Speleothem calcite farmed in situ: Modern calibration of $\delta^{18}$O and $\delta^{13}$C paleoclimate proxies in a continuously-monitored natural cave system

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Received 23 December 2010; accepted in revised form 2 June 2011; available online 16 June 2011

Abstract

Understanding the relationships between speleothem stable isotopes ($\delta^{13}$C $\delta^{18}$O) and in situ cave forcing mechanisms is important to interpreting ancient stalagmite paleoclimate records. Cave studies have demonstrated that the $\delta^{18}$O of inorganically precipitated (low temperature) speleothem calcite is systematically heavier than the $\delta^{18}$O of laboratory-grown calcite for a given temperature. To understand this apparent offset, rainwater, cave drip water, groundwater, and modern naturally precipitated calcite (farmed in situ) were grown at multiple locations inside Hollow Ridge Cave in Marianna, Florida. High resolution micrometeorological, air chemistry time series and ventilation regimes were also monitored continuously at two locations inside the cave, supplemented with periodic bi-monthly air gas grab sample transects throughout the cave.

Cave air chemistry and isotope monitoring reveal density-driven airflow pathways through Hollow Ridge Cave at velocities of up to 1.2 m s$^{-1}$ in winter and 0.4 m s$^{-1}$ in summer. Hollow Ridge Cave displays a strong ventilation gradient in the front of the cave near the entrances, resulting in cave air that is a mixture of soil gas and atmospheric CO$_2$. A clear relationship is found between calcite $\delta^{13}$C and cave air ventilation rates estimated by proxies pCO$_2$ and $^{222}$Rn. Calcite $\delta^{13}$C decreased linearly with distance from the front entrance to the interior of the cave during all seasons, with a maximum entrance-to-interior gradient of $\Delta\delta^{13}$C$_{\mathrm{CaCO}_3} = -7\%_{\text{oo}}$. A whole-cave “Hendy test” at multiple contemporaneous farming sites reveals that ventilation induces a $+1.9 \pm 0.96\%_{\text{oo}}$ $\delta^{13}$C offset between calcite precipitated in a ventilation flow path and calcite precipitated on the edge or out of flow paths. This interpretation of the “Hendy test” has implications for interpreting $\delta^{13}$C records in ancient speleothems. Calcite $\delta^{13}$C$_{\mathrm{CaCO}_3}$ may be a proxy not only for atmospheric CO$_2$ or overlying vegetation shifts but also for changes in cave ventilation due to dissolution fissures and ceiling collapse creating and plugging ventilation windows.

Farmed calcite $\delta^{18}$O was found to exhibit a $+0.82 \pm 0.24\%_{\text{oo}}$ offset from values predicted by both theoretical calculations and laboratory-grown inorganic calcite. Unlike $\delta^{13}$C$_{\mathrm{CaCO}_3}$, oxygen isotopes showed no ventilation effects, i.e. $\Delta\delta^{18}$O$_{\mathrm{CaCO}_3}$ appears to be a function of growth temperature only although we cannot rule out a small effect of (unmeasured) gradients in relative humidity (evaporation) accompanying ventilation. Our results support the findings of other cave investigators that water–calcite fractionation factors observed in speleothem calcite are higher than those measured in laboratory experiments. Cave and laboratory calcite precipitates may differ mainly in the complex effects of kinetic isotope fractionation. Combining our data with other recent speleothem studies, we find a new empirical relationship for cave-specific water–calcite oxygen isotope fractionation across a range of temperatures and cave environments:

$$1000 \ln x = 16.1(10^3 T^{-1}) - 24.6$$

with a fractionation temperature dependence of $\Delta\delta^{18}$O/$\Delta T = -0.177\%_{\text{oo}}$/°C, lower than the currently accepted $-0.206\%_{\text{oo}}$/°C. © 2011 Elsevier Ltd. All rights reserved.

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1. INTRODUCTION

Calcite (CaCO$_3$) cave formations, or speleothems, incorporate and preserve high-resolution climate signals within their crystalline matrices, allowing modern interpretation of past climate systems (Holland et al., 1964; Hendy, 1971; Schwarcz et al., 1976; Gascoyne et al., 1980; Gascoyne, 1983; Schwarcz, 1986). Variations in speleothem $\delta^{18}O$ in caves with near 100% relative humidity (insignificant drip water evaporation $\delta^{18}O$ enrichment effects) and constant temperature (insignificant temperature-induced $\delta^{18}O$ variations) are most often interpreted as either changes in meteoric water sources (Bar-Matthews et al., 2003; Wang et al., 2001, 2008; Fleitmann et al., 2003b; Cruz et al., 2005a, 2007; Cobb et al., 2007), or changes in rainfall amount and intensity in monsoon climates (Burns et al., 2002; Fleitmann et al., 2003a; Cruz et al., 2005b; Johnson et al., 2006; Wang et al., 2005, 2008; Partin et al., 2007; Cheng et al., 2009).

Speleothem $\delta^{18}O$ records on glacial to interglacial time scales broadly covary with high-latitude solar insolation (Wang et al., 2004, 2008; Dykoski et al., 2005; Cheng et al., 2006, 2009), yet can deviate significantly from global insolation-based predictions over centuries or decades (Wang et al., 2008; Cheng et al., 2009) for reasons that are not well understood but are likely local or regional in scale. Recent studies have attempted to isolate the magnitude of these inter-dependent variables (Clemens et al., 2010; Dayem et al., 2010; Lambert and Aharon, 2010). Although many cave studies have described regional and global paleoclimate records, there have been few investigations of the relationships among drip water chemistry, cave air ventilation and the isotopic composition of modern calcite – what we call “modern calibration of speleothem paleoclimate proxies.”

Oxygen isotopic fractionation in calcite is temperature dependent (Urey, 1948; McCrea, 1950; Epstein et al., 1951, 1953). Numerous laboratory-based inorganic calcite precipitation experiments have demonstrated a temperature-dependent oxygen isotopic fractionation from water to calcite of approximately $-0.23\%_{\text{o}}/{^\circ}\text{C}$ (Epstein et al., 1953; O’Neil et al., 1969; Tarutani et al., 1969; Kim and O’Neil, 1997). To reduce errors associated with assuming the initial source water composition, fossil pore-water can be extracted from micro-inclusions and subjected to $\delta^2$H and $\delta^{18}O$ analyses (Schwarcz et al., 1976; Harmon et al., 1979; Winograd et al., 1992; Rowe et al., 1998; Matthews et al., 2000; Dennis et al., 2001; McGarry et al., 2004; Vonhof et al., 2006; van Breukelen et al., 2008; Zheng et al., 2008; Griffiths et al., 2010). However, this method is sensitive to oxygen isotope re-equilibration and requires specialized equipment. We are aware of only one study that attempts to replicate cave conditions in a laboratory setting – that of Day and Henderson (2011). Instead, we have measured rain and in situ temperature and drip water $\delta^{18}O$, cave air chemistry and isotopes (CO$_2$, $^{222}$Rn, $\delta^{13}C$), and farmed calcite isotopes ($\delta^{18}O$ and $\delta^{13}C$) in a natural cave setting that we have been continuously monitoring for several years.

Speleothems form when high pCO$_2$ calcite-saturated drip waters degas, increasing pH and oversaturating the drip waters and leading to precipitation of calcite:

$$\text{Ca}^{2+} + 2\text{HCO}_3^- \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2(g) \uparrow$$  \hfill (1.1)

Calcite $\delta^{13}C$ is often interpreted as a proxy for atmospheric CO$_2$ concentration (Baskaran and Krishnamurthy, 1993) and overhead vegetation composition (C3 vs. C4: Brook et al., 1990; Dorale et al., 1992; Bar-Matthews et al., 1997; Hou et al., 2003; Denniston et al., 2007). Until recently cave air and its CO$_2$ have been considered to be stagnant, i.e. with little or no air exchange with the atmosphere, fostering paleoclimate interpretations that focused only on atmospheric CO$_2$ and vegetation contributions to soil gas. Recent work has demonstrated that ventilation-driven outgassing of cave-air CO$_2$ must control drip water degassing of CO$_2$ and thus the rate and timing of calcite precipitation (McDermott, 2004; Mickler et al., 2004, 2006; Spötl et al., 2005; Bourges et al., 2006; Banner et al., 2007; Baldini et al., 2008; Kowalczyk and Froelich, 2010) as well as the isotopic composition of drip water and subsequent calcite (Mattey et al., 2008; Cosford et al., 2009; Oster et al., 2010; Frisia et al., 2011; Lambert and Aharon, 2011). However, it is not yet clear how strong ventilation affects calcite $\delta^{18}O$ and $\delta^{13}C$ on seasonal, diurnal, and multi-decadal scales. The implication that all caves with calcite formation must breathe with outside air requires renewed evaluation of the effects of both CO$_2$ sources on $^{13}C$, and temperature and evaporation effects on $^{18}O$, a focus of this paper. The large number of dry caves in the northeast panhandle of Florida may be important for paleoclimate work because of a number of climatic factors.
Numerous studies have demonstrated a teleconnection between the sub-tropical Gulf of Mexico and high-latitude climate perturbations since the Last Glacial Maximum from marine forams in sediment cores (Poore et al., 2003, 2004, 2009; Richey et al., 2007, 2009; Ziegler et al., 2008), lake pollen records (Watts and Hansen, 1994; Willard et al., 2007), lake sediment records (Grimm et al., 1993, 2006; Mangini et al., 2007) and a few very limited speleothem records (Lachniet et al., 2004a,b; Mangini et al., 2007; van Beynen et al., 2007, 2008; Lambert, 2010). But the Southeast USA in general, and the Gulf Coast in particular, are notably lacking in high-resolution continental climate records such as those from speleothems (Lambert and Aharon, 2010). The most robust speleothem-derived paleoclimate records available are a few in which modern cave monitoring studies preceded investigation of fossil dripstones (Lambert and Aharon, 2011). We report here an extensive physical, chemical, and stable isotope data set designed to establish modern isotopic, temperature, ventilation and rainfall proxy calibrations with which to interpret paleoclimate records from ancient speleothems in north Florida.

