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

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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 δ^{13} C 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 δ^{13} C values of dissolved inorganic carbon (DIC) along discret 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 $<\sim 1\%$ to $\sim 4\%$ increase in δ^{13} C values of DIC along the flow paths. The magnitude of the increase in δ^{13} C 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 δ^{13} C value of the DIC reservoir can be accounted for by a Rayleigh distillation model with equilibrium C-isotope fractionation factors for (CO_{2(g)}-HCO_{ftaq}) and (CaCO₃-HCO_{ftaq}). As the depletion of the DIC reservoir exceeds 15% the DIC δ^{13} C values become progressively higher such that the (HCO_{ftaq})-CO_{2(g)}) fractionation values needed to explain the observations change from equilibrium values of $\sim 8\%$ to non-equilibrium values of up to $\sim 25\%$. 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

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https://doi.org/10.1016/j.gca.2018.09.027 0016-7037/© 2018 Elsevier Ltd. All rights reserved. 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; Frappier 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 biome shifts (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 δ^{13} C values in paleoclimate reconstructions as well as a detailed discussion of processes affecting speleothem δ^{13} C 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 δ^{13} C 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 air ventilation (Tochterle et al., 2017) that alters the extent of CO₂ degassing, and as we will discuss CO_2 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 colder, 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 CO_2 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 $\delta^{13}C$ 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 CO_2 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 δ^{13} C 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),



Fig. 1. Schematic diagrams of ISST (A) and ISCD (B) monitoring sites. At both sites the drip water enters the cave from the ceiling off a discreet drip (direct drip) and flows over an intermediate flowstone before dripping off a second discreet drip (Indirect drip).

1m

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 CO_2 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 $\pm 3.5\%$. Humidity and temperature were measured using a Tinytag TH-2500 hand-held thermohygrometer with an analytical precision $\pm 3\%$ RH.

3.3. Cave drip water chemistry

Elemental concentrations were measured using an Agilent 7500ce Quadrupole inductively-coupled-plasma-massspectrometer (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



Fig. 2. Time series of cave-air CO_2 concentration at site ISST and monthly average air temperature. Cave air pCO_2 is highest in the summer months when ventilation is limited due to stability induced by colder and thus denser air below ground than in the outside atmosphere. Cave air pCO_2 is the lowest in winter months when relatively cool, high density, atmosphere convectively mixes in the cave with warmer, less dense, cave air.

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 ($\pm 0.3\%$, 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 preweighed, 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, $10 \text{ cm} \times 10 \text{ cm}$ (Banner et al., 2007).

The δ^{13} C 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 septumcapped 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 CO_2 and calcite during progressive CO_2 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 HCO_3^- and verified by PHREEQ-C modelling (Parkhurst and Appelo, 2013). PHREEQ-C results are summarized in Table 1. The loss of HCO_3^- 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 HCO_3^- . The loss of DIC to CO_2 degassing was determined by subtracting the loss of DIC to calcite precipitation from the total DIC loss.

This study models the evolution of the δ^{13} C values of the DIC reservoir by the δ^{13} C 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 δ^{13} C 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

