Oxygen isotopic fractionation between drip water and speleothem calcite: A 10-year monitoring study, central Texas, USA.

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Abstract

Speleothem $\delta^{18}O$ values can serve as a paleoclimate proxy, yielding information about past temperature and rainfall. An accurate determination of the equilibrium calcite-water oxygen isotopic fractionation factor and an assessment of kinetic isotopic fractionation are required for interpretation of speleothem $\delta^{18}O$ data. In this study, $\delta^{18}O$ values were measured for calcite deposited on artificial substrates at four sites in two central Texas caves monitored for over 10 years. The results are used to evaluate the equilibrium isotopic fractionation factor and the impact of climatic and hydrologic conditions on kinetic isotopic fractionation.

The $\delta^{18}O$ values of calcite from the four sites ranged from 24.8 ‰ to 26.7 ‰ (V-SMOW), and associated drip water values ranged from -4.6 ‰ to -3.9 ‰. A comparison of predicted equilibrium calcite $\delta^{18}O$ values, calculated using a commonly used isotopic fractionation factor, with measured values indicates that 94 % of the calcite samples are not in oxygen isotopic equilibrium with respect to their associated drip water. The departure from oxygen isotopic equilibrium (expressed as $\Delta^{18}O_{cc-e}$) ranges from -0.7 ‰ to 1.4 ‰. Three of the four drip sites yield similar linear relationships between $\Delta^{18}O_{cc-e}$ and water temperature (t_w), and can be collectively expressed as: $\Delta^{18}O_{cc-e} = 0.3\, t_w - 4.7$; $r^2 = 0.56$ (n = 93). Therefore, calcite deposited during time periods of lower t_w, lower cave-air CO_2 concentration and faster calcite deposition rates, have $\delta^{18}O$ values closer to equilibrium. This contradicts conceptual models, which predict that a faster calcite deposition rate leads to a *larger* departure of calcite $\delta^{18}O$ from equilibrium.

If slower calcite deposition indeed facilitates equilibrium fractionation (i.e., $\Delta^{18}O_{cc-e} \rightarrow 0$), then the results of this study support a larger than commonly accepted value for the equilibrium calcite-water oxygen isotopic fractionation factor. Adopting a larger published value for the fractionation factor yields negative $\Delta^{18}O_{cc-e}$ values of up to -2.4 ‰. These negative values cannot be explained by existing kinetic fractionation models. Alternatively, they may reflect the trapping of a calcite "surface layer" with a lower $\delta^{18}O$ value than that of calcite in isotopic equilibrium with ambient water. The relationship between deposition rates and $\Delta^{18}O_{cc-e}$ for this study is consistent with the same relationship using data for synthetic calcite from the literature. This relationship indicates a -0.8 ‰ shift of calcite $\delta^{18}O$ for every ten-fold increase in deposition rate at 5 to 25 °C at a pH of 8.3. The significant kinetic fractionation effects observed in this study warrant consideration in applying measured speleothem calcite $\delta^{18}O$ values to interpret past climate conditions.

1. Introduction

Speleothem oxygen isotopic compositions are commonly related to $\delta^{18}O$ values of cave drip water derived from surface rainfall. Rainfall $\delta^{18}O$ values, in turn, contain climate information (Dansgaard, 1964; Rozanski et al., 1993). Recent advances in speleothem $\delta^{18}O$ studies emphasize relative $\delta^{18}O$ shifts in time series and their implications for variations of rainfall amount and temperature (e.g., Hendy and Wilson, 1968; Dorale et al., 1992; Holmgren et al., 1995; Bar-Matthews et al., 1997, 1999; Asmerom et al., 2010). These two parameters can be further related to regional or global paleoclimate conditions, including: intensity of ENSO (e.g., Lachniet et al., 2004); frequency of tropical cyclones (Frappier et al., 2007); strength of the Asian and North American Monsoon (e.g., Wang et al., 2001; Cheng et al., 2007, 2009; Dong et al., 2010); position and strength of the polar jet stream (e.g., Asmerom et al., 2010); and positions of the Intertropical Convergence Zone (e.g., Shakun et al., 2007).

Speleothem $\delta^{18}O$ values are the end result of complex interactions of environmental processes in the ocean, atmosphere, soil zone, epikarst, vadose zone, and cave system. Valid interpretations of these data depend on knowledge of the relationship between $\delta^{18}O$ values of drip water and speleothem calcite (i.e., calcite-water oxygen isotopic fractionation). If equilibrium isotopic fractionation is achieved, a given speleothem $\delta^{18}O$ value can be used to calculate a drip water $\delta^{18}O$ value using the equilibrium isotopic fractionation factor α:

$$\alpha = R_{calcite} / R_{water} \quad (1)$$

where $R_{calcite}$ and R_{water} are the ratio of $N(^{18}O)/N(^{16}O)$ in calcite and water respectively (Coplen, 2011). The $N(^{18}O)$ and $N(^{16}O)$, in turn, are the numbers of ^{18}O and ^{16}O isotopes in the substance of interests. The value of α is temperature dependent and has been determined experimentally and theoretically (e.g., McCrea, 1950; O'Neil et al., 1969; Friedman and O'Neil, 1977; Kim and O'Neil, 1997).

Both the assumption of equilibrium isotopic fractionation, and the accepted nominal value of α have been previously questioned. Non-equilibrium oxygen isotopic fractionation (termed "Kinetic isotopic fractionation") in speleothem calcite has been observed (e.g., Fantidis and Ehhalt, 1970; Mickler et al., 2004, 2006). Several mechanisms have been proposed to explain kinetic isotopic fractionation (e.g., Hendy, 1971; Michaelis et al., 1985; Mickler et al., 2004, 2006; Dreybrodt and Scholz, 2011). In model studies, it is assumed that the evolution of oxygen isotopic distributions in the dissolved inorganic carbon species (DIC, e.g., HCO_3^-, CO_3^{2-}, H_2CO_3) in the solution is the primary control on kinetic calcite-water isotopic fractionation. These models are: 1) diminishing isotopic fractionation between calcite and DIC species with increasing calcite deposition rates (e.g., Mickler et al., 2004); 2) Rayleigh distillation of oxygen isotopes of DIC (Hendy, 1971; Mickler et al., 2004); and 3) water evaporation (Fornaca-Rinaldi et al., 1968; Hendy, 1971; Gascoyne, 1992). Model 1 suggests that rapid degassing of CO_2 and calcite deposition cause consumption of almost all DIC in the solution. Rapid

loss of DIC leads to calcite inheriting the $\delta^{18}O$ values of bulk DIC (the aggregate of all DIC species). At pH=8, the predominant DIC species in a water solution is HCO_3^-, thus, calcite will have $\delta^{18}O$ values similar to those of HCO_3^-. This would eliminate the isotopic fractionation between calcite and HCO_3^- that would occur if the isotopic exchange reaction were to proceed until equilibrium. Model 2 suggests that CO_2 degassing may cause temporary enrichment of ^{18}O in the remaining DIC because it preferentially removes ^{16}O. The magnitude of the ^{18}O enrichment in the eventual calcite may be mainly a competition between time needed for CO_2 degassing, calcite deposition, water replenishment, and water-DIC oxygen isotopic buffering that eliminates the aforementioned enrichment (e.g., Dreybrodt and Scholz, 2011). Model studies suggest that equilibrium fractionation is favored at slow calcite deposition rates, high ambient pCO_2, and small drip intervals (i.e., fast drip rate, Dreybrodt and Scholz, 2011). In model 3, water evaporation increases the $\delta^{18}O$ value of the remaining water, and thereby increases the $\delta^{18}O$ of DIC and calcite. It is important to note that all three models suggest that kinetic fractionation will result in calcite with a more positive $\delta^{18}O$ than equilibrium values. Models 1 and 2 also predict a closer approach to equilibrium $\delta^{18}O$ for calcite deposited at a slower rate (smaller amount of calcite deposition in a given period of time), at a high ambient pCO_2 and large drip interval.

Hendy (1971) proposed two tests based on the above assumption to assess the attainment of equilibrium calcite-water oxygen isotopic fractionation in speleothems: 1) invariability and lack of a progressive increase of $\delta^{18}O$ values along a single growth layer as one moves away from the growth axis; and 2) lack of covariation of $\delta^{18}O$ and $\delta^{13}C$ values along a single growth layer. The "Hendy test" has been widely applied in speleothem studies (e.g., Williams et al., 2005; Hodge et al., 2008; Moreno et al., 2010). Recent studies suggest, however, that even if a speleothem fails the Hendy test, calcite near the growth axis may still be in isotopic equilibrium with respect to drip water (Dorale and Liu, 2009; Dreybrodt and Scholz, 2011).

Recent findings from naturally-deposited (Coplen, 2007; Tremaine et al., 2011) and synthetic (e.g., Dietzel et al., 2009; Day and Henderson, 2011) calcite bring the commonly accepted equilibrium α value into question. Results of an oxygen isotope study of Holocene vein calcite from Devils Hole, Nevada (Coplen, 2007), suggested that the calcite-water equilibrium oxygen isotopic fractionation may be 1.5 ‰ larger at 25 °C than determined by O'Neil et al. (1969). Tremaine et al (2011) compiled measured cave speleothem calcite $\delta^{18}O$ values from the literature to obtain a regression line for $1000\ln\alpha$ vs. $10^3/T$ that lies between those of Kim and O'Neil (1997) and Coplen (2007). In a study of $\delta^{18}O$ values of synthetic calcite and associated reaction water, Dietzel et al. (2009) suggested that previously accepted α values may not represent true equilibrium isotopic fractionation because they were obtained from fast-growth synthetic calcite that was not in isotopic equilibrium with reaction water. Day and Henderson (2011) constructed a laboratory system simulating the cave environment with controlled temperature, ambient CO_2 concentration and drip intervals. They argued that the measured fractionation between calcite and water can be

explained by the larger fractionation factor of Coplen (2007) and a rate-dependent kinetic fractionation as suggested by Dietzel et al. (2009), although the design of the system does not eliminate the impact of water evaporation on eventual calcite $\delta^{18}O$.

In this study, calcite samples were collected from artificial glass substrates placed under four drip sites in two central Texas caves every 4 to 8 weeks between 1998 and 2008. The $\delta^{18}O$ values of these samples are presented and compared to expected equilibrium values calculated using associated $\delta^{18}O$ values and temperatures of the drip water (collected at the same locations where the calcite was deposited, Pape et al., 2010). The magnitudes of the differences (i.e., departure of measured calcite $\delta^{18}O$ from the expected equilibrium value) are discussed in the sequence: 1) the applicability of previously accepted values for α; 2) controlling factors on kinetic oxygen isotopic fractionation between calcite and water; 3) applicability of a published experimental relationship of rate-dependent kinetic fractionation from synthetic calcite; and 4) implications for paleoclimate studies using speleothem $\delta^{18}O$ records.

2. Hydrogeologic Setting

The study sites are in Inner Space Cavern (IS) and Natural Bridge Caverns (NB) in central Texas (Fig. 1a). Both caves are at the eastern edge of the Edwards Plateau, approximately 130 km apart. IS is located in Williamson County. Meteorological data (for the period of 1998-2008) from a nearby National Climatic Data Center (NCDC) weather station at Lake Georgetown (Cooperative station ID: 413507) indicates a mean annual temperature (MAT) of 19.8 °C, monthly mean temperatures (MMT) from 6.2 °C to 30.6 °C, and mean annual precipitation (MAP) of ~92 cm/year. NB is located in Comal County. A nearby NCDC weather station at New Braunfels (Cooperative station ID: 416276) indicates a MAT of 20.0 °C, MMT of 7.9-30.5 °C, and a MAP of ~84 cm/year.

Moisture in local rainfall for both caves is typically derived from the Gulf of Mexico, with occasional contributions from the eastern Pacific Ocean and land-recycled moisture (Carr, 1967; Larkin and Bomar, 1983). The wettest months, on average, are May, June and October. The $\delta^{18}O$ values of rain water collected at Austin (40 km southwest of IS) typically range from -7.3 ‰ to -1.1 ‰ with an average value of -4.1 ‰. Occasional moisture from Pacific tropical cyclones may produce rainfall with $\delta^{18}O$ values as negative as -12.6 ‰ (Pape et al., 2010). Ranges of summer and winter rainfall $\delta^{18}O$ values are indistinguishable. The median $\delta^{18}O$ value of summer rainfall (June-July-August) is -3.2 ‰, which is in contrast with a median winter rainfall value of -4.0 ‰ (December-January-February, Pape et al., 2010).