2. STUDY SITE

Hollow Ridge Cave (HRC) is a wild, protected, phreatic-zone solution cave in Marianna, Florida, formed within the flat-lying Oligocene Marianna Limestone Formation, penetrating downward into the Bumpnose Limestone Formation. Hollow Ridge is hosted in the Chattahoochee Anticline and is an upland karst cave (normally dry), with unaltered entrances and few annual visitors. The cave is over lain by a thin soil veneer (average <30 cm thick) composed of Plio-Pleistocene sands and clays with multiple bedrock outcrops, and the vegetation is characterized as an “upland mixed forest” composed primarily of C3 trees and C4 shrubs and vines ( Maddox, 1993). This cave is one of dozens of similar caves that occur in the tops of local ridges along the Chipola river, including the Florida Caverns public show cave.

Mean annual precipitation in Quincy, Florida (35 km east of Marianna, Florida) is approximately 1370 mm yr$^{-1}$ (1984–2010; www.ncdc.noaa.gov), ranging from 917 mm (2007) to 2105 mm (1994). During this study, measured monthly rainfall at HRC ranged from 113 mm month$^{-1}$ (1356 mm from November 2007 to December 2008) to 123 mm month$^{-1}$ (1476 mm from December 2009 to January 2010). Mean annual atmospheric air temperature measured at HRC (2007–2010) was 18.3 °C, ranging from 8.5°C (January 2008) to 26.6°C (June 2009). The lowest elevation entrance to Hollow Ridge lies at approximately 21 m above sea level (ASL) at the edge of the flood plain of the Chipola river, which runs north-south approximately 400 m west of the study site. The highest entrance lies at 28 m ASL. The lowermost levels of the cave have experienced four river-flooding events in the past three years, events which block the lower entrances.

There are 1030 m of mapped passage within HRC (Fig. 1). The vertical throw between the lowest point (Ballroom) and the highest point (Signature Room) is 10 m, which is approximately the maximum overhead limestone thickness. Hollow Ridge passage is typically 1–2 m high, and floored by clay-mud up to 1 m thick. There is a vertical fissure that transects the cave from northwest to east-southeast, coinciding with the local limestone fault structure. The cave is owned, protected and managed by the Southeastern Cave Conservancy Inc. (SCCi). HRC is shallow and subject to large temperature gradients near the lower entrances and is thus not typical of larger deep caves which are often presumed to be at constant temperature and 100% relative humidity. Mean annual cave air temperatures measured continuously at two sites inside HRC (Fig. 1) were 18.8 °C (CS1) and 19.5 °C (CS2). However, winter airflow into Entrance-A and out Entrance-D (through-flow) can reduce in-cave air temperatures in the Entrance Room to approximately 12 °C. It is important to note that although HRC is an excellent cave in which to perform modern calibrations, temperature variations of this magnitude would require independent information for both H$_2$O–δ$^18$O and temperature for paleoclimate interpretations, and thus long-term speleothem records in the affected area near the entrance are only used here for calibration purposes. The deep interior of the cave (CS2), while ventilated (Kowalczk and Froelich, 2010), is much more stable.

We report here the second phase of an ongoing high-resolution time series cave-monitoring program that was established at Hollow Ridge Cave in November 2007 (Kowalczk, 2009). The primary goal of phase one was to instrument the cave for continuous monitoring and to investigate the rates and timing of cave ventilation. Three monitoring stations were deployed (Fig. 1): (1) an above ground micrometeorological (MET) station that records temperature (T), relative humidity (RH), barometric pressure (BP), wind velocity and direction, rainfall, and solar irradiance, all at 30-minute intervals; (2) an in-cave microchem station in the Entrance Room referred to as Cave Station 1 (CS1) that records T, RH, BP, Radon-222 ($^{222}$Rn), and air CO$_2$ concentration at one-hour intervals; and (3) a microchem station in the Signature Room referred to as Cave Station 2 (CS2) that records interior-cave T, BP, RH, $^{222}$Rn and air CO$_2$ at one-hour intervals. Details of the instrumentation and methodology are reported in Kowalczk (2009) and Tremaine (2010).

We use Radon-222 (measured with portable Durridge RAD7’s) as a cave air ventilation monitor to estimate rates at which HRC breathes with outside air (Kowalczk and Froelich, 2010). Radon-222 is a radioactive daughter of $^{226}$Ra in the $^{238}$U decay series and is constantly emitted from marine limestones. It is a heavy noble gas with very high aqueous solubility and serves as a non-reactive mass-transport proxy for CO$_2$ exchange on time scales less than five times its half-life ($\tau_{1/2} = 3.82$ days). Average atmospheric $^{222}$Rn activity above HRC is effectively zero, measured at approximately 2 dpm L$^{-1}$ on 11/10/2008, while cave air $^{222}$Rn activities range from 50 to 100 dpm L$^{-1}$ at CS1 and 65 to 400 dpm L$^{-1}$ at CS2. Detectable atmospheric $^{222}$Rn above HRC indicates that cave air is leaking upward through cracks in the cave ceiling, consistent with...
our understanding of the winter ventilation regime at HRC (warm air inside the cave is rising). Phase one data (2008–2009) were used to generate a 222Rn deficiency model to estimate CO₂ outgassing as a function of cave-air ventilation rates, and seasonal calcite deposition based on net CO₂ export from Hollow Ridge Cave (Kowalczk and Froelich, 2010). In addition to chemical monitoring, an acoustic anemometer was deployed inside the cave at a restriction near the lower entrance (Fig. 1) to record cave air advection direction and velocity at one-hour intervals.

3. MATERIALS AND METHODS

3.1. Ventilation and cave air CO₂ and δ¹³C

To fill in longitudinal data between hourly time series data at CS1 and CS2, an additional portable Durridge RAD7 radon detector was carried through the cave bi-monthly in “snapshot mode” to grab air samples to determine the extent of ventilation in rooms and passages throughout the cave that were not being continuously monitored. Air samples were also collected bi-weekly under the forest canopy and from a soil flux chamber (soil-respired CO₂) installed atop the cave. Six in-cave air CO₂ grab sample transects were performed during the study, on 5/22/2009, 7/24/2009, 10/31/2009, 11/21/2009, 1/4/2010 and 2/28/2010. Each transect was completed in less than 2 h. Grab samples were compared with in-cave monitors (CO2-Licor 820; 222Rn-RAD7) to verify that cave ventilation conditions were stable during each transect. Grab air samples were drawn into a 60 mL syringe and injected into 30 mL evacuated glass vials sealed with rubber septa. Samples (150 μL) were analyzed for CO₂ concentration and δ¹³C value on a Finnigan MAT V Delta Isotope Ratio Mass Spectrometer (IR-MS) at Florida State University (FSU) against internal standards (Electronic Annex (EA): Table EA.1) with typical 1σ analytical uncertainties of ±2.5 ppmv for CO₂ and ±0.39‰ for δ¹³C.

3.2. Drip and groundwater saturation state (Ω) and δ¹³C

To determine the calcite saturation state of drip and groundwaters, pH, [Ca²⁺], [Mg²⁺], and Total-CO₂
(TCO₂ = Total Dissolved Inorganic Carbon = DIC) were measured in waters collected at the same four locations monthly for four months (Ballroom, Duece, Smith and Jones A, Sump). Water pH was measured in situ with a Thermo Orion 210A pH meter and P9106 gel-filled semimicro pH probe after in-cave calibration with pH-7 and pH-10 buffers. Multiple water samples were collected in 8 mL glass vials (TCO₂ and isotopes) and sealed with rubber septa. Vials were filled with fluid to avoid headspace equilibration with cave air and were kept cold and dark and analyzed within 24 h.

Samples for δ¹³C and TCO₂ were treated with 0.5 mL of 105% H₃PO₄, then shaken and pressurized with helium. Samples were allowed to equilibrate for 1 h, followed by injection of head-space air (150 μL) into a Finnigan MAT V Delta IR-MS coupled to a HP 5890 Series II Gas Chromatograph at FSU. Calibrations were performed at the beginning and end of each run using in-house standards (Table EA.1). The δ¹³C (CO₂) values are reported in reference to the international VPDB scale as outlined by Coplen et al. (2006). Long-term reproducibility of the method is ±0.05‰ (1σ) for δ¹³C. TCO₂ and pH were used to calculate carbonate alkalinity and all other aqueous carbonate species using carbonate system constants at salinity (S) = 0‰ and temperatures of T_cave = 18°C (Ballroom and Duece) and T_cave = 20°C (Sump and Smith and Jones A) after Pilson (1998) (Fig. EA.1 and Table EA.2).

