Quantifying carbon isotope disequilibrium during in-cave evolution of drip water along discreet flow paths

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Received 26 June 2017; accepted in revised form 23 September 2018; available online 9 October 2018

Abstract

Paleoclimate reconstructions that use speleothem proxy data have increased our understanding of terrestrial climate change, but gaps remain in our understanding of in-cave processes that influence speleothem chemistry. The δ13C values of speleothem calcite are typically influenced by kinetic isotope effects that operate during CO2 degassing and calcite precipitation. Therefore the identification and quantification of these isotopic effects is important in interpreting speleothem stable isotope records. Here we studied the change in water chemistry and δ13C values of dissolved inorganic carbon (DIC) along discreet flow paths at multiple drip sites in Inner Space Cavern, central Texas. We quantified the extent to which the water remains in C isotopic equilibrium during flow along speleothem surfaces as CO2 degasses and calcite precipitates.

Two locations in the study cave that have long in-cave flow paths were examined to determine the geochemical evolution and its driving processes along these paths. At each location cave water was sampled at two points 1–2 meters apart along each flow path. Among the key spatial changes observed is a <1‰ to >4‰ increase in δ13C values along the flow paths. The magnitude of the increase in δ13C values is controlled by the extent of DIC loss to CO2 degassing. The extent of DIC loss and CO2 degassing is controlled by the pCO2 gradient between drip water and cave air. If the DIC loss is less than 15%, then the evolution of the δ13C value of the DIC reservoir can be accounted for by a Rayleigh distillation model with equilibrium C-isotope fractionation factors for (CO2(g)-HCO3−/CaCO3aq) and (CaCO3-HCO3−/CaCO3aq). As the depletion of the DIC reservoir exceeds 15% the DIC δ13C values become progressively higher such that the (HCO3−/CO2(g)) fractionation values needed to explain the observations change from equilibrium values of ~8‰ to non-equilibrium values of up to ~25‰. This variance in magnitude of C-isotope fractionation during CO2 degassing cannot be attributed to changes in temperature, and thus we infer significant kinetic isotope effects at higher rates of DIC loss. Such kinetic effects have significant implications for speleothem C-isotope proxy interpretations, as these kinetic isotope effects are of a similar magnitude as those used to infer past changes in drought and vegetation.

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Keywords: Speleothem; Non-equilibrium; C isotopes

1. INTRODUCTION

Speleothems are useful paleoclimate archives. Speleothem climate records have improved our understanding of the
timing of glacial-interglacial transitions (Cheng et al., 2009; Moseley et al., 2016) and the orbital and millennial variability of low (Wang et al., 2001; Shakun et al., 2007; Cruz et al., 2009; Cheng et al., 2012; Denniston et al., 2013; Lachniet et al., 2013) and mid latitude precipitation (Dorale et al., 1998; Bar-Matthews et al., 2000; Oster et al., 2009). Speleothems have also been used to study smaller, shorter term changes including ENSO events and intra-annual climate variability (Banner et al., 1996; Frapporti et al., 2002; Lachniet et al., 2004). Studies of the carbon isotopic composition of speleothems have been used to infer changes in ecosystem productivity (Genty et al., 2003), soil erosion (Bar-Matthews et al., 2003), paleoaridity (Oster et al., 2015) and bioclasts (Dorale et al., 1992) and when stacked globally record atmospheric CO₂ concentrations over the past 90 kyr (Breecker, 2017). Recent work provides more detailed discussion of the use of speleothem δ¹³C values in paleoclimate reconstructions as well as a detailed discussion of processes affecting speleothem δ¹³C values (Meyer et al., 2014; Wong and Breecker, 2015; Dreybrodt et al., 2016; Breecker, 2017; Muhlinghaus et al., 2007; Dreybrodt, 2008). These studies detail numerous processes that control speleothem δ¹³C values. The most proximal to the site of calcite precipitation are processes that occur as water flows in the cave environment and water chemistry is altered by CO₂ degassing and calcite precipitation (Baker et al., 1997; Hansen et al., 2013). These processes are influenced by cave ventilation (Tochterle et al., 2017) that alters the extent of CO₂ degassing, and as we will discuss CO₂ degassing/calcite precipitation ratios.

Carbon isotope compositions of calcite controlled by seasonality in calcite precipitation may differ from average annual climate conditions. Few studies consider the potential effect of seasonal cave ventilation on the processes that control the isotopic compositions of groundwater and speleothem calcite. Seasonal cave ventilation can occur in multiple ways: (1) when the outward movement of relatively warm less dense cave air is replaced by cooler, relatively denser outside air during colder months, (2) when relatively cooler, dense cave air rolls out of a cave entrance in caves situated on hill side terrain and is replaced by warmer, relatively less dense air. (3) A combination of these two processes in caves with multiple conduits to the outside atmosphere at multiple elevations where a chimney effect may occur that moves cave air in seasonally controlled directions (Wigley and Brown, 1976). These processes are covered in depth in Baldini et al., (2008) and James et al., (2015).

This study examines the effect of CO₂ degassing and calcite precipitation on the stable carbon isotope composition of vadose waters in a central Texas cave. We constrain these processes through an analysis of cave meteorology and drip water flow, and through the geochemistry of drip waters and the modern speleothem-analog calcite precipitating from the water. We measure the C isotope composition of calcite precipitated on artificial substrates placed under three of these drips in order to determine the extent to which (1) isotopic equilibrium is attained between the drip water and speleothem calcite and (2) temporal variations in C isotopes in vadose water, and environmental changes, are reflected by speleothem calcite. Processes that affect karst water δ¹³C values are quantitatively modeled to evaluate the magnitude of carbon isotope fractionation factors required to explain the observed groundwater evolution along a flowpath.