The drip sites studied are IS's Flowing Stone of Time (Site ISST, as in Banner et al., 2007) and Lake of the Moon (ISLM), and NB's Well Shaft (NBWS, located in the South Cave of NB) and Castle Table Top (NBCT, in the North Cave of NB). Physical and hydrogeologic aspects and meteorological conditions of the drip sites are listed in Table 2. There is clear seasonal ventilation of the sites, as demonstrated by low cave-

air CO_2 concentrations (< 1,000 ppm by volume) in the winter and high (> 2,000 ppm by volume) concentrations in the summer at all four sites (Table 2). The effect of ventilation on calcite deposition rates has been well documented at these site (e.g., Banner et al., 2007), whereby high concentrations of summer CO_2 inhibit calcite deposition from drip water.

Water supplying drip site ISST enters the cave at the ceiling, drops less than 0.3 m to a point on the northwest of the apex of the flowstone, then flows along the slope for ~1.5 m before dripping off the margin of the formation and falling ~1 m to the cave floor; it lands either on a substrate (for calcite collection) and runs off, or into a container (for water collection, Fig. 1b). At sites ISLM, NBCT and NBWS, water drops off the ceiling directly onto the substrate or into the collection container. The drip at site NBCT is complex in that water discharges from multiple, closely spaced (<10 cm) drips and falls a relatively long distance of ~10 m. This causes difficulty in collecting drip water from one unique drip consistently, and substrates placed at this site occasionally move a few cm due to the impact of the drip waters.

Water samples were collected at the same locations as the glass substrates. Drip water samples were collected every 4 to 8 weeks; collection procedures and $\delta^{18}O$ values are detailed in Pape et al. (2010). In contrast to surface rainfall, measured drip water $\delta^{18}O$ values are relatively invariable. For ISST and ISLM, most water $\delta^{18}O$ values are within the range of -4.4±0.2 ‰, while NBCT and NBWS water have $\delta^{18}O$ values of -4.3±0.2 ‰ (Table 3, Pape et al., 2010). Four additional ISST drip water samples were collected weekly from February 20th to March 20th of 2003, encompassing two rainfall events (Feb. 21st and Mar. 4th) that produced 28 mm and 44 mm of rainfall, respectively (NCDC). These drip water $\delta^{18}O$ values are -4.5 ‰, -4.6 ‰, -4.6 ‰ and -4.5 ‰, respectively (Pape et al., 2010). These values are within the aforementioned range of -4.4±0.2 ‰. The similarity suggests that drip waters are well homogenized with respect to $\delta^{18}O$ values and that significant variation of drip water $\delta^{18}O$ values between two consecutive measurements taken every 4 to 8 weeks seems unlikely. The mean values of -4.4 (IS) and -4.3 (NB) ‰ for drip water are more negative than the weighted average Austin rainfall $\delta^{18}O$ value of -4.1 ‰. This suggests that large rainfall events with more negative $\delta^{18}O$ values may have contributed proportionally more to the water reservoir of IS and NB sites, as has been found in multiple tropical settings (Jones and Banner, 2003).

3. Samples and Methods

The methods of collection and isotopic analyses of water samples were presented in Pape et al. (2010). Upon collection, an aliquot of drip water (several ml) was analyzed on site for pH and temperature using a Myron L Co. Ultrameter II 6P, which was calibrated before each trip.

Glass substrates (10 x 10 cm plates) were frosted using glass beads to facilitate calcite nucleation. The substrates were cleaned and placed under the drip site to receive drip water and calcite deposition following procedures detailed in Mickler et al. (2004) and Banner et al. (2007). Substrates were harvested and renewed every 4 to 8 weeks. Harvested

substrates were rinsed with DI water on site and dried in a laminar flow hood. The calcite deposition rate (in mg/day) for each substrate was determined by weighing the substrate before and after deployment. Weighing procedures and uncertainties are described in Banner et al. (2007). The deposition rate is also expressed as "R_c" (in μmol hr^{-1} m^{-2}) for some substrates. The calculation of R_c assumed 1) the surface area of each substrate is 100 cm^2 ($\pm 5\%$), and 2) calcite deposited on the substrates uniformly. The latter assumption has uncertainties due mainly to the uneven distribution of calcite on a typical glass plate substrate sample.

Sampling of the substrate calcite was carried out in a laminar flow hood, where ~200 μg of calcite was gently scraped off the surface. Sampling areas range from ~0.3 to ~10 cm^2, depending on the thickness of calcite. Up to sixteen samples were collected from different areas on each substrate to assess spatial variations in calcite $\delta^{18}O$. Because of inhibitive effects of high cave-air CO_2 concentration on calcite deposition during the summer months (Banner et al., 2007), substrates from these months have little to no calcite deposition. Therefore, some of these substrates were not sampled. On each substrate, samples collected within a 4×4 cm square area centered on the approximate impact point between the drip water and substrate are referred to as "center samples", and samples collected outside this area are termed "edge samples".

Isotopic analyses of calcite samples were carried out at the University of Texas at Austin (PRISM II dual-Inlet MS, Thermo Finnigan MAT 253), the Minnesota Stable Isotope Lab (Thermo Finnigan MAT 252), or the University of California at Davis (GV Instruments Optima) using the modified method of McCrea (1950). In summary, 100-200 μg of calcite powder was reacted with 100 % H_3PO_4 at elevated temperature (70-90 °C). The resultant gaseous mixture of H_2O and CO_2 was cryogenically separated, and CO_2 was transferred into the mass spectrometer for measurement of $\delta^{18}O$ values. The long term average value of NBS-19 in the Minnesota Stable Isotope Lab is -2.24 $\pm$ 0.10 (2σ) ‰ (V-PDB) for $\delta^{18}O$. Eleven NBS-19 standards were run with the samples at University of California Davis and have a mean value of -2.20 $\pm$ 0.12 ‰ for $\delta^{18}O$ (V-PDB). Fifteen NBS-19 standards were run with the samples at the University of Texas Austin and have a mean value of -2.20 $\pm$ 0.12 ‰ for $\delta^{18}O$ (V-PDB). Isotopic results are reported relative to V-PDB standard (Vienna Pee Dee Belemnite, Craig, 1957) by individual laboratories on a normalized scale such that $\delta^{18}O$ of NBS-19 is -2.2 ‰. These results were converted to V-SMOW/SLAP (Vienna Standard Mean Ocean Water, Standard Light Antarctic Precipitation, Gonfiantini, 1978) using the following equation (Coplen et al., 2002):

$$\delta_{V\text{-}SMOW} = 1.03091\delta_{V\text{-}PDB} + 30.91 \qquad (2)$$

Results are expressed on the normalized scale such that $\delta^{18}O$ of SLAP is -55.5 ‰ (Coplen, 1996).

The δ notation is defined as:

$$\delta = R_{sample} / R_{standard} - 1$$
$$(3)$$

For $\delta^{18}O$, R_{sample} and $R_{standard}$ are the isotopic ratios of $N(^{18}O)/N(^{16}O)$ in the sample and standard respectively (Coplen, 2011).

4. Results

All analyzed substrates from sites ISST (n = 77), NBCT (n=6) and NBWS (n=7) presented in this study were completely covered by calcite deposition. The petrographic characters of the substrate calcite are the same as those in Banner et al. (2007). There are growth patterns on many of the studied substrates. Thirteen of the ISST substrates (~30 %) display concentric, doughnut-shaped patterns. These patterns are not exclusive to a certain season. More than 30 of 46 substrates from ISLM display concentric patterns, whereby denser calcite deposition can be seen in a circular area with an approximate diameter of ~3-6 cm, centered on the impact points between drip water and substrates. Outside the circular area, there is little visible calcite deposition. The center area (~1-2 cm in diameter) of four NBWS substrates are covered by less calcite deposition than the remainder of the substrates.

Calcite $\delta^{18}O$ values ($\delta^{18}O_{cc}$) ranged from 24.8 ‰ to 26.7 ‰ for all samples (V-SMOW, Supplementary Table 1). The $\delta^{18}O_{cc}$ values of ISST center samples had the same range, with a mean of 25.6 ‰. ISLM center samples had a smaller range of 25.3 ‰ to 26.0 ‰. NBCT center samples ranged from 24.8 ‰ to 25.3 ‰, while NBWS center samples ranged from 24.9 ‰ to 26.1 ‰ (Table 3). Edge samples (mostly from ISST substrates) encompass the full range above. $\delta^{13}C$ results will be presented and discussed in a separate paper (Feng et al., in prep.).

Measured drip water temperatures (t_w) and $\delta^{18}O$ values ($\delta^{18}O_w$) are also listed in Table 3. In order to represent the temperature of calcite deposition, t_w is the average of the two water temperatures taken when the substrate was deployed and when it was collected. For ISST, t_w values ranged from 14.9 °C to 21.6 °C for the period of 2000-2008 (Fig. 2). A single low t_w value of 14.9 °C is 2.3 °C lower than the range of 61 other t_w measurements (mean value is 20.2 °C, standard deviation (S.D.) is 1.1 °C; Table 3) and was not associated with a decrease in surface air temperature. This erroneous value is not considered further. Similarly, a single low $\delta^{18}O_w$ value of -5.5 ‰ (for drip water collected in January of 2003) is ~1 ‰ more negative than all other values (mean value is -4.4 ‰, S.D. = 0.15), and was not associated with a large amount of rainfall or a more negative rainfall $\delta^{18}O$ value (Pape et al., 2010). This value is also likely erroneous and not considered further. For ISLM, t_w values ranged from 20.7 to 22.4 °C (Table 3). The narrower range is consistent with reduced ventilation and more stable conditions at this site. For NBCT and NBWS, measured t_w values ranged from 20.5 to 22.3 °C, and from 18.5 to 22.6 °C respectively. These ranges of t_w values at all drip sites are smaller than those of surface MMT (Table 2). Calculated calcite deposition rates range from 0.45 mg/day to 106 mg/day (Table 3), with higher rates occurring in the winter months at all four sites when the caves were well ventilated (Banner et al., 2007).

5. Discussion

There is no statistically significant relationship between measured $\delta^{18}O_{cc}$ values and cave-air CO_2 concentration, t_w, or drip interval (t_d). In this discussion, measured $\delta^{18}O_w$ values of associated drip water (Pape et al., 2010) and t_w are used to calculate equilibrium, or $\delta^{18}O_e$, values for substrate calcite with the commonly accepted equilibrium

fractionation factor (α) of Kim and O'Neil (1997). These calculated equilibrium $\delta^{18}O_e$ values are subsequently compared to measured $\delta^{18}O_{cc}$ values to assess if substrate calcite was deposited in isotopic equilibrium with associated drip water. The *magnitude* of the difference between $\delta^{18}O_{cc}$ and $\delta^{18}O_e$ (termed "$\Delta^{18}O_{cc-e}$", calculated as $\delta^{18}O_{cc}-\delta^{18}O_e$, Table 1) is used to assess the control of calcite-water kinetic isotopic fractionation.

5.1 Equilibrium status of measured calcite $\delta^{18}O_{cc}$

Measured isotopic fractionation (α_m) can be calculated for the studied substrate calcite (Table 1). On a plot of $1000\ln\alpha$ vs. t_w, results of this study from four different sites in NB and IS yield no significant linear relationship. The results plot away from the "equilibrium lines" predicted by previously published "equilibrium" isotopic fractionation factors (e.g., Friedman and O'Neil, 1977; Kim and O'Neil, 1997; Coplen, 2007; Tremaine et al., 2011; Fig. 3). These two observations indicate the influence of kinetic oxygen isotopic fractionation in the studied substrate calcites.

To quantitatively assess the kinetic fractionation, the departures of the measured calcite $\delta^{18}O_{cc}$ from predicted equilibrium values were calculated using the following approach. If calcite was deposited in oxygen isotopic equilibrium with the associated drip water, its $\delta^{18}O$ value ($\delta^{18}O_e$) can be predicted using water $\delta^{18}O$ values ($\delta^{18}O_w$) and the calcite-water equilibrium oxygen isotopic fractionation factor (α). Values of α have been obtained by experimental studies (McCrea, 1950; O'Neil et al., 1969; Friedman and O'Neil, 1977; Tarutani et al., 1969; Kim and O'Neil, 1997; Jiménez-López et al., 2001; Beck et al., 2005; Dietzel et al., 2009) or theoretical calculations (Kieffer, 1982; Dove et al., 1992; Watson, 2004; Chacko and Deines, 2008). Among published results, the equation given by Kim and O'Neil (1997) is commonly used:

$$1000\ln\alpha = 18.03 \times 10^3\, T^{-1} - 32.42 \quad (4)$$

where T is temperature in Kelvin. Eq. 4 was acquired using an acid-fractionation factor of 1.01050 at 25 °C (Kim and O'Neil, 1997), as opposed to the commonly accepted value of 1.01025 (Friedman and O'Neil, 1977). Some studies have applied a 0.25 ‰ correction to the constant of 32.42 (e.g., Zhou and Zheng, 2003); such a correction does not affect the discussion below. Calculated $\delta^{18}O_e$ values range from 24.6 ‰ to 25.1 ‰ (ISST, n=62), 24.6 ‰ to 24.9 ‰ (ISLM, n=8), 24.3 ‰ to 25.4 ‰ (NBWS, n=7), and 24.6 ‰ to 25.0 ‰ (NBCT, n=6). Some of the $\delta^{18}O_e$ values for ISST and ISLM were calculated using an assumed $\delta^{18}O_w$ of -4.4 ‰ when no measured value was available (Table 3). This nominal value was selected based on the observation that ISST drip water samples had mostly invariable $\delta^{18}O_w$ values for the period of 2000-2004 (Pape et al., 2010).

