\text{C}_{\text{CO}_2}$ values were near the atmospheric air endmember of ~ -9 ‰ V-PDB, supporting that the cave was well ventilated bringing CO_2 with more positive $\delta^{13}\text{C}$ values from outside the cave (Figure 3). However, $\delta^{13}\text{C}_{\text{CO}_2}$ reached values as low as -13.9 ‰ V-PDB demonstrating that the cave was occasionally less ventilated. Cave ventilation can also be determined from cave air $p\text{CO}_2$ measurements, which were not made. The $\delta^{13}\text{C}_{\text{CO}_2}$ values decrease with distance from the entrance. The most negative values were from the West Room suggesting that this was the least ventilated, a fact also supported by its distance from the two entrances. The $\delta^{13}\text{C}_{\text{CO}_2}$ values from the second level location near the third level were elevated because of ventilation from the shaft entrance located nearby.

On shorter timescales, we note that the periods of lower $\delta^{13}\text{C}_{\text{CO}_2}$ were observed in June 2012, December 2012, November 2013, and April 2014. Such periods of decreased ventilation could be driven by variations in soil $\delta^{13}\text{C}_{\text{CO}_2}$ value, temperature, and wind direction (James et al., 2015; Noronha et al., 2017). Studies have also shown that seasonally, ventilation can be impacted by the temperature difference between the cave and the outside. When caves remain warmer than the outside, a resultant airflow into the cave can occur, if the geometry of the cave allows (Noronha et al., 2017). This temperature phenomenon occurs in HBC during the winter months, unfortunately, the cave air $\delta^{13}\text{C}_{\text{CO}_2}$ measurements were not made at a temporal resolution for determining seasonality in ventilation. Despite the fact that less ventilated caves are generally preferable for climate studies, we note that research suggest that well-ventilated areas may still preserve high-resolution climatic information (Carlson et al., 2018).

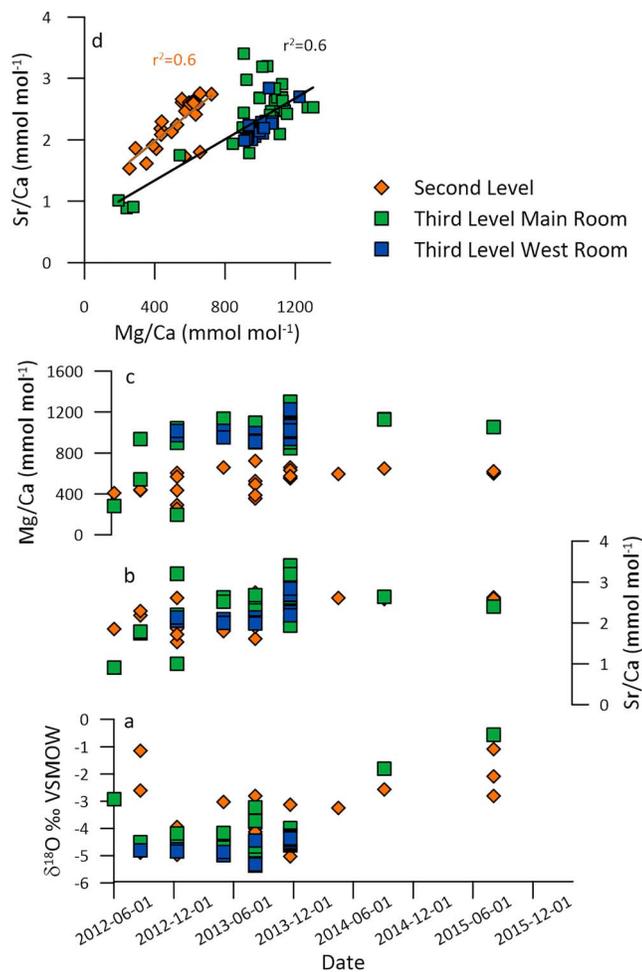


Figure 5. Dripwater chemistry results. Second level results are shown as orange diamonds, third level Main Room results are shown as green squares and third level West Room results are blue squares. (a) $\delta^{18}\text{O}_w$ values by location plotted with time. (b) Sr/Ca results by location with time. (c) Mg/Ca results by location with time. (d) Mg/Ca versus Sr/Ca results for dripwater samples. Note that the relationship for the third level is dominated by four points which are low in Mg and Sr and when these points are removed, the $r^2 = 0.1$.