2. STUDY AREA AND HYDROGEOLOGY

The cave studied here, Inner Space Cavern (IS), was developed in the cavernous zone of the Edwards Formation, which overlies the Comanche Peak Formation and is capped by the Del Rio Clay (Kastning, 1983). Limestone, dolostone and chert make up the majority of the Edwards Formation. The portion of the Edwards that Inner Space has formed in is relatively pure limestone interbedded with dolomite strata and chert lenses (Kastning, 1983). Sampling sites in Inner Space Cavern are located between 12 and 18 meters below the surface and at least 100 meters from the cave entrance. The vegetation of this area consists of mostly grasses, cacti, oak, elm and juniper trees. The soils of this area range between 10 cm and 50 cm, are moderately calcareous, and there is little exposed bedrock (Banner et al., 2007). In addition, impervious asphalt surfaces exist over the cave and as indicated in Meyer et al. (2014)

2.1. Study site hydrogeology and ventilation setting

In this study, and likely most other central Texas caves, the cave studied is located under relatively level terrain, and cave air exchange occurs by process 1 described above. In the summer months cool, dense cave air does not convectively exchange CO₂ with the outside warmer, less dense air, and CO₂ exchange with the outside atmosphere occurs by less effective means. CO₂ degassing from cave waters and gas phase transport through epikarst fractures (Breecker et al., 2012) increases cave air CO₂ concentrations which reduces the gradient between cave air CO₂ concentrations and cave water dissolved inorganic carbon (DIC), reducing calcite precipitation rates. In cooler winter months, the now relatively warmer lower density, higher CO₂ cave air is convectively replaced by cooler higher density, lower CO₂ outside air which decreases the cave air CO₂ concentrations and increases cave water DIC gradient engendering calcite precipitation (Spötl et al., 2005; Banner et al., 2007). Drip waters emerging from the cave ceiling, with high pCO₂ from the epikarst, must degas CO₂ in order to equilibrate with the lower pCO₂ cave atmosphere, engendering calcite supersaturation and precipitation. CO₂ degassing and calcite precipitation can result in kinetic fractionation of C isotopes between drip water and the precipitated calcite and along flowpath shifts in drip water DIC δ¹³C values (Mickler et al., 2004, 2006).

2.2. Site descriptions and hydrological characteristics

Three sites were chosen for study in Inner Space caverns, ISST, ISCD and ISSR-8. Two of the sites, ISST and ISCD, have unique characteristics that made this study possible (Fig. 1). Specifically, these characteristics are that the water enters the cave at a discrete stalactite (Direct drip site),
drips onto a calcite flowstone and then drips off a lower stalactite (Indirect drip site). Because of this unique geometry the cave water could be collected at two points along its flow path: (1) as it entered the cave environment from the cave roof (allowing its chemical and isotopic composition to be measured before exchanging with the cave atmosphere and (2) as it dripped off a lower stalactite where the water’s chemical and isotopic composition could be measured again. The effects of CO2 degassing and calcite precipitation on the water as it moved over the flowstone intermediate between the two drip sites can be assessed by comparing the drip-water chemistry between the two sites. Finally, an artificial substrate was placed under the lower stalactites at ISST and ISCD to collect modern cave calcite.

The ISSR-8 site was chosen to compare and contrast to the ISST and ISCD sites. At ISSR-8, water enters the cave and drips off a discreet stalactite before falling onto a lower stalagmite. This represents a more conventional drip site that may be used in other cave studies and may be more applicable to stalagmite carbon isotope records.

Surface air temperatures above the cave show strong seasonality with monthly average temperatures highest in August, approximately 31 °C, and lowest in December, approximately 7 °C. Inner Space Cavern receives an average of 84 cm of rain a year.

Cave-air temperatures are dampened compared to surface air temperatures, ranging from a high of 22.7 to a low of 17.4 °C. Cave air and surface air temperatures were roughly equal in October. Relative humidity in Inner Space Cavern ranges from 89 to 98% (Banner et al., 2007). CO2 concentrations in the cave air range from 7700 to 400 mg/LV. CO2 concentrations show a strong correlation with seasonality: highest CO2 concentrations occur in the summer months and the lowest CO2 concentrations occur in the winter months (Fig. 2).

3. METHODS

3.1. Atmospheric conditions

Surface air temperatures and precipitation data are from a nearby weather station with data available from www.noaa.gov. The station located closest to Inner Space Cavern, approximately 8 km to the north, is the Georgetown station Coop ID number 413506.

3.2. Cave-air conditions

Cave-air CO2 concentrations, humidity and temperature were recorded during monthly or bi-monthly sampling trips. A Vaisala GM70 meter with a GMP222 probe was used to measure CO2 concentrations with an analytical precision of ±3.5%. Humidity and temperature were measured using a Tinytag TH-2500 hand-held thermohygrometer with an analytical precision ±3% RH.

3.3. Cave drip water chemistry

Elemental concentrations were measured using an Agilent 7500ce Quadrupole inductively-coupled-plasma-mass-spectrometer (ICP-MS) at the University of Texas at Austin. Waters were collected for cation analysis in 15 ml acid-cleaned polypropylene bottles and acidified with ultrapure HNO3 at the University of Texas. Cave waters were refrigerated between collection and analysis. Field
measurements of water temperature, and pH, were conducted during each sampling visit with field meters.

Waters were collected and analyzed for DIC concentrations and carbon isotope composition by injecting 0.4 milliliters of drip water into He-flushed septum-capped Exetainer vials in the field (Meyer et al., 2014). In the lab, these were reacted with 103% orthophosphoric acid at 40 °C for 8 hours. The liberated CO₂ gas was analyzed using a GasBench II coupled to a Thermo Scientific MAT 253 mass spectrometer (modified from method of Spötl and Venneman, 2003). An in-house NaHCO₃ standard, itself calibrated to VPDB scale by comparison to NBS 18 and NBS 19 following Coplen et al. (1996), was dissolved in DI water at various concentrations and analyzed alongside unknowns. Analytical precision (±0.3 ‰, 1 sigma) was determined by replicate analyses of the aqueous NaHCO₃ standard. The NaHCO₃ standard was also used to quantify DIC concentrations. A detailed description of DIC concentration methods are in Meyer et al. (2014).