The calculated $\delta^{18}O_e$ values would be identical with measured $\delta^{18}O_{cc}$ values, i.e., $\Delta^{18}O_{cc-e} = 0$, if the studied substrate calcite was in equilibrium with drip water, while non-zero $\Delta^{18}O_{cc-e}$ values outside of analytical uncertainty are indicative of kinetic isotopic fractionation. The $\Delta^{18}O_{cc-e}$ values of the studied substrate calcite are listed in Table 3 and range from -0.7 ‰ to 1.4 ‰ (Table 3). The calcite from all but six substrates display kinetic fractionation with the associated drip water ($|\Delta^{18}O_{cc-e}| > 0.1$ ‰).

The largest $\Delta^{18}O_{cc-e}$ data set (ISST, n=62) was examined as a time series and compared to meteorological parameters inside and outside the cave (Fig. 2) to explore possible causes of kinetic fractionation between $\Delta^{18}O_{cc-e}$ and associated drip water. While there is no apparent correlation between $\Delta^{18}O_{cc-e}$ and water chemistry, such as Ca^{2+} concentration ($r^2 = 0.01$), the $\Delta^{18}O_{cc-e}$ and t_w (Fig 2) show similar time-series variations, and are linearly correlated (Fig. 4):

$$\Delta^{18}O_{cc-e} = 0.3\, t_w - 5.1; \quad r^2 = 0.56 \quad (5a)$$

Similar correlations were also observed for ISLM and NBWS samples:

$$\text{ISLM}: \quad \Delta^{18}O_{cc-e} = 0.3\, t_w - 5.6; \quad r^2 = 0.49 \quad (5b)$$

$$\text{NBWS}: \quad \Delta^{18}O_{cc-e} = 0.2\, t_w - 3.4; \quad r^2 = 0.45 \quad (5c)$$

Collectively, results from ISST, ISLM and NBWS yield:

$$\Delta^{18}O_{cc-e} = 0.3\, t_w - 4.7; \quad r^2 = 0.56 \quad (5d)$$

The lack of significant correlation between $\Delta^{18}O_{cc-e}$ and t_w for NBCT calcite may be attributed to the aforementioned unique characteristics of this particular site, which makes the location of the substrate's center of calcite deposition difficult to identify. If there were differences in $\delta^{18}O$ values between center and edge calcite sample, the NBCT results in Table 3 may not represent the center calcite $\delta^{18}O$ values and may not yield a true relationship between $\Delta^{18}O_{cc-e}$ and t_w. For the other three sites, the similarity of both slopes and intercepts indicates that the mechanism controlling the kinetic effects acts on scale greater than an individual drip site. While there is insufficient evidence to suggest a cause and effect between t_w and $\Delta^{18}O_{cc-e}$, Eq. 5a-d describes a temporal correlation between the two. It shows that, using the α values of Kim and O'Neil (1997), calcite of closer-to-equilibrium $\delta^{18}O_{cc}$ was deposited *during periods of low t_w* (in the winter), when cave-air CO_2 concentrations are low, and calcite deposition is relatively rapid. Similarly, Eq. 5d indicates that calcite with further-from equilibrium $\delta^{18}O_{cc}$ was deposited *during periods of high t_w* (in the summer), when cave-air CO_2 concentrations are high, and calcite deposition is slow in rate and low in magnitude (see Banner et al., 2007 for the impact of cave ventilation on the cave-air CO_2 concentration and calcite deposition rate). This observation is further strengthened 1) by the similarities in slopes and intercepts among different sites from different caves, and 2) because the slow-depositing ISLM calcite (Banner et al., 2007) has $\Delta^{18}O_{cc-e}$ values indicating further departure from equilibrium (Fig. 4). This observation contrasts with most

published conceptual models of calcite-water kinetic fractionation (e.g., Hendy, 1971; Mickler et al., 2004). These models predict a closer-to-equilibrium calcite $\delta^{18}O_{cc}$ for a slower calcite deposition rate (smaller amount of calcite deposition in a given period of time) and high ambient CO_2, while further departure from equilibrium (a larger $\Delta^{18}O_{cc-e}$) occurs at fast calcite deposition and low ambient CO_2.

Water evaporation is not an important factor in this discussion for several reasons. First, this study compares water collected just before it strikes the substrate (Fig. 1b). Any evaporation effect would be limited to that occurring while the water is resident on the substrate. The maximum possible effect of evaporation during this residence can be estimated by assuming $RH = 81\%$ (the minimum value associated with the caves), an air velocity of 5 cm/s, air and water temperatures of 20 °C, a 300 μm water thickness on the substrate, a drop size of 0.1 ml, and a 63 second drip interval (the maximum observed during the study period). Using these conditions, the equation of Carrier (1918) shows that evaporation would remove ~11 mg or 0.37% of the water on the substrate in the time between each drip. Assuming 1) Rayleigh fractionation and an equilibrium water-water vapor oxygen isotopic fractionation factor of 1.0098, 2) repeated 63 second evaporation intervals, and 3) thorough mixing of a 0.1 ml drip every 63 seconds, evaporation would yield a maximum enrichment of ~0.05‰ in $\delta^{18}O_w$ when the system reaches steady-state. This enrichment is within the analytical precision. Furthermore, the above estimate represents an extreme scenario, as air velocities at the studied sites are below detection, and the average t_d values for each sites is much smaller than the value used in the estimate and do not vary significantly from summer to winter (Table 2, average t_d values are 1.5 s for ISST, 0.5 s for NBCT, 0.9 s for NBWS, 16 s for ISLM). Therefore the extent of water evaporation is likely 4 to 130 times smaller than that estimated above. Additionally, the $\Delta^{18}O_{cc-e}$ value is much less affected by water evaporation than $\delta^{18}O_{cc}$, because evaporation results in increases in both water and calcite $\delta^{18}O$ values. For an increase of Δ in water $\delta^{18}O_w$ by evaporation, calcite $\delta^{18}O$ will increase by an amount $\alpha * \Delta$. The impact of evaporation on the value of $\Delta^{18}O_{cc-e}$ would be $(\alpha_m - \alpha)\Delta$. Here, α is the equilibrium fractionation factor, while α_m is the measured fractionation factor (Table 1). The values of $(\alpha_m - \alpha)$ for the studied substrate calcite range from -0.0004 to 0.0014 (Table 3). If evaporation was responsible for the observed $\Delta^{18}O_{cc-e}$ of up to 1.4 ‰, Δ would be *at least* 1000 ‰, which is very unlikely.

5.2 Re-evaluating the calcite-water equilibrium isotopic fractionation factor

If slower calcite deposition rates (during periods of higher CO_2 and t_w) indeed facilitate equilibrium fractionation, the calcite from the present study with slower deposition rates should have smaller $\Delta^{18}O_{cc-e}$ values that are close to zero, instead of the observed positive values (Table 3). Since the $\Delta^{18}O_{cc-e}$ values are calculated using measured $\delta^{18}O_{cc}$ and $\delta^{18}O_w$ values, and the assumed α of Kim and O'Neil (1997), it is likely that this commonly accepted α value is too small to describe the calcite-water equilibrium oxygen isotopic fractionation in these natural low temperature cave environments. As noted earlier, several recent studies have

reached similar conclusions. Coplen (2007) measured $\delta^{18}O$ of naturally deposited slow-growth Holocene vein calcite in Devils Hole, Nevada. The results suggest that the commonly accepted equilibrium oxygen isotopic fraction of O'Neil et al. (1969) might be 1.5 ‰ too low at 25 °C. Tremaine et al (2011) compiled published speleothem calcite studies and proposed a fractionation factor that is between those of Kim and O'Neil (1997) and Coplen (2007), although evidence is not presented that those speleothems were deposited in oxygen isotopic equilibrium with their associated drip waters. Dietzel et al. (2009) experimentally synthesized calcite by spontaneous deposition at relatively slow rates. These authors examined postulated the oxygen isotopic fractionation between the resultant calcite and the reaction water and concluded that the "equilibrium oxygen isotopic fractionation factor might be greater than the commonly accepted value". Day and Henderson (2011) studied slowly deposited calcite in a simulated cave environment with controlled ambient CO_2, drip interval, and air temperature. The resultant calcites have $\delta^{18}O$ values more positive than predicted by the α of Kim and O'Neil (1997), which prompted Day and Henderson (2011) to adopt the larger α of Coplen (2007). However, because the water analyzed by Day and Henderson (2011) was not collected at the same place where the drip hits the calcite deposition surface, the effect of evaporation was unconstrained.

The present study compares measured $\delta^{18}O$ values of substrate calcite and associated drip water at a high temporal resolution in two natural caves. The results are in accord with findings of Coplen (2007), Tremaine et al (2011), Dietzel et al. (2009) and Day and Henderson (2011) in that they support a larger equilibrium α value at 20°C, which is the approximate deposition temperature of the studied substrate calcites. The revised fractionation factor of Coplen (2007) is hereafter adopted as a working model:

$$1000 \ln \alpha = 17.4 \times 10^3 \, T^{-1} - 28.6 \quad (6)$$

Eq. 6 was proposed for the temperature range of 13 to 40 °C, and was obtained using a measured equilibrium α value of 1.0285 ± 0.0001 at 33.7 °C and a commonly accepted $d\alpha/dT$ value of -0.0002 K^{-1} (Epstein et al., 1953). Using Eq. 6, the $\Delta^{18}O_{cc-e}$ values were recalculated for studied substrate calcites (expressed here as $\Delta^{18}O_{cc-e}{}^{\#}$, and listed in Table 3). These values range from -2.4 ‰ to -0.4 ‰. For each substrate, the $\Delta^{18}O_{cc-e}{}^{\#}$ value is more negative than the $\Delta^{18}O_{cc-e}$ value calculated using Eq. 4. All samples still have non-zero $\Delta^{18}O_{cc-e}{}^{\#}$ values (Table 3), which suggests that kinetic oxygen isotopic fractionation remains a significant factor. Using the proposed equilibrium fractionation factor of Tremaine et al. (2011), instead of Coplen (2007), would yield smaller, but still none-zero and mostly negative, $\Delta^{18}O_{cc-e}$ values (Fig. 3).

5.3 Mechanisms for negative departure from equilibrium $\delta^{18}O$

The $\Delta^{18}O_{cc-e}{}^{\#}$ values calculated using the fractionation factor of Coplen (2007) are all negative. This is in contrast to the predictions of existing kinetic fractionation models (three models as described in Introduction section), none of which

yields a negative $\Delta^{18}O_{cc-e}{}^{\#}$ value. Therefore, other mechanism(s) must be responsible for the observed negative $\Delta^{18}O_{cc-e}{}^{\#}$ values.

Consistent with the results of Dietzel et al (2009), the results of the current study support the hypothesis that a negative $\Delta^{18}O_{cc-e}{}^{\#}$ value may be a result of entrapment formation of calcite as proposed by Watson and Liang (1995) and Watson (1996, 2004). This model suggests that a thin, nanometer-scale layer of calcite exists at the mineral surface. Because this surface layer is primarily formed by attachment of $CO_3{}^{2-}$ and Ca^{2+} (Watson, 2004, Dietzel et al., 2009), it may have a $\delta^{18}O$ value similar to that of $CO_3{}^{2-}$ in the solution, which is 6.8 ‰ more negative than the inner lattice (Watson, 2004). When the mineral grows, a new surface layer forms, and the former surface layer is trapped in the inner lattice (Fig. 5). Subsequently, isotopic exchange between the inner lattice and former surface layer occurs via slow ion diffusion, and will evolve the $\delta^{18}O$ of the former surface layer to a high value that is in equilibrium with bulk DIC and water. If calcite deposition rates are sufficiently high, however, such exchange will be limited and therefore the relatively low $\delta^{18}O$ values of the surface layer would be preserved. It can be speculated that the maximum negative shift of calcite $\delta^{18}O_{cc}$ from the equilibrium value would be expected when a calcite crystal is completely composed of multiple trapped "surface layers". This maximum negative shift may therefore be approximated as the value of equilibrium isotopic fractionation between calcite and $CO_3{}^{2-}$ ($\Delta^{18}O_{CC-CO_3{}^{2-}}$), which would be 5.6 ‰ at 20 °C. (Beck et al., 2005; Coplen, 2007).