6.2. Drivers of Dripwater Chemistry

The $\delta^{18}\text{O}_w$ and $\delta^2\text{H}_w$ values of the dripwaters fall along the GMWL (Figure 4) suggesting that dripwater samples have not undergone significant evaporation and reflect the original meteoric water composition (Craig et al., 1963). Variation in $\delta^{18}\text{O}_w$ values of the dripwaters were observed spatially within the cave, which may be a result of seasonal variations in the $\delta^{18}\text{O}_w$ values of rainfall with more negative $\delta^{18}\text{O}_w$ values during the wet season (because of the amount effect) and the deeper parts of the cave being recharged when rainfall is high and $\delta^{18}\text{O}_w$ values are

Table 3
Mean and Standard Deviations of Isotopic and Minor Element Results for the Calcite Precipitates for the Locations Within the Cave

Location	$\delta^{13}\text{C}_c$ (‰ V-PDB)	stdev	$\delta^{18}\text{O}_c$ (‰ V-PDB)	stdev	Sr/Ca (mmol/mol)	stdev	Mg/Ca (mmol/mol)	stdev	$\mu\text{moles CaCO}_3$ ($\text{cm}^{-2}\cdot\text{day}^{-1}$)	n
Main Room	-8.86	-1.50	-4.00	0.86	0.46	0.10	34.55	5.33	1.00	19
West Room	-10.11	-1.61	-4.51	0.96	0.33	0.10	27.14	5.88	2.55	10

more negative (Baldini et al., 2007; Dansgaard, 1964). In addition, although few samples were analyzed, the $\delta^{18}\text{O}_w$ values were more positive and more variable in the second and third levels from September 2014 to August 2015 (Figure 5a) which corresponded to a period of very low calcite precipitation rates (Figure 6).

Similar to the $\delta^{18}\text{O}$ values of the dripwater, variations in the concentrations of minor elements of the dripwater also varied between levels. The relationship between Mg/Ca and Sr/Ca ratios from the second level fall on a line with a steeper slope with respect to the third level (Figure 5d), potentially supporting a greater Sr bedrock contribution to the second level dripwaters and/or an increasing Mg bedrock source to the third level (Tremaine & Froelich, 2013). These differences may be because of changes in the bedrock type with depth. For example, cores from nearby Abaco Island demonstrate dolomite presence below 25 m, and such bedrock variability may be present in Eleuthera (Kaldi & Gidman, 1982).

PCP is considered the primary driver of minor element variability in dripwater and calcites from many caves (Fairchild & Baker, 2012). The observed positive trend between Sr/Ca and Mg/Ca ratios for the dripwaters (Figure 5d) was primarily driven by three outliers, making the interpretation of the dripwater Sr/Ca and Mg/Ca difficult. However, for the calcite precipitates, the observed positive trend between the Sr/Ca and Mg/Ca ratios for the precipitated calcites (Figure 7d), supports that PCP was a driver of the elemental chemistry in HBC. In addition, we note that lower Mg/Ca and Sr/Ca ratios were observed in the West Room calcites which suggests potentially less PCP here compared to the Main Room, as increasing PCP tends to drive Sr and Mg calcite concentrations higher (Tremaine & Froelich, 2013). While this difference could be because of variations in flow rates, with faster flow rates discouraging PCP, drip rates were not measured and therefore this hypothesis could not be tested. Increased cave ventilation can also affect PCP with decreased $p\text{CO}_2$ of the cave resulting in increased PCP (Sherwin & Baldini, 2011; Wong et al., 2011). Such a mechanism would also explain the reduced PCP in the West Room.

6.3. Drivers of Calcite Precipitation Rate

Calcite precipitation rates were lower in the Main Room than the West Room (Figure 6). Such spatial variations within the cave might be a result of the routing path of the water, differences in calcite saturation states, and/or ventilation driven degassing processes (Sherwin & Baldini, 2011).

Calcite precipitation rates were lowest from September 2014 to August 2015, a period coinciding with increased $\delta^{18}\text{O}_w$ values in the dripwaters. Such temporal trends were probably a result of a reduction in rainfall amount, which was observed at LLNPP during this period (Figure 6). However, when comparing the mean daily calcite precipitation rate to the mean daily rainfall amount, no significant correlation was observed, although there may be a lag between rainfall and calcite precipitation rate, or spatial variations in rainfall events for the island of Eleuthera. We note that previous studies have demonstrated a minimal lag between rainfall and drip rate (Partin et al., 2013), while other studies have shown the response of drip rate to rainfall can be variable within a cave (Wong et al., 2011).