Table 1

PHREEQC modelling results showing the distribution of C specie	es and calcite and aragonite saturation indices
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Site	Date	Total C	HCO ₃ ⁻ (Mol/L)	CO2 (Mol/L)	CO_3^{-2} (Mol/L)	SI Calcite	SI aragonite	% HCO ₃
ISST Direct	8/16/2013	0.013440	0.012330	0.000857	0.000022	0.8	0.6	91.7
ISST Indirect	8/16/2013	0.011850	0.011170	0.000443	0.000035	0.9	0.8	94.3
ISST Direct	9/29/2013	0.006040	0.005579	0.000333	0.000011	0.5	0.4	92.4
ISST Indirect	9/29/2013	0.004998	0.004742	0.000135	0.000020	0.7	0.6	94.9
ISST Direct	10/19/2013	0.005492	0.005176	0.000178	0.000019	0.7	0.6	94.2
ISST Indirect	10/19/2013	0.003809	0.003638	0.000051	0.000031	0.9	0.7	95.5
ISST Direct	11/16/2013	0.004876	0.004547	0.000219	0.000011	0.5	0.4	93.3
ISST Indirect	11/16/2013	0.003802	0.003595	0.000026	0.000059	1.1	1.0	94.6
ISST Direct	12/16/2013	0.004598	0.004366	0.000119	0.000020	0.7	0.6	95.0
ISST Indirect	12/16/2013	0.003290	0.003149	0.000037	0.000032	0.8	0.7	95.7
ISST Direct	1/20/2014	0.004656	0.004345	0.000211	0.000011	0.5	0.4	93.3
ISST Indirect	1/20/2014	0.003177	0.003033	0.000030	0.000036	0.9	0.8	95.5
ISST Direct	2/15/2014	0.007226	0.006854	0.000190	0.000031	0.9	0.8	94.9
ISST Indirect	2/15/2014	0.005556	0.005315	0.000060	0.000057	1.1	0.9	95.7
ISST Direct	3/29/2014	0.009487	0.008534	0.000793	0.000011	0.5	0.3	90.0
ISST Indirect	3/29/2014	0.007341	0.007020	0.000087	0.000069	1.2	1.0	95.6
ISCD Direct	8/16/2013	0.007978	0.007477	0.000379	0.000017	0.5	0.4	93.7
ISCD Indirect	8/16/2013	0.008073	0.007591	0.000354	0.000020	0.6	0.4	94.0
ISCD Direct	9/29/2013	0.003254	0.003048	0.000156	0.000007	0.2	0.0	93.7
ISCD Indirect	9/29/2013	0.002859	0.002687	0.000126	0.000007	0.2	0.0	94.0
ISCD Direct	10/19/2013	0.003093	0.002877	0.000175	0.000005	0.0	-0.1	93.0
ISCD Indirect	10/19/2013	0.003263	0.002617	0.000616	0.000001	-0.6	-0.1	80.2
ISCD Direct	11/16/2013	0.003433	0.003277	0.000062	0.000020	0.7	0.6	95.5
ISCD Indirect	11/16/2013	0.003327	0.003174	0.000043	0.000027	0.8	0.7	95.4
ISCD Direct	12/16/2013	0.003112	0.002924	0.000127	0.000008	0.3	0.2	94.0
ISCD Indirect	12/16/2013	0.003031	0.002846	0.000127	0.000007	0.3	0.1	93.9
ISSR-8	8/16/2013	0.012200	0.011520	0.000380	0.000044	1.1	0.9	94.4
ISSR-8	9/29/2013	0.005370	0.005095	0.000110	0.000028	0.9	0.8	94.9
ISSR-8	10/19/2013	0.004887	0.004622	0.000042	0.000062	1.2	1.1	94.6
ISSR-8	11/16/2013	0.004289	0.003976	0.000022	0.000086	1.4	1.3	92.7
ISSR-8	12/16/2013	0.004991	0.004676	0.000029	0.000090	1.4	1.2	93.7
ISSR-8	1/20/2014	0.004646	0.004360	0.000029	0.000078	1.3	1.2	93.8
ISSR-8	2/15/2014	0.007725	0.007260	0.000047	0.000136	1.5	1.4	94.0
ISSR-8	3/29/2014	0.009338	0.008820	0.000066	0.000145	1.5	1.4	94.5

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, αp -r, by the following equations.

$$\alpha(p-r) = (X)\alpha 1 + (X-1)\alpha 2 \tag{1}$$

X is the determined fraction of C lost to CO_2 degassing and X – 1 is the fraction of C lost to calcite precipitation, $\alpha 1$ is the fractionation factor between $CaCO_3$ (s) and HCO_3^- (aq), $\alpha 2$ 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.