5.4 Correlation between $\Delta^{18}O_{cc-e}{}^{\#}$ and calcite deposition rate

Both the model study of Watson (2004) and the experimental study of Dietzel et al. (2009) suggest that the magnitude of $\Delta^{18}O_{cc-e}$ may be related to the deposition rate (R_c). Dietzel et al. (2009) further demonstrated linear relationships between the kinetic calcite-water oxygen isotopic fractionation and R_c. These relationships, if confirmed, may be useful in adjusting speleothem $\delta^{18}O$ records to enable more accurate interpretation.

Such relationships are difficult to obtain from the data of the current study, because R_c is not the only factor affecting the eventual calcite-water oxygen isotopic fractionation. For example, the experimental results of Dietzel et al. (2009) demonstrated an impact of solution composition on kinetic fractionation at higher deposition rate. Other factors may include ambient air CO_2 concentration and drip interval (Dreybrodt and Scholz, 2011). The substrate calcite of the current study was deposited in a much less constrained environment. Variable water pH, t_w, and drip interval, together with uncertainties related to the calculation of R_c (see section 3. Samples and Method), make a precise rate-dependent fractionation factor difficult to determine. A linear regression between $\Delta^{18}O_{cc-e}{}^{\#}$ and R_c is not statistically significant. However, it is possible to compare the results of the current study to the experimental study of Dietzel et al. (2009) to assess the applicability of a $\Delta^{18}O_{cc-e}$ - R_c relationship based on measurements of synthetic calcite to results from a natural cave environment.

Dietzel et al. (2009) synthesized calcite at a range of deposition rates ($1.8 < \log R_c < 4.4$ μmol m^{-2} h^{-1}), pH (8.3-10.5) and temperatures (5 °C, 25 °C and 45 °C). The study did not yield a calcite sample in isotopic equilibrium. To calculate $\Delta^{18}O_{cc-e}$ values for the synthetic calcite, an expected $\delta^{18}O_e$ value must be determined for the experimental temperature. In this study, the equilibrium fractionation factor of Coplen (2007) was adopted to calculate $\delta^{18}O_e$ and $\Delta^{18}O_{cc-e}$ for 25 °C and pH=8.3 (commonly observed in cave environments). In a plot of $\Delta^{18}O_{cc-e}$ vs. R_c, a linear regression yields (Fig. 6a):

$$\Delta^{18}O_{cc-e} = -0.77 \log R_c \qquad r^2=0.70, \quad n=12 \qquad (7)$$

It was not possible to calculate an exact $\Delta^{18}O_{cc-e}$ vs. $\log R_c$ relationship for 5°C because Eq. 6 is only applicable to temperatures of 13-40 °C (Coplen, 2007). Nevertheless, the results of Dietzel et al. (2009) suggest that for both 5 °C and 25 °C, the regression slopes for plots of $\Delta^{18}O_{cc-e}$ vs. $\log R_c$ would be similar. If this inference is correct, then the slope of Eq. 7, i.e., $\Delta^{18}O_{cc-e}$ / $\log R_c$, suggests that at a pH of 8.3 and temperatures of 5 to 25 °C, every ten-fold increase in R_c may cause an approximately -0.8 ‰ shift in the calcite $\delta^{18}O$ value without a change in the drip water $\delta^{18}O$ value. There is considerable scatter in the data of Dietzel et al. (2009). Examining individual samples indicates the values of $\Delta^{18}O_{cc-e}/\log R_c$ ranged from -1.1 to -0.3 ‰ (Fig. 6b).

Using data of the current study, the departure of $\delta^{18}O_{cc}$ from the equilibrium value for every ten-fold increase of deposition rate can be calculated as $\Delta^{18}O_{cc-e}{}^{\#}$ / $\log R_c$ for each of the studied substrates (Table 3). Substrates of this study have $\Delta^{18}O_{cc-e}{}^{\#}$ / $\log R_c$ values that ranged from -0.8 ‰ to 0 ‰ (for ISST, average -0.4 ‰, n=53), -0.7 ‰ to -0.2 ‰ (for ISLM, average -0.4 ‰, n=18), -0.9 ‰ to -0.3 ‰ (for NBCT, average -0.5 ‰, n=6), and -0.7 ‰ to -0.3 ‰ (NBWS, average -0.5 ‰, n=7) These ranges are comparable to each other, and to the range of -1.1 to -0.3 ‰ for the synthetic calcite of 25 °C experiments (Fig. 6b, Dietzel et al., 2009). The mean values of -0.4 ‰ (ISST, ISLM) and -0.5 ‰ (NBCT, NBWS) are smaller (in absolute value) than -0.8 ‰ suggested by Eq. 7, although the maximum value of -0.8 ‰ is identical. The smaller $\Delta^{18}O_{cc-e}{}^{\#}/\log R_c$ of this study may be a result of lower pH values for the drip water (6.8-8.4, Table 2), the effects of which is demonstrated in the experimental study of Dietzel et al. (2009). Based on the agreement among different natural drip sites (this study), and with the results of synthetic calcite (Dietzel et al., 2009), it is speculated that both the negative shifts of $\delta^{18}O_{cc}$ from equilibrium values and the quantitative impact of calcite deposition rates on the kinetic fractionation (-0.8 ‰ / $\log R_c$) may be applicable to other settings.

5.5 Spatial variations of calcite $\delta^{18}O$ values on substrates

Center samples have more negative $\delta^{18}O_{cc}$ values than edge samples for each individual substrate (Fig. 7, Table 4). A similar center-to-edge trend was previously observed in substrate calcites grown over 12-18 months in a cave in Barbados, West Indies (Mickler et al., 2004, 2006). The maximum center-to-edge $\delta^{18}O_{cc}$ shift measured for each of the 65 substrates range from 0 to 1.4 ‰, although these values may

not represent the true maximum differences due to potential sampling bias. The 40 % of the substrates show no difference within analytical uncertainty, while 30 % show a difference of up to 0.3 ‰.

The observed center to edge shifts could be due to slower calcite deposition at the edge than at the center. The water film at the edge of the substrates may contain less Ca^{2+} and DIC due to longer exposure to the cave-air and earlier calcite deposition in the center. Slower deposition rates may result in calcite with more positive $\delta^{18}O_{cc}$ than the center sample (i.e., Dietzel et al., 2009). However, DIC loss in the water film is likely small, (Feng et al., in prep). Similar center to edge positive shifts are observed for the $\delta^{13}C$ of substrate calcite (Feng et al., in prep). Because water evaporation does not affect the carbon isotopic distribution among DIC species, these $\delta^{13}C$ and $\delta^{18}O$ shifts from center to edge indicate a negligible role for water evaporation in determining the isotopic compositions

5.6 Implications for paleoclimate studies based on speleothem $\delta^{18}O$ records

Results of this study suggest that the fractionation factor of Coplen (2007) may better describe the calcite-water equilibrium oxygen isotope fractionation for low temperature environments. At 13-40 °C, this fractionation factor indicates a ~1.5 ‰ larger calcite-water fractionation than that predicted by the previously accepted equilibrium fractionation factors of O'Neil et al. (1969) and Kim and O'Neil (1997). The current study supports the entrapment formation of calcite and a control of calcite deposition rate in leading to negative departures of calcite $\delta^{18}O$ from the equilibrium value (Watson, 2004; Dietzel et al., 2009). Results of the current study support the experimental study of synthetic calcite (Dietzel et al., 2009), which indicates a -0.8 ‰ shift of calcite $\delta^{18}O$ value for every ten-fold increase in calcite deposition rate at 25 °C and a pH of 8.3. These results lead to several important implications for paleoclimate studies based on speleothem $\delta^{18}O$ records.

5.6.1 Paleo-rainfall $\delta^{18}O$ values inferred from speleothem $\delta^{18}O$ values

Similar to modern rainfall, paleo-rainfall $\delta^{18}O$ values can be affected by multiple factors, such as distance from the moisture source (i.e., continental effect), amount of rainfall, temperature, altitude, and seasonality (e.g., Dansgaard, 1964; Rozanski et al., 1993). Stable isotope variations of near-surface materials such as paleosols (e.g., Yapp, 1993, 2008; Feng and Yapp, 2009) and speleothems (e.g., Dorale et al., 1992) may serve as proxies for contemporaneous rainfall $\delta^{18}O$ values and climate conditions. The two common methods of inferring paleoclimate conditions from speleothem calcite $\delta^{18}O$ are: 1) solving the equation for equilibrium isotopic fractionation (e.g., Eqs. 4, 6) for cave-air temperature using measured speleothem $\delta^{18}O$ values and independently estimated $\delta^{18}O_w$ values (e.g., Gascoyne, 1992); 2) using measured speleothem $\delta^{18}O$ values and independently estimated temperature to calculate paleo-water $\delta^{18}O_w$ values, which can be related to surface temperature or amount of rainfall (e.g., Hendy and Wilson, 1968; Bar-Matthews et al., 2003). For these quantitative calculations of

paleoclimate conditions, the calcite-water oxygen isotopic fractionation factor is essential.

If the equilibrium calcite-water oxygen isotopic fractionation is indeed ~1.5 ‰ larger than commonly assumed for commonly observed temperatures (Coplen, 2007; Dietzel et al., 2009; this study), the paleo-rainfall $\delta^{18}O$ value inferred from a given speleothem calcite sample would be ~1.5 ‰ more positive than that calculated using previously accepted equilibrium fractionation factors (e.g., O'Neil et al., 1969; Kim and O'Neil, 1997), thereby impacting paleoclimate inferences. Taking the speleothem $\delta^{18}O$ geothermometer as an example (method 1 above), a temperature calculated using a larger value for α would be ~7 °C warmer than that calculated using previously accepted values for α. In method 2 above, a larger α would result in a ~1.5 ‰ more positive value for the inferred rainfall $\delta^{18}O$ (in contrast to using Eq. 4). Using a meteoric water $\delta^{18}O$- temperature relationship of -0.58 ‰/°C (Rozanski et al., 1993), more positive rainfall $\delta^{18}O$ values would lead to a 3 °C underestimation of the temperature calculated using the equilibrium isotopic fractionation factor of Kim and O'Neil (1997). Similarly, using a $\delta^{18}O$ - rainfall amount relationship of -1.0 ‰ / 200 mm (Bar-Matthews et al., 2003), a 1.5 ‰ more positive water $\delta^{18}O$ value would lead to 300 mm underestimation of local annual rainfall amount.

Negative shifts of $\delta^{18}O$ due to kinetic calcite-water isotopic fractionation, as observed in all substrate calcite of the current study, may also contribute to inaccurate estimates of climatic conditions using speleothem $\delta^{18}O$ values. Again, using the speleothem calcite $\delta^{18}O$ geothermometer as an example, if speleothem calcite $\delta^{18}O$ values are more negative than equilibrium values due to faster deposition, the inferred contemporaneous water $\delta^{18}O$ value would also be more negative. This would result in an underestimation of temperature or overestimation of local rainfall amount.

5.6.2 Non-climate driven $\delta^{18}O$ shifts in speleothem time series

In paleoclimate studies, negative shifts of speleothem $\delta^{18}O$ values in a time series are commonly interpreted as an indication of 1) wetter climate conditions due to the "amount effect" (e.g., Bar-Matthews et al., 1997, 1999; Wang et al., 2001; Frappier et al., 2007; Asmerom et al., 2007, 2010; Cheng et al., 2009; Wagner et al., 2010), and/or 2) warmer temperatures (e.g., Hendy and Wilson, 1968; Dorale et al., 1992; Holmgren et al., 1995; Lauritzen, 1995). These interpretations are based on the premise that for a given speleothem, $\delta^{18}O$ values of all calcite samples are related to contemporaneous surface rainfall $\delta^{18}O$ values by either the equilibrium fractionation factor, or by a common kinetic fractionation factor. Results from this study indicate that this interpretation may not always be valid, because kinetic calcite-water isotopic fractionation is observed for a wide range of deposition rates and varies with deposition rates. Therefore, a speleothem with a varying growth rate history can display variations in a $\delta^{18}O$ time series with no changes in the $\delta^{18}O$ value of corresponding drip water.

During the last glacial period, the climate of the southwestern U.S. has been inferred to have been much wetter

compared with present day (Toomey et al., 1993; Musgrove et al., 2001; Asmerom, et al., 2007, 2010; Wagner et al., 2010). During this period, speleothem growth rates were up to two orders of magnitude faster than during the Holocene (Musgrove, 2000; Musgrove et al., 2001; Asmerom et al., 2010; Wagner et al., 2010). Based on the relationship determined in Eq. 7, this growth rate increase could have caused up to a -1.6 ‰ shift in speleothem $\delta^{18}O$ values independent of variations in surface rainfall $\delta^{18}O$ values. Because growth rate variations in speleothems are common and span several orders of magnitude (e.g., Musgrove et al., 2001), this is an important factor to consider when interpreting $\delta^{18}O$ shifts in a speleothem time series.