3.4. Modern speleothem calcite

Modern speleothem calcite was collected by placing pre-weighed, clean, sandblasted glass plates directly under drips that were actively precipitating speleothems. The plates were positioned very close to but slightly off level to limit the presence of standing water on the plate. Plates were left from 4 to 6 weeks to accumulate calcite. Plates were then rinsed with deionized water to prevent the precipitation of calcite due to evaporation, and dried in a laminar flow hood overnight. Plates were weighed on a Sartorius balance to the 5th decimal place with an precision of ±0.00007 g. Calcite growth rates were calculated by determining the weight of the precipitated calcite (Weight of plate with calcite – weight of plate before experiment) and dividing by the time the plate was deployed. Natural drift in the balance was corrected for by normalizing the data to a reference plate such that the (weight of the reference plate minus the accepted weight of the reference plate) was subtracted from the weight of the precipitated calcite. All plates were approximately the same size, 10 cm × 10 cm (Banner et al., 2007).

The δ¹³C values of modern speleothem-analog calcite were determined by collecting approximately 200 micrograms of calcite from each plate using a scalpel and binocular microscope. Calcite samples were placed in septum-capped Exetainer vials, flushed with He, and reacted with 103% anhydrous orthophosphoric acid at 50 °C for 2 h. The liberated CO₂ gas was analyzed using a Gasbench II coupled to a Thermo Scientific MAT 253 mass spectrometer (Spötl and Venneman, 2003). Carbon isotope ratios were normalized to the VPDB scale following Coplen et al. (1996) and are reproducible within ±0.12 ‰ (1 sigma).

3.5. Equilibrium and non-equilibrium isotope fractionation assessment methods

The extent to which DIC remained in C isotope equilibrium with degassed CO₂ and calcite during progressive CO₂ degassing and calcite precipitation at the ISST and ISCD sites was determined by calculating the loss of DIC between the direct and indirect drip sites, assumed to be predominately HCO₃⁻ and verified by PHREEQC modelling (Parkhurst and Appelo, 2013). PHREEQC results are summarized in Table 1. The loss of HCO₃⁻ to calcite precipitation was determined by assuming any loss of Ca from the water was due to calcite precipitation and there was a stoichiometric loss of HCO₃⁻. The loss of DIC to CO₂ degassing was determined by subtracting the loss of DIC to calcite precipitation from the total DIC loss.

This study models the evolution of the δ¹³C values of the DIC reservoir by the δ¹³C values of the corresponding drip water, the temperature of the drip water and temperature-dependent fractionation factors between calcite and HCO₃⁻ (aq) and between CO₂ and HCO₃⁻ (Deines et al., 1974). This study also models the evolution of δ¹³C values of the HCO₃⁻ reservoir by taking into consideration variations in the CO₂ degassing and calcite precipitation ratio, which are often considered to be 1. To model the isotopic composition of the HCO₃⁻ (aq) reservoir as degassing of CO₂ and the
precipitation of calcite proceed, the combination of the HCO$_3^-$ (aq)-CO$_2$(g) fractionation factor and the CaCO$_3$(s)-HCO$_3^-$ (aq) fractionation factor is used. These two fractionation factors together produce the fractionation between the dissolved inorganic carbon and a bulk product calculated from the relative proportions of carbon dioxide gas and calcite removed from the HCO$_3^-$ (aq) reservoir. We calculate the fractionation factor between the HCO$_3^-$ (aq) reservoir and the bulk product, $\delta_{p-r}$, by the following equations.

\[ x(p - r) = (X')\delta_1 + (X - 1)\delta_2 \]  

(1)

$X$ is the determined fraction of C lost to CO$_2$ degassing and $X - 1$ is the fraction of C lost to calcite precipitation, $\delta_1$ is the fractionation factor between CaCO$_3$(s) and HCO$_3^-$ (aq), $\delta_2$ is the fractionation between HCO$_3^-$ (aq) and CO$_2$(g). Using this combination fractionation factor and the Rayleigh distillation described below by Eq. (2), the change in the carbon isotope composition of the HCO$_3^-$ (aq) remaining during equilibrium calcite precipitation can be calculated.

\[ \frac{(\delta - 1000)}{(\delta_t + 1000)} = f^{(\delta_{p-r}-1)} \]  

(2)

3.6. Non-equilibrium fractionation factor determination

The $\delta^{13}$C values of some DIC samples in this study cannot be explained by equilibrium calcite precipitation and CO$_2$ degassing and suggest that non-equilibrium fractionation is occurring. We model the evolution of DIC $\delta^{13}$C values from the direct drip site to the indirect drip site at both ISST and ISCD using a Rayleigh distillation model of CO$_2$ degassing and calcite precipitation (Eq. (2)), where $\delta$ is the C isotope composition of DIC at the indirect drip site, $\delta_0$ is the initial C isotope composition of DIC at the direct drip site, $f$ is the fraction of DIC remaining during the reaction progress calculated from the difference in DIC concentrations from the direct to indirect drip site, and $\delta_{p-r}$ is the equilibrium fractionation factor between the bulk product and the HCO$_3^-$ (aq) reactant. The fractionation factor must take into account both the relative proportions of both calcite precipitation and carbon dioxide degassing.

The HCO$_3$(aq)-CO$_2$(g) kinetic fractionation factor, hereafter referred to as $\varepsilon$ which is equivalent to 1000 ln, can be estimated by assuming the CaCO$_3$(s)-HCO$_3$(aq) fractionation factor is approximately equal to the equilibrium value. Direct incorporation of HCO$_3^-$ (aq) into calcite during rapid calcite precipitation, such that isotopic fractionation...
Table 2
Summary of field parameters and general chemistry for samples collected at the ISST, ISCD, ISSR-8 drip sites. These parameters were used to calculate loss of Ca and DIC between direct and indirect drip sites and proportion the loss of DIC between calcite precipitation and CO₂ degassing.