$$\frac{(\delta + 1000)}{(\delta_0 + 1000)} = f^{(\alpha_{p-r} - 1)} \tag{2}$$

3.6. Non-equilibrium fractionation factor determination

The δ^{13} C values of some DIC samples in this study cannot be explained by equilibrium calcite precipitation and CO₂ degassing and suggest that non-equilibrium fractionation is occurring. We model the evolution of DIC δ^{13} C values from the direct drip site to the indirect drip site at both ISST and ISCD using a Rayleigh distillation model of CO₂ degassing and calcite precipitation (Eq. (2)), where δ is the C isotope composition of DIC at the indirect drip site, δ_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 α_{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 $HCO_{faq}^{-}-CO_{2(g)}$ kinetic fractionation factor, hereafter referred to as \mathcal{E} which is equivalent to $1000\ln\alpha$, can be estimated by assuming the $CaCO_{3(s)}$ - HCO_{faq}^{-} 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
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Site Date T (°C) pН Ca (mg/L)DIC (mg/L)DIC δ^{13} C Loss of Loss of Fraction of Fraction Fraction (PDB) Ca (mmol) DIC (mmol) HCO₃ lost of HCO₃⁻ lost of DIC to calcite to CO₂ remaining precipitation degassing ISST Direct 8/16/2013 22.5 7.48 85.2 151.7 -10.10ISST Indirect 8/16/2013 21.7 7.73 79.5 138.0 -9.570.141 1.141 0.12 0.88 0.91 ISST Direct 9/29/2013 21.4 7.56 87.0 68.9 -10.4ISST Indirect 9/29/2013 21.9 7.88 73.1 59.0 -8.830.345 0.824 0.42 0.58 0.86 ISST Direct 10/19/2013 24.7 7.78 79.6 64.4 -10.22ISST Indirect 10/19/2013 22.2 8.19 46.0 -7.180.444 0.29 61.8 1.532 0.71 0.71 ISST Direct 11/16/2013 7.65 84.5 56.3 -9.99ISST Indirect 11/16/2013 21.9 8.48 62.0 47.0 -6.860.561 0.774 0.72 0.28 0.83 12/16/2013 ISST Direct 23.8 7.89 69.6 54.4 -9.6712/16/2013 **ISST** Indirect 21.9 8.27 53.0 39.9 -5.950.414 0.34 0.66 0.73 1.205 ISST Direct 1/20/2014 7.65 79.7 53.7 -9.86ISST Indirect 1/20/2014 21.8 8.35 54.1 38.8 -6.100.638 1.245 0.51 0.49 0.72 2/15/2014 ISST Direct 23.6 7.88 77.0 85.4 -9.71Indirect 2/15/2014 21.4 8.29 57.5 67.5 -6.250.484 1.494 0.32 0.68 0.79 ISST Direct 77.3 3/29/2014 23.9 7.35 104.7 -9.76Indirect 3/29/2014 63.5 88.9 -8.230.85 21.8 8.24 0.344 1.318 0.26 0.74 ISCD direct 8/16/2013 21.7 7.63 56.17 91.7 -11.5ISCD Indirect 8/16/2013 22.7 56.09 93.2 0.002 7.66 -11.11-0.125-0.021.02 1.02 ISCD direct 9/29/2013 20.6 7.64 53.89 37.4 -11.430.88 ISCD Indirect 9/29/2013 20.2 7.68 53.91 33.0 -11.06-0.0010.366 0.001.00 ISCD direct 10/19/2013 20.1 7.57 47.58 35.2 -11.04ISCD Indirect 10/19/2013 20.3 6.98 46.98 31.8 -10.510.015 0.281 0.05 0.95 0.90 ISCD direct 11/16/2013 20.1 8.07 66.72 41.1 -10.60ISCD Indirect 11/16/2013 20.9 40.2 -10.320.001 0.068 0.01 0.99 0.98 8.21 66.69 ISCD direct 12/16/2013 20.3 7.71 36.1 -10.8366.62 ISCD Indirect 12/16/2013 -10.55-0.0030.082 0.97 20.2 7.70 66.73 35.1 -0.031.03 ISSR-8 8/16/2013 21.4 7.81 92.86 143.2 -10.30ISSR-8 9/29/2013 21.4 8.00 87.87 64.1 -10.60ISSR-8 10/19/2013 22 8.38 76.53 60.1 -9.53ISSR-8 11/16/2013 21.5 8.59 86.12 54.0 -9.65ISSR-8 12/16/2013 21.7 8.54 75.43 62.2 -9.76ISSR-8 1/20/2014 21.7 8.51 75.82 57.8 -9.44ISSR-8 2/15/2014 21.5 8.52 78.45 96.0 -9.30ISSR-8 3/29/2014 21.4 8.46 79.29 115.3 -10.05