6.4. Carbon and Oxygen Isotopes

A positive correlation between $\delta^{13}\text{C}_c$ and $\delta^{18}\text{O}_c$ values was observed from the cave calcite results (Figure 7). Although evaporative processes

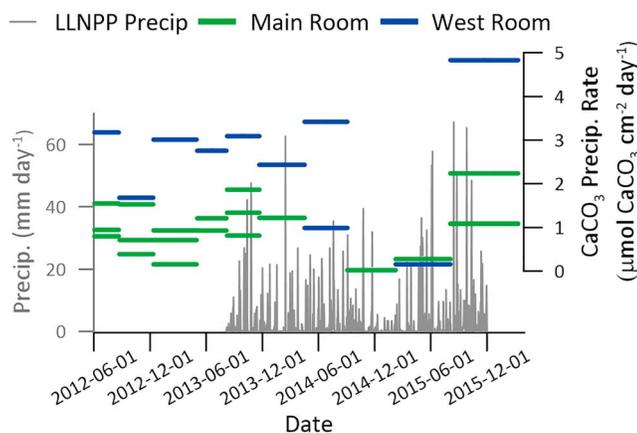


Figure 6. Calcite precipitated per day plotted by date. Green lines are slides deployed in the Main Room, blue lines are slides deployed in the West Room with the length of the bar representing the period the slide was in the cave. Total daily precipitation from the LLNPP is shown in gray. LLNPP = Leon Levy Native Plant Preserve.