5.6.3 The Hendy Test

Previous studies have questioned the validity of using the Hendy test to assess if speleothem calcite has formed in oxygen isotopic equilibrium with its associated drip water (Mickler et al., 2006; Dorale and Liu, 2009). One concern is the difficulty of sampling calcite along a single growth layer (e.g., Dorale et al., 2009). Simulations have suggested (Dreybrodt and Scholz, 2011) that although drip water could gradually be enriched in ^{18}O while on a speleothem surface, the enrichment may not be recorded in calcite deposited near the growth axis. This is because at a site with rapidly dripping water, water on the speleothem surface is rapidly replaced by new water. Therefore, calcite near the growth axis is always deposited from newly arrived drip water, and the ^{18}O enrichment in the "old water" is not recorded in the growth-axis calcite (e.g., Dreybrodt and Scholz, 2011). Furthermore, some speleothem calcite studies show negative shifts of calcite $\delta^{18}O$ values along a growth layer, away from the growth axis (e.g., Williams et al., 2005; Moreno et al., 2010).

Results of this study suggest that the model simulations of the evolution of oxygen isotopic distribution in DIC species which support the utility of the Hendy test do not account for all factors controlling kinetic calcite-water oxygen isotopic fractionation. The Hendy test does not account for the entrapment formation at the mineral surface and rate dependent kinetic fractionation, as suggested by Watson (2004) and supported by other studies (Dietzel et al., 2009, Day and Henderson, 2011, this study). As such, the Hendy test may not be valid for all speleothem studies.

One of the principal criteria of Hendy (1971) is that the invariability of calcite $\delta^{18}O$ values along a single growth layer implies attainment of equilibrium isotopic fractionation between calcite and water. If the calcite deposition rate is the primary control on kinetic oxygen isotopic fractionation, then invariable $\delta^{18}O$ values could indicate invariable calcite deposition rates along the growth layer. Invariable deposition rates along the growth layer, however, do not necessarily imply a *slow* calcite deposition rate, which is required for equilibrium isotopic fractionation.

6. Summary and Conclusions

Almost all calcite (94 %) deposited on artificial glass substrates for the period of 1998-2008 at four drip sites in two central Texas cave was not in oxygen isotopic equilibrium with associated drip water, based on the commonly accepted oxygen isotopic fractionation factor of Kim and O'Neil (1997). The magnitude of the departures from expected equilibrium values ($\Delta^{18}O_{cc-e}$) were mostly positive, and were positively correlated with temperature of associated drip water. The closer-to-equilibrium $\delta^{18}O$ values are achieved during time intervals when temperature and cave-air CO_2 is low and calcite deposition is rapid. This is in contrast to previously proposed kinetic fractionation mechanisms that predict a positive departure from equilibrium values at faster calcite deposition rates. These results indicate that a re-evaluation of equilibrium fractionation factors and the controlling factors on kinetic fractionation are required and lead to the following conclusions:

1. The commonly accepted equilibrium oxygen isotopic fractionation factor (Kim and O'Neil, 1997) between calcite and water may be too low at the studied temperature of ~20 °C, which is typical of many natural environments. Results of this study support the equilibrium fractionation factor of Coplen (2007), which predicts a ~1.5 ‰ larger equilibrium calcite-water oxygen isotopic fractionation at the studied temperature.

2. Observed negative departure of $\delta^{18}O_{cc}$ from equilibrium values can be explained by the surface attachment formation theory of Watson (2004). This negative shift may have an upper limit of -5.6 ‰. Therefore, variations of speleothem growth rates may cause shifts in speleothem calcite $\delta^{18}O$ values in the absence of changes in drip water $\delta^{18}O$ values. This has implications for paleoclimate studies based on oxygen isotope studies of speleothems.

3. Results of this study support the applicability of the published experimental study of synthetic calcite (Dietzel et al., 2009), which suggests a shift of about -0.8 ‰ in calcite $\delta^{18}O$ for every ten-fold increase in growth rate at 5-25 °C and a pH of 8.3.

4. The Hendy test may not adequately assess the attainment of oxygen isotopic equilibrium. Invariable $\delta^{18}O$ values along a speleothem growth layer do not necessarily indicate that the calcite was deposited in isotopic equilibrium with respect to the associated drip water.

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Tables

Table 1. Symbols and terms used in this paper

α	Equilibrium calcite-water oxygen isotopic fractionation factor
α_m	Kinetic calcite-water oxygen isotopic fractionation factor, calculated as $(\delta^{18}O_{cc} + 1)/(\delta^{18}O_w + 1)$[1]
R_c	Calcite deposition rate, in $\mu mol\ m^{-2}\ h^{-1}$
RH	Relative Humidity
t_d	Time elapsed between two consecutive drips
$\delta^{18}O_{cc}$	Measured calcite oxygen isotopic composition
$\delta^{18}O_w$	Measured drip water oxygen isotopic composition
$\delta^{18}O_e$	Equilibrium calcite oxygen isotopic composition, calculated using $\delta^{18}O_w$ and the α of Kim and O'Neil (1997)
$\Delta^{18}O_{cc-e}$	$\Delta^{18}O_{cc-e} = \delta^{18}O_{cc} - \delta^{18}O_e$
$\Delta^{18}O_{cc-e}{}^{\#}$	$\Delta^{18}O_{cc-e} = \delta^{18}O_{cc} - \delta^{18}O_e{}^{\#}$, $\delta^{18}O_e{}^{\#}$ is predicted equilibrium calcite oxygen isotopic composition, calculated using the α of Coplen (2007)
$\Delta^{18}O_{cc-CO_3{}^{2-}}$	Equilibrium oxygen isotopic fractionation between calcite and $CO_3{}^{2-}$ in the water

[1] as defined by Coplen (2011)

Table 2. Summary of conditions of the studied sites

| Site | distance from entrance[1] (m) | Depth (m) | Temperature (°C) | | RH (%) | drip characteristics | | | CO_2 (ppm)[5] | pH |
			Surface Air[2]	Water		rate (ml/min)	Size (ml)[3]	Interval, t_d (s)[4]		
ISST	230	17	6.2-30.6	14.9-24.1	83-100	0.12-18.5		0.1-63	400-7000	7.5-8.4
mean			19.8	20.2	92	3.3	~0.1	1.5	1100	8.1
Summer mean[6]			28.3	21.0	92	7.8		1.3	2100	7.8
winter mean			10.4	19.0	93	5.6		2	600	8.2
ISLM	350	20		20.7-24.6	81-100	0.1-3.4		9.3-56	400-8500	7.1-8.4
mean				21.7	93	0.8	~0.2	16	3100	7.8
summer mean				21.8	92	1.3		17	4500	7.6
winter mean				21.5	94	0.5		15	970	8.0
NBCT			7.9-30.5	17.1-27	85-100	6.9-200		0.2-5.7	380-9300	6.8-8.3
mean			20.0	22.2	93	46	~0.4	0.5	2600	7.8
summer mean			28.3	23.0	92	41		0.5	4800	7.6
winter mean			10.9	21.0	94	40		0.8	770	8.0
NBWS				17.5-26	81-100	2.9-300		0.2-3.3	600-33000	6.8-8.2
mean				21.8	92	48	~0.7	0.9	6700	7.6
summer mean				22.6	92	70		1.5	10000	7.4
winter mean				20.6	93	31		0.6	1700	7.9

[1] commercial entrance. [2] Monthly mean temperature (Data from NCDC). [3] Calculated as ratio of the averaged drip rate in ml/min to the averaged drip rate in drops/min. [4] Each drip interval value was averaged over 1-3 measurements using a stop watch during each cave visit. [5] Measurements made using a Telaire 7001 CO_2 meter (in ppm by volume, the accuracy of the volume fraction is the greater of ± 50 ppm or 5%),calibrated monthly at $CO_2 = 0$ ppm using a N_2 filled container. [6] Summer refers to the months of June, July and August; winter refers to the months of December, January and February.

Table 3. Results of calcite $\delta^{18}O_{cc}$, meteorological conditions, calcite deposition rates, and values of $\Delta^{18}O_{cc-e}$

Date	$\delta^{18}O_{cc}$ V-SMOW (‰)[1]	t_W (°C)[2]	deposition rate (g/d)	Log R_c (µmol cm^2 h^{-1})	$\delta^{18}O_w$ V-SMOW (‰)[2,4]	$\alpha_m - \alpha$ [5]	$\delta^{18}O_e$ V-SMOW (‰)[6]	$\Delta^{18}O_{cc-e}$ V-SMOW (‰)	$\Delta^{18}O_{cc-e}$ [#] V-SMOW (‰)	1000ln α_m
ISST										
12/10/1998	25.4									
1/11/1999	25.6									
2/12/1999	25.7									
3/21/1999	25.2									
4/29/1999	25.2									
6/12/1999	25.2									
7/28/1999	24.9				-4.5					29.1
9/13/1999	26.1				-4.5					30.3
11/2/1999	26.3				*-4.4*					30.3
12/31/1999	26.7				*-4.4*					30.7
2/17/2000	25.2				-4.4					29.3
3/20/2000	25.1				-4.3					29.1
4/20/2000	25.7				-3.9					29.2
5/18/2000	25.8				-3.9					29.3
6/15/2000	25.7				-4.3					29.6
9/23/2000	25.9	*20.5*			-4.5	0.0011	24.8	1.1	-0.6	30.0
10/21/2000	25.9	20.7			-4.5	0.0011	24.7	1.2	-0.6	30.0
11/21/2000	25.9	20.3			-4.4	0.0010	24.9	1.0	-0.7	30.0
1/1/2001	25.4	20.7			-4.4	0.0006	24.8	0.6	-1.1	29.5
2/10/2001	25.6	21.1	0.013		-4.4	0.0009	24.7	0.9	-0.9	29.7
3/16/2001	25.3	20.0			-4.4	0.0004	25.0	0.3	-1.4	29.4
4/20/2001	25.4	20.2	0.014	2.75	-4.4	0.0004	24.9	0.5	-1.3	29.5
5/23/2001	25.5	21.4	0.013	2.73	-4.4	0.0009	24.7	0.8	-0.9	29.6
6/24/2001	25.4	21.2	0.017	2.84	-4.5	0.0008	24.6	0.8	-1.0	29.6

Date										
9/24/2001	25.7	21.2			-4.5	0.0011	24.6	1.1	-0.7	29.9
10/22/2001	25.7	20.8	0.03	3.1	-4.5	0.0010	24.7	1.0	-0.7	29.9
11/26/2001	25.6	21.3	0.022	2.96	-4.4	0.0009	24.7	0.9	-0.8	29.7
12/31/2001	25.7	20.7	0.032	3.12	-4.4	0.0009	24.8	0.9	-0.9	29.8
1/29/2002	25.6	19.8	0.015	2.79	-4.4	0.0006	25.0	0.6	-1.2	29.7
2/26/2002	25.6	*19.7*	0.011	2.65	-4.4	0.0006	25.0	0.6	-1.1	29.7
3/29/2002	25.5	*20.2*	0.01	2.63	-4.4	0.0005	24.9	0.6	-1.2	29.6
4/27/2002	25.4	20.5	0.007	2.44	-4.4	0.0005	24.9	0.5	-1.2	29.4
5/23/2002	25.3	21.0	0.006	2.37	-4.4	0.0006	24.8	0.5	-1.1	29.4
6/23/2002	25.7	21.0	0.006	2.4	-4.3	0.0008	24.9	0.8	-0.9	29.7
9/27/2002	25.6	21.2	0.017	2.85	-4.4	0.0009	24.7	0.9	-0.8	29.7
10/29/2002	25.7	20.9	0.036	3.18	-4.4	0.0009	24.8	0.9	-0.9	29.7
11/26/2002	25.7	20.2	0.015	2.81	-4.5	0.0008	24.8	0.9	-0.9	29.8
12/27/2002	25.5	19.7	0.022	2.96	-4.5	0.0006	24.9	0.6	-1.1	29.7
2/2/2003	25.5	19.3	0.022	2.95	-4.5	0.0005	25.0	0.5	-1.2	29.7
2/24/2003	25.2	18.9	0.014	2.76	-4.5	0.0001	25.1	0.1	-1.6	29.4
4/3/2003	25.6	19.4	0.011	2.67	-4.5	0.0006	25.0	0.6	-1.1	29.8
5/21/2003	25.5	20.1	0.003	2.16	-4.6	0.0008	24.8	0.7	-1.0	29.8
6/21/2003	25.5	20.2	0.004	2.2	-4.6	0.0008	24.7	0.8	-0.9	29.8
10/5/2003	26.2	19.9	0.01	2.62	-4.6	0.0014	24.8	1.4	-0.3	30.4
12/13/2003	26.2	19.2	0.018	2.87	-4.5	0.0011	25.1	1.1	-0.6	30.3
2/12/2004	25.8	18.8	0.015	2.79	-4.6	0.0007	25.0	0.8	-1.0	30.0
4/10/2004	25.3	19.1	0.016	2.82	-4.6	0.0003	25.0	0.3	-1.4	29.6
6/13/2004	25.3	19.6	0.014	2.78	-4.6	0.0005	24.9	0.4	-1.2	29.6
8/11/2004	25.4	19.9	0.002	1.88	-4.6	0.0007	24.8	0.6	-1.1	29.7
10/7/2004	25.4	19.7	0.014	2.75	-4.6	0.0006	24.8	0.6	-1.2	29.7
11/21/2004	25.1	19.4	0.016	2.83	-4.6	0.0002	24.9	0.2	-1.5	29.4
12/25/2004	25.2	19.2			-4.5	0.0001	25.1	0.1	-1.6	29.4
2/9/2005	25.1	18.9	0.028	3.07	*-4.4*	-0.0002	25.2	-0.1	-1.9	29.2