<table>
<thead>
<tr>
<th>Site</th>
<th>Date</th>
<th>T (°C)</th>
<th>pH</th>
<th>Ca (mg/L)</th>
<th>DIC (mg/L)</th>
<th>DIC δ¹³C (PDB)</th>
<th>Loss of Ca (mmol)</th>
<th>Loss of DIC (mmol)</th>
<th>Fraction of HCO₃⁻ lost to calcite precipitation</th>
<th>Fraction of HCO₃⁻ lost to CO₂ degassing</th>
<th>Fraction of DIC remaining</th>
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<td>22.5</td>
<td>7.48</td>
<td>85.2</td>
<td>151.7</td>
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<td>0.12</td>
<td>0.88</td>
<td>0.91</td>
</tr>
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<td>138.0</td>
<td>9.83</td>
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<td>0.42</td>
<td>0.58</td>
<td>0.86</td>
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<td>68.9</td>
<td>8.33</td>
<td>−11.0</td>
<td>0.57</td>
<td>0.42</td>
<td>0.58</td>
<td>0.95</td>
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<td>10.22</td>
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is minimized (Michaelis et al., 1985) may overestimate the HCO$_3$-CO$_2$ fractionation factor by an amount equivalent to the difference between the actual and equilibrium fractionation factor between CaCO$_3$-HCO$_3$-HCO$_3$. This overestimation is likely small because the CaCO$_3$-HCO$_3$ fractionation factor is small, in this study approximately 2‰. Variations in the CaCO$_3$-HCO$_3$-HCO$_3$ fractionation factor, in this study, are also likely limited by the relatively small variation in drip water temperature, between 20.1°C and 24.7°C at the ISST and ISCD sites. By calculating the $\varepsilon$ (HCO$_3$-CO$_2$ fraction) value over $\varepsilon$ (CaCO$_3$-HCO$_3$-HCO$_3$) values from 0 to 2, the effect of the uncertainty in the CaCO$_3$-HCO$_3$ fractionation factor is bracketed.

4. RESULTS

4.1. Drip-water chemistry

The drip sites have seasonal pH, DIC and Ca fluctuations (Table 2). DIC values show the strongest seasonality with the highest concentrations occurring in August and winter month concentrations decreasing down to ~30% of the summertime maximum, a drop from 151.7 mg/L to 39 mg/L at the ISST direct drip site. At the ISST site, DIC concentrations are consistently lower in the indirect drip site. The ISCD drip site also shows seasonal changes in DIC concentrations with a summertime maximum of 93.2 mg/L and a winter time minimum of 31.8 mg/L, a decrease to 34% of maximum. Unlike the ISST site, the ISCD site does not show a decrease in DIC concentrations between the direct and indirect drip site, suggesting that no CO$_2$ degassing or calcite precipitation occurs during the water’s time on the flowstone between these distinct drip sites.

The Ca concentrations of the drip water mirror the DIC concentrations at the ISST and ISSR-8 sites, where Ca concentrations are highest in the summer months and are generally lower in the winter months. At the ISST site, Ca concentrations are higher at the direct drip than at the indirect drip suggesting loss to calcite precipitation. The ISCD site does not show a systematic change in Ca concentrations with season or a decrease in concentration between the direct and indirect drip site.

The pH at the three sites show similar trends (Table 2) where the measured pH is lowest in the summer months at the ISST, ISCD and ISSR-8 sites (7.4, 7.0 and 7.8 respectively) and increase into the winter months (8.5, 8.2 and 8.6 respectively). The increase in drip water pH is correlated with the decrease in DIC values. The pH systematically increases between the direct and indirect drip sites at the ISST site suggesting that pH increases with progressive CO$_2$ degassing and calcite precipitation. We do not observe a systematic increase in pH between the direct and indirect drip sites at ISCD where no CO$_2$ degassing or calcite precipitation is suspected.

4.2. Water C isotope composition

The $\delta^{13}$C values of cave waters generally show seasonal fluctuations with the lowest values occurring during the summer and the highest values occurring during the winter months (Table 2). At the ISST site, the magnitude of increases in $\delta^{13}$C value of the DIC between the direct and indirect drip sites varies seasonally; it is relatively small in August 2013 (~10.1‰ to ~9.6‰) and relatively large in 12/2013 (~9.7‰ to ~6.8‰). The ISCD site has lower $\delta^{13}$C variability between the direct and indirect drip sites and in seasonal $\delta^{13}$C variability. The lowest $\delta^{13}$C values occurring in August of 2013 where the $\delta^{13}$C value of DIC increases between the direct and indirect drip sites from ~11.5‰e to ~11.1‰e in 7/2013. Higher $\delta^{13}$C values occurring in 12/2013 where $\delta^{13}$C values increase between the direct and indirect drip sites from ~10.8‰e to ~10.55‰e. The ISSR-8 site shows similar variability as the ISST site, however, because this site does not have a direct and indirect drip site like the other sites, the effect of progressive calcite precipitation and CO$_2$ degassing could not be identified. The $\delta^{13}$C value of DIC at the ISSR-8 site increases from ~10.30 in 7/2013 to ~9.44 in 1/2014.

4.3. Calcite growth rates and $\delta^{13}$C values

Average daily growth rates were measured at ISST (5/2001 to 3/2015), ISCD (9/2013 to 3/2015) and ISSR-8 (5/2009 to 3/2015) sites (Fig. 3). Although significant variability exists in the data some generalities can be observed by analyzing average growth rates by month (Banner et al., 2007). Calcite growth rates at the ISST and ISSR-8 sites are near 0 in August and September and highest
between November and May or June, with average growth rates \(\sim 11\) mg/d at ISSR-8 and \(\sim 8\) mg/d at ISST. Maximum calculated growth rates were \(35\) mg/d in 1/2013 at ISSR-8 and \(39\) mg/d in 12/2014 at ISST.

Although the ISCD site contained flowstone calcite between the direct and indirect drips the plate placed under the indirect drip was consistently lower in weight after collection than before. This suggests that no calcite was precipitated on the plate and a small portion of the glass plate dissolved into the drip water (Cooper and Cox, 1996).

