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Interpretation of speleothem calcite δ^{13} C variations: Evidence from monitoring soil CO₂, drip water, and modern speleothem calcite in central Texas

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Abstract

We studied the sources and transport of carbon in two active karst systems in central Texas, Inner Space Cavern (IS) and Natural Bridge North and South Caverns (NB), to provide new insights into the interpretation of speleothem (cave calcite deposit) carbon isotope compositions. We have determined the δ^{13} C values of soil CO₂ (δ^{13} C_s) in grassland and savanna above these caves with δ^{13} C values of cave drip water (δ^{13} C_{HCO₂}) and modern speleothem calcite grown on artificial substrates $(\delta^{13}C_{cc})$. We compare $\delta^{13}C_{HCO_{\tau}}$ values from direct drip sites, where water was sampled immediately upon discharging from the cave ceiling, to values from indirect sites, where water was sampled after flowing along a prolonged path within the cave that allowed for longer CO₂ degassing and have found that direct drip sites yield consistently lower $\delta^{13}C_{HCO_{\overline{1}}}$ values. The $\delta^{13}C_{HCO_{\overline{3}}}$ values of direct drip water below savanna (-10.6 ± 0.5% and -12.6 ± 0.2% in NB and IS, respectively) are indistinguishable from (IS) or similar to (NB) calculated $\delta^{13}C_{HCO_3}$ values in equilibrium with measured soil CO₂ beneath trees (-13.5% to -11.3% for juniper trees above NB, and -13.6% to -12.6% for mixed oak and elm trees above IS, respectively). At IS, the $\delta^{13}C_{HCO_{\overline{1}}}$ values of direct drip water are higher below grassland $(-9.7 \pm 0.3\%)$ than below savanna $(12.6 \pm 0.2\%)$. These results suggest that the $\delta^{13}C_{HCO_{\overline{1}}}$ values of drip waters that initially enter the caves are controlled by deep-rooted plants, where present, and are minimally influenced by host-rock dissolution and/or prior calcite precipitation (PCP). The $\delta^{13}C_{HCO_{T}}$ values of indirect drip water vary seasonally with relatively low values during the summer $(-10.8 \pm 0.8)_{\infty}$ and $-9.2 \pm 0.4)_{\infty}$ under juniper savanna at NB and under grassland at IS, respectively) that are similar to the direct drip $\delta^{13}C_{HCO_{3}}$ values $(-10.6 \pm 0.5\%$ and $-9.7 \pm 0.3\%$ under savanna at NB and under grassland at IS, respectively). The relatively high $\delta^{13}C_{HCO_{3}}$ - values of indirect drip sites during the winter ($\delta^{13}C_{HCO_{\overline{3}}} = -8.6 \pm 0.8\%$ at NB and $8.0 \pm 0.1\%$ at IS) result from CO₂ degassing of water along in-cave flow paths. We also present decade-long records of modern calcite δ^{13} C values from direct and indirect drip sites at IS. The $\delta^{13}C_{cc}$ values vary seasonally with lower values during the summer and higher values during the winter, and with smaller amplitude variations at the direct drip site. Such seasonal variations can be used as a geochronological tool in some speleothems that do not contain visible lamina. The summer $\delta^{13}C_{cc}$ values of direct drip calcite are similar to $\delta^{13}C_{cc}$ values predicted from soil CO₂ collected beneath trees above that drip site. The occurrence of highest $\delta^{13}C_{cc}$ values during the winter, when cave CO₂ concentrations are low, highlights the significance of ventilation-driven changes in cave-air pCO₂. Modern calcite δ^{13} C values are also negatively correlated with drip rate, which suggests that $\delta^{13}C_{cc}$ variations are controlled by kinetic effects during degassing and calcite precipitation associated with the drip water

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exposure time to a low- pCO_2 environment. In all, at the caves we investigated, variability in speleothem $\delta^{13}C_{cc}$ values primarily reflect presence/absence of deep-rooted vegetation and kinetic isotope effects. We therefore infer that increased aridity may result in higher $\delta^{13}C$ values of vegetation, lower drip rates and more drip water degassing, and thus higher $\delta^{13}C_{cc}$ values of speleothem calcite.

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1. INTRODUCTION

Speleothems (i.e., cave calcite deposits) serve as important terrestrial proxies for paleoenvironmental and paleoclimatic conditions (McDermott, 2004; Fairchild et al., 2006). Hendy and Wilson (1968) first evaluated the potential of speleothem oxygen isotope compositions (δ^{18} O) in preserving climatic information. The development of uraniumseries geochronology (e.g., Edwards et al., 1986; Musgrove et al., 2001) allowed for precise age constraints of changes in speleothem δ^{18} O values. Since then, variations in speleothem calcite δ^{18} O values have been used to document environmental and climatic changes associated with, among others, Heinrich events (Bar-Matthews et al., 1999), East-Asian monsoon intensity (Wang et al., 2001) and shifts in the Intertropical Convergence Zone (Dykoski et al., 2005). In general, speleothem δ^{18} O values are controlled by the δ^{18} O value and temperature of the water entering a cave and to a variable extent by kinetic isotope effects (termed "kinetic effects" hereafter) occurring during CO₂ degassing and calcite precipitation (Hendy and Wilson, 1968; Hendy, 1971; Mickler et al., 2004, 2006; Feng et al., 2012).

Speleothem calcite carbon isotope compositions ($\delta^{13}C_{cc}$) have also been employed for paleoclimate reconstructions (e.g., Dorale et al., 1992). The interpretations of $\delta^{13}C_{cc}$ values are myriad, complex, and often region- or case-specific. Proposed factors affecting speleothem calcite δ^{13} C values include: the δ^{13} C value of atmospheric CO₂ (Baskaran and Krishnamurthy, 1993), the relative proportions of C_3 and C₄ vegetation above caves (Dorale et al., 1992; Dorale, 1998), the soil/vegetation productivity affected by temperature and precipitation (Genty et al., 2006), carbon isotope fractionation during decomposition of soil organic matter (Baker et al., 2011), the proportion of host rock carbon (e.g., Hendy, 1971; Genty et al., 2001; Fairchild et al., 2006), and in-cave kinetic effects (Mickler et al., 2004, 2006; Spötl et al., 2005; Mattey et al., 2010; Baker et al., 2011; Frisia et al., 2011; Lambert and Aharon, 2011). The kinetic effects are primarily caused by two mechanisms: (1) degassing, whereby ¹²CO₂ preferentially escapes from oversaturated waters resulting in higher δ^{13} C values of residual dissolved inorganic carbon (DIC): and (2) precipitation. whereby carbonate ions are incorporated into rapidly precipitating CaCO₃ without equilibrium isotope exchange between solid CaCO₃ and solution.

This study aims to determine the factors controlling the δ^{13} C values of speleothem calcite in three central Texas caves by investigating the processes that influence C isotope compositions during transmission of water from the surface to the site of speleothem growth. We measured δ^{13} C values

of soil CO₂ ($\delta^{13}C_s$), DIC in drip waters (particularly focused on the carbonate species of bicarbonate, HCO₃; $\delta^{13}C_{HCO_3}$), and modern calcite grown on artificial substrates ($\delta^{13}C_{cc}$) in the caves. A two-phase approach was adopted to investigate: (1) processes in soil and epikarst that influence $\delta^{13}C_{HCO_3}$ value before water enters caves; and (2) in-cave processes that influence the $\delta^{13}C$ value of drip water DIC and calcite.

2. BACKGROUND

2.1. The formation of karst landscapes

Speleothems in most regions are cave-calcite deposited from groundwater that travels through the vadose zone dissolution region and into the calcite precipitation region (Fairchild et al., 2006). The dissolution region constitutes the soil horizon and the epikarst (the weathered/fractured bedrock where groundwater conduits and flow paths develop). In this region, CO_2 respired by plants and microbial communities dissolves into vadose zone waters and dissociates into a series of carbon-bearing ions, collectively known as dissolved inorganic carbon (DIC), according to the following reactions:

$$CO_{2(g)} \leftrightarrow CO_{2(aq)}$$
 (1a)

$$H_2O + CO_{2(aq)} \leftrightarrow H_2CO_{3(aq)} \tag{1b}$$

$$H_2CO_{3(aq)} \leftrightarrow H^+ + HCO^-_{3(aq)}$$
 (1c)

$$HCO_{3(aq)}^{-} \leftrightarrow H^{+} + CO_{3(aq)}^{2-}$$
(1d)

The resulting waters are acidic, and dissolve host limestone. The pH of water interacting with limestone bedrock is commonly between 7.5 and 8.5, such that the dominant DIC species is bicarbonate (HCO₃⁻). Water containing Ca²⁺_(aq) and DIC is transported by matrix, fracture, or conduit flow to open cavities in the subsurface (Atkinson, 1977; White and White, 2005). The calcite precipitation region is defined by the entrance of these waters into any void space within the subsurface with a lower pCO_2 than the epikarst, and where precipitation of calcite occurs by the overall reaction:

$$\operatorname{Ca}_{(\mathrm{aq})}^{2+} + 2\operatorname{HCO}_{3(\mathrm{aq})}^{-} \leftrightarrow \operatorname{CaCO}_{3(\mathrm{s})} + \operatorname{CO}_{2(\mathrm{g})} + \operatorname{H}_2O_{(\mathrm{l})}$$
(2)