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.

is minimized (Michaelis et al., 1985) may overestimate the $HCO_{\bar{f}aq}$ - $CO_{2(g)}$ fractionation factor by an amount equivalent to the difference between the actual and equilibrium fractionation factor between $CaCO_{3(s)}$ - $HCO_{\bar{f}aq}$). This overestimation is likely small because the $CaCO_{3(s)}$ - $HCO_{\bar{f}aq}$) fractionation factor is small, in this study approximately 2%. Variations in the $CaCO_{3(s)}$ - $HCO_{\bar{f}aq}$ 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 \mathcal{E} ($HCO_{\bar{f}aq}$)- $CO_{2(g)}$) value over \mathcal{E} ($CaCO_{3(s)}$ - $HCO_{\bar{f}aq}$) values from 0 to 2, the effect of the uncertainty in the $CaCO_{3(s)}$ - $HCO_{\bar{f}aq}$) 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 $\sim 30\%$ 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 than direct drips, and this shows the effects of CO₂ degassing and calcite precipitation on the flowstone between these distinct drip sites. 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 CO₂ degassing or calcite precipitation occurs during the water's time on the flowstone between these distinct drip sites. The ISSR-8 site also shows seasonal DIC variability with a summertime high value of 143 mg/L and a wintertime low of 54 mg/l, a decrease to 37% of the summertime high (Table 2).

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 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 δ^{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 δ^{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 -6.0%). The ISCD site has lower δ^{13} C variability between the direct and indirect drip sites and in seasonal δ^{13} C variability. The lowest δ^{13} C values occurring in August of 2013 where the δ^{13} C value of DIC increases between the direct and indirect drip sites from -11.5% to -11.1% in 7/2013. Higher δ^{13} C values occurring in 12/2013 where δ^{13} C values increase between the direct and indirect drip sites from -10.83% to -10.55%. 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 CO2 degassing could not be identified. The δ^{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 δ^{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



Fig. 3. Average daily calcite growth rate and maximum daily growth rate vs month for the ISST indirect drip site and ISSR-8 site. Calcite was grown on glass plates placed under ISST indirect drip and the ISSR-8 drip sites.

Table 3

Summary of the δ^{13} C values of DIC and the corresponding plate calcite at the ISST indirect and ISSR-8 drip sites. The difference between the δ^{13} C value of calcite and DIC is considered the ϵ (Calcite-HCO_{3 (aq)}). Note, the ϵ (Calcite-HCO_{3 (aq)}) value is between 0 and equilibrium values of approximately 2.

Site	Date collected	Calcite δ^{13} C (PDB)	DIC δ^{13} C (PDB)	ε(Calcite-HCO _{3 (aq)})	
ISSR-8	10/19/2013	-8.43	-9.53	1.10	
ISSR-8	11/16/2013	-8.80	-9.65	0.85	
ISSR-8	12/16/2013	-8.04	-9.67	1.63	
ISSR-8	1/20/2014	-8.43	-9.44	1.01	
ISSR-8	2/15/2014	-8.29	-9.30	1.01	
ISSR-8	3/29/2014	-8.36	-10.05	1.69	
ISST	10/19/2013	-6.92	-7.18	0.03	
ISST	11/16/2013	-5.82	-6.86	1.04	
ISST	12/16/2013	-5.07	-5.95	0.09	
ISST	1/20/2014	-5.30	-6.10	0.80	
ISST	2/15/2014	-5.34	-6.25	0.91	
ISST	3/29/2014	-6.68	-8.23	1.55	