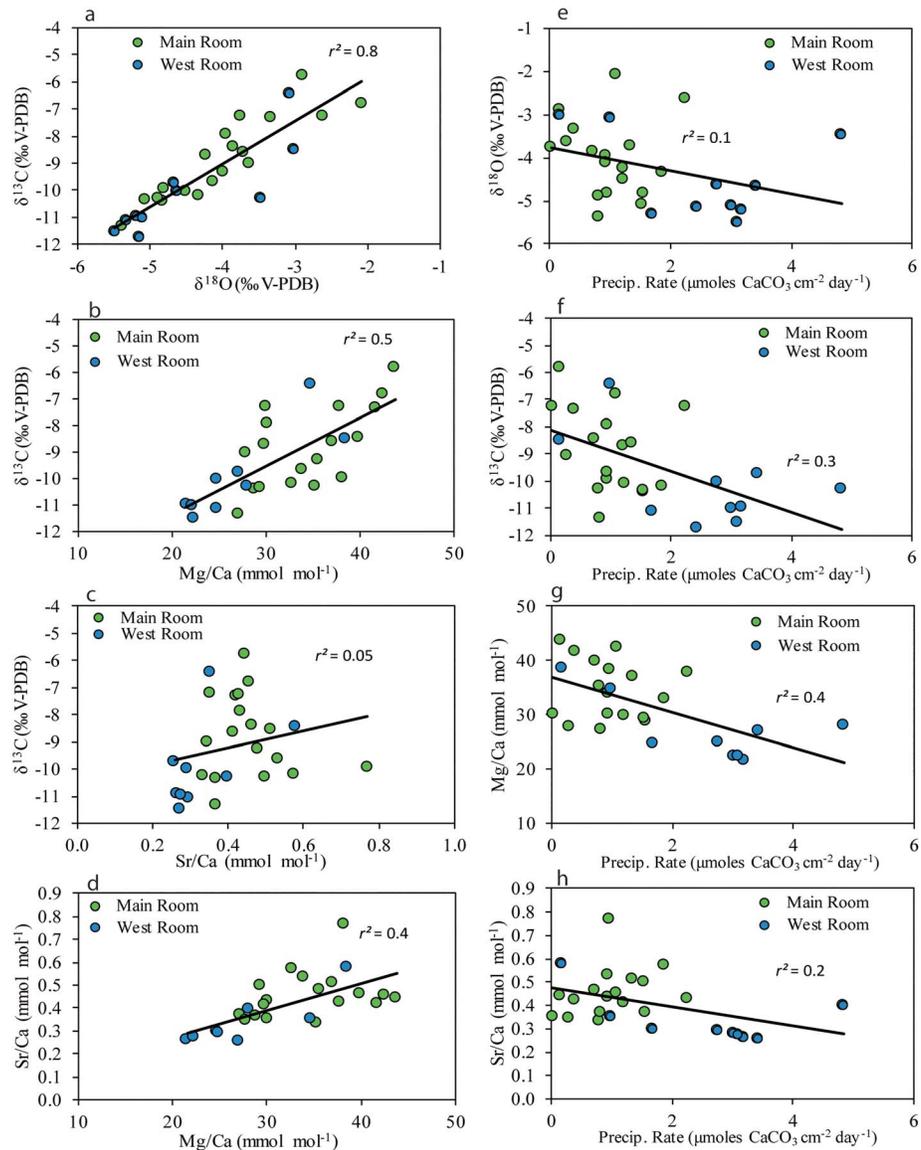


Figure 7. Isotope and minor element results from farmed calcite. Main Room results are shown in green and West Room results in blue. $\delta^{13}\text{C}_c$ values plotted against (a) $\delta^{18}\text{O}_c$, (b) Mg/Ca, and (c) Sr/Ca. (d) Sr/Ca versus Mg/Ca ratios. (e) $\delta^{18}\text{O}_c$ values; (f) $\delta^{13}\text{C}_c$ values; (g) Mg/Ca ratios; and (h) Sr/Ca ratios plotted against calcite precipitation rates.

in the soil zone or in the cave can lead to the oxygen isotopes of the water and hence the precipitated calcite to become progressively more positive (Tremaine et al., 2011), the occurrence of the dripwaters near the GMWL, precludes evaporation being a major driver of the $\delta^{18}\text{O}_w$ values. Degassing processes during calcite precipitation can also affect the $\delta^{13}\text{C}_c$ and $\delta^{18}\text{O}_c$ values. For example, an increased rate of

Table 4
The $\delta^{18}\text{O}$ Offset Between Measured $\delta^{18}\text{O}_c$ and Calculated $\delta^{18}\text{O}_c$ Values

Room	Tremaine et al. (2011; % offset)	Kim and O'Neil (1998; % offset)	Affek and Zaarur (2014; % offset)
Main Room	0.56	1.61	0.83
West Room	0.36	1.41	0.63

Note. Values were calculated using three water-calcite oxygen isotope fractionation relationships from Tremaine et al. (2011), Kim and O'Neil (1997), and Affek and Zaarur (2014) and inputting the mean $\delta^{18}\text{O}_w$ of dripwaters and cave temperature. Calculated $\delta^{18}\text{O}_c$ values were then subtracted from the measured $\delta^{18}\text{O}_c$ values (measured – calculated). For these calculations, only samples collected from June 2012 to April 2014 were used.

degassing may result in the remaining HCO_3^- (aq) becoming progressively enriched in ^{13}C (Lambert & Aharon, 2011; Mickler et al., 2004; Tremaine et al., 2011), while during slow degassing reequilibration of HCO_3^- (aq) occurs. Degassing rates are impacted by ventilation, with more ventilation resulting in faster degassing (Kowalczyk & Froelich, 2010; Lambert & Aharon, 2011). In addition, during degassing the $\delta^{13}\text{C}$ values of dripwater can become progressively more positive because of the DIC- CO_2 exchange with ventilated cave air (Tremaine et al., 2011). These degassing processes similarly can affect the $\delta^{18}\text{O}_c$ value and possibly result in the positive correlation between $\delta^{13}\text{C}_c$ and $\delta^{18}\text{O}_c$ values. Measurement of drip water DIC and $\delta^{13}\text{C}$ values of DIC would have strengthened the interpretation of the carbon isotopes of the calcite.

The $\delta^{18}\text{O}_c$ values precipitated closer to predicted equilibrium in the West room relative to the Main Room. Using the measured $\delta^{18}\text{O}_w$ values and the temperature at the time of formation, the expected $\delta^{18}\text{O}_c$ values can be calculated using Kim and O'Neil (1997; equation (3)) and Tremaine et al. (2011; equation (4)). To compare these various equations with the results from HBC, averaged $\delta^{18}\text{O}_w$ values of dripwaters from June 2012 to November 2013 (-4.1‰ and -4.8‰ VSMOW for Main and West Rooms respectively) and cave temperature (23.4 °C) were used to calculate the $\delta^{18}\text{O}_c$ values. The results demonstrate an increased offset in the Main Room relative to the West Room, with the Tremaine et al. (2011) equation most closely representing HBC (Table 4). The enhanced offset in the Main Room is thought to be caused by increased ventilation driven degassing rates resulting in increased kinetic fractionation. We also note that the HBC calcite offsets may be because of the variability in the $\delta^{18}\text{O}_w$ of dripwaters ($\pm 0.6\text{‰}$ and $\pm 0.2\text{‰}$ for the Main and West Rooms respectively, from June 2012 to November 2013).