2.2. Surface and shallow-subsurface processes: Soil horizon and the epikarst

Several factors control the δ^{13} C values of soil pore space CO₂ (i.e., soil CO₂; δ^{13} C_s). Soil CO₂ is a mixture of atmospheric CO₂ and soil-respired CO₂, which is derived from root/rhizosphere respiration and soil organic matter (SOM) decomposition. Therefore, the first factors

controlling δ^{13} C values of soil CO₂ are the contributing endmember δ^{13} C values of atmospheric CO₂ and soil-respired CO₂. The δ^{13} C value of atmospheric CO₂ is relatively invariant (approximately -8.5% at each study site) in comparison with δ^{13} C values of soil-respired CO₂, which vary widely. The δ^{13} C values of soil-respired CO₂ are closely related to both the δ^{13} C values of organic matter in soils and the δ^{13} C value of plant tissue. For instance, δ^{13} C values of soil-respired CO₂ are typically within 1% of the δ^{13} C values of SOM (Bowling et al., 2008). The δ^{13} C values of SOM, and corresponding speleothem calcite, have been argued to vary with the relative abundance of C_3 versus C₄ plants (Farquhar et al., 1989; Dorale et al., 1992; Ehleringer and Monson, 1993). The observed ranges of δ^{13} C values of C₃ and C₄ plant tissues are -35% to -21%and $-20\%_{00}$ to $-9\%_{00}$, respectively (Badeck et al., 2005). It is also important to note that the δ^{13} C values of individual C₃ plant species can vary ($\sim 1-2\%$) due to water availability (e.g., Hartman and Danin, 2010).

The second factor that controls soil CO₂ δ^{13} C values is the relative proportion of atmospheric versus soil-respired CO₂. Decreases in soil respiration rate can result in elevated soil CO₂ δ^{13} C values; this effect is particularly prominent when soil CO₂ concentrations decrease below approximately 2000 ppm. Surface aridity could therefore affect the δ^{13} C value of drip water DIC entering caves and that of speleothem calcite both through changes in surface vegetation (i.e., C₃–C₄ transition or changes in the δ^{13} C values of C₃ plants) and soil CO₂ productivity (e.g., Genty et al., 2006), and through change in the endmember δ^{13} C value of the organic carbon source, as described previously.

Diffusion is the final factor governing δ^{13} C values of soil CO₂. Higher diffusivity of ¹²CO₂ (relative to ¹³CO₂) through soil pore spaces results in soil CO₂ δ^{13} C values that are 4.4‰ higher (or more if respiration rates are low) than δ^{13} C values of the organic carbon source for respiration (Cerling, 1984; Cerling et al., 1991). Carbon isotope fractionation during diffusion must therefore be taken into account when comparing δ^{13} C values of soil CO₂, cave air CO₂, DIC and calcite (Breecker et al., 2012).

Whereas these factors and the empirical work supporting them are well-established for soils, comparatively little is known about the controls on δ^{13} C values of CO₂ in the deeper vadose zone beneath soils, which are perhaps more closely related to δ^{13} C values of speleothem calcite. Relevant to this, Breecker et al. (2012) determined that in the mixed C₃-C₄ ecosystems of central Texas and southern Arizona (including the locations studied here), deep-rooted C₃ vegetation is the primary source of CO₂ entering caves. In this paper, we address the question of whether or not this bias towards deep-rooted vegetation also holds for DIC in drip water and resultant cave calcite.

2.3. Host-rock influences

The incorporation of host-rock carbonate (CO_3^{2-}) into solution can also affect $\delta^{13}C$ values of DIC and thus speleothems (Hendy, 1971; Fairchild et al., 2006). This effect is modulated by open versus closed system conditions. An open system allows for complete and continuous isotope exchange between solution DIC and vadose zone CO₂, such that the host-rock contribution can be overwhelmed if the flux of CO₂ through the vadose zone is large enough. In contrast, closed systems involve groundwater that is isolated from exchange with vadose zone CO₂ and thus more susceptible to the carbon isotope exchange between host-rock and the solution (Hendy, 1971; Fairchild et al., 2006). The δ^{13} C values of Cretaceous carbonates in the study area range between 0.8‰ and 2.3‰ (Keith and Weber, 1964; Lee et al., 1997). If host-rock influence is significant, it will shift the drip water and subsequent speleothem calcite δ^{13} C values higher and away from the δ^{13} C_{DIC} values in equilibrium with soil CO₂.

2.4. In-cave processes affecting calcite δ^{13} C values

Speleothem calcite δ^{13} C values are controlled by the temperature dependent equilibrium carbon isotope fractionation factors between CO₂ gas, DIC species, and calcite. Published studies lack agreement on the magnitude and temperature sensitivity of the CaCO₃–HCO₃⁻ fractionation factor (Polag et al., 2010). Most studies report a CaCO₃–HCO₃⁻ fractionation factor of ~1‰ at common cave temperatures of 10–30 °C, but values ranging from ~0‰ to 2‰ have been reported over this temperature range (e.g., Deines et al., 1974; Romanek et al., 1992; Mook, 2002; Polag et al., 2010).

Kinetic isotope effects may also affect speleothem $\delta^{13}C_{cc}$ values. Model studies have addressed influences of drip rate, mixing ratio between a new drip and the existing film on a speleothem surface (Mühlinghaus et al., 2007), equilibrium isotopic exchange between cave-air and water (Scholz et al., 2009; Dreybrodt and Scholz, 2011), drip intervals (Deininger et al., 2012) and varying open versus closed-system scenarios (Fohlmeister et al., 2011; Riechelmann et al., 2013). Wiedner et al. (2008) experimentally demonstrated that δ^{13} C values of calcite increased along a continuous flow-path. The magnitude of increase varied as a function of the water exposure time (t_{exp}) to the low pCO_2 caveair, and the surface-area-to-volume ratio of the drip water. Additionally, Baker et al. (2011) and Riechelmann et al. (2013) showed that drip rate controls the δ^{13} C values of calcite and DIC.

2.4.1. Kinetic isotope effects associated with in-cave CO_2 degassing

When drip water enters a cavity with substantially lower pCO_2 than that with which the water last equilibrated, rapid degassing occurs, whereby ${}^{12}CO_2$ preferentially escapes from solution relative to ${}^{13}CO_2$ (Hendy, 1971; Fairchild et al., 2006). This may cause kinetic effects in DIC and subsequently precipitated speleothem calcite (Mickler et al., 2004, 2006). The rate of CO₂ degassing from drip water is influenced by cave ventilation, which is likely to be seasonal in temperate and subtropical cave systems (James and Banner, 2008). In deeper portions of caves, cave-air (and drip water) temperatures remain relatively constant throughout the year (Spötl et al., 2005; Banner et al., 2007). This leads to colder (and denser) cave-air than outside air in the summer, and therefore little ventilation.

Without adequate ventilation, elevated cave-air pCO_2 results in minimal degassing and insignificant kinetic effects in δ^{13} C values of DIC and calcite. In contrast, cave-air is warmer than outside air during the winter, which promotes density-driven ventilation by surface air of relatively low pCO₂, maximizing the water-to-cave-air CO₂ gradient and the potential for kinetic effects. This seasonal variation in cave-air CO₂ concentrations is observed in both undeveloped and tourist caves in central Texas (Banner et al., 2007; Cowan et al., 2013), and is responsible for seasonal variations in calcite precipitation rate as has been established in previous work in various cave systems, including those from this study where higher precipitation rates are observed in the winter (Spötl et al., 2005; Banner et al., 2007; Mattey et al., 2010; Frisia et al., 2011; Feng et al., 2012). Note that other factors such as the cave morphology, passage tortuosity, and entrance position/orientation can also affect the timing, magnitude and duration of the season of maximum ventilation.

2.4.2. Prior calcite precipitation

The process of calcite precipitation from solution before reaching the drip site is referred to as prior calcite precipitation (PCP). This process preferentially removes ${}^{13}C$ over ${}^{12}C$ from solution, resulting in progressively lower $\delta^{13}C_{DIC}$ values along the flow path (Fairchild et al., 2006). However, PCP is typically driven by CO₂ degassing, making it difficult to separate the effects of either of these individual processes on δ^{13} C values of DIC and speleothem calcite. PCP can occur in any void or region in the epikarst that groundwater or drip water is able to degas CO₂. The overall impact of PCP is assessed at the first entry of water to the cave due to the inaccessibility of the epikarst to sampling. Such assessments can be made using trace and major element ratios $(Mg^{2+}/$ Ca^{2+} , Sr^{2+}/Ca^{2+} , Ba^{2+}/Ca^{2+} , Cd^{2+}/Ca^{2+} , and Co^{2+}/Ca^{2+}) as partition coefficients for these trace elements differ significantly from 1, yielding, for example, elevated Mg²⁺/Ca²⁺ ratios and lower Cd^{2+}/Ca^{2+} ratios in both solution and subsequently precipitated calcite (Fairchild et al., 2000; Sinclair, 2011; Wong et al., 2011; Oster et al., 2012; Sinclair et al., 2012; Day and Henderson, 2013).