The \(\delta^{13}C\) value of calcite at the ISST and ISSR-8 drip sites vary between 0.3‰ and 1.7‰ higher (average value of \(\sim 1.1%\) higher) than the \(\delta^{13}C\) value of DIC of the corresponding indirect drip water (Table 3). No calcite was collected at the ISCD site and the \(\text{CaCO}_3^{\text{(aq)}}-\text{HCO}_3^{\text{(aq)}}\) fractionation factor could not be determined. Note the \(\epsilon\) \((\text{Calcite}-\text{HCO}_3^{\text{(aq)}})\) values used to determine the non-equilibrium fractionation factor between \(\text{HCO}_3^{\text{(aq)}}-\text{CO}_2\) are 0 to 2, which brackets all observed differences in \(\text{CaCO}_3\) \((\epsilon^{\text{Calcite-HCO}_3^{\text{(aq)}}})\) pairs.

### 4.4. Loss of DIC and CO\(_2\) degassing: calcite precipitation ratios

The loss of DIC between the direct and indirect drip site at ISST increased from an August value of 91% of 151.7 mg/L C remaining to a wintertime value of 72% of 53.7 mg/L C in January (Table 2). The loss of DIC was calculated to be 71% of 64.4 mg/L C in October but we use the lower DIC value in January as the lower DIC loss endmember because of the lower DIC concentrations and the October loss of DIC may be overestimated.

The loss of DIC is predominately by \(\text{CO}_2\) degassing in August when the \(\text{CO}_2\) degassing to calcite precipitation ratio was 88:12, the highest ratio measured at ISST. Correspondingly, the loss of DIC in January was equally distributed between \(\text{CO}_2\) degassing and calcite precipitation with a \(\text{CO}_2\) degassing: calcite precipitation ratio of 49:51. This ratio is lower than the theoretical value of 50:50, the value and likely due to analytical error and this value can be considered 50:50. The loss of DIC to calcite precipitation between the direct and indirect drip sites represents calcite precipitated on the flowstone along the flowpath between these sites. The calcite growth rates discussed above represent loss of DIC after flowing off the indirect site and do not consider any loss of DIC to calcite precipitation on the flowstone between the direct and indirect sites.

The \(\text{CO}_2\) degassing: calcite precipitation ratio of 28:72 calculated for November at ISST is problematic. We believe a ratio lower than 50:50 is not possible in a natural cave setting and this value is due to error in the direct drip Ca concentration measurement, the value is likely too high.

The loss of DIC at the ISCD site was significantly different than the ISST site. We could not detect any loss of DIC due to calcite precipitation despite the fact there was a flowstone over which the water flowed over intermediate of the direct and indirect drip sites. The Ca concentrations remained within analytical error between the direct and indirect drip sites and no calcite was collected on the glass plate below the indirect drip site. The loss of DIC between the direct and indirect drip site changed from near 100% of 91.7 mg/L C (no loss of DIC due to \(\text{CO}_2\) degassing) in August to 88% of 37.4 mg/L C in October. All \(\text{CO}_2\) degassing: calcite precipitation ratios measured at ISCD site were \(\sim 100\%\).

The \(\text{CO}_2\) degassing: calcite precipitation ratio could not be determined along flow path at ISSR-8 because water was dripping from a single stalactite at this site. An attempt was made to estimate the ratio by assuming the water entering the cave had a consistent chemistry that was equivalent to the August values where cave p\(\text{CO}_2\) was highest and no calcite was precipitated on the glass plate, suggesting minimal \(\text{CO}_2\) degassing and calcite precipitation. However, we will show that this assumption is wrong and the initial drip water chemistry varies seasonally. This assumption overestimates the loss of DIC along flowpath and underestimates the fractionation factor between \(\text{HCO}_3^{\text{(aq)}}-\text{CO}_2\).

The drip water in August had a DIC concentration of 143 mg/L C and a Ca concentration of 93 mg/L. The lowest DIC and Ca concentrations were measured in November, 54 mg/L C and 86 mg/L respectively. If the drip water entering the cave in November started with a chemistry

### Table 3

Summary of the \(\delta^{13}C\) values of DIC and the corresponding plate calcite at the ISST indirect and ISSR-8 drip sites. The difference between the \(\delta^{13}C\) value of calcite and DIC is considered the \(\epsilon\) \((\text{Calcite}-\text{HCO}_3^{\text{(aq)}})\). Note, the \(\epsilon\) \((\text{Calcite}-\text{HCO}_3^{\text{(aq)}})\) value is between 0 and equilibrium values of approximately 2.

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<th>DIC (\delta^{13}C) (PDB)</th>
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approximated by the August values then 38% of the 143 mg/L C remained after the drip water travelled along the stalactite and the CO₂ degassing; calcite precipitation ratio was 98.2. This loss of DIC and the CO₂ degassing; calcite precipitation ratio are much larger than what was observed, by direct measurements along flowpaths, for winntertime months at the ISST and ISCD sites.

4.5. Calculated fractionation factors between (HCO₃(aq)-CO₂(g))

A rayleigh distillation model (Eq. (2)) was used to calculate the kinetic fractionation factor between \( -\text{HCO}_3^-\text{(aq)-CO}_2\text{(g)} \) necessary to explain the downflow shift in water chemistry and isotopic composition. When the loss of DIC between the direct and indirect drip sites was less than 15%, the observed \( \delta^{13}C \) value of the DIC at the indirect site was consistent with values predicted by the Rayleigh distillation model using equilibrium fractionation factors between calcite and HCO₃ (aq) and CO₂ and HCO₃ (aq) (Fig. 4). In all these cases glass plates placed under the indirect drip measured no calcite growth. However, a loss of Ca at ISST between the direct and indirect drip sites suggests some calcite precipitated on the intermediate flowstone (1 out of 6 cases).

When the loss of DIC was 15% or greater, the Rayleigh distillation model was unable to predict the \( \delta^{13}C \) value of the DIC at the indirect drip site using equilibrium fractionation factors (7 out of 7 cases). When the measured CO₂ degassing; calcite precipitation ratio was used, rather than assuming a ratio of 50:50, the predicted \( \delta^{13}C \) values of the DIC at the indirect site were generally close to those observed but the observed DIC values were still up to 2.8‰ higher than modelled values. The 11/2013 date was problematic because of the likely incorrect CO₂ degassing; calcite precipitation ratio discussed earlier. In all these cases, the loss of Ca between the direct and indirect drip sites suggests calcite formation on the intermediate flowstone and calcite was grown on the glass plate positioned under the indirect drip.