Unfiltered cation samples (Ca²⁺ and Mg²⁺) were diluted to approximately 1 ppm [Ca] and measured on an Agilent Quadrupole 7500cs ICP-MS in 2‰ Optima HNO₃ spiked with 10 ppb Sc and 1 ppb Y internal standards following multiple-element standard- bracketing ICP-MS methods at FSU (methods modified from Yu et al., 2005). Calibration standards are shown in Table EA.1. See Tremaine (2010) for further details.

3.3. Drip and groundwater δD and δ¹⁸O

Drip and groundwater samples were collected bi-weekly for a period of 20 months from June 2008 through February 2010 at multiple sites throughout the cave, including the Ballroom (drip), Sump (ground), Duece (drip) and Smith and Jones Room A (drip) (Fig. 1). Water was collected unfiltered into 8-mL glass vials and sealed with rubber septa. Vials were filled with fluid to avoid headspace equilibration with cave air and were kept cold and dark and analyzed within 24 h.

Samples for δ¹³C and TCO₂ were treated with 0.5 mL of 105% H₃PO₄, then shaken and pressurized with helium. Samples were allowed to equilibrate for 1 h, followed by injection of head-space air (150 μL) into a Finnigan MAT V Delta IR-MS coupled to a HP 5890 Series II Gas Chromatograph at FSU. Calibrations were performed at the beginning and end of each run using in-house standards (Table EA.1). The δ¹³C (CO₂) values are reported in reference to the international VPDB scale as outlined by Coplen et al. (2006). Long-term reproducibility of the method is ±0.05‰ (1σ) for δ¹³C. TCO₂ and pH were used to calculate carbonate alkalinity and all other aqueous carbonate species using carbonate system constants at salinity (S) = 0‰ and temperatures of T_cave = 18°C (Ballroom and Duece) and T_cave = 20°C (Sump and Smith and Jones A) after Pilson (1998) (Fig. EA.1 and Table EA.2).

Acid digestion of calcite standards and samples was performed at 25°C, and the acid fractionation factor ([ACD]) was assumed to be 1.01030 (Kim et al., 2007). Reported values are the calibrated values of 10 replicate sample measurements. The δ¹³C and δ¹⁸O values were calibrated based on measurements of three sets each of four different carbonate standards (Table EA.1) processed with each batch of samples and are reported in reference to the international carbonate VPDB scale. Calibration scales were anchored with NBS-19 (δ¹⁸O = -2.20‰, δ¹³C = +1.95‰ VPDB) as outlined in Coplen (1996). The analytical precision (based on replicate analyses of lab standards processed with each batch of samples) is ±0.1‰ (1σ) or better for both δ¹³C and δ¹⁸O.

3.4. Modern calcite farming and calcite δ¹⁸O and δ¹³C

In November 2008 calcite “farming” was initiated under active drip sites in the Ballroom on standard glass microscope slides. Expansions of the farming project occurred in summer 2009, and again in fall 2009. Before deployment, slides were pre-weighed and then fixed tilted with a flexible wire mesh atop actively growing (dripping) stalagmites similar to the methods of Frisia et al. (2000), Mickler et al. (2004), Banner et al. (2007), and Boch et al. (2009) (Fig. EA.2). We did not attempt to attach seed crystals, so initial growth was undoubtedly delayed. After visual verification of calcite growth, slides were periodically removed and replaced. In this fashion, the farms were monitored for growth through seven three-month seasons. Recovered slides were rinsed with DDW, dried and weighed. Low-magnesium calcite growth was verified using visual microscopy of crystal habit and X-ray diffraction (Tremaine, 2010). No aragonite or vaterite were observed. Approximately 250-μg samples were removed from each plate into pre-cleaned glass vials and placed in an oven at 80°C for 48 h to remove water. Vials were subsequently capped and flushed with helium and the samples acidified with 105% H₃PO₄, prepared following the standard procedure (Sharp, 2007), and left to react for 24 h at 25°C. The resulting CO₂ was then introduced via an on-line, continuous-flow system (Finnigan GasBench II) into the IR-MS at FSU for isotopic analysis. The continuous flow method operates on the basis of identical treatment of standards and samples, resulting in identical acid fractionation factors (Werner and Brand, 2001; Paul and Skrzypek, 2007) which are inherently incorporated into our four-point calibration. Thus acid fractionation factors are not reported here although they can be calculated from the gas calibration data in Tremaine (2010).

Acid digestion of calcite standards and samples was performed at 25°C, and the acid fractionation factor ([ACD]) was assumed to be 1.01030 (Kim et al., 2007). Reported values are the calibrated values of 10 replicate sample measurements. The δ¹³C and δ¹⁸O values were calibrated based on measurements of three sets each of four different carbonate standards (Table EA.1) processed with each batch of samples and are reported in reference to the international carbonate VPDB scale. Calibration scales were anchored with NBS-19 (δ¹⁸O = -2.20‰, δ¹³C = +1.95‰ VPDB) as outlined in Coplen (1996). The analytical precision (based on replicate analyses of lab standards processed with each batch of samples) is ±0.1‰ (1σ) or better for both δ¹³C and δ¹⁸O.
4. RESULTS

4.1. Seasonal ventilation regimes

Hollow Ridge Cave experiences diurnal ventilation driven by two distinct regimes: winter and summer (Kowalczk and Froelich, 2010) (Fig. 2). During the winter, cold, dry and dense air enters the bottom of HRC through Entrance A and is moisturized and convectively heated by cave walls, becoming more buoyant and rising to exit through cracks in the cave ceiling at the east end of the cave. The air is accelerated through relatively small openings at the top of the cave (a “ceiling leak”) creating a pressure differential, which in turn draws more dense cold air into the bottom of the cave through Entrance A at up to 1.2 m s\(^{-1}\) (Fig. 2). These types of “ceiling leak” ventilation pathways are undiscoverable without detailed in-cave and atop-cave \(^{222}\text{Rn}\) snooping. This style of ventilation results in near-atmospheric levels of \(\text{CO}_2\) (385–450 ppmv) and relatively low levels of \(^{222}\text{Rn}\) activity (40–120 dpm L\(^{-1}\)) in the ventilation flow path. Winter air is cooler than the cave at night and can often becomes warmer during the day. Because cave wall temperatures are virtually constant, the system can switch back and forth diurnally from inflow at entrance-A and outflow through the ceiling leaks late at night (20:00–09:00 h) to stagnant or sluggish inflow at the ceiling leak and outflow at entrance-A during day-time heating (10:00–18:00 h).

In the summer, outside air temperatures rise rapidly after sunrise (07:00 h) from approximately 20 °C to 35 °C. Convective cooling then induces down-drafting through the same small openings in the top of the cave. Atmospheric air (warmer than cave-air) is entrained downward through the ceiling leaks, becoming cooler and increasingly more dense from interaction with cave walls. Similar to the winter ventilation regime, the cave walls impart moisture to summer air (which is already fairly high water content), decreasing the density contrast. The downward velocity of the entrained air mass is reduced by this added buoyancy, resulting in flow velocities out of Entrance A of less than 0.4 m s\(^{-1}\) (Fig. 2). Due to slower summer air advection and increased soil gas \(\text{CO}_2\) production, summer time cave-air \(\text{CO}_2\) and \(^{222}\text{Rn}\) levels are elevated and often display periods of stagnation with little to no ventilation.

During spring and autumn ventilation, evening outside air temperatures are slightly cooler than the cave, often resulting in inflow at Entrance A. Daytime temperatures are warmer than the cave, resulting in downdraft through the ceiling leak and outflow through Entrance A. During these “change” seasons, HRC experiences a bimodal diurnal flow with an equal amount of inflow and outflow. When outside air densities are identical to cave wall temperatures, ventilation slows dramatically and the cave experiences ‘stagnation’. Thus, spring and fall ventilation regimes are characterized by morning inflow, a period of stagnation,
and afternoon outflow through the lower entrances. Spring and fall ventilation results in high-amplitude diurnal variation in cave air CO$_2$ and 222Rn (Kowalczk and Froelich, 2010). Prolonged periods of stagnation were observed when Chipola River flooding events seal off the lower entrances of HRC, eliminating ventilation altogether. The highest 222Rn activity (1200 dpm L$^{-1}$C0$_1$) and ingrowth rates (40 dpm L$^{-1}$C0$_1$ h$^{-1}$) were measured during these flooding events (Kowalczk, 2009; Tremaine, 2010).

4.2. Cave air CO$_2$ and calcite growth rates

Kowalczk and Froelich (2010) observed a ventilation-driven mixing relationship between cave air CO$_2$ and 222Rn (Kowalczk and Froelich, 2010). Prolonged periods of stagnation were observed when Chipola River flooding events seal off the lower entrances of HRC, eliminating ventilation altogether. The highest 222Rn activity (1200 dpm L$^{-1}$) and ingrowth rates (40 dpm L$^{-1}$ h$^{-1}$) were measured during these flooding events (Kowalczk, 2009; Tremaine, 2010).