3. METHODS

3.1. Study sites

We conducted this study in and above three central Texas caves: Inner Space Cavern (IS; 30°36'28" N, 97°41'16" W, WGS84), and Natural Bridge Caverns North Cavern and South Cavern (NB; 29°41'31" N, 98°20'34" W, WGS84). The caves are located at the intersection of the Balcones Fault Zone and the Edwards Plateau (Maclay and Small, 1983).

Cave IS is located ~3 km south of Georgetown, Texas. Study sites include: (1) cave drip sites, at which we measured δ^{13} C values of DIC and, in limited cases, δ^{13} C values of modern calcite; and (2) corresponding surface sites above the cave, where we measured the concentration and carbon isotope composition of soil pore space CO₂ (Fig. 1). We established precise locations of these sites relative to one another using the locations of access and ventilation shafts that connect surface to subsurface. Studied drip sites are located \sim 24 m below the surface. Highway IH-35 extends over the cave and the natural vegetation (oak and elm savanna) has been replaced by grassland (Fig. 1).

The NB caves are located ~ 24 km west of New Braunfels, Texas. The two NB caves are separated by collapse and may still be connected in terms of cave-air circulation, but exhibit different ranges in cave-air pCO_2 (Elliot and Veni, 1994; Banner et al., 2007; Wong et al., 2011; Cowan et al., 2013). The drip sites are located ~ 50 m beneath the surface.

In both caverns, cave-air and drip water temperatures remain largely constant throughout the year, with averages of 20 and 22 °C at IS and NB, respectively (Banner et al., 2007; Feng et al., 2012). Mean annual temperature above both caves is 20.8 °C and mean annual precipitation is 82.0 and 87.0 cm/year at IS and NB, respectively (for 1981–2010, National Climatic Data Center).

Our soil gas sampling locations were chosen based on vegetation. Patchy, mixed grassland-woodland vegetation (subtropical savanna) occurs above the caves and across central and southern Texas including the Edwards Plateau and Balcones Fault Zone (Jessup et al., 2003; Bai et al., 2009, 2012). Soils in the region are 0-45 cm thick Lithic Argiustolls and Lithic Haplustolls (Godfrey et al., 1973; Cooke et al., 2007). The region provides habitat to native and non-native species of C3, C4, and CAM vegetation, and has been undergoing extensive woodland (C_3) encroachment since the mid-19th century (Jessup et al., 2003; Bai et al., 2009, 2012). Southern live oak (Ouercus virginiana) and ashe juniper (Juniperus ashei) are the dominant tree species responsible for this encroachment (Jessup et al., 2003). This biome allows for stark variations in the proportions of C₃, C₄, and CAM plant types. The surface vegetation above both caves is dominated by Q. virginiana and J. ashei with limited stands of cedar elm (Ulmus crassifolia) (woodlands), King Ranch bluestem (Bothriochloa ischaemum; C_4) and cedar sedge (*Carex planostachys*; C_3) (grasslands). Patches of Texas prickly pear (Opuntia engelmanii; CAM) and other mixed C3-C4 grasses are also present (Breecker et al., 2012).

At NB, soil gas was collected at four sites (four depths per site) at depths ranging from 6 to 34 cm. Wells were installed above the cave in grassland soils and beneath the canopy of juniper trees. At IS, soil gas was collected from five locations above site D-ISLM-d (Lake of the Moon; see Table B6, Supplementary Material), three locations in a grove of live oak and cedar elm trees and two wells in a patch of prickly pear cactus. Soil CO₂ measurements in the grassland near the highway above sites D-ISST-i and D-ISST-d (Breecker et al., 2012, reproduced in Table B6) are used in this study for comparison with drip water and calcite δ^{13} C values from this part of cave IS.

3.2. CO₂ sampling

We measured CO_2 respired by tree roots, in soils above the caves and in cave-air. To measure CO_2 respired by tree roots, we collected ashe juniper rootlets from ~15 cm depth



Fig. 1. Composite images of cave maps superimposed on surface satellite imagery for Natural Bridge Caverns (A) and Inner Space Cavern (B) adapted from Elliot and Veni (1994), regional location of both field localities (C), and schematic maps for both IS (D) and NB (E). The locations of NB drip sites (D-NBCH-d, D-NBCT-i) and soil gas wells (S-NB1, S-NB2, S-NB3, S-NB4) are shown. At Inner Space Cavern, line A–A' is the approximate transect we followed for transient soil gas well sampling. IS drip sites (D-ISST-i and D-ISST-d, ISLM) and the location of permanent soil gas wells (S-IS1, S-IS2, S-IS3, S-IS4, S-IS5) are also depicted. These are the same sampling locations as used in Breecker et al. (2012). The dotted lines indicate approximate area of the composite images, relative to the entire cave system. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

in the NB woodland. The rootlets were cleaned of soil and debris and rinsed with deionized water, dried, and placed in He-flushed, septum-capped 12 ml Labco Exetainer[®] vials incubated at 25 °C to mimic surface temperature at the time of collection. We sampled the headspace with a 1 ml Luer-Lock[™] syringe after 8 and 18-day intervals for carbon isotope analysis of CO₂.

We collected soil gas samples for measurement of the concentration and δ^{13} C values of soil CO₂. Soil gas samples were collected from septum-capped soil gas wells. The same wells were used for soil CO2 measurements reported in Breecker et al. (2012). Briefly, soil gas wells consist of 1/4" O.D. stainless steel tubes, crimped shut at the bottom and perforated on the side of the well. Wells were driven into the soil using a cordless drill and capped with rubber septum in Swagelok® fittings. Soil gas samples were collected from the wells by syringe at 4-8 week intervals and stored in He-flushed 12 ml Labco Exetainer® vials for a period of no longer than 1 week before analysis. Cave-air and surface atmospheric pCO_2 and air temperatures were determined using Telaire[®] 7001 CO₂ meters, Vaisala[®] GM70 Handheld CO₂ meters, and mercury/ethanol thermometers (uncertainties $\leq \pm 5\%$, Banner et al., 2007).

Cave-air samples were collected by syringe in similar fashion to the soil CO_2 samples by storage in Exetainer[®] vials and duration of storage. Collection sites are near drip site D-ISST-d (Inner Space Flowing Stone of Time) in cave IS, and near drip site D-NBCH-d (Natural Bridge Chandelier) in cave NB. They were sampled evenly between the cave floor and ceiling at ~1–2 m height.

3.3. Drip water sampling

We classified drip sites inside the caves as either: (1) 'directly-sourced', from stalactites/soda-straws where water enters the cave from the epikarst and is exposed to the cave atmosphere for less than 30 s prior to collection; or (2) 'indirectly-sourced', from in-cave flow-paths with some unknown, longer period of exposure time (\gg 30 s) to cave-air prior to drip formation. Drip water samples were collected on the same day as soil gas samples during the 2011–2012 collection period. Archived drip water data were from a 2004 to 2006 collection period (Guilfoyle, 2006). Single aliquots (0.4 ml) of drip water were subsampled from ~3 to 5 ml collected in 20 ml HDPE Nalgene[®] bottles and were transferred in the cave into Ultra High Purity (UHP) He-flushed Exetainer[®] vials using 1 ml Luer-LockTM syringes with 25G needles. The 3–5 ml sample was then dumped, and recollected with fresh drip water three additional times resulting in four 0.4 ml replicates transferred for isotopic analysis. Collection time for each 3–5 ml and 0.4 ml subsample was <30 s, which placed the lower-limit time constraint on sampling drip water from directlysourced sites. Sites for drip water collection (suffix "i" for indirect sites; suffix "d" for direct sites) are D-ISST-i, D-ISST-d, and D-ISLM-d at IS, and D-NBCH-d and D-NBCT-i at NB (Fig. 1). All sites except D-NBCH-d and D-ISST-d have been previously studied (Banner et al., 2007; Wong et al., 2011; Cowan et al., 2013; Appendix C, Supplementary Material).

In-cave degassing experiments were carried out on drip water samples collected from the D-ISST-d and D-NBCHd sites. The objective of these experiments was to investigate the rate at which $\delta^{13}C_{DIC}$ values change with degassing. At D-ISST-d, ~5 ml of drip water were collected in 30 ml HDPE Nalgene[®] bottles resulting in a water layer thickness of ~1.5 cm. CO₂ was allowed to degas into the cave atmosphere (*p*CO₂ = 540–740 ppm) for 270 min and was sampled every 30 min. A similar experiment was also conducted at D-NBCH-d on five 30 ml drip water samples in five 14 cm diameter glass petri dishes with a water film thickness of ~1 mm. We sampled water in the petri dishes every ~30 min for 150 total minutes (cave-air *p*CO₂ = 670–770 ppm).

3.4. Modern calcite growth and sampling

 10×10 cm sand-blasted, acid-cleaned glass substrates were placed under IS and NB drip sites to collect modern calcite precipitated at 4–6 week intervals for over 12 years. The oxygen isotope results of this effort from 1998 to 2008 were presented and discussed in a prior study (Feng et al., 2012).