3/24/2005	24.8	18.8	0.023	2.97	*-4.4*	-0.0004	25.2	-0.4	-2.1	28.9
4/25/2005	25.0	19.4	0.008	2.54	*-4.4*	-0.0001	25.1	-0.1	-1.8	29.1
5/26/2005	25.0	20.4	0.008	2.5	*-4.4*	0.0001	24.9	0.1	-1.6	29.1
6/26/2005	25.0	21.1	0.004	2.24	*-4.4*	0.0003	24.7	0.3	-1.4	29.1
10/21/2005	25.7	20.4	0.01	2.64	*-4.4*	0.0008	24.9	0.8	-0.9	29.8
11/17/2005	25.8	20.2	0.011	2.66	*-4.4*	0.0009	24.9	0.9	-0.8	29.9
12/22/2005	25.9	20.1	0.015	2.79	*-4.4*	0.0009	25.0	0.9	-0.8	30.0
1/21/2006	25.6	19.6	0.001	1.58	*-4.4*	0.0005	25.1	0.5	-1.2	29.7
4/29/2006	25.9	21.1	0.005	2.35	*-4.4*	0.0011	24.7	1.2	-0.6	30.0
6/4/2006	25.9	21.6	0.003	2.05	*-4.4*	0.0012	24.6	1.3	-0.5	29.9
1/3/2007	25.4	*14.9*			*-4.4*		26.1	-0.7	-2.4	29.5
2/8/2007	25.4	17.2	0.009	2.58	*-4.4*	-0.0002	25.6	-0.2	-1.9	29.5
3/11/2007	25.4	19.8	0.015	2.79	*-4.4*	0.0004	25.0	0.4	-1.3	29.5
6/13/2007	25.9	21.3	0.01	2.61	*-4.4*	0.0012	24.7	1.2	-0.6	29.9
11/4/2007	25.8	*21.1*	0.011	2.67	*-4.4*	0.0011	24.7	1.1	-0.7	29.9
11/29/2007	25.9	21.4	0.015	2.79	*-4.4*	0.0012	24.7	1.2	-0.5	30.0
12/25/2007	25.9	20.8	0.013	2.73	*-4.4*	0.0011	24.8	1.1	-0.6	30.0
1/28/2008	25.7	20.2	0.01	2.61	*-4.4*	0.0008	24.9	0.8	-0.9	29.8
3/2/2008	25.7	20.4	0.009	2.58	*-4.4*	0.0008	24.9	0.8	-0.9	29.8
3/26/2008	25.9	*20.4*	0.004	2.22	*-4.4*	0.0010	24.9	1.0	-0.7	30.0
4/25/2008	25.9	20.5	0.02	2.91	*-4.4*	0.0010	24.9	1.0	-0.7	30.0
5/25/2008	25.9	21.0	0.027	3.05	*-4.4*	0.0012	24.8	1.1	-0.6	30.0
6/19/2008	25.7	21.4	0.011	2.65	*-4.4*	0.0010	24.7	1.0	-0.7	29.8
7/14/2008	25.4	21.3	0.002	1.95	*-4.4*	0.0007	24.7	0.7	-1.0	29.5
ISLM										
1/29/2002	25.8	21.4	0.005	2.32	*-4.4*	0.0011	24.7	1.1	-0.7	29.8
3/29/2002	25.7	*21.3*	0.006	2.39	*-4.4*	0.0010	24.7	1.0	-0.7	29.8
4/27/2002	25.8	21.6	0.003	2.15	*-4.4*	0.0011	24.6	1.2	-0.6	29.8

5/23/2002	25.5	21.9	0.002	1.89	-4.4	0.0009	24.6	0.9	-0.8	29.6
6/23/2002	25.5	22.0	0.002	1.97	-4.4	0.0010	24.6	0.9	-0.8	29.6
11/26/2002	25.5	21.1	0.001	1.55	-4.4	0.0007	24.7	0.8	-1.0	29.6
12/27/2002	25.7	21.2	0.005	2.29	-4.5	0.0011	24.6	1.1	-0.7	29.9
2/2/2003	25.5	21.8	0.008	2.52	-4.4	0.0009	24.6	0.9	-0.8	29.6
2/24/2003	25.6	20.7	0.002	1.89	-4.4	0.0007	24.8	0.8	-1.0	29.7
3/17/2003	25.5	20.7	0.001	1.72	-4.4	0.0006	24.8	0.7	-1.1	29.6
4/26/2003	25.5	20.7	0.003	2.11	-4.3	0.0006	24.9	0.6	-1.1	29.5
5/21/2003	25.3	20.8	0.006	2.42	-4.5	0.0006	24.7	0.6	-1.1	29.5
6/21/2003	25.3	20.9	0.001	1.57	-4.4	0.0005	24.8	0.5	-1.2	29.4
12/13/2003	25.6		0.006	2.38	-4.3					29.6
2/12/2004	25.6		0.008	2.54	-4.3					29.5
4/10/2004	25.5		0.004	2.21	-4.4					29.6
6/13/2004	25.5		0.001	1.74	-4.4					29.6
10/7/2004	25.6		0	0.88	-4.4					29.7
11/19/2004	25.4		0	1.17	-4.3					29.4
12/18/2004	25.4		-0.026	0	-4.4					29.5
2/4/2005	25.5		0.006	2.39	-4.5					29.7
3/24/2005	25.5		0.006	2.38	-4.4					29.6
4/25/2005	25.5		0.004	2.25	-4.4					29.6
5/26/2005	25.4		0.003	2.16	-4.4					29.5
6/26/2005	25.5		0.002	1.92	-4.4					29.6
12/17/2005	25.7	22.2	0.006	2.42	-4.4	0.0012	24.5	1.2	-0.5	29.8
1/21/2006	25.7	22.4	0.002	2	-4.4	0.0012	24.5	1.2	-0.5	29.8
2/24/2006	25.6		0.007	2.47	-4.4					29.7
3/30/2006	25.5		0.006	2.36	-4.4					29.6
4/24/2006	25.4		0.009	2.59	-4.4					29.5
5/30/2006	25.5		0.002	1.81	-4.4					29.6
7/19/2006	25.5		0	1.27	-4.4					29.6

11/25/2006	25.5		0.001	1.61	*-4.4*					29.6
1/3/2007	25.6		0.005	2.31	*-4.4*					29.7
2/8/2007	25.4		0.005	2.32	*-4.4*					29.5
3/11/2007	25.4		0.005	2.34	*-4.4*					29.5
4/13/2007	25.5		0.006	2.41	*-4.4*					29.6
11/4/2007	25.6	*21.0*	0.003	2.12	*-4.4*	0.0009	24.8	0.8	-0.9	29.7
11/29/2007	25.7		0.003	2.16	*-4.4*					29.7
12/25/2007	25.8		0.006	2.38	*-4.4*					29.9
1/28/2008	26.0	*21.2*	0.007	2.44	*-4.4*	0.0013	24.7	1.3	-0.5	30.1
3/2/2008	25.7	20.9	0.007	2.46	*-4.4*	0.0010	24.8	0.9	-0.8	29.8
3/26/2008	25.8		0.005	2.35	*-4.4*					29.9
4/25/2008	25.7		0.006	2.41	*-4.4*					29.8
6/30/2008	25.6		0.001	1.52	*-4.4*					29.7
8/15/2008	25.7		0.002	1.85	*-4.4*					29.8
NBCT										
7/16/2004	25.3	22.3	0.026	3.03	-4.3	0.0008	24.6	0.7	-1.0	29.3
9/22/2004	24.8	22.3	0.001	1.75	-4.2	0.0001	24.7	0.1	-1.6	28.7
11/25/2004	25.3	21.4	0.046	3.28	-4.2	0.0005	24.9	0.4	-1.3	29.2
1/20/2005	25.2	20.5	0.036	3.17	-4.3	0.0003	25.0	0.2	-1.5	29.2
3/8/2005	25.3	20.8	0.106	3.65	-4.4	0.0005	24.8	0.5	-1.2	29.4
5/12/2005	25.0	22.1	0.031	3.11	-4.3	0.0002	24.8	0.2	-1.5	29.0
NBWS										
4/23/2003	25.3	22.6	0.015	2.78	-4.5	0.0010	24.3	1.0	-0.7	29.5
11/16/2003	25.4	19.6	0.011	2.64	-4.4	0.0004	25.1	0.3	-1.3	29.5
1/12/2004	25.5	18.7	0.037	3.19	-4.3	0.0002	25.4	0.1	-1.5	29.5
3/8/2004	25.3	20.6	0.031	3.10	-4.2	0.0003	25.1	0.2	-1.4	29.2
5/8/2004	25.4	21.2	0.033	3.14	-4.2	0.0005	24.9	0.5	-1.2	29.3

1/20/2005	26.1	18.6	0.056	3.37	-4.3	0.0007	25.4	0.7	-1.0	30.0
3/8/2005	24.9	18.5	0.038	3.2	-4.4	-0.0004	25.3	-0.4	-2.1	29.0

[1] Where multiple center samples were analyzed for a substrate, the average $\delta^{18}O_{cc}$ value is shown.

[2] Most values are the average of the two measurements taken when the substrate was deployed and when is was collected. Occasionally, a single measurement, taken during the deployment or pick up of the substrate is used (in italic).

[3] R_c was calculated as (deposition rate (g/d)) $\times 10^6/24$, assuming surface area of each substrate is 10×10 cm, microscopic observation confirms that the calcite covers the full surface of ISST, NBCT, NBWS substrates.

[4] Data from Pape et al. (2010).

[5] See Table 1 for the definition of α and α_m, the values of α are calculated using Eq. 4 (Kim and O'Neil, 1997).

[6] When there is no measured $\delta^{18}O_w$, a value of -4.4 ‰ was assumed (in italic), as described in the text.

Table 4. Spatial distribution of $\delta^{18}O$ on the studied substrate

Date	$\delta^{18}O_{max} - \delta^{18}O_{min}$ $_{V-SMOW}$ (‰)[1]	Date	$\delta^{18}O_{max} - \delta^{18}O_{min}$ (‰) $_{V-SMOW}$ (‰)[1]
ISST			
12/10/1998	0.1	4/26/2003	0.2
1/11/1999	0.0	5/21/2003	0.2
2/12/1999	0.2	6/21/2003	0.1
3/21/1999	0.4	2/12/2004	0.2
4/29/1999	0.5	4/10/2004	0.4
6/12/1999	0.5	6/13/2004	0.0
9/13/1999	0.0	8/11/2004	0.2
2/17/2000	0.0	10/7/2004	0.3
3/20/2000	0.3	12/25/2004	0.1
11/21/2000	0.1	2/9/2005	0.5
2/10/2001	0.1	6/26/2005	0.2
4/20/2001	1.3	10/21/2005	0.1
5/23/2001	0.4	11/17/2005	0.2
6/24/2001	0.2	12/22/2005	0.2
9/24/2001	0.8	1/21/2006	0.0
10/22/2001	0.2	3/30/2006	0.4
11/26/2001	0.4	4/29/2006	0.1
12/31/2001	0.3	6/4/2006	0.7
1/29/2002	0.2	1/3/2007	0.2
3/29/2002	0.2	2/8/2007	0.1
4/27/2002	0.0	3/11/2007	0.1
5/23/2002	0.2	6/13/2007	0.3
6/23/2002	0.3	11/4/2007	0.6
9/27/2002	0.2	11/29/2007	0.3
10/29/2002	0.2	12/25/2007	0.8
11/26/2002	0.4	3/2/2008	0.1
12/27/2002	0.3	4/25/2008	0.6
2/2/2003	0.2	5/25/2008	0.2
2/24/2003	0.2	6/19/2008	0.1
4/3/2003	0.4		
ISLM			
1/28/2008	1.4		
NBWS			
4/23/2003	0.4	3/8/2004	0.3
11/16/2003	0.7	5/8/2004	0.1

1/12/2004   1.0

[1] $\delta^{18}O_{max}$ and $\delta^{18}O_{min}$ are the maximum and minimum $\delta^{18}O_{cc}$ values measured for calcite on a substrate (when two or more samples were analyzed from a substrate).