between November and May or June, with average growth rates $\sim 11 \text{ mg/d}$ at ISSR-8 and $\sim 8 \text{ mg/d}$ 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 δ^{13} C value of calcite at the ISST and ISSR-8 drip sites vary between 0.3‰ and 1.7‰ higher (average value of ~1.1‰ higher) than the δ^{13} C value of DIC of the corresponding indirect drip water (Table 3). No calcite was collected at the ISCD site and the CaCO_{3(s)}-HCO_(faq) fractionation factor could not be determined. Note the ε (CaCO_{3(s)}-HCO_(faq)) values used to determine the nonequilibrium fractionation factor between HCO_(faq)-CO₂ are 0 to 2, which brackets all observed differences in CaCO₃ (s)⁻HCO_{faq} pairs.

4.4. Loss of DIC and CO₂ 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 remaining 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 CO₂ degassing in August when the CO₂ 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 CO₂ degassing and calcite precipitation with a 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 CO₂ 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 place 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 CO₂ degassing) in August to 88% of 37.4 mg/L C in October. All CO₂ degassing: calcite precipitation ratios measured at ISCD site were ~100:0.

The CO₂ 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 pCO₂ was highest and no calcite was precipitated on the glass plate, suggesting minimal CO₂ 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 HCO_{faq})-CO_{2(g)}.

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

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 wintertime months at the ISST and ISCD sites.

4.5. Calculated fractionation factors between $(HCO_3^-(aq)-CO_2(g))$

A rayleigh distillation model (Eq. (2)) was used to calculate the kinetic fractionation factor between $-\text{HCO}_3^-(\text{aq})-\text{CO}_2(\text{g})$ 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 δ^{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 HCO_3^- (aq) and CO_2 and HCO_3^- (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 δ^{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 δ^{13} C values of the DIC at the indirect site were generally closer to those observed but the observed DIC values were still up to 2.8‰ higher than modelled values. The 11/2013 date was



Fig. 4. The calculated ϵ (HCO_(aq)-CO_{2(g)}) vs. fraction of DIC remaining for the ISST and ISCD sites.

problematic because of the likely incorrect CO_2 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 \mathcal{E} (HCO₃⁻(aq)-CO₂(g)) value (Table 4) assuming the 1000ln α (CaCO₃-HCO_(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 \mathcal{E} (HCO₃⁻(aq)-CO₂(g)) despite the fact that the observed DIC δ^{13} C values were close to equilibrium values. For instance, the calculated \mathcal{E} (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 E (HCO_{faq}) - $CO_{2(g)}$) varied between -13.6% and -26.3%when the 1000ln α between (CaCO₃-HCO_{faq}) was 2% (Fig. 4). If we set the value for $1000 \ln \alpha$ between (CaCO₃- $HCO_{faq}^{-})$ to 0, the \mathcal{E} (HCO_{faq}^{-} - $CO_{2(g)}$) 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 E (HCO⁻_{faq)}-CO_{2(g)}) decreases away from equilibrium values to modelled values around -26%. Previous studies have identified lower than equilibrium $\mathcal{E}(HCO_{flag}^{-}-CO_{2(g)})$ values (Spötl et al., 2005; Breecker et al., 2012; Frisia et al., 2011) that shift the δ^{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 δ^{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 \mathcal{E} (HCO_{faq})-CO_{2(g)}) needed to model the observed results was increased from equilibrium values of ~-8.2% to values between -0.74% and -3.00%. 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). Table 4

Summary of predicted DIC δ^{13} C values for ISST and ISCD indirect drip sites using 50:50 calcite precipitation/CO₂ degassing ratios and the measured calcite precipitation/CO₂ degassing ratios. Measured DIC δ^{13} C values are included in Table 2. Also summarized are the calculated $\mathcal{E}_{CO2-bicarb}$ needed to fit observed δ^{13} C values measured at the indirect drip sites. These values are graphically represented in Fig. 5.