In this study, we report on calcite from sites D-ISST-i, D-ISST-d, D-ISLM-d, and D-NBCT-i. Drip site D-NBCH-d was established in 2011 and has not been monitored for calcite collection. One method of calcite collection used a flow-channel made from 1/2-inch Lexan[®] sheets and outfitted with Gorillapod[®] legs and slots for 10×10 cm glass substrates (Fig. A2, Supplementary Material). Due to the central Texas drought that began in 2011, the ISST drip site was dry for the first time in 12 years of monitoring, resulting in a lapse of the time-series.

Calcite was collected from the center of the drip water impact region on substrates (referred to as "center samples") and from the edge away from the drip water impact ("edge samples", Table B7, Supplementary Material). The calcite was sampled for analyses by scraping from the substrate in a class-100 clean hood using dental tools to obtain a 5–20 mm² area of sample material, following the methods outlined in Banner et al. (2007). The amount sampled depends on the season, whereby sample yields are low in the summer and high in the winter.

3.5. Isotopic analysis by continuous-flow IRMS

Isotopic analyses were carried out at the University of Texas at Austin (PRISM II dual-Inlet MS, Thermo

Electron MAT 253, Thermo MAT 253 IRMS), the University of Minnesota (Finnigan Delta E) and the University of California at Davis (GV Instruments Optima). Soil CO2 samples were transferred via valved svringe (valve closed during transfer) to a separate He-flushed, septum-capped 12 ml Labco Exetainer[®] vials for sample dilution. Samples were then cryo-focused in a liquid nitrogen trap before introduction to the IRMS. A CO2-in-air standard calibrated to the Vienna Pee Dee Belemnite (VPDB) scale at CU-INSTAAR in Boulder, Colorado was used to calibrate an internal laboratory CO2-in-air standard for use in determining the δ^{13} C values of soil CO₂ samples. Soil CO₂ concentrations were determined by IRMS from the soil gas collection volume, the collection vial volume, the transfer volume and the mass 44 peak area, calibrated to measure moles of CO₂ by analyzing various volumes of standard gas. DIC and calcite samples were analyzed via multiple loop injections using a GasBench II. Inorganic carbon was exsolved from drip water samples by reaction with 103% H₃PO₄ at 25 °C for 12-40 h (Salata et al., 2000). The 0.4 ml drip water samples yielded 4-8 V signals in the mass spectrometer. For substrate calcite samples, 200-500 µg of calcite sample were placed in 12 ml Exetainer® vials and flushed with UHP helium before reaction with 103% H₃PO₄ for 2 h at 50 °C. Drip water and calcite samples were measured against internal laboratory NaHCO₃ (both as a solid and in solution) and marble standards. The 0.5 L standard NaHCO₃ solution was prepared by dissolving NaHCO₃ in DI water to achieve 1-10 meq/L as HCO_3^- . The range of HCO_3^- concentrations in the standard solutions allowed calibration of mass 44 peak area as a measure of HCO_3^- concentration. During analysis, 0.4 ml of each standard solution was transferred to UHP He-flushed vials and prepared identically to the drip water samples. Both solid and solution standards were calibrated to Carrara marble, NBS-18, and NBS-19. Measured δ^{13} C values of the standards are reproducible within $\pm 0.1\%$ (2σ) . All isotope analysis results are reported relative to VPDB.

3.6. Calculation of $\delta^{13}C_r$ and $\delta^{13}C_{HCO_{\overline{3}}}$ values

The calculations described here are summarized in a flow chart in Fig. 2. The δ^{13} C values of soil-respired CO₂ (δ^{13} C_r) were calculated from measured concentrations and δ^{13} C values of soil CO₂ using the equation below (Davidson, 1995):

$$\delta^{13}C_{r} = \frac{\delta^{13}C_{s} - 4.4 + 4.4\frac{C_{a}}{C_{s}} - \delta^{13}C_{a}\frac{C_{a}}{C_{s}}}{1.0044(1 - \frac{C_{a}}{C_{s}})}$$
(3)

where C_a is the atmospheric CO_2 concentration (395 ppm), C_s is the soil CO_2 concentration, and $\delta^{13}C_a$ is the carbon isotope composition of atmospheric CO_2 (-8.5‰). The $\delta^{13}C$ values of bicarbonate ($\delta^{13}C_{HCO_3}$) in drip waters were calculated from measured $\delta^{13}C_{DIC}$ values by first speciating DIC using measured drip water pH values and then calculating the $\delta^{13}C$ value of each DIC species by carbon isotope mass balance. We also predicted $\delta^{13}C_{HCO_3}$ values from $\delta^{13}C_s$ values to facilitate comparison between soil CO_2



Fig. 2. Flow-chart depicting the calculation of δ^{13} C values of respired CO₂, epikarst CO₂, bicarbonate and calcite from values measured at site D-ISLM-d. Arrows represent carbon isotope fractionations or the selection of certain values as described in text. Measured soil CO₂ is from soil beneath oak and elm trees above cave drip site D-ISLM-d. Ranges of predicted δ^{13} C values of epikarst CO₂ were estimated from measured soil CO₂ values. The upper end of the δ^{13} C range was calculated from δ^{13} C values of soil CO₂ samples with pCO₂ > 2000 ppm (see text). The lower end of the δ^{13} C range was determined by calculating δ^{13} C values of soil-respired CO₂ from measured soil CO₂ values and then adding 4.4₀₀ to account for diffusion. Ranges for δ^{13} C values of HCO₃⁻ and calcite were calculated by applying the appropriate fractionation factors.

and drip water. $\delta^{13}C_{HCO_{\bar{i}}}$ values were calculated from $\delta^{13}C$ values of CO2 after Zhang et al. (1995) using an enrichment factor of $\varepsilon_{\rm HCO3-g} = -0.141T$ (°C) + 10.78% and mean annual drip water temperatures of 22.7 °C (NB) and 22.5 °C (IS). This was done in two ways to generate a range of predicted $\delta^{13}C_{HCO_{3}}$ values: (1) measured $\delta^{13}C_{s}$ values were used in the equilibrium calculation; and (2) $\delta^{13}C_{r}$ values +4.4 ‰ were used in the equilibrium calculation. The range of predicted $\delta^{13}C_{HCO_{3}}$ calculated with these two approaches accounts for uncertainty in the CO₂ concentration in the epikarst where drip water acquires its $\delta^{13}C$ values. The first approach assumes epikarst CO2 concentrations are equal to soil CO₂ concentrations. This is a minimum estimate for epikarst pCO_2 and results in a maximum estimate of $\delta^{13}C_{HCO_3}$ values. The second approach assumes epikarst CO2 concentrations are sufficiently high (>2000 ppm) that mixing with atmospheric CO_2 does not influence the epikarst pore space $CO_2 \delta^{13}C$ values. This is a maximum estimate for epikarst CO2 and results in minimum estimates of $\delta^{13}C_{HCO_{\overline{1}}}$ values.

4. RESULTS

4.1. Soil and soil-respired CO₂

We report both measured δ^{13} C values of soil CO₂ (δ^{13} C_s; Fig. 3) and calculated δ^{13} C values of soil-respired CO₂ (δ^{13} C_r), where the δ^{13} C_s values for soil CO₂ samples with pCO₂ > 2000 ppm. Averages for all samples are compared with the averages of samples with pCO₂ > 2000 ppm in Table B6. There are different numbers of values for δ^{13} C_r



Fig. 3. Comparison of measured and predicted drip water $\delta^{13}C_{HCO_3}$ values. The values for D-NBCH-d are calculated from measured drip water $\delta^{13}C_{DIC}$ values. The values for S-NB4, S-NB3, S-NB2 and S-NB1 are predicted values in equilibrium with measured soil CO₂ $\delta^{13}C_s$ values (samples with $pCO_2 > 2000$ ppm only) using the enrichment factor of Zhang et al. (1995) and mean annual temperature at Natural Bridge Caverns. S-NB4 and S-NB3 sites have mixed C₃-C₄ vegetation whereas S-NB2 and S-NB1 are dominated by deep-rooted trees (C₃). Box plots depict the median (centerline of the box), 25th and 75th percentiles (bounds of the box), 10th and 90th percentile values (black circles) for each site.

than $\delta^{13}C_s$ because soil CO₂ concentration, required to calculate $\delta^{13}C_r$, was not measured for every sample.

For soil under mixed C_3-C_4 grasses above NB, the mean $\delta^{13}C_s$ and $\delta^{13}C_r$ values are $-14.7 \pm 1.1\%$ ($n = 17, 1\sigma$) and $-19.7 \pm 0.9\%$ ($n = 6, 1\sigma$), respectively (Table B6). For soil under ashe juniper trees (C₃) at NB, mean $\delta^{13}C_s$ was $-18.8 \pm 0.9\%$ (n = 25) and $\delta^{13}C_r$ was $-25.3 \pm 2.0\%$ (n = 56). The $\delta^{13}C$ value of CO₂ respired during laboratory incubation of juniper roots was $-23.6 \pm 0.1\%$ after 8 days and $-24.9 \pm 0.9\%$ after 18 days. Soil CO₂ concentrations increased with depth at all sites above NB and $\delta^{13}C_s$ values decreased with depth in the top 20 cm by an average of $2.3 \pm 1.4\%$ (n = 27). Soil CO₂ concentrations, $\delta^{13}C_s$ values, and $\delta^{13}C_r$ values also varied temporally during the period of study (Fig. A1, Table B6, Supplementary Material).