The Rayleigh distillation model was used to predict the \( \epsilon \) (HCO₃(aq)-CO₂(g)) value (Table 4) assuming the 1000lnx (CaCO₃-HCO₃(aq)) was 2‰ (Deines et al., 1974) and 0‰ (Mickler et al., 2006). When the DIC loss was less than 12‰, analytical errors produced large variations in the predicted \( \epsilon \) (HCO₃(aq)-CO₂(g)) despite the fact that the observed DIC \( \delta^{13}C \) values were close to equilibrium values. For instance, the calculated \( \epsilon \) (HCO₃(aq)-CO₂(g)) was −64‰ at the ISCD site in 8/2013. These data will be excluded from discussion of kinetic fractionation factors.

When the loss of DIC was greater than 15‰, the \( \epsilon \) (HCO₃(aq)-CO₂(g)) varied between −13.6‰ and −26.3‰ when the 1000lnx between (CaCO₃-HCO₃(aq)) was 2‰ (Fig. 4). If we set the value for 1000lnx between (CaCO₃-HCO₃(aq)) to 0, the \( \epsilon \) (HCO₃(aq)-CO₂(g)) is lowered by 2‰, which is farther from equilibrium (Table 4). The 11/2013 value of −65.6‰ was excluded from consideration because the CO₂ degassing; calcite precipitation ratio was thought to be in error. Generally, as the loss of DIC to calcite precipitation and CO₂ degassing increases the value of \( \epsilon \) (HCO₃(aq)-CO₂(g)) decreases away from equilibrium values to modelled values around −26‰. Previous studies have identified lower than equilibrium \( \epsilon \) (HCO₃(aq)-CO₂(g)) values (Spölöt et al., 2005; Breecker et al., 2012; Frisia et al., 2011) that shift the \( \delta^{13}C \) value of cave air CO₂ towards values lower than those predicted by equilibrium degassing.

At the ISSR-8 drip site, the initial water chemistry had to be estimated because the water could only be collected at one location along the flowpath. Therefore, the seasonal decrease in DIC and Ca concentrations and the increase in drip water DIC \( \delta^{13}C \) values were assumed to be from CO₂ degassing and calcite precipitation on the drip water’s stalactite prior to sample collection. The 8/2013 ISSR-8 water chemistry was assumed to be the initial water chemistry as the water entered the cave system because the high cave pCO₂ would limit CO₂ degassing and calcite precipitation. This approach assumes there is little or no seasonal variability in the initial water chemistry as it first enters the cave system and the observed seasonality at ISSR-8 is due to the water exchanging with the cave atmosphere prior to collection. The same assumption can be made for the seasonality of the water chemistry at the direct drip site for both ISST and ISCD (Table 5). We will show that these assumptions are not valid and the initial water chemistry is not seasonally invariable.

The relatively large decrease in fraction of DIC remaining from summer to winter months at ISSR-8, a maximum of 38‰, had large effects on the Rayleigh distillation model. The \( \epsilon \) (HCO₃(aq)-CO₂(g)) needed to model the observed results was increased from equilibrium values of −8.2‰ to values between −0.74‰ and −3.0‰. Similar results are obtained when the 8/2013 chemistry at the ISST direct drip site is used as the initial drip water chemistry when modelling the seasonal variability at these sites (Table 5).
These findings are in direct contradiction to the $\varepsilon (\text{HCO}_3^{-}\text{aq}-\text{CO}_2(g))$ values obtained by modelling DIC $\delta^{13}C$ spatial evolution between the direct and indirect drips at ISST and ISCD, systems where the initial water chemistry was directly measured and not assumed. Carbon isotopic exchange between the cave water film on the speleothem and the cave atmosphere is likely occurring but could not be quantified. Bergel et al. (2017) measured both cave air and soil CO$_2$ at Inner Space Cavern. The $\delta^{13}C$ values of cave-air CO$_2$ ranged from $-22.3\%e$ to $-14.8\%e$, with an average of $-17.3\%e$. Carbon isotope exchange between the water film on the speleothem surface and the cave air will buffer the $\delta^{13}C$ values of the HCO$_3^{-}(aq)$ reservoir requiring lower negative $\varepsilon (\text{HCO}_3^{-}\text{aq}-\text{CO}_2(g))$ values than those calculated. We chose to ignore possible carbon isotopic exchange between the cave-water film and the cave atmosphere and our calculated $\varepsilon (\text{HCO}_3^{-}\text{aq}-\text{CO}_2(g))$ values may be conservative.

5. DISCUSSION

5.1. Seasonal variations in cave-water chemistry

Inner Space Cavern shows seasonal changes in the following cave meteorology and cave drip water chemistry: 1. Cave air CO$_2$ concentrations show strong seasonality with low concentrations occurring in the winter months and high concentrations occurring during the summer months. Cave air CO$_2$ concentrations show a positive relationship with atmospheric air temperatures. 2. Drip water chemistry shows intra-annual variability with lower pH and higher Ca concentrations in the summer months. The $\delta^{13}C$ values of cave water DIC and plate calcite are lower in the summer months. 4. Calcite precipitation rates are higher in the winter months.

The observed changes in cave air meteorology and cave water chemistry can be explained by seasonal cave ventilation, driven by the changing density gradients between outside air and cave air, as discussed in the introduction (James et al., 2015). Drip waters are thus exposed to seasonally-changing CO$_2$ concentrations as they enter the cave. It is therefore necessary to assess the extent to which such degassing of CO$_2$ and/or calcite precipitation may account for the variations in the $\delta^{13}C$ values of the host drip waters and precipitated modern speleothem calcite.

All the sites in this study have a negative correlation between cave air CO$_2$ concentrations and DIC $\delta^{13}C$ values. Since the degassing of CO$_2$ increases the $\delta^{13}C$ value of the residual HCO$_3^{-}$ reservoir, this inverse relationship supports the hypothesis that variations in the $\delta^{13}C$ values of these cave waters are controlled by CO$_2$ degassing (with or without calcite precipitation).