In addition to covariation between $\delta^{13}\text{C}_c$ and $\delta^{18}\text{O}_c$ values, the $\delta^{13}\text{C}_c$ and $\delta^{18}\text{O}_c$ values are also positively correlated with Mg/Ca ratios. In turn, Mg/Ca ratios are negatively correlated with calcite precipitation rates (Figure 7). Therefore, in addition to PCP, the Mg/Ca may be impacted by variations in the amount of precipitation and water/rock interactions. During periods of reduced rainfall, water/rock interactions would increase, $\delta^{18}\text{O}_w$ values would increase and calcite precipitation rates would decrease, resulting in the observed covariations.

7. Linkages to Bahamas Paleoclimate Studies

The HBC is one of the few caves in the Bahamas in which speleothems are currently forming and this monitoring study was initiated to aid with the interpretation of the Pleistocene stalagmites collected from nearby Abaco Island in the Bahamas (Figure 1). However, care must be taken when using modern observations to interpret paleorecords as each cave exhibits its own environment, geology, and ventilation patterns. In Arienzo et al. (2015) and Arienzo et al. (2017), the four stalagmites studied formed between 64,000 and 13,200 year BP. Utilizing the $\delta^{18}\text{O}_w$ values of the fluid inclusions from one speleothem it was concluded that the main driver of $\delta^{18}\text{O}_c$ value was temperature, rather than changes in the $\delta^{18}\text{O}_w$ value of the fluid (Arienzo et al., 2015). In contrast to the Pleistocene stalagmite, temperature was not a major driver of the $\delta^{18}\text{O}_c$ value of the precipitated calcite in HBC. The fluid inclusion isotopic results from the Pleistocene stalagmite fell on GMWL (Arienzo et al., 2015), similar to the modern dripwaters. In the modern, PCP was a driver of the elemental chemistry of the precipitated calcite as identified by covarying Mg/Ca and Sr/Ca ratios. In contrast, the Pleistocene samples did not exhibit covarying Mg/Ca and Sr/Ca ratios, which suggests that PCP did not significantly influence the calcite chemistry (Arienzo et al., 2017). In HBC, a positive covariation between Mg/Ca and $\delta^{13}\text{C}_c$ and $\delta^{18}\text{O}_c$ values and a negative covariation between Mg/Ca ratios and calcite precipitation rates was attributed to increasing water/rock reactions. Similarly, in the Pleistocene samples, a positive covarying trend between Mg/Ca and $\delta^{13}\text{C}_c$ values was attributed to increased water/rock interactions because of increased aridity associated with climate events (Arienzo et al., 2017). The HBC results provide additional confidence in our interpretation of the Pleistocene speleothem record, demonstrating similar trends. Interestingly, the Mg/Ca ratios are similar between the dolomite influenced Pleistocene samples (Arienzo et al., 2017) and the modern samples. This is possibly because of the presence of high-magnesium calcite in the overlying bedrock of HBC.

8. Conclusions

The HBC monitoring study in the Bahamas was conducted to understand the drivers of calcite chemistry in HBC located in Eleuthera, Bahamas, and to aid with the interpretation of records obtained from ancient stalagmites. Air temperature, $\delta^{13}\text{C}_{\text{CO}_2}$, dripwater chemistry, and calcite chemistry have been leveraged to understand the drivers of calcite chemistry in HBC. We note additional measurements would have enhanced this study and recommend future work in tropical caves include additional calcite chemistry measurements, higher resolution $\delta^{13}\text{C}_{\text{CO}_2}$ and $p\text{CO}_2$ measurements, dripwater DIC concentrations, $\delta^{13}\text{C}$ values of DIC, and alkalinity. However, from this study, dripwater $\delta^{18}\text{O}_w$ values were shown to be more negative deeper in the cave and the $\delta^{13}\text{C}_{\text{CO}_2}$ values were the most negative in the third floor West Room because of reduced ventilation. The West Room also exhibited less PCP than the Main Room and the $\delta^{18}\text{O}$ values of the precipitated calcite in the West Room were also closer to equilibrium, which was proposed to be a result of reduced ventilation and slower degassing rates. Overall, the calcite chemistry appears to indicate that in the modern, PCP, water-rock interactions and ventilation are the greatest drivers of variations in speleothem chemistry. Within HBC, the Main Room $\delta^{18}\text{O}$ calcite values precipitated farther from equilibrium and kinetic effects may overprint the subtler original rainfall isotopic signatures in the Main Room precipitated calcite.

When comparing between the modern cave monitoring results and the Pleistocene stalagmites, similarities and differences were observed. Such differences may be because of differences in the caves themselves (e.g., ventilation regime, temperature, geometry of the cave). We note that both the modern and Pleistocene stalagmites demonstrated the influence of water/rock interactions on the elemental chemistry.

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