4.2.1. Atmospheric (under canopy) air CO$_2$ seasonality

Kowalczk and Froelich (2010) observed a ventilation-driven mixing relationship between cave air CO$_2$ and $\delta^{13}$C in HRC that follows the Keeling relationship (Keeling, 1958). They found that the average soil gas CO$_2$ endmember ($\delta^{13}$C = $-20.7\%_o$ at 4077 ppmv) mixes with 'outside' (under canopy) air CO$_2$ ($\delta^{13}$C = $-10.7\%_o$ at 513 ppmv) to produce ventilation gradients inside the cave. A soil gas endmember of $\delta^{13}$C = $-20.7\%_o$ requires a 35% contribution of C4 plant respiration and a 65% C3 tree respiration (assuming $\delta^{13}$C = $-11\%_o$ and $-26\%_o$ for C4 and C3, respectively), which is typical for a “mixed upland forest” (Maddox, 1993). Following the protocol established in Kowalczk (2009), high-resolution bi-weekly samples of atmospheric, soil gas, and cave-air CO$_2$ and $\delta^{13}$C were collected. New data from the present study were then plotted with data from Kowalczk and Froelich (2010) (Fig. 3). The best-fit line through in-cave air grab samples extends directly through both endmember averages indicating that CO$_2$ concentrations in cave air and $\delta^{13}$CO$_2$ cave air represent a ventilation-driven mixture between only two endmembers: soil gas and outside atmosphere. The significance of this cave air mixing relationship in Fig. 3 is that stalagmites and their drip solutions at fixed locations inside a cave are experiencing a range of both CO$_2$ and $^{13}$C depending on proximity to the cave entrance or cave interior and the ventilation regime that are being seasonally modulated (direction of flow and turbulence).

4.2.2. Atmospheric (under canopy) air CO$_2$ seasonality

CO$_2$ endmembers in Fig. 3 are expanded in Fig. 4 to demonstrate seasonal cycles in soil gas and canopy air.
Fig. 4. Seasonal cycles of soil gas and atmospheric CO₂ endmembers. (A) Soil gas [CO₂] time series from April 2009 to February 2010. (B) Soil gas δ¹³C time series from April 2009 through February 2010. (C) Keeling plot of soil gas endmember; δ¹³CO₂ vs. 1/[CO₂]. (D) Under canopy [CO₂] time series from April 2009 to February 2010. (E) Atmospheric δ¹³C time series from April 2009 through February 2010. (F) Keeling plot of atmospheric endmember; δ¹³CO₂ vs. 1/[CO₂]. (A and D) were generated as inverse (1/[CO₂]) and plotted as a linear [CO₂] y-axis. Filled circles and squares in (C and F) are the same as in Fig. 3. Open triangles represent seasonal averages of data with corresponding colors. Parentheses around two data points in (C) signify data that are believed to have been improperly sampled and are not included in the average. Double-ended arrows in (C and F) indicate the vectors along which seasonal shifts occur in endmember values. Soil gas (C) shifts from higher δ¹³C and high pCO₂ to lower δ¹³C and less concentrated CO₂ as plant populations change from summer (C4 and C3) to winter (C3 only) (Ehleringer et al., 1997). Atmospheric gas (F) shifts from higher δ¹³C and lower CO₂ concentration in the winter to lower δ¹³C and higher CO₂ concentrations in the summer. The atmospheric shift indicates that air trapped between the tree canopy and the cave exhibits simple mixing between atmosphere (−8%o, 390 ppmv) and soil gas (−20.7 ± 0.66%o (1σ range), 4077 ppmv).
Atmospheric air samples collected above the cave and under the forest canopy (Fig. 4D through F) exhibit the least depleted $\delta^{13}$CO$_2$ ($-9.6_{\text{‰}}$) and lowest pCO$_2$ (440 ppmv) in the winter, a slightly more depleted $\delta^{13}$CO$_2$ ($-11.4_{\text{‰}}$) and higher pCO$_2$ (500 ppmv) in fall and spring $\delta^{13}$CO$_2$ ($-10.8_{\text{‰}}$), and highest CO$_2$ (575 ppmv) ($\delta^{13}$CO$_2$ = $-11.3_{\text{‰}}$) concentrations during summer. The linear trend in average values from low pCO$_2$-high $\delta^{13}$CO$_2$ (winter) to high pCO$_2$-low $\delta^{13}$CO$_2$ (summer) falls on the extended mixing line in Fig. 3, and reveals that ‘under canopy’ atmospheric air samples represent a mixture of soil gas (ventilated from soils and from inside the cave) and true atmosphere mixes into the understory. In addition as deciduous trees shed some of their leaves, a higher percentage of “free” atmosphere mixes into the understory.

### 4.2.2. Soil gas CO$_2$ seasonality

Soil gas exhibits the most depleted $\delta^{13}$CO$_2$ ($-21.5_{\text{‰}}$) and lowest pCO$_2$ (2600 ppmv) in the winter, with less depleted $\delta^{13}$CO$_2$ ($-21_{\text{‰}}$) and higher pCO$_2$ (3300 ppmv) in fall, and the highest pCO$_2$ (4700 ppmv) and least depleted $\delta^{13}$CO$_2$ ($-20.3_{\text{‰}}$) in spring and summer (Fig. 4C). The average seasonal values trend from low pCO$_2$-low $\delta^{13}$CO$_2$ (winter) to high pCO$_2$-high $\delta^{13}$CO$_2$ (summer), orthogonal to an extension of the cave air mixing line. This trend suggests that plant root respiration is highest in the spring and summer (high CO$_2$), and that the C4 plant productivity (respired $\delta^{13}$CO$_2$ = $-11$ to $-14_{\text{‰}}$ VPDB) is higher in the warmer months resulting in $^{13}$C-enriched soil gas (Ehleringer et al., 1997). This soil gas seasonal cycle was not observed in cave air.

One of the fundamental questions in speleothem-based paleoclimate studies involves whether high temporal resolution geochemical signals of seasons are preserved in ancient calcite. Results from this study show that summer calcite growth in the interior of Hollow Ridge Cave is one to two orders of magnitude slower than growth at the same locations in fall, spring and winter (Table EA.3). These results support the hypothesis that slower summer ventilation rates result in elevated cave-air CO$_2$, which in turn slows drip water CO$_2$ degassing rates and thus speleothem precipitation rates. Ancient speleothems far from the entrances in Hollow Ridge Cave do not precipitate enough calcite during the summer to allow seasonal resolution of trace element and isotopic records. Therefore, we predict that paleoclimate interpretations from Hollow Ridge Cave stalagmites will be more reflective of winter and fall conditions, which could alias annual interpretations.

### 4.3. Drip water chemistry and calcite saturation state ($\Omega$)

Calcite precipitation rate is expected to be directly proportional to drip water oversaturation ($\Omega > 1$) (Teng et al., 2000; De Yoreo et al., 2009). To establish the relationship between ventilation and saturation state (precipitation rate), drip and groundwaters were analyzed throughout a 4-month study from 10/31/2009 to 2/28/2010 (Table EA.4). Drip and groundwaters were both always supersaturated with respect to calcite ($\Omega_{\text{range}}$ = 3.6–73). Our aequous chemistry data are typical of data from other caves. TCO$_2$, pH, $\delta^{13}$C, [Ca$^{2+}$], [Mg$^{2+}$], and calcite saturation state were similar to cave waters measured by Plummer et al. (2000), Mickler et al. (2004), Spöll et al. (2005), Banner et al. (2007), and Lambert and Aharon (2011) (Table EA.5). Ballroom drip water samples were found to be in chemical equilibrium with cave air CO$_2$, while Duece, Smith and Jones A and the Sump were still degassing at the time of sampling (Fig. 5A). If drip water
Craig, 1961; Dansgaard, 1964) and the Tallahassee Meteoric Water Line (GMWL – blue line; \( \delta = 8.6^{18}O + 10 \); Craig, 1961; Dansgaard, 1964) and the Tallahassee Meteoric Water Line (TMWL – red line; \( \delta = 8.2^{18}O + 13 \)). Red open circles designate Tallahassee Rainfall. Black open circles and squares represent data from Kowalczk (2009) from April 2008 to January 2009. Colored circles are cave data from the current study (January 2009 to February 2010). Cave water samples exhibit much less variation than rain samples, indicating water homogenization in the epikarst reservoir and phreatic zone.

CO\(_2\) (aq) is in chemical equilibrium with cave air CO\(_2\) (g) then the saturation state of water (\( \Omega \)) with respect to calcite (after impingement upon a speleothem) should be a function of cave air CO\(_2\) on timescales of seconds (Zeebe et al., 1999; Schulz et al., 2006; Dreybrodt and Scholz, 2011). Indeed, we find a hyperbolic relationship between cave air pCO\(_2\) and drip water saturation state (Fig. 5B) described by:

\[
\Omega = 7.3 \times 10^6 / (\text{pCO}_2)^2 \quad R² = 0.76 \tag{4.3.1}
\]

Although this experiment was relatively short and should be repeated over several seasons, this relationship reveals that drip water saturation state (and therefore precipitation rate) increases rapidly below cave air pCO\(_2\) values of approximately 700 ppmv (Fig. 5). Eq. (4.3.1) can be used to predict drip water saturation state as a continuous function of cave air pCO\(_2\), which is a potential predictive tool when coupled with pCO\(_2\) time series. Summer cave-air pCO\(_2\) inside HRC averages approximately 1084 ppmv while winter cave-air pCO\(_2\) averages 445 ppmv (Tremaine, 2010). These findings are consistent with the hypothesis that slower summer time ventilation in HRC leads to high cave air CO\(_2\) that greatly reduces calcite precipitation rates. Example calculations are shown in Table EA.2.