This inverse relationship suggests that as DIC is removed from the water by CO$_2$ degassing, the residual C in the water evolves to higher $\delta^{13}C$ values. In addition, variable extents of carbonate dissolution in the vadose zone above the cave can control DIC concentration and $\delta^{13}C$ values of waters entering caves. Increased DIC concentrations caused by the dissolution of the host limestone bedrock would move the $\delta^{13}C$ value of the HCO$_3^{-}$ reservoir towards the $\delta^{13}C$ value of the host limestone. The $\delta^{13}C$ values of limestone and dolostones in the Edwards Group near the Balcones fault zone relatively near the cave systems vary from $-0\%e$ to $4\%e$ (Abbott and Woodruff, 1986). Increased dissolution of host limestone would therefore likely increase HCO$_3^{-}$ $\delta^{13}C$ values and DIC concentrations, which is the inverse of the relationship seen in this study. It is likely that in most cave systems the $\delta^{13}C$ values of the host carbonate aquifer rocks is higher than the $\delta^{13}C$ values of the dissolved HCO$_3^{-}$ reservoir, such that increased host carbonate
Table 5
Parameters and calculation used to determine $\varepsilon_{\text{CO}_2-\text{bicarb}}$ through the study period assuming the initial drip water chemistry at the direct drip site can be approximated using the August drip water chemistry. Note, the authors do not agree with these fractionation factors and they are included here to compare and contrast to the directly measured $\varepsilon_{\text{HCO}_3-\text{CO}_2}$ outlined in Table 4.

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<th>$\delta$ calculated CO$_2$ degassing/calcite precip ratio and equilibrium frac factors</th>
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dissolution would produce a positive correlation between HCO₃⁻ δ¹³C values and DIC concentrations.

5.2. Calcite precipitation/CO₂ degassing ratio

As a further test of the ventilation hypothesis, CO₂ degassing with calcite precipitation would be evident in a negative correlation between a drip water Ca²⁺ concentration and DIC δ¹³C value. Sites ISSST, ISSR-8 and ISCD show such a negative correlation (Table 2). The variations in δ¹³C values observed at these sites are most likely due to the combination of CO₂ degassing (which results in higher residual HCO₃⁻ δ¹³C values) and calcite precipitation (which results in lower Ca²⁺).

If the effects of CO₂ degassing and calcite precipitation on the δ¹³C values of the precipitated calcite are to be modeled successfully using Rayleigh distillation, the ratio of C lost to calcite precipitation vs. CO₂ degassing must be known. The calcite precipitation/CO₂ degassing ratio has a large effect on the fractionation factor between the HCO₃⁻ (aq) reservoir and the bulk product, p-r (see Methods section). For example, the equilibrium fractionation factor (used in this study) between HCO₃⁻ (aq) and CO₂ (g) is ~8.2‰ (Deines et al., 1974, Mook et al., 1974, and the equilibrium fractionation factor between CaCO₃ (s) and HCO₃⁻ (aq) is ~2.0‰ (Deines et al., 1974). The equilibrium fractionation factor between the HCO₃⁻ (aq) reservoir and the bulk product, p-r changes from ~3.1‰ to ~8.2‰ when the calcite precipitation/CO₂ degassing ratio changes from 50:50 to 1:100. Loss of C by CO₂ degassing alone will have a larger effect on the δ¹³C value of the HCO₃⁻ (aq) reservoir because of the larger HCO₃⁻ δ¹³C values and calcite precipitation, relative to equilibrium values. These large negative fractionation factors result in large down flow path changes in the δ¹³C values of the HCO₃⁻ (aq) reservoir during CO₂ degassing with or without calcite precipitation, relative to equilibrium values. These changes to the δ¹³C values of the HCO₃⁻ (aq) reservoir are inherited by the calcite precipitated on the speleothem surface. Large shifts in the δ¹³C values of speleothems may therefore be a result of changes in the rate and amount of CO₂ degassing and to a lesser extent calcite precipitation during seasonal cave ventilation.

5.3. Model results for Non-equilibrium fractionation factor determination

At site ISSST, direct drip water collected during 8/2013 had a δ¹³C value of −10.10‰, a DIC concentration of 151.7 mg/L C, and a Ca concentration of 85.2 mg/L. Subsequent months show the DIC concentration decrease, as did the calcium concentration (Table 2). Based on this loss of Ca and HCO₃⁻, the proportions of C loss due to calcite precipitation and CO₂ degassing were calculated. Because the fractionation factors between HCO₃⁻ and CaCO₃ and HCO₃⁻ and CO₂ vary greatly in magnitude and direction, the proportion of C lost from the HCO₃⁻ reservoir to CO₂ degassing and calcite precipitation must be known to accurately apply Rayleigh distillation models. The necessary assumption is that the decrease in Ca concentration each subsequent month is from the precipitation of calcite, not from the lack of dissolution of calcite. This is a safe assumption since the δ¹³C values of the drip waters are also increasing as Ca is lost.

The CO₂ degassing/calcite precipitation ratio, the fraction of DIC remaining and the combined equilibrium fractionation factors allowed for the calculation of the theoretical δ¹³C value of the drip waters at the indirect sites (Table 4). The theoretical δ¹³C values of the indirect drip water are within error of the observed δ¹³C values when loss of DIC is <15% and evidence of calcite precipitation is absent. When the loss of DIC is >15% and evidence of calcite precipitation is seen on glass plates below the indirect drip, the calculated δ¹³C values that are not within error of the observed δ¹³C values and are up to 2.8‰ higher than theoretical values. The theoretical δ¹³C values calculated using equal proportions of C loss due to calcite precipitation and CO₂ degassing is also represented in Table 4, to illustrate that the theoretical values calculated using the measured (CO₂ degassing):(calcite growth) ratios provide values closer to the observed δ¹³C values (Fig. 5).