At cave IS, we observed similar relationships between $\delta^{13}C_s$ values and the type of vegetation present. For soil CO₂ under oak and elm trees, mean $\delta^{13}C_s$ was $-20.0 \pm 2.0\%_{00}$ (n = 12) and $\delta^{13}C_r$ was $-25.5 \pm 2.8\%_{00}$ (n = 22). For soil CO₂ under prickly pear cactus, $\delta^{13}C_s$ was $-17.7 \pm 2.5\%_{00}$ (n = 8) and $\delta^{13}C_r$ was $-23.7 \pm 1.9\%_{00}$ (n = 14). For soil CO₂ under grassland, pCO_2 was <2000 ppm for all samples measured and the mean $\delta^{13}C_s$ was $-13.7 \pm 1.2\%_{00}$ (n = 3) and $\delta^{13}C_r$ is $-20.3 \pm 1.2\%_{00}$ (n = 3; Table B6). In addition to new data reported here, we also include published soil CO₂ data (Breecker et al., 2012, Table B6). Depth profiles were not measured in soils above IS and seasonal cycles were not as clear as in soils above NB.

Predicted $\delta^{13}C_{HCO_{3}}$ values based on soil CO₂ measurements above cave NB are $-7.2 \pm 1.1\%_{00}$ (n = 13) for a patch of grassland, $-8.9 \pm 1.2\%_{00}$ (n = 17) in a mixed-vegetation streambed, $-11.4 \pm 1.0\%_{00}$ (n = 25) for ashe juniper trees (Fig. 2, Table B6). Predicted mean $\delta^{13}C_{HCO_{3}}$ values at IS were $-6.2 \pm 1.2\%_{00}$ (n = 3) under grassland, $-10.2 \pm 1.7\%_{00}$ (n = 8) under prickly pear and $-12.6 \pm 2.0\%_{00}$ (n = 12) under oak and elm trees (Table B6).

4.2. $\delta^{13}C_{HCO_{\overline{1}}}$ of directly- and indirectly-sourced drip water

Directly-sourced drip water $\delta^{13}C_{HCO_{\overline{3}}}$ values were only calculated from 2011 to 2012 (Table B2) to best correspond to the soil gas samples, which were only collected during this interval. The mean $\delta^{13}C_{HCO_{7}}$ values of direct drip water were $-10.6 \pm 0.5\%$ (D-NBCH-d; $n = 10, 1\sigma$), $-9.7 \pm 0.3\%$ (D-ISST-d; n = 9, 1σ) and $-12.6 \pm 0.1\%$ (D-ISLM-d, n = 3, 1σ) (Fig. 4). Measured $\delta^{13}C_{HCO_{\overline{3}}}$ values at D-NBCH-d (-10.6 ± 0.5‰) are similar to $\delta^{13}C_{HCO_{\overline{3}}}$ values predicted from contemporaneous soil CO2 under juniper trees at NB (-11.4% to -13.5%). Measured $\delta^{13}C_{HCO_{\overline{1}}}$ values at site D-ISLM-d $(-12.6 \pm 0.1\%)$; n = 3, 1σ) are indistinguishable from values predicted from penecontemporaneous soil CO₂ under oak and elm trees (-13.6%) to -12.6_{00}° (Table B6). Measured $\delta^{13}C_{HCO_{\overline{3}}}$ at site D-ISSTd are intermediate between values predicted from soil CO2 under trees and soil CO2 under grassland (Tables B2 and B6).

The mean $\delta^{13}C_{HCO_3}$ values for indirectly-sourced drip water were $-8.6 \pm 0.8\%$ (D-ISST-i; n = 4; S.D. $= 1\sigma$) and $-9.6 \pm 1.5\%$ (D-NBCT-i; n = 9, S.D. $= 1\sigma$). At both sampling intervals (2004–2006 and 2011–2012), the $\delta^{13}C_{HCO_{3}}$ values of indirectly-sourced drip water varied seasonally (~4–6‰ and ~3‰ difference between summer and winter, respectively), whereas $\delta^{13}C_{HCO_{3}}$ values of directly-sourced drip water did not (Fig. 4). During the in-cave degassing experiments, $\delta^{13}C_{DIC}$ values increased at a rate of 0.24‰/h, with a water film thickness of ~1.5 cm, and 0.47‰/h with a film thickness of ~1 mm (Fig. A5, Supplementary Material). Drip water $\delta^{13}C_{DIC}$ values from this study are placed in the context of published drip water values from other studies in Fig. 5 (Spötl et al., 2005; Mattey et al., 2010; Frisia et al., 2011; Riechelmann et al., 2011; Tremaine et al., 2013).

4.3. Modern calcite δ^{13} C values

The $\delta^{13}C_{cc}$ values of D-ISST-i center samples spanning 1998–2008 range from -8.6% to -3.9% (n = 64, Fig. 6, Table B7, Supplementary Material). The $\delta^{13}C_{cc}$ values of D-ISLM-d center samples have $\delta^{13}C_{cc}$ values ranging from -11.7% to -10.2% (*n* = 40, Fig. 6, Table B7, Supplementationtary Material, $\delta^{18}O_{cc}$ values of these samples were presented in a prior study, Feng et al., 2012). The D-ISST-i $\delta^{13}C_{cc}$ values peak (range of peak values between -7.2% and -3.9%) every winter in the record spanning 1998-2008 (Fig. 6). For the edge samples, $\delta^{13}C_{cc}$ values ranged from -10.4_{00}° to -3.9_{00}° at all sites. Given the susceptibility of edge samples to large kinetic effects by precipitation and degassing, they were not considered for further discussion. The $\delta^{13}C_{cc}$ values from sites D-NBCT-i and D-ISST-i spanning 2011-2012 ranged from -8.3% to -7.5% (D-NBCT-i) and -8.7% to -8.1% (D-ISST-i). The D-ISST-i $\delta^{13}C_{cc}$ values correlate inversely with drip rate ($r^2 = 0.58$, after 5-point moving average; Fig. 8).

For all sites evaluated at both IS and NB, $\delta^{13}C_{DIC}$ and $\delta^{13}C_{cc}$ values were within 1.5% of one another. For the comparison of substrate calcite to drip water δ^{13} C values, we were unable to determine $\delta^{13}C_{HCO_{\overline{3}}}$ due to pH not being measured for the samples collected from 2004 to 2006. $\delta^{13}C_{DIC}$ and $\delta^{13}C_{cc}$ values were well correlated during 2011-2012 for both directly (D-ISST-d) and indirectly (D-ISST-i) sourced drip water in cave IS ($r^2 = 0.82$; Fig. A4, Supplementary Material). The $\delta^{13}C_{cc}$ values did deviate from values predicted by the equilibrium fractionation factor (Romanek et al., 1992) between HCO_3^- and $CaCO_3$ (Fig. A4, Supplementary Material). The magnitudes of the deviation can be expressed as the difference between measured and equilibrium $\delta^{13}C_{cc}$ values, $\Delta^{13}C_{m-e}$. During the 2011-2012 sample collection period, the values of $\Delta^{13}C_{m-e}$ range from -1.2% to +0.2% at D-NBCT-i and 0.0% to +3.7% at D-ISST-d (including edge samples). Additionally, $\varDelta^{13}C_{m-e}$ values for calcite collected at D-ISST-i between 2004 and 2006 ranged from -1.2% to -0.2% (center samples only, Table B7, Supplementary Material). The magnitude of variations in center plate sample $\Delta^{13}C_{m-e}$ values from central Texas caves overlaps with those observed in Harrison's Cave, Barbados (Mickler et al., 2004; approximately $\pm 1.0\%$ to -2.5%), but with a smaller overall range.





Fig. 4. Drip water $\delta^{13}C_{HCO3-}$ values for Natural Bridge Caverns (A) and Inner Space Cavern (B). Values for direct and indirect drip sites are similar during the summer months when CO₂ degassing from drip water is minimized; $\delta^{13}C_{HCO_{\bar{x}}}$ values of indirect drip sites increased during the winter with enhanced cave ventilation and CO₂ degassing. Arrows indicate the direction of change in $\delta^{13}C_{HCO_{\overline{x}}}$ values associated with kinetic isotope effects by CO₂ degassing. Dashed lines indicate the $\delta^{13}C_{HCO_7}$ values predicted from $\delta^{13}C_s$ values (top line, for samples with soil $CO_2 > 2000$ ppm only) and $\delta^{13}C_r + 4.4\%$ (bottom line) under trees.