4.4. Rainfall and drip water \( \delta^{18}O \) & \( \delta D \)

Rain water was collected monthly and the amount-weighted average of Tallahassee rainfall \( \delta^{18}O \) during this study period (February 2009 to February 2010) was \(-3.56 \pm 1.18\%_o\) (2σ range) (Fig. 6). Hollow Ridge drip water \( \delta^{18}O \) during this study ranged from \(-3.05\%_o\) to \(-4.16\%_o\) with an average of \(-3.75 \pm 0.33\%_o\) (2σ range) (Fig. 6). Tropical Storm Fay (August 22nd, 2008) delivered approximately 80 mm of isotopically light rain (\( \delta^{18}O = -14\%_o\) VSMOW) to Marianna, Florida. However, this excursion was not observed in drip waters (Kowalczk, 2009, his Fig. 4.14). Limited \( \delta^{18}O \) variability of cave drips indicates that the epikark-storage reservoir is relatively large and its water residence time sufficiently long (at least 2 weeks) to homogenize the isotopic composition of drips. This limited range in drip water \( \delta^{18}O \) simplifies calculation of temperatures based on water–calcite oxygen isotopic fractionation (Lachniet, 2009).

4.5. Predicted and measured calcite \( \delta^{18}O \)

Farming modern calcite under drips of known isotopic composition in a cave that is well-monitored for temperature and ventilation is essentially a “natural laboratory” (Poulson and White, 1969; Coplen, 2007) that allows calibration of the temperature-dependence on speleothem calcite \( \delta^{18}O \) (\( \Delta \delta^{18}O_{\text{calcite}}/\Delta T \)). We will consider that only evaporation, temperature, and drip water \( \delta^{18}O \) variation can have significant impact on \( \text{in situ} \) calcite \( \delta^{18}O \) assuming that calcite forms very close to oxygen isotopic equilibrium with drip water. The oxygen atom content of water is \( ~55 \text{ molar} \) while HCO\(_3\)\(^-\) is in the 1–3 mM range and thus DIC-water oxygen isotope exchange should control the bulk isotopic composition of the carbonic acid system (O’Neil and Truesdell, 1991; Kim and O’Neil, 1997). Cave air relative humidity in the interior of HRC is always 97–100% (Tremaine, 2010), which minimizes the effects of evaporation and reduces calcite \( \delta^{18}O \) composition to a function of drip water isotopic composition (\( \delta^{18}O = -3.75 \pm 0.33\%_o\) and formation temperature (T)). Measured atmospheric (MET station directly atop Hollow Ridge Cave – Fig. 1) and cave air temperatures (CS1 and CS2) combined with in-cave transects allows estimation of air temperatures at each farming location to within \( \pm 0.5 \text{ °C} \).

Measured \( \delta^{18}O \) values of drip water and \( \text{in situ} \) temperatures were used to calculate predicted calcite \( \delta^{18}O \) values based on both the O’Neil et al. (1969) equation (Eq. (4.5.1)) and the Kim and O’Neil (1997) equation (Eq. (4.5.2)) (data are in Table 1). The O’Neil et al. (1969) equation, as modified by Friedman and O’Neil (1977) and hereafter referred to as O’Neil et al. (1969), is based on extrapolation from their high-temperature (250–700 °C) fractionation line through two low-temperature experimental data points (0 and 25 °C), thus having the form \( 10^\delta T^{-2} \). The Kim and O’Neil (1997) equation, as modified by Kim et al. (2007) and hereafter referred to as Kim and O’Neil (1997), is based on low-temperature (10–40 °C) experimental calcite precipitation and has the form of \( 10^\delta T^{-1} \).
Table 1
Predicted and measured calcite δ¹⁸O values. Predicted values based on drip water δ¹⁸O of −3.75 ± 0.33‰ (2σ) (VSMOW) (Tremaine, 2010). Measured calcite values represent the average value for each location during that growing season. Averages were calculated as Σδ¹⁸O/n where n is the number of individual analyses.

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<th>Predicted from O'Neil et al. (1969) b δ¹⁸O (VPDB)</th>
<th>Predicted from Chacko and Deines (2008) c δ¹⁸O (VPDB)</th>
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a As modified by Kim et al. (2007) temperature equation: 1000 ln x = 18.03 (10⁶/T) − 31.17.

b As modified by Friedman and O'Neil (1977) temperature equation: 1000 ln x = 2.78 (10⁶/T²) − 2.89.

c Chacko and Deines (2008) temperature equation was constructed by us from their published reduced partition coefficient data as: 1000 ln x = 2.5733 (10⁶/T²) − 0.869.

d Horita and Clayton (2007) temperature equation: 1000 ln x = 0.9521 (10⁹/T²) + 11.59 (10¹/T) − 21.56.
$1000 \ln a = \frac{2.78 \times (10^6)}{T^2} - 2.89$ (4.5.1)

O’Neil et al. (1969), Friedman and O’Neil (1977)

$1000 \ln a = \frac{18.03 \times (10^3)}{T} - 32.17$ (4.5.2)


$x = \frac{\delta_{CaCO_3} - \delta_{H_2O}}{1000} = \frac{1000 + \delta_{CaCO_3}}{1000 + \delta_{H_2O}}$ (4.5.3)

$\Delta \delta^{18}O_{CaCO_3}/\Delta T = -0.206^{\delta\text{/oC}}$ Kim and O’Neil (1997) (4.5.4)

$T = \text{Kelvin.}$

Predicted calcite $\delta^{18}O$ values were then compared to measured calcite $\delta^{18}O$ values. Measured farmed calcite $\delta^{18}O$ values are consistently offset from predicted values by:

<table>
<thead>
<tr>
<th>Authors</th>
<th>Offset ($^\circ\text{VPDB}$)</th>
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<td>Horita and Clayton (2007)</td>
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</table>

Hollow Ridge Cave calcite is more enriched in $^{18}O$ than predicted by Kim and O’Neil (1997) for their 5 mmol initial $[\text{Ca}^{2+}]$ solution, which they interpreted as “the slowest” kinetics and thus closest to isotopic equilibrium (Fig. 7). Note that the $[\text{Ca}^{2+}]$ concentrations in HRC drips are 0.7–1.8 mmol. Speleothem studies at different latitudes, altitudes, and temperatures have reported similar “too high” offsets (Desmarchelier et al., 2000; Plagnes et al., 2002; Genty et al., 2003; Mickler et al., 2004, 2006; Coplen, 2007; Sinha et al., 2007; Boch et al., 2009) as summarized and discussed by McDermott et al. (2006). Additionally, fluid inclusion investigations have revealed corresponding offsets (McDermott et al., 2006; van Breukelen et al., 2006).

Fig. 7. 1000 ln $a$ vs. $10^3 \ T^{-1}$ For Calcite from Laboratory, Theoretical, and Cave Studies where the right y-axis is HRC calcite $\delta^{18}O$ (VSMOW), and the top x-axis is temperature (°C) plotted for Hollow Ridge Cave calcite (black open squares). HRC data shown are average values for each farming site by season. Other modern cave studies (solid and crossed squares), laboratory-based inorganic precipitation values (circles), and theoretical calculations (lines) are reported from those studies that reported calcite $\delta^{18}O$–$H_2O$ data. The red line is the best-fit line from Kim and O’Neil (1997) as modified by Kim et al. (2007): $10^3 \ ln a = 18.83 \times (10^2 \ T^{-1}) - 32.17$. Not shown are Kim and O’Neil (1997); 15 mmol L$^{-1}$ $[\text{Ca}^{2+}]$ where 1000 ln $x = 21.69 \times (10^2 \ T^{-1}) - 43.55$; and 25 mmol L$^{-1}$ $[\text{Ca}^{2+}]$ where 1000 ln $x = 21.56 \times (10^2 \ T^{-1}) - 42.55$. Hollow Ridge Cave drip samples ranged from 0.6 to 1.8 mmol L$^{-1}$ $[\text{Ca}^{2+}]$ and average drip $\delta^{18}O$ was $-3.75 \pm 0.33^{\text{min}}$ (2σ range) (VSMOW). The light-blue dashed line through cave data is the linear best-fit line $1000 \ ln x = [16.1 \pm 0.65] \times (10^3 \ T^{-1}) - [24.6 \pm 2.2] \times (98\% \ C.I.) (R^2 = 0.94)$ for all cave deposits. This result is significantly different from Kim and O’Neil (1997) 5 mmol data line at the 98% confidence interval. Equations for theoretical calculations are shown in Table EA.6. Analytical uncertainty for single measurements during the Hollow Ridge Cave study was less than $0.14^{\text{min}}$ (1σ), $1000 \ ln x = 1000 \times \ln [(1000 + \delta^{18}O_{\text{Calcite}})/(1000 + \delta^{18}O_{\text{Drip \ H2O}})]$ where for HRC $\delta^{18}O_{\text{Drip \ H2O}} = -3.75 \pm 0.33^{\text{min}}$ (VSMOW).
Authors of cave studies often state that their calcite was precipitated at or approaching equilibrium with water δ18O, statements that are virtually unprovable. Coplen (2007) defended that Devil’s Hole submerged vein calcite (enriched in δ18O by 1.5‰ over that predicted by Kim and O’Neil, 1997 at 33.7 °C) had precipitated in isotopic equilibrium by proving that: (1) there is <0.2‰ variation along the axis of the vein calcite δ18O (sample DHC2-8) over the last 10 ka (constant water temperature), (2) there is <0.1‰ variation in contemporary calcite δ18O at various sites throughout the cave (no gradients inside the submerged cave), and (3) U-series dating revealed that DHC2-8 precipitation rates of 0.1–0.8 mm/ka are much lower than laboratory experiments, and are thus less likely to induce kinetic fractionation. It is important to note that Devil’s Hole calcite precipitated in an open vertical shaft from ground water approximately 30 m below the water surface, and therefore solution–mineral precipitation kinetics are different from thin film degassing from splash drips atop a speleothem.