Supplementary Table 1: calcite $\delta^{18}O$ analyses results

Date	location on substrate[1]	$\delta^{18}O$ V-PBD (‰)	Date	location on substrate	$\delta^{18}O$ V-PDB (‰)
ISSL					
12/10/1998	c	-5.3	9/27/2002	c	-5.2
12/10/1998	c	-5.4	9/27/2002	c	-5.1
1/11/1999	c	-5.2	9/27/2002	e	-5.0
1/11/1999	c	-5.2	9/27/2002	e	-5.1
2/12/1999	c	-5.1	9/27/2002	e	-5.0
2/12/1999	e	-4.9	10/29/2002	c	-5.1
3/21/1999	c	-5.7	10/29/2002	e	-4.9
3/21/1999	c	-5.3	10/29/2002	e	-5.0
4/29/1999	c	-5.8	11/26/2002	c	-5.1
4/29/1999	c	-5.3	11/26/2002	c	-5.1
4/29/1999	e	-5.6	11/26/2002	e	-5.0
6/12/1999	c	-5.3	11/26/2002	e	-4.7
6/12/1999	c	-5.8	12/27/2002	c	-5.2
6/12/1999	e	-5.8	12/27/2002	e	-4.9
7/28/1999	c	-5.8	12/27/2002	e	-5.0
9/13/1999	c	-4.7	12/27/2002	e	-5.2
9/13/1999	c	-4.7	12/27/2002	e	-5.1
11/2/1999	c	-4.5	2/2/2003	c	-5.2
12/31/1999	c	-4.1	2/2/2003	c	-5.3
2/17/2000	c	-5.5	2/2/2003	e	-5.0
2/17/2000	c	-5.5	2/2/2003	e	-5.2
3/20/2000	c	-5.8	2/24/2003	c	-5.5
3/20/2000	c	-5.5	2/24/2003	e	-5.3
4/20/2000	c	-5.1	2/24/2003	e	-5.3
5/18/2000	c	-5.0	4/3/2003	c	-5.2
6/15/2000	c	-5.1	4/3/2003	c	-5.2
9/23/2000	c	-4.9	4/3/2003	e	-4.8
10/21/2000	c	-4.9	4/3/2003	e	-5.2
11/21/2000	c	-4.9	4/26/2003	e	-5.3
11/21/2000	c	-4.8	4/26/2003	e	-5.1
1/1/2001	c	-5.3	5/21/2003	c	-5.2
2/10/2001	c	-5.1	5/21/2003	e	-5.1
2/10/2001	c	-5.2	5/21/2003	e	-5.1
3/16/2001	c	-5.4	6/21/2003	c	-5.3
4/20/2001	c	-5.3	6/21/2003	c	-5.2

4/20/2001	c	-5.3	10/5/2003	c	-4.6
4/20/2001	c	-5.5	12/13/2003	c	-4.6
4/20/2001	c	-5.4	2/12/2004	c	-5.1
4/20/2001	e	-5.2	2/12/2004	c	-5.0
4/20/2001	e	-5.2	2/12/2004	c	-4.9
4/20/2001	e	-4.2	4/10/2004	c	-5.4
4/20/2001	e	-4.2	4/10/2004	c	-5.7
5/23/2001	c	-5.2	4/10/2004	c	-5.3
5/23/2001	c	-5.2	6/13/2004	c	-5.4
5/23/2001	c	-5.2	6/13/2004	c	-5.4
5/23/2001	c	-5.2	8/11/2004	c	-5.4
5/23/2001	e	-4.8	8/11/2004	c	-5.2
5/23/2001	e	-5.0	10/7/2004	c	-5.5
6/24/2001	c	-5.4	10/7/2004	c	-5.2
6/24/2001	c	-5.4	11/21/2004	c	-5.6
6/24/2001	c	-5.3	12/25/2004	c	-5.6
6/24/2001	c	-5.4	12/25/2004	c	-5.5
6/24/2001	e	-5.2	2/9/2005	c	-6.0
6/24/2001	e	-5.2	2/9/2005	c	-5.6
6/24/2001	e	-5.3	2/9/2005	c	-5.7
9/24/2001	c	-5.1	2/9/2005	c	-5.5
9/24/2001	c	-5.1	2/9/2005	c	-5.6
9/24/2001	c	-5.0	3/24/2005	c	-5.9
9/24/2001	e	-5.0	4/25/2005	c	-5.7
9/24/2001	e	-5.5	5/26/2005	c	-5.7
9/24/2001	e	-4.9	6/26/2005	c	-5.8
9/24/2001	e	-4.7	6/26/2005	c	-5.7
10/22/2001	c	-5.1	6/26/2005	c	-5.6
10/22/2001	c	-5.0	10/21/2005	c	-5.1
10/22/2001	c	-5.1	10/21/2005	c	-5.0
10/22/2001	c	-5.1	11/17/2005	c	-4.8
10/22/2001	e	-4.9	11/17/2005	c	-5.0
10/22/2001	e	-4.9	11/17/2005	c	-5.0
10/22/2001	e	-5.0	12/22/2005	c	-5.0
11/26/2001	c	-5.1	12/22/2005	c	-4.8
11/26/2001	c	-5.2	12/22/2005	c	-4.8
11/26/2001	c	-5.2	1/21/2006	c	-5.2
11/26/2001	c	-5.1	1/21/2006	e	-5.1
11/26/2001	e	-4.8	3/30/2006	e	-4.7

11/26/2001	e	-5.0	3/30/2006	e	-5.1
11/26/2001	e	-5.1	4/29/2006	c	-4.9
11/26/2001	e	-4.9	4/29/2006	e	-4.9
11/26/2001	e	-4.9	6/4/2006	e	-4.2
11/26/2001	e	-5.0	6/4/2006	e	-4.9
11/26/2001	e	-5.0	6/4/2006	c	-4.9
11/26/2001	e	-4.9	6/4/2006	e	-4.8
11/26/2001	e	-4.9	10/27/2006	e	-4.1
11/26/2001	e	-4.8	11/25/2006	e	-4.4
11/26/2001	e	-4.9	1/3/2007	c	-5.3
11/26/2001	e	-4.9	1/3/2007	e	-5.1
12/31/2001	c	-5.1	2/8/2007	c	-5.4
12/31/2001	c	-5.0	2/8/2007	c	-5.3
12/31/2001	c	-5.1	3/11/2007	c	-5.3
12/31/2001	c	-5.1	3/11/2007	e	-5.2
12/31/2001	e	-4.9	6/13/2007	c	-4.9
12/31/2001	e	-4.9	6/13/2007	e	-4.6
12/31/2001	e	-5.0	10/6/2007	e	-4.7
12/31/2001	e	-4.9	11/4/2007	c	-4.9
12/31/2001	e	-4.9	11/4/2007	c	-5.0
12/31/2001	e	-4.9	11/4/2007	e	-4.4
12/31/2001	e	-4.9	11/4/2007	e	-4.9
12/31/2001	e	-4.9	11/4/2007	e	-4.5
12/31/2001	e	-4.8	11/29/2007	c	-4.9
12/31/2001	e	-4.9	11/29/2007	c	-4.9
12/31/2001	e	-5.0	11/29/2007	e	-4.6
12/31/2001	e	-4.9	12/25/2007	e	-4.7
1/29/2002	c	-5.1	12/25/2007	e	-4.8
1/29/2002	c	-5.3	12/25/2007	e	-4.0
1/29/2002	c	-5.1	12/25/2007	c	-4.9
1/29/2002	e	-5.1	12/25/2007	e	-4.8
1/29/2002	e	-5.1	1/28/2008	c	-5.0
2/26/2002	c	-5.1	3/2/2008	c	-5.1
3/29/2002	c	-5.3	3/2/2008	c	-5.0
3/29/2002	c	-5.2	3/26/2008	c	-4.9
3/29/2002	e	-5.3	4/25/2008	c	-4.9
3/29/2002	e	-5.1	4/25/2008	c	-4.8
4/27/2002	c	-5.4	4/25/2008	e	-4.3
4/27/2002	e	-5.4	5/25/2008	e	-4.8

5/23/2002	c	-5.4	5/25/2008	e	-4.8
5/23/2002	e	-5.3	5/25/2008	e	-4.8
5/23/2002	e	-5.2	5/25/2008	c	-4.9
6/23/2002	c	-5.1	5/25/2008	c	-4.8
6/23/2002	c	-5.1	5/25/2008	e	-4.7
6/23/2002	c	-5.0	6/19/2008	c	-5.1
6/23/2002	e	-4.8	6/19/2008	c	-5.1
7/24/2002	e	-5.1	7/14/2008	c	-5.3
ISLM					
1/29/2002	c	-5.0	5/26/2005	c	-5.4
3/29/2002	c	-5.1	6/26/2005	c	-5.3
4/27/2002	c	-5.0	12/17/2005	c	-5.0
5/23/2002	c	-5.2	1/21/2006	c	-5.1
6/23/2002	c	-5.2	2/24/2006	c	-5.1
11/26/2002	c	-5.3	3/30/2006	c	-5.2
12/27/2002	c	-5.1	4/24/2006	c	-5.3
2/2/2003	c	-5.2	5/30/2006	c	-5.3
2/24/2003	c	-5.2	7/19/2006	c	-5.2
3/17/2003	c	-5.3	11/25/2006	c	-5.2
4/26/2003	c	-5.2	1/3/2007	c	-5.2
5/21/2003	c	-5.5	2/8/2007	c	-5.3
6/21/2003	c	-5.4	3/11/2007	c	-5.3
12/13/2003	c	-5.2	4/13/2007	c	-5.2
2/12/2004	c	-5.2	11/4/2007	c	-5.1
4/10/2004	c	-5.2	11/29/2007	c	-5.1
6/13/2004	c	-5.2	12/25/2007	c	-4.9
10/7/2004	c	-5.2	1/28/2008	c	-4.8
11/19/2004	c	-5.4	1/28/2008	e	-3.4
12/18/2004	c	-5.3	3/2/2008	c	-5.0
2/4/2005	c	-5.2	3/26/2008	c	-4.9
3/24/2005	c	-5.3	4/25/2008	c	-5.0
4/25/2005	c	-5.3	6/30/2008	c	-5.1
			8/15/2008	c	-5.1
NBCT					
7/16/2004	c	-5.4	1/20/2005	c	-5.5
9/22/2004	c	-5.9	3/8/2005	c	-5.4
11/25/2004	c	-5.4	5/12/2005	c	-5.7

NBWS					
3/18/2003	e	-5.4	5/8/2004	c	-5.3
4/23/2003	c	-5.4	1/20/2005	c	-4.7
11/16/2003	c	-5.3	3/8/2005	c	-5.8
1/12/2004	c	-5.2	12/20/2005	e	-5.0
3/8/2004	c	-5.4			

[1] c = center, e = edge. See text for further explanation

Figure Captions

Fig. 1. a) Map of the Edwards Plateau and its location in central Texas, locations of Inner Space Cavern and Natural Bridge Caverns, and b) schematic of site ISST. Water travels along the slope of the ISST flowstone before dripping onto the deployed substrate. Other monitored sites drip directly off the cave ceiling.

Fig. 2. Time series of ISST substrate calcite $\delta^{18}O_{cc}$ (shaded diamonds) and meteorological conditions outside and inside Inner Space Cavern. Plotted, top to bottom, are Austin area surface rainfall amount (solid line), drip interval (t_d, in seconds, filled triangle), monthly mean outside air temperature (°C, shaded squares), RH (%, filled diamonds), cave-air CO_2 concentration (shaded triangles, dashed line represents average value of the outside air CO_2 concentration), drip water temperature (t_w, shaded circles), $\Delta^{18}O_{cc-e}$ (‰, filled circles, dashed line represents equilibrium fractionation, that is $\Delta^{18}O_{cc-e}$ = 0), drip water Ca^{2+} concentration (ppm by mass, open circles), rainfall $\delta^{18}O$ values (open diamonds), drip water $\delta^{18}O_w$ values (filled squares), measured calcite $\delta^{18}O_{cc}$ values (shaded diamonds), and expected equilibrium calcite $\delta^{18}O_e$ values (open squares) calculated using drip water $\delta^{18}O_w$ (when measured $\delta^{18}O_w$ was not available, a value of -4.4 ‰ was used based on the invariability of measured $\delta^{18}O_w$), t_w and α values of Kim and O'Neil (1997). Plotted values for t_d, t_w, RH, and CO_2 are averaged over the two consecutive measurements before and after the deployment of the substrate.