5. DISCUSSION

-4

-6

-8

-10

5¹³C_{HCO3}. (‰, VPDB)

A

11 4%

Ranae of $\delta^{13}C$

values predicted from soil CO, under mixed C_3 - C_4 grasses

5.1. The source of carbon in drip water and speleothem calcite

The objective of measuring soil CO_2 in this study was to investigate the source of carbon in drip water and speleothem calcite. Direct comparison between δ^{13} C values of soil CO₂ and either drip water bicarbonate or speleothem calcite are somewhat obscured by the intervening epikarst, which is difficult to sample. The thin soils above the caves experience widely ranging moisture and temperature conditions resulting in large seasonal and interannual variations in soil CO₂ concentrations and, thus, $\delta^{13}C_s$ values. These large amplitude variations that occur near the surface are typically dampened with depth. Therefore we would expect, in the absence of respiration in the epikarst, that epikarst CO₂ concentrations would approximate mean annual soil

CO₂ concentrations. In reality, epikarst CO₂ concentrations are probably higher than mean annual soil CO₂ concentrations because roots extending into the epikarst in this region (Jackson et al., 1999) likely produce CO₂ (Wong and Banner, 2010) that would elevate epikarst CO₂ concentrations. Some soil gas samples have very low CO2 concentrations (Table B6). Below approximately 2000 ppm, $\delta^{13}C_s$ values are strongly influenced by the atmospheric CO₂ component. Above 2000 ppm, the influence of the atmospheric component declines substantially. For these reasons, we argue that $\delta^{13}C_s$ values for soil gas samples with CO₂ concentrations higher than approximately 2000 ppm are most likely to be representative of the epikarst, and thus drip water. We therefore predict $\delta^{13}C_{HCO_3}$ values for comparison with measured drip water $\delta^{13}C_{HCO_3}$ values using $\delta^{13}C_s$ values for soil gas samples with $CO_2 > 2000 \text{ ppm}$ (Table B6). This provides an upper limit on expected



Fig. 5. Drip water $\delta^{13}C_{DIC}$ values from published studies across Europe and North America. Data are from IS and NB caves (this study), Lascaux and Cussac Caves (Peyraube et al., 2013), Bunker Cave (Riechelmann et al., 2011), Hollow Ridge Cave (Tremaine et al., 2011), Grotta di Ernesto (Frisia et al., 2011), St. Michaels Cave (Mattey et al., 2010), and Obir Caves (Spötl et al., 2005). To minimize the effects of PCP or KIE, we only evaluated the range of $\delta^{13}C_{DIC}$ values corresponding to the period of minimum cave ventilation documented in each study. Ranges of predicted $\delta^{13}C$ values of bicarbonate in equilibrium with soil CO₂ under C₃ and C₄ vegetation are shown for comparison with measured $\delta^{13}C_{DIC}$ values. These predicted $\delta^{13}C$ values of bicarbonate were calculated using the ranges of $\delta^{13}C$ values of C₃ and C₄ plants reported by Badeck et al. (2005). A constant 4.4‰ was added to the plant $\delta^{13}C$ values to calculate $\delta^{13}C$ values of soil CO₂ and then equilibrium $\delta^{13}C$ values of bicarbonate were calculated from those soil CO₂ $\delta^{13}C$ values using a temperature of 22 °C (mean temperature at NB caverns, calculation not sensitive to temperature) and the enrichment factor of Zhang et al. (1995). Accurate comparison with predicted $\delta^{13}C_{HCO_{3}}$ values requires calculation of $\delta^{13}C_{HCO_{3}}$ from measured $\delta^{13}C_{DIC}$ values. The pH of the Lascaux and Cussac Caves is as low as 7.15, resulting in $\delta^{13}C_{HCO_{3}}$ 1.5‰ higher than the $\delta^{13}C$ values of total DIC shown, but still within the expected range for C₃ vegetation. The drip waters in the other caves have pH around 8 and therefore the $\delta^{13}C$ values of HCO₃⁻ are at most several tenths of a per mil higher than shown and thus all within the C₃ range. *Denotes regions with mixed C₃-C₄ vegetation, the remaining localities have almost exclusively C₃ vegetation.



Fig. 6. Modern calcite δ^{13} C values ($\delta^{13}C_{cc}$) from center plate samples precipitated on glass substrates at Inner Space Cavern (Table B7, Supplementary Material). Both sites have a vegetation baseline (indicated by horizontal dashed lines) from which δ^{13} C values increase each winter. Dashed lines indicate the $\delta^{13}C_{cc}$ values predicted from $\delta^{13}C_s$ values (top line of each range, for samples with soil CO₂ >2000 ppm only) and $\delta^{13}C_r + 4.4_{oo}$ (bottom line of each range) under grassland (upper range) and under oak and elm trees (lower range). The directly-sourced drip site (D-ISLM-d) demonstrates low-magnitude variability and spatially corresponds to a grove of live oak trees above the site. The indirectly-sourced drip site (D-ISST-i) exhibits higher-magnitude variability and corresponds to a mixed C₃-C₄ grassland (woody plants removed) above the drip site.

 $\delta^{13}C_{HCO_{3}}$ and $\delta^{13}C_{cc}$ values whereas the use of $\delta^{13}C_{r} + 4.4_{00}^{\circ}$ provides a lower limit.

Soil-respired CO_2 is from both plant root-respiration and the decomposition of SOM with proportions varying between 10% and 90% root respiration (Hanson et al., 2000; Sulzman et al., 2005; Davidson and Janssens, 2006; Trumbore, 2006). The mean δ^{13} C value of CO₂ produced during juniper root incubations in the present study

(-24.3%) was indistinguishable from the mean $\delta^{13}C_r$ value determined from soil gas samples from underneath the live juniper tree $(-24.1 \pm 1.1\%, n = 14, 1\sigma, \text{ values correspond})$ to soil CO₂ concentrations >2000 ppm). Therefore, soil CO₂ generated by SOM decomposition is either negligible in this region, or has δ^{13} C values similar to ashe juniperrespired CO₂. Some studies have focused on measuring the δ^{13} C values of CO₂ respired by analyzing: (1) SOM fractions that have been separated (Crow et al., 2006), (2) samples from physical manifolds placed around plant limbs, leaves, and in isolated sections of soil (Damesin et al., 2005; Wingate et al., 2010) or (3) CO₂ efflux from the land surface to the atmosphere measured from different sections of forest canopies and various biomes (Hanson et al., 2000; Sulzman et al., 2005: Davidson and Janssens, 2006: Trumbore, 2006). Future work could evaluate the percent carbon and δ^{13} C values of respective organic and inorganic fractions of the soil at each field locality that may resolve the contribution of SOM decomposition to $\delta^{13}C_s$ values. For the purpose of this study, we assume that combined root respiration and SOM decomposition comprise total soil respiration.

The similarity between $\delta^{13}C_{HCO_{\overline{3}}}$ values at D-ISLM-d and those expected from vadose waters equilibrated with oak and elm soil CO2 above cave IS suggests that trees control the drip water $\delta^{13}C_{HCO_{\overline{3}}}$ values at this site, with minimal influence from host-rock dissolution. The overlap between measured and predicted $\delta^{13}C_{HCO_{\overline{x}}}$ values at D-NBCH-d also suggests a large component of tree-derived carbon in drip water DIC (Fig. 3). Based on the ranges of measured and predicted values, we cannot rule-out carbon contributions from grassland CO₂ as large as 20% (D-ISLM-d) and 60% (D-NBCH-d), from host-rock dissolution as large as 6% (D-ISLM-d) and 20% (D-NBCH-d) or some combination from each. For D-ISLM-d, we do not think the CO_2 from the streambed or the prickly pear cactus soil are substantial components given the small areal distribution of this vegetation across the field area, and that the streambed does not cross over the drip site. However, supply of drip water by preferential recharge through streambeds is a potential consideration for other caves. Figs. 3 and 4 suggest that trees control the $\delta^{13}C_{HCO_{\overline{3}}}$ values of drip water in the NB caves, with minimal influence from host-rock dissolution. Measured $\delta^{13}C_{HCO_{3}}$ values at D-ISST-d are 3% higher than at D-ISLM-d, and are intermediate between $\delta^{13}C_{HCO_{\overline{3}}}$ values predicted from soil CO₂ under trees and from soil CO2 in the current grassland above this part of the cave (Fig. 4). These intermediate values may result from a lag in the response of the cave to changes in surface vegetation (e.g., Dorale et al., 1992) due to the slow decay of tree roots that likely grew deep into the epikarst in this area before the highway was constructed in 1963. Together, the results suggest that, if present, trees control the δ^{13} C values of drip water and speleothems in these caves. We suggest that the mechanism for the tree-bias is that downward percolating groundwater exchanges carbon with CO₂ from deep roots (7-9 m for ashe juniper and cedar elm, up to 25 m for oak at various central Texas caves, including cave NB; Jackson et al., 1999) before it enters caves, which may reset the $\delta^{13}C_{HCO_{\overline{2}}}$

values acquired in the soil. This open system exchange between percolating waters and respired CO₂ cycling through the epikarst likely also overwhelms the effect of host-rock interaction, resulting in a nearly pure vegetation signal at direct drip water at D-ISLM-d and a vegetationdominated signal at D-NBCH-d.

The nearly constant, vegetation-controlled $\delta^{13}C_{HCO_{\overline{2}}}$ values measured at direct drip sites (Fig. 4) provide a useful reference frame, which we term the 'vegetation baseline'. The lowest $\delta^{13}C_{HCO_{3}}$ values at indirect drip sites (D-ISST-i and D-NBCT-i) coincide with the vegetation baseline, indicating that both direct and indirect drip sites might record a nearly pure vegetation signal. Lambert and Aharon (2011) also observed baseline δ^{13} C values of drip water DIC that they interpreted to be primarily controlled by vegetation with some ($\sim 23\%$) influence from host rock dissolution. These vegetation baselines provide context for the effect of in-cave processes on drip water and speleothem calcite δ^{13} C values (discussed in the following section), which are most prominent at the indirect sites in our study. Seasonal to interannual scale departures from vegetation baselines are likely the result of in-cave processes. Over longer timescales, vegetation baselines likely shift with vegetation change.