5.4. Equilibrium vs. non-equilibrium calcite precipitation

This study and others (Mickler et al., 2006) have identified non-equilibrium isotope effects operating during calcite precipitation. If the effects of CO₂ degassing and calcite precipitation on the δ¹³C values of the precipitated calcite are to be modeled accurately using Rayleigh distillation, the fractionation factor between the HCO₃⁻ (aq) reservoir and the bulk product must be known. This study shows that when calcite precipitation rates are the highest, and presumably when the bulk of speleothem calcite is being deposited, the fractionation factor between the HCO₃⁻ (aq) reservoir and the bulk product decreases from near equilibrium values between −3.7‰ to −8.4‰ to non-equilibrium values of −25‰. These large negative fractionation factors result in large down flow path changes in the δ¹³C values of the HCO₃⁻ (aq) reservoir during CO₂ degassing with or without calcite precipitation, relative to equilibrium values. These changes to the δ¹³C values of the HCO₃⁻ (aq) reservoir are inherited by the calcite precipitated on the speleothem surface. Large shifts in the δ¹³C values of speleothems may therefore be a result of changes in the rate and amount of CO₂ degassing and to a lesser extent calcite precipitation during seasonal cave ventilation. Environmental variability that controls the amount of time water has to degas CO₂ (Meyer et al., 2014), the gradient between drip water pCO₂ and cave air pCO₂, such as changing vegetation, below ground respiration rates and/or temperature seasonality, may therefore influence speleothem δ¹³C values. In addition, changes in temperature seasonality outside the cave system may influence a cave’s ventilation regime, and thus the fractionation factor between the HCO₃⁻ (aq) reservoir and the bulk product. Larger seasonally controlled temperature variation may result in larger non-equilibrium fractionation factors and higher speleothem δ¹³C values. We expect this process to be most pronounced in temperate climates where seasonal temperature changes drive cave ventilation James et al. (2015).

5.5. Seasonal epikarst controls on cave water chemistry

We modelled the seasonal evolution of the cave water at ISSR-8 and the direct drip sites at ISSST by assuming the initial chemistry of the cave water could be approximated by the August values (Table 5). The results were in contradiction to the direct measurements made between the direct and indirect drip sites at ISSST and ISCD. This suggests that the initial chemistry of the cave water, as it first enters the
cave system and before it has started to equilibrate with the lower pCO2 cave environment, changes seasonally. Processes in the epikarst produce cave water with higher DIC concentrations, and potentially higher Ca concentrations in summer months than in winter months possibly due to higher subsurface respiration rates and/or seasonal ventilation of epikarst fractures (Bergel et al., 2017). The cave water, as it first enters the cave and before it begins equilibrating with the cave atmosphere and can be collected for analysis, cannot be assumed to be seasonally invariant.

6. IMPLICATIONS FOR SPELEOTHEM CLIMATE RECONSTRUCTIONS

Speleothem records may be influenced by non-equilibrium isotope effects during the precipitation of speleothem calcite. The extent of these non-equilibrium isotope effects can be controlled by several factors including: 1. Calcite precipitation/CO2 degassing ratios that are not equal. 2. Changes in non-equilibrium fractionation factors, to much larger negative values, that control the fractionation between HCO3-(aq) and degassed CO2 from that HCO3-(aq) reservoir. 3. Seasonally controlled cave ventilation lowering cave air CO2 concentrations and therefore increasing the gradient between cave water DIC and cave air CO2 concentrations. The kinetic effects identified in this study have significant implications for speleothem C-isotope proxy interpretations. These effects are of a similar magnitude as those used to infer past changes in drought and vegetation from speleothem records.

Speleothem C isotope studies will benefit from assessing the ventilation regime of specific cave systems, (James et al., 2015, Noronha et al., 2017) and assessing flow paths and the δ13C evolution along those paths for individual speleothem precipitation sites (Mühlhaus et al., 2007, Dreybrodt et al., 2016, Dreybrodt and Romanov, 2016, Hansen et al., 2013). More judicious sample selection will help conserve the fragile/limited resource of speleothems and ensure the most paleoclimate information can be assessed from collected speleothems.

7. CONCLUSIONS

Our results allow the first determination of a kinetic isotope fractionation factor between the cave water HCO3 reservoir and a theoretical bulk product, predominantly composed of degassed CO2. The ability to determine both the (CO2 degassing):(calcite growth) ratio and the kinetic isotope fractionation factor between the HCO3(aq) reservoir and a theoretical bulk product are essential to accurately model the δ13C evolution of cave drip water and the speleothem calcite precipitated from that drip water. The ability to accurately model the δ13C evolution of modern cave calcite will help identify the controls on speleothem δ13C compositions. In this study, modern speleothem calcite grown at the drip sites shows strong seasonal δ13C variations. In the cool season, calcite δ13C values are higher than warm season values, consistent with drip water δ13C evolution.

Inner Space Cavern drip sites exhibit a strong seasonality in cave-air CO2, speleothem calcite growth rate, and drip-water δ13C values, pH, and DIC concentrations. These data are consistent with a mechanism involving seasonal cave-air ventilation driven by regional air temperature, in turn driving cool-season CO2 degassing and calcite growth, and concomitant C isotope evolution of cave drip water. Detailed spatial and temporal analysis at two drip sites reveal changes in drip water pH, HCO3 and δ13C along flow paths that indicates (1) a strong seasonality in the extent of drip water chemical and isotopic evolution, with much larger effects in the cool season; and (2) equilibrium isotope fractionation factors cannot account for the C-isotope evolution of the drip waters. Whereas equilibrium precipitation of speleothem calcite necessitates a one-for-one ratio of (CO2 degassing):(calcite growth) of 50:50, equilibrium Rayleigh distillation modeling of the C-isotope reservoirs of the present study requires ratios in excess of the limit of 100:0, a theoretical impossibility that would lead to zero calcite growth. (CO2 degassing):(calcite growth) ratios are calculated by comparing monthly changes in drip-water Ca and HCO3 concentrations, and show that in the majority of cases CO2 degassing greatly exceeds calcite precipitation. The observed evolution of the δ13C values of the drip water HCO3 reservoir are best explained by a combination of (CO2 degassing):(calcite growth) ratios in excess of 50:50 and kinetic effects between the HCO3 reservoir and a theoretical bulk product.
REFERENCES


*Associate editor: Frank F. McDermott*