Three basic factors control isotope fractionation during mineral–solution interaction: (1) forward reaction rate and kinetic fractionation factor (Rf and s); (2) the equilibrium fractionation factor (sF); and (3) the backward (dissolution) reaction rate (Rb) defined as the difference between the net precipitation rate and the forward reaction rate (Rf – Rb) (DePaolo, 2011). Calcite will form close to oxygen isotopic equilibrium under the conditions of (Rf/Rb < 1), in other words the net precipitation rate is very slow with respect to the gross forward and backward reactions. At faster net precipitation rates, the forward kinetic fractionation factor will control the isotope system (Rf/Rb > 1). Calcite growth kinetics studies (e.g., Teng et al., 2000) have demonstrated that calcite growth rate is directly proportional to the extent of supersaturation (Ω > 1), i.e. higher Ω results in faster Rf. Higher values of Ω also decrease the solubility of CaCO3(s), resulting in reduced gross dissolution or RB. From this reasoning we suggest that calcite precipitated very slowly in a cave environment from natural drips at low Ω is likely closer to oxygen isotope equilibrium than lab-based experiments performed at high Ω. Additional rationale for this assessment will be explored in Section 5.1.

4.6. Predicted and measured calcite δ13C – ventilation effects

Several studies have quantified the effects of ventilation, fast degassing and carbon isotope exchange in the calcite–water–soil gas system in natural systems (Spötl et al., 2005; Frisia et al., 2011; Lambert and Aharon, 2011), in laboratory settings (Wiedner et al., 2008; Polag et al., 2010), and from a theoretical perspective (Scholz et al., 2009; Mühlinghaus et al., 2009; Dreybrodt and Scholz, 2011). In order to constrain the extent of ventilation-driven disturbances in equilibrium precipitation, it is necessary to know or assume the following: (1) carbon source endmember isotopic compositions; and (2) extent of isotopic exchange between drip water and cave air CO2. We follow Mühlinghaus et al. (2009), Scholz et al. (2009) and Frisia et al. (2011) in assuming little or no 13C fractionation between dissolved HCO3- and CaCO3 based on the negligible temperature dependence (HCO3- → CaCO3 + 13CO2 + Δ13C = –0.03‰) at 6.5 °C as reported by Mook and de Vries, 2000.

Stoichiometric contributions of bedrock and soil gas CO2-derived DIC are an ideal starting point for prediction of drip water DIC. The predicted drip water DIC for soil gas CO2 (δ13C = –20.7 ± 0.66‰) combined with Oligocene limestone (assumed δ13C = –2.0‰) is δ13C = –11.35‰. As discussed in Section 4.3, three drip sites (Duce, Smith and Jones A, and Ballroom) were sampled once monthly for four months to determine TCO2 and carbonate speciation. Drip water DIC at those sites was measured to be δ13C = –11.5 ± 1‰ (1σ range) (Table EA.4), indicating that measured values are in good agreement with predicted δ13C values and that stoichiometric carbon transport through the soil-epikarst system is an acceptable assumption, at least for winter time conditions.
Most of the calcite plates display δ13C values that are heavier than their respective drips (Fig. 8). Calcite grown at Ballroom, Smith and Jones Site B, Smith and Jones A2, as well as Lucky, and Larry (both near Entrance A—Fig. 1) exhibit a +1.5‰ to +2.7‰ enrichment in δ13C during spring and summer (weak ventilation), and a +2.7‰ to +5.5‰ enrichment during winter and fall (strong ventilation regime). Larry and Lucky are closest to Entrance A, and show winter time enrichments of +5.5‰ over predicted values. Sites Duece and Smith and Jones A1 precipitate calcite δ13C that are consistent with predicted values during spring and summer, and are enriched in 13C by +0.7‰ to 1.0‰ during fall and winter, about half that of the other sites. Site Richard precipitates calcite consistent with predicted δ13C values during summer, spring, and winter, but exhibit a +1.8‰ enrichment during fall.

4.7. Whole cave Hendy test relationships

Calcite grown at sites within the faster ventilation pathways of the cave (Larry, Lucky, Ballroom, Smith and Jones Site B, Smith and Jones Site A2) all have isotopic signatures...
Temperatures. The dashed black line with slope \(Dd\) and cave air CO\(_2\)-derived DIC (\(d\)) cave entrance drives rapid drip water CO\(_2\) degassing, preferentially removing the light isotope (\(^{12}\)CO\(_2\)) and enriching the remaining HCO\(_3^-\) – \(^{13}\)C (aq) reservoir (and consequent calcite); and (2) the initial aqueous HCO\(_3^-\) in the drip water which is also a mixture of soil gas and \(^{13}\)C enriched atmospheric air (\(\delta^{13}\)CO\(_2\) = −10%o), the composition of which is dependent on seasonal and diurnal ventilation gradients as depicted in Figs. 3 and 4.

To test the effects of ventilation on farmed calcite \(^{13}\)C and \(^{18}\)O, we constructed a modified “Hendy test” diagram of our farmed calcite \(^{18}\)O vs. \(^{13}\)C data (Fig. 10). Hendy (1971) predicted that rapid \(^{12}\)CO\(_2\) degassing from drip waters would drive the carbon isotopic composition of calcite toward higher \(^{13}\)C values with no change in \(^{18}\)O, provided that the degassing rate is slow enough to allow continuous \(^{18}\)O equilibrium exchange with the water oxygen isotope reservoir. Alternatively, drip water degassing and rapid precipitation would drive both \(^{13}\)C and \(^{18}\)O toward higher values. The “Hendy test” is often employed along a growth layer in a stalagmite to establish if a speleothem was precipitated out of oxygen isotopic equilibrium with drip water, and assumes a “closed” carbon system.

In order to test this conceptual model, we first predict what the temperature-induced changes in \(^{13}\)C\(_{\text{DIC}}\) and \(^{13}\)C\(_{\text{CaCO}_3}\) would be at isotopic equilibrium by calculating the temperature-dependent slope based on the results of Deines et al. (1974) and Kim and O’Neil (1997) (Eq. (4.5.4)):

\[
[\Delta^{13}\text{C}/\Delta T]/[\Delta^{18}\text{O}/\Delta T] = -0.09\%_\text{oo} / -0.206\%_\text{oo} = 0.44 \quad (4.7.1)
\]

This “slope of the slopes” is then the predicted change in \(^{13}\)C and \(^{18}\)O of calcite precipitated under equilibrium conditions from a homogeneous aquatic reservoir of fixed isotopic composition due only to changes in temperature. Note that slight differences in which temperature coefficients one chooses (which literature values) makes very little difference in this value. This slope is plotted on Fig. 10 near the bottom.

The Hendy test should then be judged against this equilibrium slope. It is important to make the distinction that the Hendy model is a Rayleigh fractionation model of calcite precipitated from an isolated and increasingly isotopically heavy solution, whereas we apply the concept not to one stalagmite growth layer but to an entire cave system in both time and space. Our farmed calcite was precipitated at many locations during different growth seasons throughout the cave, and the \(^{13}\)C/\(^{18}\)O of each sample is controlled by (1) temperature of formation (\(^{13}\)C\(_{\text{O}}\)), (2) the \(p\text{CO}_2\) gradient between water and air driving drip water \(\text{CO}_2\) degassing (\(^{13}\)C\(_{\text{DIC}}\)), and (3) the equilibrated fraction of cave air-derived DIC in drip water (\(^{13}\)C\(_{\text{DIC}}\)). Two groupings are observed in our farmed calcite (Fig. 10): (1) those precipitated in carbon equilibrium with drip water, and (2) those precipitated in a strongly ventilated flow path. The two groupings have very similar slopes (\(\Delta^{13}\text{C}/\Delta^{18}\text{O} = 1.7\) and 1.9) which are steeper than predicted for temperature equilibration only (0.44). But those in the ventilated flow path are offset in \(^{13}\)C from those outside the flow path by \(\sim 1.9 ± 0.6\%_\text{oo}\) (1σ). Both groupings exhibit \(\text{CO}_2\) ventilation effects as indicated by a slope steeper than predicted (\(\sim 1.8\) versus 0.44 – Eq. (4.7.1)). But unlike \(^{13}\)C, the 2.2\%_\text{oo} range in \(^{18}\)O is a result of the 9.5 °C temperature difference between farming.
sites as indicated by the top x-axis in Fig. 10 \((\Delta \delta^{18}O_{CaCO3}/\Delta T \sim -0.23\%/^{\circ}F)\). We therefore assume, but can not prove, that the calcite \(\delta^{18}O\) increase is due entirely to temperature-induced fractionation effects and not due to enhanced evaporation along the ventilation pathway (for example, see Day and Henderson, 2011). Relative humidity measured at CS1 and CS2 always fell between 97% and 100%, suggesting minimal evaporation effects. More work is needed to document this effect.