The vegetation baselines observed in the drip water $\delta^{13}C_{HCO_3}$ records also occur in the longer modern speleothem calcite records (1998–2008). D-ISST-i and D-ISLMd $\delta^{13}C_{cc}$ baselines differ by ~3‰ (the lowest $\delta^{13}C_{cc}$ values; D-ISST-i: $-8.2 \pm 0.3‰$ and D-ISLM-d: $-11.1 \pm 0.2‰$). This difference is consistent with the differences between $\delta^{13}C_{HCO_3}$ vegetation baselines at these two sites (Table B6, Supplementary Material) and, as suggested above for $\delta^{13}C_{HCO_3}$, can be explained by an upward shift in the D-ISST-i baseline due to the removal of trees next to the highway above this site. This interpretation suggests that speleothems in this part of the cave may record the recent vegetation change and that cave calcite $\delta^{13}C$ values in IS reflect the spatial distribution of vegetation on the surface.

To test whether the bias toward trees (or other deeply rooted plants) is an isolated occurrence or is typical of caves, we compiled measured $\delta^{13}C_{DIC}$ values of drip water from caves in Gibraltar, Italy, Austria, Germany, France and the United States (Fig. 5, Spötl et al., 2005; Mattey et al., 2010; Frisia et al., 2011; Riechelmann et al., 2011; Tremaine et al., 2011; Peyraube et al., 2013). All compiled $\delta^{13}C_{DIC}$ values fall in the range expected for water in equilibrium with soil CO₂ influenced by C₃ plants, including values for the caves with mixed C_3 - C_4 vegetation. C_4 trees and shrubs are rare among C_4 vegetation (C_4 only represent $\sim 3\%$ of plant species globally; Sage, 2004), therefore, in ecosystems with mixed C₃-C₄ vegetation and the presence of trees or shrubs, we would expect deep-rooted C₃ plants to bias the $\delta^{13}C_{DIC}$ of drip water. Certain ecosystems such as tallgrass prairies, in which grasses root deeper than forbs, and some shrublands might be exceptions to the C₃ bias (e.g., Pearcy and Troughton, 1975). Comparisons between $\delta^{13}C$ values of soil CO₂ and cave drip waters in these specific ecosystems would help further test this hypothesis.

5.2. The effect of in-cave process on $\delta^{13}C_{DIC}$ and $\delta^{13}C_{cc}$ values

The seasonal variation of indirectly-sourced drip water $\delta^{13}C_{HCO_{\overline{1}}}$ values is best interpreted in the context of vegetation baselines. For instance, $\delta^{13}C_{HCO_3}$ values approach the vegetation baseline at D-NBCT-i during summer months and are elevated above the vegetation baseline during the winter and spring (Fig. 4). The deviation from the vegetation baseline occurs when the cave is ventilated (maximum ventilation during winter. Banner et al., 2007) and thus the rates of drip water degassing and calcite precipitation are relatively high. Kinetic effects associated with CO₂ degassing are likely the primary factors responsible for positive deviation from the vegetation baseline. Elevated winter drip water $\delta^{13}C_{DIC}$ values in DeSoto Caverns were also interpreted to result from such kinetic effects (Lambert and Aharon, 2011). The deviation of indirect (D-NBCT-i and D-ISST-i) but not direct (D-NBCH-d and D-ISST-d) $\delta^{13}C_{HCO_{\overline{2}}}$ values from the vegetation baseline during the winter can be explained by considering the extended drip water exposure time (t_{exp}) of indirectly-sourced drip water and the documented increase in $\delta^{13}C_{\text{DIC}}$ with t_{exp} (+0.24‰/h to $+0.47^{\circ}_{\circ\circ}/h$). We argue that the observed deviations from the vegetation baselines at indirect drip sites are not explained by seasonal variations in the soil because: (1) there are no such deviations at direct drip sites; and (2) seasonal variation in $\delta^{13}C_s$ or $\delta^{13}C_r$ values are inconsistent with measured variations in $\delta^{13}C_{HCO_3}$ at indirect drip sites (Table B6).

Comparison of the decade-long modern calcite $\delta^{13}C$ records from D-ISST-i and D-ISLM-d supports the interpretation that deviations from the vegetation baseline result from CO₂ degassing inside the cave, which is enhanced during the winter. The seasonal variability of directly sourced drip water $\delta^{13}C_{HCO_{\overline{2}}}$ values in cave IS (Table B6) suggests that the seasonal variability in modern calcite δ^{13} C values is controlled by in-cave processes as opposed to epikarst processes. However, it should be noted that Peyraube et al. (2013) observed ~2% variability in δ^{13} C values of CO₂ in the epikarst, which is of similar magnitude as observed for site D-ISLM-d in this study. The difference between the amplitude of $\delta^{13}C_{cc}$ variations at the two sites is likely the result of larger kinetic effects at the indirectlysourced drip site (D-ISST-i), which is also closer to the cave entrance and therefore better ventilated than D-ISLM-d. Maximum departures from the vegetation baseline during the winter in the D-ISST-i $\delta^{13}C_{cc}$ record are consistent with the departures being controlled by kinetic isotope effects during ventilation-mediated degassing of CO₂ from drip water. A seasonally-resolved speleothem record reported by Johnson et al. (2006) also shows higher winter and lower summer $\delta^{13}C_{cc}$ with an amplitude of $\sim 1_{00}^{\circ}$ and with $\delta^{13}C_{cc}$ values that are consistent with a pure C_3 carbon source. Deviations from the vegetation baseline during winter months may be common in temperate and sub-tropical caves. In tropical caves, however, we expect lower seasonal variability in calcite δ^{13} C values (e.g., Mickler et al., 2004) due to calcite formation operating by small diurnal variations in cave ventilation being the primary mechanism behind CO₂ degassing of drip water.

We have also documented significant inverse correlation between drip rate and $\delta^{13}C_{cc}$ values at site D-ISST-i ($r^2 = 0.58$, after moving average, Figs. 7 and 8).We infer this correlation to result from decreased drip rate allowing for prolonged CO₂ degassing causing increase of the exposure time, t_{exp} , to a relatively low pCO_2 environment in the cave. Variability in speleothem $\delta^{13}C_{cc}$ values will occur under low pCO_2 conditions modulated by drip rate, which must be slow enough in order for these changes in $\delta^{13}C_{DIC}$ and $\delta^{13}C_{cc}$ values to be observable. This correlation between drip rate and $\delta^{13}C_{cc}$ is also observed in a study of St. Michaels Cave, Gibraltar (Fig. A6, Supplementary Material; Mattey et al., 2010), which suggests this relationship may apply in other temperate and subtropical cave systems.

The quantitative influence of t_{exp} on the δ^{13} C values of drip water DIC and speleothem calcite has been estimated in modeling studies (Mühlinghaus et al., 2007; Romanov et al., 2008; Scholz et al., 2009; Dreybrodt and Scholz, 2011). Experimental calcite precipitation results (Wiedner et al., 2008; Hansen et al., 2013), and empirical data from Bunker Cave (Riechelmann et al., 2013) also determined t_{exp} to govern changes in $\delta^{13}C_{cc}$ values. Our empirical results agree with theoretical constraints reported by these studies on the evolution of $\delta^{13}C_{DIC}$ and $\delta^{13}C_{cc}$ values and stress the importance of interaction between t_{exp} and cave-air pCO_2 on speleothem $\delta^{13}C_{cc}$ values.

5.3. Calcite δ^{13} C values and interpretations of a 10-year modern calcite record

Many substrate calcite samples followed trends of increasing δ^{13} C values from the center to the edge of the substrate. This is presumably due to kinetic effects as water moved outward from the locus of drip impact (Mickler et al., 2006). We believe that additional drip water to the substrate contributes to and 'refreshes' the existing film of water residing on the glass substrate, with undetermined flux of water off the substrate at the margins. This flux in the water film would then presumably establish a steadystate condition where the margins were continually more degassed than the center. We acknowledge that film thickness on a substrate or feature within the cave would play a role in governing the extents of degassing, and we encourage further work in this regard. Therefore only center samples are considered here but all values are included in Table B7 of the Supplementary Material. For sites D-NBCT-i, D-ISLM-d, D-ISST-i and D-ISST-d, $\delta^{13}C_{cc}$ values closely followed drip water $\delta^{13}C_{DIC}$. The $\Delta^{13}C_{m-e}$ values (deviation of calcite δ^{13} C values from expected equilibrium values) of center samples range from -1.2% to +0.2%(Fig. A4, Supplementary Material), we attribute to possible temperature sensitivities in the equilibrium fractionation factor between DIC and calcite, and/or kinetic effects from calcite precipitation. Note that this assessment of $\Delta^{13}C_{m-e}$ values uses the fractionation factor of Romanek et al. (1992), which determined an invariant CaCO₃-HCO₃⁻ 'enrichment factor', $\varepsilon_{\text{calcite}-\text{HCO3-}}$ (where $\varepsilon = (\alpha - 1)^*$ 1000), of $\sim 1\%$ for the temperature range of 10–40 °C. Recent studies suggest that the enrichment factor may be