Fig. 3. 1000 ln α vs. 1000/T. Filled circles denote the results of this study. Lines show the expected relationships according to published equilibrium calcite-water oxygen isotopic fractionation factors (Friedman and O'Neil, 1977; Kim and O'Neil, 1997; Coplen, 2007; Tremaine et al., 2011).

Fig. 4. $\Delta^{18}O_{cc-e}$ vs. t_w for drip sites ISST, ISLM, NBWS, and NBCT. Line indicates linear regression of data from ISST, ISLM and NBWS. $\Delta^{18}O_{cc-e}$ values are calculated as $\delta^{18}O_{cc}$ - $\delta^{18}O_e$, where $\delta^{18}O_e$ values are calculated using measured $\delta^{18}O_w$ where available (a nominal value of -4.4 ‰ was assumed for some ISST and ISLM substrates, see Table 3) and α value of Kim and O'Neil (1997). Conservative uncertainty estimates of ± 0.3 in t_w and ±0.2 ‰ in $\Delta^{18}O_{cc-e}$ are shown in the lower right.

Fig. 5. Schematic for the trapping of a calcite surface layer during mineral growth. This surface layer may have $\delta^{18}O$ value that is identical to the $\delta^{18}O$ value of CO_3^{2-} in the solution, which is more negative than the calcite deposited in oxygen isotopic equilibrium with DIC species and water. At faster deposition rates, the surface layer is preserved in the calcite crystal, this "trapping" causes the overall calcite crystals to have more negative $\delta^{18}O$ value than equilibrium fractionation predicts (Watson, 2004).

Fig. 6. The $\Delta^{18}O_{cc-e}$ values plotted against log R_c. a) results for thirteen calcite samples synthesized (filled circles, Dietzel et al., 2009) and one hypothetical calcite in isotopic equilibrium with ambient water (open circle, Coplen, 2007) at 25 °C and pH=8.3. The regression slope ($\Delta^{18}O_{cc-e}$ /log R_c) suggests a -0.8 ‰ shift in $\delta^{18}O$ values for every ten-fold increase in deposition rate; b) Histogram of $\Delta^{18}O_{cc-e}{}^{\#}$/log R_c for results of this study (shaded and textured columns). Frequencies of the occurrence were counted after rounding the calculated $\Delta^{18}O_{cc-e}{}^{\#}$/log R_c values to two significant figures. Results of 25 °C experiments (filled columns) of Dietzel et al. (2009) are plotted for comparison.

Fig. 7. Spatial variability of $\delta^{18}O_{cc}$ on two typical ISST substrates. Numbers are measured calcite $\delta^{18}O_{cc}$, shaded areas represent the sampling locations, and contours are for 0.2 ‰. Light gray lines indicate the estimated contours while black lines are for contours drawn based on measured calcite $\delta^{18}O_{cc}$ values. a) Substrate deployed from December of 2001 to January of 2002 shows a spatial variation of 0.3 ‰, relative to an analytical uncertainty of ±0.1 ‰; b) Substrate deployed between April and May of 2001 shows a spatial variation of 1.3 ‰. The variation observed in (a) is typical of most substrates, whereas the variation observed in (b) is the maximum observed at ISST. In both substrates, there is an enrichment of ^{18}O in calcite collected near the edge of the substrate relative to the center.
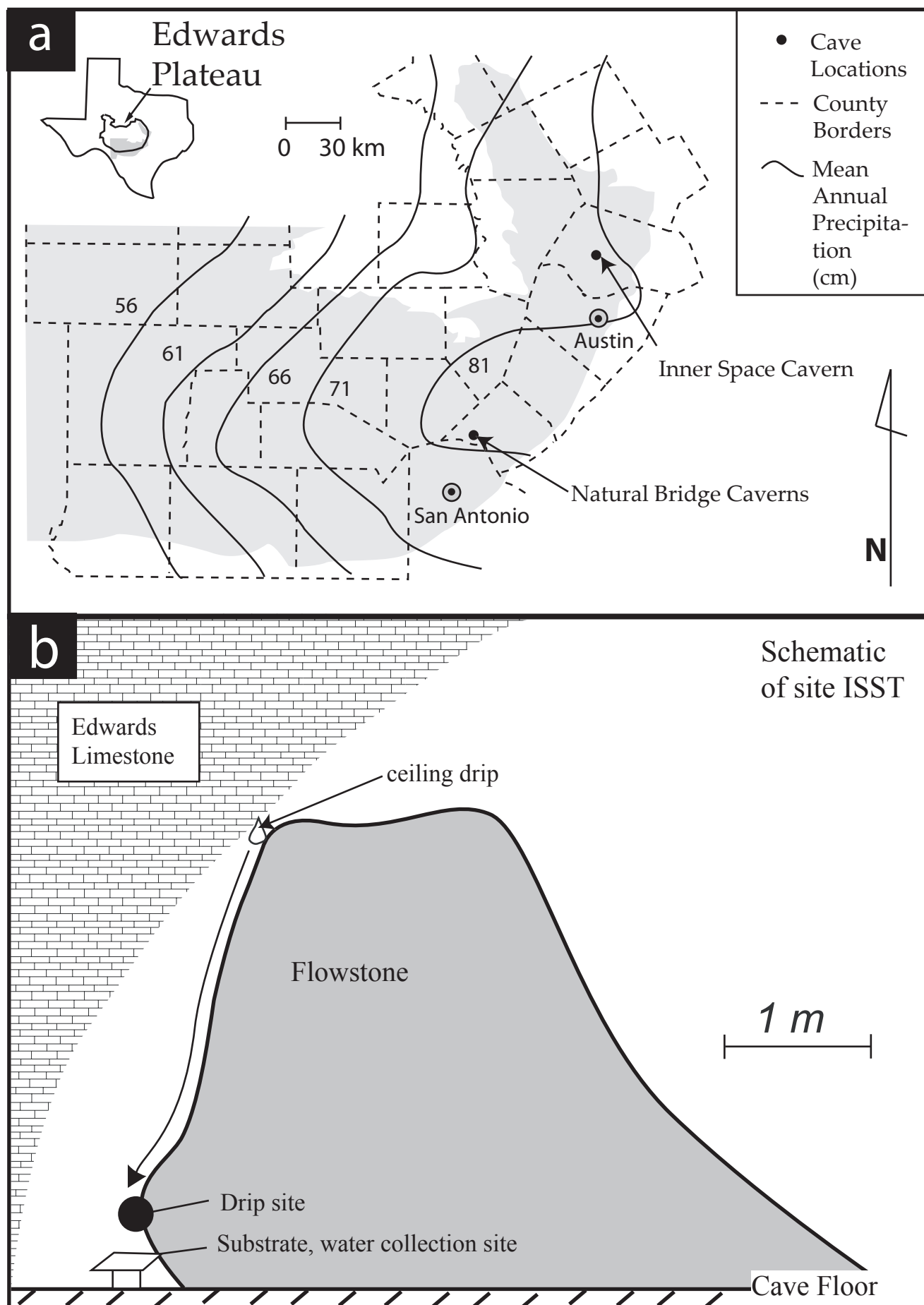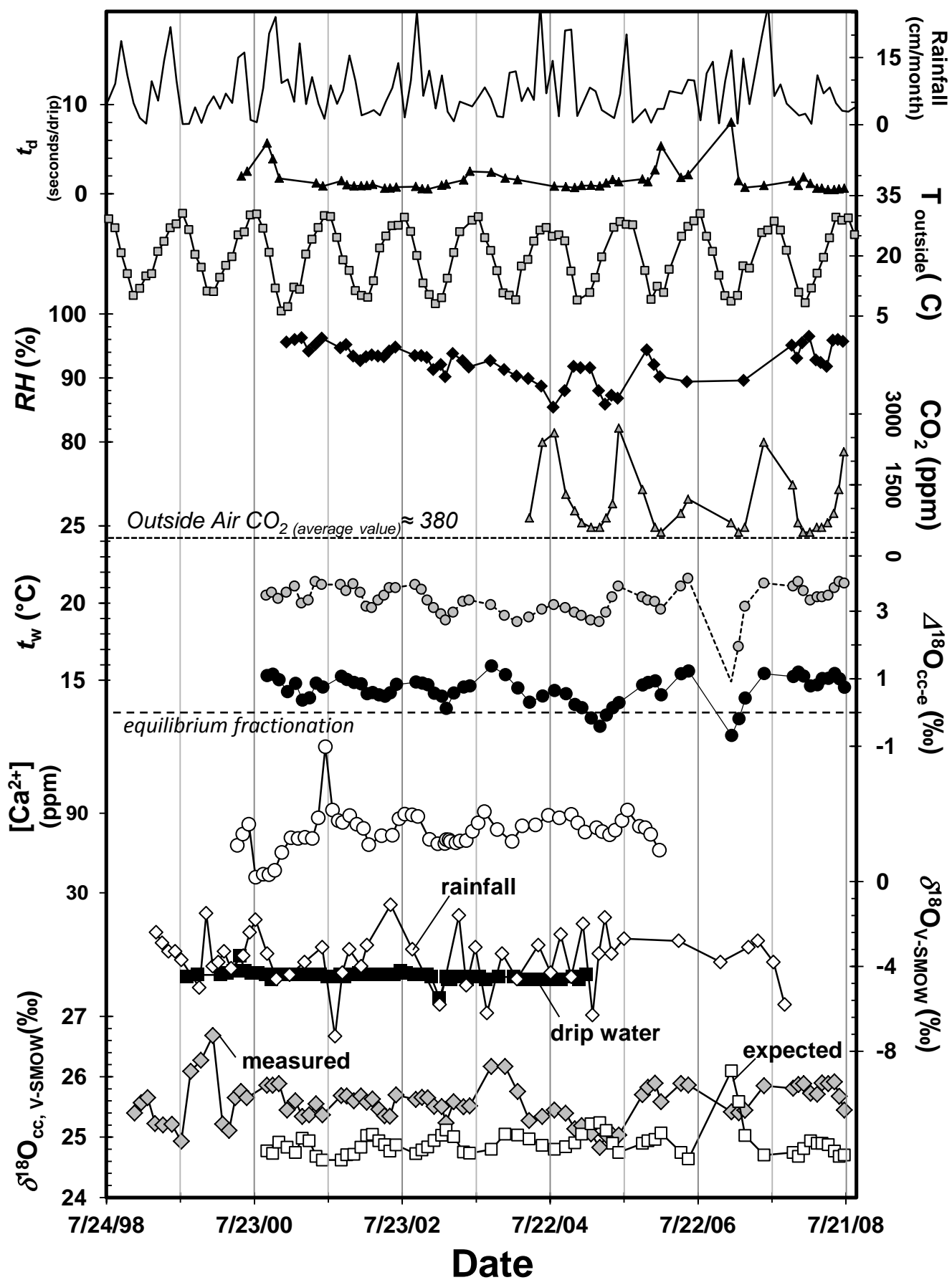
Fig. 1

a Edwards Plateau

0   30 km

- Cave Locations
- - - County Borders
- ⌇ Mean Annual Precipitation (cm)

56

61

66 71

81

Austin

San Antonio

Inner Space Cavern

Natural Bridge Caverns

N

b Schematic of site ISST

Edwards Limestone

ceiling drip

Flowstone

1 m

Drip site

Substrate, water collection site

Cave Floor

Fig. 2

Fig. 3

Fig. 3

Fig. 4

Legend (on plot):
- ○ ISST
- ■ ISLM
- ◇ NBCT
- ▲ NBWS

For ISST, ISLM, and NBWS
$y = 0.3x - 4.7$; $r^2 = 0.56$

Y-axis: $\Delta^{18}O_{cc-e, \text{ V-SMOW}}$ (‰)

X-axis: t_w (° C)

Fig. 5

Surface layer with $\delta^{18}O$ values close to $\delta^{18}O$ values of CO_3^{2-}

Growth Surface

Growth Surface

Trapped former "surface layer"

calcite inner lattice

calcite inner lattice

Slow calcite growth

Fast calcite growth

Fig. 6

a) y = -0.77x; r^2 = 0.70

Plot showing $\Delta^{18}O_{cc-e, v-SMOW}$ (‰) versus log R_c (μmol m^{-2} h^{-1}).

b) Slopes of $\Delta^{18}O_{cc-e}^{\#}$ vs. log R_c

Legend: ISST, ISLM, NBCT, NBWS, Dietzel et al. (2009)

Histogram of Frequency versus $\Delta^{18}O_{cc-e}^{\#}$ / log R_c.

Fig. 7

a) Dec, 01 to Jan, 02

26.0　25.9　25.9

25.9　25.7　25.7　25.9

25.9　25.7　25.8　25.9

25.9　25.9　25.9

b) Apr, 01 to May, 01

26.6　26.6

25.2　25.3

25.4　25.4

25.5　25.5