The +1.9\(^{\circ}O\) offset in the \(\delta^{13}C\) gradients (Fig. 10) represents a difference between sites that are only slightly ventilated and those that are vigorously ventilated. Since the oxygen isotopic composition is (in this case) a ventilation-independent variable, the slope of each line is set by the air-water pCO\(_2\) gradient along the flow path. The observed shift in \(\delta^{13}C\) is not likely due to differences in degassing rates since there is no accompanying change in the \(\Delta \delta^{18}O/\Delta \delta^{13}C\) slope between groupings. Instead, we argue that the shift is due to equilibrium precipitation with a mixture of soil gas (\(\delta^{13}C = -20.7^{\circ}O\)) and limestone (\(\delta^{13}C \sim -2.1^{\circ}O\)) derived DIC and cave air CO\(_2\)-derived DIC (\(\delta^{13}C\) is variable – see Fig. 3).

Air grab transects throughout Hollow Ridge Cave at different times of year reveal that significant portions of the cave are ventilated as a function of depth into the cave interior. Summer cave-air CO\(_2\) in the stream of the ventilation flow path can be 75% atmospheric air, and during periods of vigorous winter ventilation, cave air samples are often 100% forest canopy air (–10\(^{\circ}O\), at 450 ppmv – Fig. 4F). Using predicted ranges in drip water \(\delta^{13}C_{DIC}\), measured calcite \(\delta^{13}C\), and measured ranges in cave air \(\delta^{13}C\), we performed a simple mass balance to determine the fraction of DIC equilibration with cave air necessary to produce the observed offsets in calcite \(\delta^{13}C\):

\[
\delta^{13}C_{CaCO3} = f_{DIC(SG)} \times \delta^{13}C_{DIC(SG)} + f_{DIC(Cave Air)} \times \delta^{13}C_{DIC(Cave Air)}
\]

\[1 = f_{DIC(SG)} + f_{DIC(Cave Air)}
\]

where \(f_{DIC(SG)}\) and \(f_{DIC(Cave Air)}\) are the respective fractions of soil gas and cave air-derived DIC, and \(\delta^{13}C_{DIC(SG)}\) and \(\delta^{13}C_{DIC(Cave Air)}\) are the predicted isotopic compositions of soil gas and cave air-derived DIC. We assume no fractionation between DIC-\(\delta^{13}C\) and CaCO\(_3\)-\(\delta^{13}C\). Isotope mass balance for Hollow Ridge Cave calcite indicates that the entire range of variation in \(\delta^{13}C_{CaCO3}\) can be accounted for with a 30–60% cave air contribution to drip water DIC (consistent with the mixing in Fig. 3), while calculations of Frisia et al. (2011) demonstrate a cave air-CO\(_2\) contribution to drip water DIC on the order of 25–30%.

The question often arises whether the CO\(_2\) released from direct calcite precipitation is a significant proportion of the CO\(_2\) inside a cave. We again take a mass balance approach to determine the relative contribution of degassed CO\(_2\) as a control on calcite isotopic composition. We estimate the proportion of degassed CO\(_2\) in cave air by taking an average calcite deposition rate of 121 \(\mu mol m^{-2} h^{-1}\) (Table EA.3), an estimated cave area of 3324 m\(^2\) (approximately 10% of which is actively precipitating calcite), and the stoichiometric weight fraction of CO\(_2\) in calcite (44 g CO\(_2\)/100 g CaCO\(_3\)) as follows:

\[
121 \mu mol m^{-2} h^{-1} \times \frac{3324 m^{2}}{10} \times \frac{44.01 g CO_{2}}{100.09 g CaCO_{3}} = 17.68 \text{ mmol CO}_2 h^{-1}
\]

Compared to average summer and winter CO\(_2\) fluxes from Hollow Ridge Cave exhaled to the atmosphere as calculated by Kowalecz and Froelich (2010) of 5 mol h\(^{-1}\) (summer), and 0.5 mol h\(^{-1}\) (winter), the calcite-released CO\(_2\) contribution to the total CO\(_2\) reservoir (cave air and drip water) is approximately 0.35–3.5% mol fraction. Thus calcite \(\delta^{13}C\) is not likely to be significantly impacted by re-equilibration with calcite-derived CO\(_2\).

Although these results need to be repeated in other cave systems, we suggest that since all caves that precipitate calcite speleothems must breathe to remove CO\(_2\) and to oversaturate drips with respect to calcite (Kowalecz and Froelich, 2010), then all speleothems are susceptible to these ventilation effects on \(\delta^{13}C\). Whether these ventilation effects may also affect \(\delta^{18}O\) due to evaporation along airways is yet to be established.

5. DISCUSSION

5.1. Approaching oxygen isotope equilibrium precipitation

Low-temperature (LT) laboratory calcite precipitation experiments are usually performed by dissolving reagent grade CaCO\(_3\) in CO\(_2\) charged distilled water, or by adding metal salts (CaCl\(_2\), MgCl\(_2\), etc.) to a NaHCO\(_3\) solution (Table EA.6). Calcium carbonate precipitation is then driven by bubbling molecular nitrogen (N\(_2\)) through the solution to strip dissolved CO\(_2\) out of solution. Such experiments give broadly reproducible results, and are generally in accord with theoretical predictions based on statistical-mechanical calculations of reduced partition functions such as those carried out by Urey (1947), Chacko et al. (1991), Dove et al. (1992), Watson (2004), Horita and Clayton (2007) and most recently Chacko and Deines (2008). However, it is virtually impossible to prove in laboratory or cave settings that calcium carbonate precipitated at LT from aqueous solution is in oxygen isotopic equilibrium.

Precipitation processes in LT lab experiments are most likely to approach oxygen isotopic equilibrium when performed at extremely slow rates of precipitation (Horita and Clayton, 2007; DePaolo, 2011). Kim and O’Neil (1997) performed inorganic precipitation experiments at three temperatures (10, 25 and 40 \(^{\circ}C\)) with three solutions containing varying calcium concentrations; [Ca\(^{2+}\)] = 5, 15, and 25 mmol L\(^{-1}\). They argued that the 5 mmol L\(^{-1}\) starting solution was most like natural waters and was most likely in isotopic equilibrium. Their 15 and 25 mmol L\(^{-1}\) solutions showed much larger fractionation at 10 and 25 \(^{\circ}C\) and were thus thought to have precipitated calcite out of equilibrium. Moreover, increased initial oversaturation (precipitation rate) resulted in an increase in the apparent temperature dependence (steeper slope of 1000 ln z vs. 10\(^{3}\) T\(^{-1}\)) of oxygen isotopic fractionation. Because the slope
of the Kim and O’Neil (1997) 5 mmol L\(^{-1}\) experimental line
closely agreed with earlier studies that included extrapolated
lines from high temperature ‘equilibrium’ experiments
and biogenic calcite (O’Neil et al., 1969; Grossman and Ku,
1986; Patterson et al., 1993), and because more dilute solu-
tions reportedly gave fractionation factors that approached
a limiting value, the 5 mM experiment was accepted as most
likely to represent equilibrium precipitation. However, Kim
and O’Neil (1997) admitted that these were “only plausibil-
ity arguments as attainment of isotopic equilibrium can not be
proved.” Furthermore, they stated that future experiments
involving extremely dilute solutions would be performed,
ostensibly to discover the lower limit. Later experiments
(Kim et al., 2007) served to lower the y-intercept to
−32.17 as a result of adopting an acid fractionation factor
(\(\alpha_{\text{CO}_2(\text{ACID})-\text{Calcite}}\)) of 1.01030\(^{\circ}\) instead of the previously
calculated 1.01055\(^{\circ}\). However the lower limits of the tem-
perature dependence (slope of 1000 ln \(x\) vs. \(10^3 T^{-1}\)) were
not investigated.

Kim and O’Neil (1997) stated that “we judge the smallest
fractionation factors obtained to be the best representation of
equilibrium fractionation factors. This judgment may seem
counterintuitive to those who would expect kinetically-con-
trolled, non-equilibrium fractionations to be too small.” In
contrast, Coplen (2007) noted that “Kinetic considerations
may suggest preferential incorporation of the isotopically
light species (e.g., CO\(_3^{2-}\)) during rapid precipitation.” In
other words, during rapid precipitation there should be less
discrimination against \(^{18}\)O, which would result in isotopi-
cally lighter calcite and lower fractionation factors. Values
of \(\delta^{18}\)O in inorganic carbonates precipitated in laboratory
settings have been reported to be independent of growth
rate (Tarutani et al., 1969; Kim and O’Neil, 1997; Jimen-
ез-Lozep et al., 2001). However, our calculations
(Table EA.7) show that the initial starting concentrations
of Kim and O’Neil (1997) result in solutions that are one
to three orders of magnitude more supersaturated with
respect to calcite than those measured in HRC and Devil’s
Hole, possibly driving the kinetic effects cited by the
authors. As previously discussed, higher \(\Omega\) drives increased
forward reaction (\(R_0\)) and decreased dissolution (\(R_6\)), thus
kinetic fractionation becomes the dominant control of calcite
\(\delta^{18}\)O. Therefore carbonates grown under conditions of
\(\Omega \gg 1\) should not be expected \textit{a priori} to precipitate in oxy-
gen isotope equilibrium with the parent solution (DePaolo,
2011).