Fig. 7. Surface air temperature and cave-air pCO_2 (top panel), and drip rate and $\delta^{13}C_{cc}$ (bottom panel, note $\delta^{13}C_{cc}$ axis is inverted) for site D-ISST-I. Results indicate that $\delta^{13}C_{cc}$ values (collected from center plate samples) were modulated by drip rate under low pCO_2 conditions. The highest $\delta^{13}C_{cc}$ values occurred when pCO_2 and drip rate were both at a minimum (e.g., January of 2004, 2006, 2007 and 2008). Cave-air pCO_2 is strongly seasonal in nature, whereas both drip rate and $\delta^{13}C_{cc}$ depict greater inter-annual variability. After applying a 5-point moving average to smooth high-frequency variations in the data, $\delta^{13}C_{cc}$ and drip rate yielded $r^2 = 0.58$ (Fig. 8), and between $\delta^{13}C_{cc}$ and cave-air pCO_2 $r^2 = 0.02$ (Fig. A7, Supplementary Material). No drip rate data were recorded for this site prior to 2002, therefore we limited our comparison to contemporaneous $\delta^{13}C_{cc}$ values. The precipitation data are from archived NOAA principally through the Meteorological Assimilation Data Ingest System (MADIS) program, and were measured in nearby Georgetown, Texas.

temperature-sensitive, but the magnitude of this sensitivity has proven variable (Polag et al., 2010). Near zero values of ε may occur due to kinetic effects, such as rapidly precipitated calcite 'inheriting' the δ^{13} C values of drip water DIC (Mickler et al., 2004). Riechelmann et al. (2013) also highlighted difficulties in determining equilibrium versus disequilibrium conditions for calcite precipitation based on which fractionation factor was used. Ultimately, a reevaluation of the equilibrium fractionation factor and an assessment of kinetic fractionation between CaCO₃ and HCO₃⁻ may be necessary.

5.4. Implications for central Texas speleothem records

Two primary factors appear to control modern speleothem $\delta^{13}C_{cc}$ values in central Texas caves: (1) the $\delta^{13}C$ values of deep-rooted vegetation that define a vegetation

baseline; and (2) kinetic isotope effects leading to deviation from the vegetation baseline, mostly associated with degassing at variable t_{exp} and the gradient between cave-air pCO_2 and cave drip water DIC concentrations. Due to the deeprooted C₃ plant biasing effect on cave-air and drip water δ^{13} C values observed in this and a prior study (Breecker et al., 2012), speleothems may not quantitatively record small changes in relative abundances of C3 and C4 plants. In fact, speleothems may record C_3 to C_4 transitions only if the relative abundance of deep-rooted plants crosses below some undetermined threshold that would allow transfer of the signal from shallow-rooted plants to caves. A reduction in the surface coverage by deep-rooted vegetation would likely be manifested as a gradual (decadal to millennial) change in speleothem δ^{13} C values due to the slow overturn of organic matter deep in soils and epikarst (e.g., Dorale et al., 1992; Breecker et al., 2012).



Fig. 8. Measured drip rate and $\delta^{13}C_{cc}$ correlation statistics from plate calcite (center samples) collected at Inner Space Cavern (IS), determined by first performing a linear interpolation of the $\delta^{13}C_{cc}$ values to be contemporaneous with drip rate sampling dates (A), followed by a linear regression (B). After the interpolation, some artificial discrepancies arise in the interpolation where points have suffered from aliasing in the data due to no seasonal accumulation of calcite (e.g., summer/fall 2006). We resolve this in panel (C) the data were smoothed using a 5-point moving average to limit the high-frequency noise associated with the contrasting sampling methodologies, and again followed by a linear regression (D). The 5-point moving average represents a timeframe of approximately 4–5 months. In the context of the 6-year section of the plate calcite record the 4–5 month averaging represents smoothing over intervals of 5–7% of the time-series, and is intended to best divide the data into single-season intervals.

Alternatively, encroachment of deep-rooted species could be manifested rapidly (decadal or faster) in speleothem δ^{13} C values.

Generally speaking, a large-magnitude increase in speleothem δ^{13} C temporally may simply reflect the onset of more arid surface conditions, via one or some combination of the following: reduced drip rates, a change in the ventilation regime of the cave, decreases in the magnitude of photosynthetic discrimination by C₃ plants, and/or a change in the type of or complete/nearly complete loss of deep-rooted plants. Importantly, decreases in aridity in semiarid climates could favor C₄ grasses over deeply-rooted C₃ shrubs (e.g., Monger et al., 2009) and thus increases in the δ^{13} C values of vegetation baselines do not necessarily record increases in aridity. If they can be resolved analytically, shifts in speleothem δ^{13} C values of vegetation baselines will be best interpreted in the context of regional biomes and in conjunction with speleothem δ^{18} O values.

Coupled study of speleothem δ^{13} C and δ^{18} O values may help evaluate the mechanisms that could cause temporal changes in $\delta^{13}C_{cc}$ values. Changes in speleothem δ^{18} O values are generally interpreted to reflect changes in cave temperature, the δ^{18} O values of precipitation, and the degree of vadose groundwater evaporation (Mickler et al., 2006). The δ^{18} O of precipitation, in turn, may be affected by aridity, temperature and moisture sources, among other factors (e.g., Rozanski et al., 1993; Lachniet, 2009). For example, if a large decrease in speleothem δ^{18} O values were to be interpreted as an increase in cave temperature related to increased aridity, a synchronous increase in speleothem δ^{13} C values would be expected, assuming increased temperature resulted in more arid surface conditions and increased t_{exp} . The correlations (Bar-Matthews et al., 1999; Frumkin et al., 2000; Bar-Matthews et al., 2003; Genty et al., 2006; Mickler et al., 2006; Spötl et al., 2008), or lack thereof, between speleothem δ^{13} C and δ^{18} O values may limit the number of likely interpretations of a speleothem record.

The seasonal shifts of $\delta^{13}C_{cc}$ values in the ISST decadal record emphasize potential use as a chronological tool. Annual laminae in speleothems are commonly attributed to surface climate forcing (e.g., Baker et al., 2008). Common types of annual laminae include UV fluorescence, visible calcite banding, changes in trace-element ratios, and stable oxygen and carbon isotope variability (Johnson et al., 2006; Baker et al., 2008). Counting annual and subannual laminae allows for the estimation of speleothem growth rate at intervals of interest unresolvable by radiometric dating. In cases where the sampling resolution is sufficiently high to resolve these shifts, along with U-series geochronologic constraints supporting annual cycles, a complete cycle of positive to negative shifts in δ^{13} C values (VPDB) may be used as an indicator of annual laminae in temperate and subtropical speleothems. Recent advances in analytical methods have allowed measurement of speleothem stable isotopic compositions at 10 µm resolution at an uncertainty of $\pm 0.3\%$ for oxygen isotope values (2σ , Orland et al., 2009), allowing for resolution of sub-annual variations in stable isotopic compositions for some fastgrowing speleothems.

6. CONCLUSIONS

Long-term monitoring study of soil CO₂, drip water and speleothem calcite δ^{13} C indicates that the decomposition of, or respiration from, deep plant roots (if present) controls the δ^{13} C values of vadose groundwater entering central Texas caves NB and IS as drip water. Throughout the year, directly-sourced cave drip water (i.e., the drip water that resides in the cave atmosphere for less than 30 s prior to contacting a feature or artificial substrate) $\delta^{13}C_{HCO_3}$ values reflect $\delta^{13}C_s$ values under deep-rooted plants. This indicates that the epikarst zone in this region is likely functioning as an open system, allowing for equilibrium isotope exchange between groundwater and CO₂ respired in the soil horizon and the epikarst. Therefore vegetation defines "baseline" $\delta^{13}C$ values for water entering the caves.

Inside the caves, the kinetic isotope effects of CO2 degassing from cave drip water are an additional control on $\delta^{13}C_{HCO_{\overline{3}}}$ and thereby $\delta^{13}C_{cc}$. For all studied sites, $\delta^{13}C_{cc}$ values closely track the $\delta^{13}C_{HCO_{\overline{3}}}$ values of drip water, but the differences between contemporaneous $\delta^{13}C_{HCO_3}$ and $\delta^{13}C_{cc}$ values are variable. We suggest that largemagnitude variability of speleothem δ^{13} C records occurs by: (1) marked changes in surface vegetation in terms of C_3 rooting depth (as opposed to the ratio of C_3 versus C_4 biomass); (2) changes in t_{exp} as influenced by drip rate in the presence of a persistently low, albeit variable, pCO_2 environment; and/or (3) seasonal ventilation of the cave atmosphere. Low-resolution sampling of speleothems may not sufficiently disentangle these factors; however, sampling at a sub-annual resolution may be able to distinguish a vegetation baseline change from changes in t_{exp} . Therefore, temperate/subtropical speleothem δ^{13} C records may be used as a means of investigating paleo-aridity and the influence of climate change on vegetation. In cases where t_{exp} is sufficiently long, there exists the potential for seasonal cycles resulting from cave ventilation to be preserved in speleothem calcite δ^{13} C values, highlighting calcite δ^{13} C variability as a geochronological tool.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.gca.2014.07.027.

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