		Predicted δ^{13} C values	at indirect drip sites	Calculated $\mathcal{E}_{CO2\text{-bicarb}}$ needed to fit observed $\delta^{13}C$ Values at indirect drip sites		
Site Date		Predicted DIC d ¹³ C values assuming 50:50 calcite precip and CO ₂ degas	Predicted DIC d ¹³ C values using measured calcite precip: CO ₂ degas ratio	ε (HCO _{faq})-CO _{2(g)}) assuming equilibrium between HCO ₃ and calcite (epsilon = 2)	\mathcal{E} (HCO _(kaq) -CO _{2(g)}) assuming no fractionation between HCO ₃ and calcite (epsilon = 0)	
ISST	8/16/2013	-9.81	-9.45	-6.76	-6.48	
ISST	9/29/2013	-9.93	-9.80	-19.20	-17.74	
ISST	10/19/2013	-9.20	-8.50	-13.75	-12.92	
ISST	11/16/2013	-9.44	-9.85	-71.24	-65.60	
ISST	12/16/2013	-8.73	-8.24	-19.66	-18.59	
ISST	1/20/2014	-8.86	-8.91	-26.27	-24.11	
ISST	2/15/2014	-8.99	-8.57	-23.11	-22.13	
ISST	3/29/2014	-9.27	-8.87	-13.59	-12.87	
ISCD	8/16/2013	-10.15	-10.23	-63.95	-63.98	
ISCD	9/29/2013	-11.04	-10.40	-2.98	-2.99	
ISCD	10/19/2013	-10.72	-10.27	-5.78	-5.66	
ISCD	11/16/2013	-10.54	-10.44	-14.38	-14.36	
ISCD	12/16/2013	-10.74	-10.59	-9.91	-9.98	

These findings are in direct contradiction to the \mathcal{E} (HCO_{faq})-CO_{2(g)}) values obtained by modelling DIC δ^{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 speleothems and the cave atmosphere is likely occurring but could not be quantified. Bergel et al. (2017) measured both cave air and soil CO₂ at Inner Space Cavern. The δ^{13} C values of cave-air CO₂ ranged from -22.3% to -14.8%, with an average of -17.3%. Carbon isotope exchange between the water film on the speleothem surface and the cave air will buffer the δ^{13} C values of the HCO_(faq) reservoir requiring larger negative \mathcal{E} (HCO_(faq)-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 \mathcal{E} (HCO_(faq)-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 CO₂ concentrations show strong seasonality with low concentrations occurring in the winter months and high concentrations occurring during the summer months. Cave air CO₂ 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. 3. The δ^{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 CO₂ concentrations as they enter the cave. It is therefore necessary to assess the extent to which such degassing of CO₂ and/or calcite precipitation may account for the variations in the δ^{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 CO₂ concentrations and DIC δ^{13} C values. Since the degassing of CO₂ increases the δ^{13} C value of the residual HCO₃⁻⁻ reservoir, this inverse relationship supports the hypothesis that variations in the δ^{13} C values of these cave waters are controlled by CO₂ degassing (with or without calcite precipitation).

This inverse relationship suggests that as DIC is removed from the water by CO₂ degassing, the residual C in the water evolves to higher δ^{13} C values. In addition, variable extents of carbonate dissolution in the vadose zone above the cave can control DIC concentration and δ^{13} C values of waters entering caves. Increased DIC concentrations caused by the dissolution of the host limestone bedrock would move the δ^{13} C value of the HCO₃⁻ reservoir towards the δ^{13} C value of the host limestone. The δ^{13} C values of limestone and dolostones in the Edwards Group near the Balcones fault zone relatively near the cave systems vary from ~0% to 4% (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 δ^{13} C values of the host carbonate aquifer rocks is higher than the δ^{13} C values of the dissolved HCO_3^- reservoir, such that increased host carbonate

Parameters and calculation used to determine $\mathcal{E}_{CO2-bicarb}$ 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 $\mathcal{E}HCO_3^--CO_2$ outlined in Table 4.