Another major difference between laboratory and cave
experiments is that nitrogen is bubbled through lab solu-
tions to strip CO\(_2\) (aq) out of solution to drive CaCO\(_3\) pre-
cipitation. Active nitrogen (N\(_2\)) bubble degassing of bulk
fluids is very different from passive CO\(_2\) degassing through
a thin film from a liquid droplet or rivulet. In cave air the
minimum pCO\(_2\) is set by the local ventilation regime (Figs. 2
and 3), and a completely ventilated cave has a minimum
pCO\(_2\) condition of atmospheric air at approximately
390 ppmv. During drip water degassing cave air CO\(_2\) dif-
fuses into the drip while CO\(_2\) (aq) diffuses out of the drip,
with a net CO\(_2\) loss from the drip, analogous to the surface
ocean (Zeebe et al., 1999). During this process, water CO\(_2\)
slowly reaches isotopic equilibrium with cave air CO\(_2\) on
the order of minutes (Dreybrodt and Scholz, 2011), and
aqueous carbonate species, almost all bicarbonate ions,
contain oxygen that is near or at equilibrium with drip
water. In contrast, bubbling N\(_2\) in the laboratory experi-
ment essentially exposes the solution to a 0 ppmv CO\(_2\)
atmosphere which strips CO\(_2(aq)\) out of solution much more
quickly. Such CO\(_2\) transport is essentially a one-way pro-
cess with no avenue of re-equilibration. It is possible that
N\(_2\) bubbling causes large kinetic fractionation between car-
bonate species, which may involve the preferential deproto-
nation of isotopically light HCO\(_3^-\) and the incorporation of
the light CO\(_3^{2-}\) isotopologues as proposed by Kim et al.

Dietzel et al. (2009) attempted to circumvent N\(_2\) bub-
bling by introducing a high pCO\(_2\) NaHCO\(_3\) solution to a
low pCO\(_2\) CaCl\(_2\) solution through a semi-permeable poly-
ethylene membrane (Dietzel and Usdowski, 1996). At con-
stant pH, Dietzel et al. (2009) and Kim et al. (2006) both
demonstrated a systematic increase in \(\alpha_{\text{CaCO}_3-H_2O}\)
with increasing experimental duration (slower precipitation).
However, based on our interpretation of the disequilibrium
isotope offset, calcite precipitated by Dietzel et al. (2009)
is the farthest from equilibrium, for reasons that are not
understood.

Coplen (2007) and Dietzel et al. (2009) provide compel-
ling arguments that laboratory inorganic calcite precipita-
tion experiments \textit{underestimate} equilibrium fractionation
factors between water and calcite. A linear best-fit line
through data from a large number of modern cave studies
(Fig. 7) suggests that the equilibrium fractionation of cal-
cite in a “natural cave laboratory” is:

\[
1000 \ln x = [16.1 \pm 0.65] (10^3 T^{-1}) - [24.6 \pm 2.2] \\
R^2 = 0.94 \text{ (98% C.I.)} \tag{5.1.1}
\]

\[
\Delta \delta^{18}O \text{CaCO}_3/\Delta T = -0.177 \% / ^\circ\text{C} \tag{5.1.2}
\]

This “cave calcite” line describes samples that were pre-
cipitated at many different latitudes, altitudes, and tempera-
tures. In Fig. 7 the “cave” line intersects the O’Neil et al.
(1969) line at T = 0 \(^\circ\)C, which suggests a systematic offset
between the “cave” line and laboratory predictions at high-
er temperatures. Although we cannot fully explain the sys-
tematic offset, it is clear that additional empirical calibra-
tions of this nature are essential to the interpretation of
paleoclimate and paleotemperature data from caves.

5.2. Ventilation

We have demonstrated that ventilation in a shallow
cave can have significant impacts on calcite \(\delta^{13}\)C, and that
seasonal ventilation regimes control the rate and timing of
calcite precipitation. In general, atmospheric CO\(_2\) mixes
with soil gas inside the cave, and calcite precipitates in
equilibrium with a \(^{13}\)C-enriched DIC reservoir as a func-
tion of distance along the ventilated flow path. At present
micro-mill sampling resolution (50–500 \(\mu m\)) ventilation-
induced seasonal variations in calcite \(\delta^{13}\)C are likely over-
printed by climate-driven long-term changes in cave air
CO\(_2\). However, significant calcite \(\delta^{13}\)C shifts could arise
from long-term changes in ventilation without concomitant changes in either vegetation or atmospheric CO2. Modern HRC calcite exhibits a $-7\%$ $\Delta^{13}C$ gradient along the ventilation pathway from cave entrance to interior during the winter. Entrance collapse would slow ventilation, and calcite near the entrance would take on the isotopic signature of DIC, thus eliminating the gradient. Conversely, the introduction of a new ventilation pathway to the interior of the cave may drive calcite to less $^{13}C$ depleted values. Such an excursion might be mistakenly interpreted as a rapid increase in the ratio of C4/C3 vegetation overlying the cave. Thus, it may be useful to begin thinking of rapid changes in calcite $\delta^{13}C$ as possible perturbations in the dominant paleo-ventilation regime, as cave openings come and go with the evolving karst hydrology.

6. CONCLUSIONS

Calcite farming in continuously monitored Hollow Ridge Cave (HRC) has revealed for the first time a direct connection between calcite growth rates, seasonal calcite $\delta^{13}C$ and ventilation-driven pCO2 gradients inside a cave. Calcite $\delta^{13}C$ decreases along the ventilation pathway suggesting that calcite $\delta^{13}C$ is a potential proxy not only for overlying vegetation or atmospheric CO2, but also for cave air ventilation. Indeed, seasonal ventilation-driven variations in speleothem $\delta^{13}C$ would not likely be obvious without high-resolution calibrations in both time and space. As in other caves, summer-time air stagnation inside HRC leads to high cave air pCO2 that reduces drip water CO2 degassing and thus lowers calcite precipitation rates. We predict that this reduction would result in seasonal aliasing of the calcite climate signal toward winter-time climates. Since all caves with actively growing formations must experience ventilation to remove cave air CO2 that drive the precipitation reaction, these inferences are generally applicable to all caves that breathe.

Modern in situ calibration of calcite $\delta^{18}O$-temperature fractionation factors in HRC farmed calcite has demonstrated that inorganic calcite precipitated very slowly from slightly supersaturated drip solutions is more enriched in $^{18}O$ (+0.82 ± 0.24‰) than predicted from laboratory-based inorganic calcite precipitation experiments. Based on our calibrations and data from other cave investigations, we propose a new empirical isotope-temperature fractionation relationship for inorganic cave calcite:

$$1000 \ln \alpha = 16.1 \left(10^3 \, T^{-1}\right) - 24.6$$

This equation defines a temperature-dependent oxygen isotope fractionation of approximately $\Delta^{18}O$ CaCO3/ $\Delta T = -0.177$‰/°C. We suggest that laboratory-based inorganic calcite precipitation experiments suffer from poorly understood kinetic isotope effects that drive the perceived ‘classic’ temperature dependence higher, to $-0.206$‰/°C.

Although water-calcite oxygen isotope equilibrium is not likely to be achieved either in caves or in laboratories, we suggest that natural cave calcite is precipitated more slowly and is likely closer to equilibrium than laboratory experiments. Modified “Hendy tests” from in situ farmed HRC calcite produce $\Delta^{13}C/\Delta^{18}O$ relationships with slopes (~1.8) that are higher than that predicted based on equilibrium temperature alone (~0.44). Similar relationships have been reported from numerous cave studies, further suggesting the possibility that nature, while seemingly reproducible, may not precipitate calcite in isotopic equilibrium. However, we demonstrate that this slope and concomitant $\delta^{13}C$ offsets are the result of small temperature differences in $\Delta^{18}O$ and large cave air ventilation effects in $\Delta^{13}C$. Thus the application of a whole-cave “Hendy test”, commonly used to discriminate “equilibrium” calcite precipitation in speleothem growth layers, may in fact be an extremely useful ventilation proxy in the absence of traditional proxy measurements such as CO2 or $^{222}$Rn.

ACKNOWLEDGMENTS

This research is conducted in conjunction with the Southeastern Cave Conservancy Inc. (SCCi), PO Box 71857, Chattanooga, TN 37407-0857, Chairman: B. Krebs, with financial support from D. Baker, Plum Creek Timber, Seattle, WA. We thank A. Mosler, HRC SCCi cave steward for allowing unrestricted access to HRC and for generous field support. We thank A. Kowalczk for creating and deploying the cave monitoring equipment, and B. Kilgore for continuous field support, sample collection, and anion analyses, and J. Chanton, S. Misra, Y. Xu, C. Langford, and J. Corbett for analytical assistance. We thank D. Nof for his input on ventilation dynamics and the cartoon of cave ventilation. We thank M. Humayun, W. Burnett, and T. Coplen for internal reviews of earlier drafts. We thank Mira Bar-Matthews for meticulous editorial handling and three anonymous reviewers for their thoughtful criticism that helped focus and refine this manuscript. This work was funded by Florida State University Francis Eppes Foundation and NSF grant #AGS-1032402 to P.N.F., and by an FSU-Oceanography teaching assistantship to D.T.

APPENDICES A AND B. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.gca.2011.06.005.

REFERENCES

Baldini J., McDermott F., Hoffmann D., Richards D. and Clipson N. (2008) Very high-frequency and seasonal cave atmosphere CO2 variability: implications for stalagmite growth and
Modern calibration of speleothem paleoclimate proxies 4947