		-				•	-		
Date	Loss of Ca from 8/2013	Loss of DIC from 8/ 2013	% HCO ₃ lost to calcite	% HCO ₃ lost to CO ₂	Fraction of DIC remaining	δ calculated 50:50 and ratio equilibrium frac factors	δ calculated CO ₂ degassing/calcite precip ratio and equilibrium frac factors	$\mathcal{E}(CO_{2(g)})$ -HCO _{3(aq)}) assuming equilibrium between HCO ₃ and calcite	$\mathcal{E}(CO_{2(g)}-HCO_{3(aq)})$ assuming $\alpha(HCO_3$ and calcite) = 1 no fractionation
ISST Direct									
9/29/2013	-0.08	6.90	0.00	1.00	0.45	-7.68	-3.68	0.38	0.38
10/19/2013	0.14	7.27	0.02	0.98	0.42	-7.62	-3.59	0.11	0.15
11/16/2013	0.02	7.95	0.00	1.00	0.37	-7.21	-2.36	-0.12	-0.11
12/16/2013	0.39	8.10	0.05	0.95	0.36	-7.09	-2.50	-0.55	-0.45
1/20/2014	0.14	8.16	0.02	0.98	0.35	-7.05	-2.08	-0.27	-0.24
2/15/2014	0.29	5.52	0.05	0.95	0.56	-8.41	-5.87	-0.83	-0.72
3/29/2014	0.28	3.91	0.07	0.93	0.69	-9.01	-7.45	-1.14	-0.99
ISSR-8									
9/29/2013	0.12	6.59	0.02	0.98	0.45	-7.84	-3.92	0.34	0.38
10/19/2013	0.41	6.93	0.06	0.94	0.42	-7.67	-3.81	-1.08	-0.96
11/16/2013	0.17	7.43	0.02	0.98	0.38	-7.32	-2.60	-0.73	-0.69
12/16/2013	0.43	6.74	0.06	0.94	0.43	-7.76	-4.10	-0.84	-0.71
1/20/2014	0.43	7.12	0.06	0.94	0.40	-7.54	-3.50	-1.15	-1.02
2/15/2014	0.36	3.93	0.09	0.91	0.67	-9.08	-7.43	-3.00	-2.80
3/29/2014	0.34	2.32	0.15	0.85	0.81	-9.75	-8.90	-1.88	-1.36

dissolution would produce a positive correlation between $HCO_3^- \delta^{13}C$ values and DIC concentrations.

5.2. Calcite precipitation/CO₂ degassing ratio

As a further test of the ventilation hypothesis, CO_2 degassing with calcite precipitation would be evident in a negative correlation between a drip water Ca^{2+} concentration and DIC $\delta^{13}C$ value. Sites ISST, ISSR-8 and ISCD show such a negative correlation (Table 2). The variations in $\delta^{13}C$ values observed at these sites are most likely due to the combination of CO_2 degassing (which results in higher residual $HCO_3^- \delta^{13}C$ values) and calcite precipitation (which results in lower Ca^{2+}).

If the effects of CO₂ degassing and calcite precipitation on the δ^{13} C 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 HCO_3^- (aq) reservoir and the bulk product, αp-r (see Methods section). For example, the equilibrium fractionation factor (used in this study) between HCO_3^- (aq) and CO_2 (g) is \sim 8.2‰ (Deines et al., 1974, Mook et al., 1974, and the equilibrium fractionation factor between $CaCO_3$ (s) and HCO_3^- (aq) is $\sim 2.0\%$ (Deines et al., 1974). The equilibrium fractionation factor between the HCO_3^- (aq) reservoir and the bulk product, αp -r changes from -3.1% to -8.2% when the calcite precipitation/CO₂ degassing ratio changes from 50:50 to 0:100. Loss of C by CO₂ degassing alone will have a larger effect on the δ^{13} C value of the HCO₃ (aq) reservoir because of the larger HCO_3^- (aq) reservoir and the bulk product, ap-r fractionation factor.

5.3. Model results for Non-equilibrium fractionation factor determination

At site ISST, direct drip water collected during 8/2013 had a $\delta 13C$ 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 HCO_3^- and $CaCO_3$ and HCO_3^- and CO_2 vary greatly in magnitude and direction, the proportion of C lost from the HCO_3^- reservoir to CO_2 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 δ^{13} C 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 δ^{13} C value of the drip waters at the indirect sites (Table 4). The theoretical δ^{13} C values of the indirect drip water are within error of the observed δ^{13} C 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 δ^{13} C values that are not within error of the observed δ^{13} C values and are up to 2.8% higher than theoretical values. The theoretical δ^{13} C 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 δ^{13} C 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 δ^{13} C values of the precipitated calcite are to be modeled accurately using Rayleigh distillation, the fractionation factor between the HCO_3^- (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 HCO_3^- (aq) reservoir and the bulk product decreases from near equilibrium values between -3.7% to -8.4% to non-equilibrium values of \sim -25%. These large negative fractionation factors result in large down flow path changes in the δ^{13} C values of the HCO_{3}^{-} (aq) reservoir during CO₂ degassing with or without calcite precipitation, relative to equilibrium values. These changes to the δ^{13} C value of the HCO₃ (aq) reservoir are inherited by the calcite precipitated on the speleothem surface. Large shifts in the δ^{13} C 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 δ^{13} C 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 HCO_3^- (aq) reservoir and the bulk product. Larger seasonally controlled temperature variation may result in larger nonequilibrium fractionation factors and higher speleothem δ^{13} C 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 ISST 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 ISST 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 pCO_2 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 nonequilibrium 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 HCO_3^- (aq) and degassed CO_2 from that HCO_3^- (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

ISST and ISCD Predicted and observed d13C values of DIC vs. fraction of DIC remaining



Fig. 5. The δ^{13} C value of DIC measured at the ISST and ISCD direct and indirect drip sites vs. fraction of DIC reservoir remaining. Also included are the theoretical δ^{13} C values of DIC at the indirect drip sites calculated from equilibrium fractionation factors and the fraction of DIC remaining for both the 50:50 CO₂ degassing/calcite precipitation ratio and the observed CO₂ degassing/calcite precipitation ratio.

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 δ^{13} C evolution along those paths for individual speleothem precipitation sites (Muhlinghaus 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 $HCO_3^$ 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 HCO_3^- reservoir and a theoretical bulk product are essential to accurately model the δ^{13} C evolution of cave drip water and the speleothem calcite precipitated from that drip water. The ability to accurately model the δ^{13} C evolution of modern cave calcite will help identify the controls on speleothem $\delta^{13}C$ compositions. In this study, modern speleothem calcite grown at the drip sites shows strong seasonal δ^{13} C variations. In the cool season, calcite δ^{13} C values are higher than warm season values, consistent with drip water $\delta^{13}C$ evolution.

Inner Space Cavern drip sites exhibit a strong seasonality in cave-air CO₂, speleothem calcite growth rate, and drip-water δ^{13} C 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 δ^{13} C 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 HCO_3^- concentrations, and show that in the majority of cases CO₂ degassing greatly exceeds calcite precipitation. The observed evolution of the δ^{13} C values of the drip water HCO_3^- reservoir are best explained by a combination of (CO₂ degassing):(calcite growth) ratios in excess of 50:50 and kinetic effects between the HCO_3^- reservoir and a theoretical bulk product.

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