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Controls on oxygen isotope variability in precipitation and cave drip waters, central Texas, USA

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SUMMARY

This study investigates the factors that control the oxygen isotopic composition of precipitation and cave drip waters in central Texas. Precipitation samples collected in Austin, Texas at monthly to bimonthly intervals between 1999 and 2007 have $\delta^{18}O$ values between −12.6‰ and −1.1‰ VSMOW and a weighted average value of −4.1‰. This weighted average value likely reflects the isotopic composition of precipitation generated predominantly by moisture masses that originate from the Gulf of Mexico. Samples with the lowest $\delta^{18}O$ values (−12.6 ± 0.1‰) are associated with precipitation from moisture masses related to Pacific tropical cyclones. Precipitation amount appears to be an important control on the oxygen isotope composition of rainfall during summertime periods with the warmest weather, but does not account for the variability of the precipitation isotopic data for colder months. Drip-water samples collected at monthly to quarterly intervals from multiple drip sites in three regionally distributed central Texas caves between 1998 and 2007 have $\delta^{18}O$ values between −5.5‰ and −0.6‰ with individual drip sites generally varying by no more than 1‰ of their average values. This much narrower range of $\delta^{18}O$ values relative to those for rainfall is consistent with mixing of meteoric water in the unsaturated zone. Average drip-water $\delta^{18}O$ values of all caves are lower than the weighted average of Austin precipitation, which may indicate that a threshold of precipitation amount must be exceeded to provide recharge to drip sites. Unlike Austin precipitation, drip waters at most sites lack seasonal variations and therefore must have a residence time in the unsaturated zone of approximately annual scale or greater. Drip waters from six caves from central Texas to eastern New Mexico display a spatial gradient in which their drip-water $\delta^{18}O$ values are lower for caves located further inland from the Gulf of Mexico. This likely reflects a combination of continental and temperature effects on precipitation above the caves. The observed spatial gradient in drip-water $\delta^{18}O$ values emphasizes the utility of comparing speleothem paleoclimate records from regionally distributed caves. Past variations in such a gradient may imply changes in prevailing storm paths or moisture source region.

Introduction

In seeking to better understand past climate variations, paleoclimatological studies have used both computer models and a variety of environmental proxies. One such environmental proxy – the oxygen isotope composition of cave calcite deposits (speleothems) – has been used to interpret past temperature and precipitation variations in paleoclimate reconstructions (Dorale et al., 1992; Fleitmann et al., 2003; Hu et al., 2008). In regions affected by tropical cyclones, high resolution sampling of speleothems for oxygen isotopes can be used for paleotempestology (e.g., Frappier et al., 2007). Speleothems have several advantages as a paleoclimate proxy: (1) they are terrestrial and easily accessible, (2) they are widespread in a variety of climates, (3) they can grow continuously for thousands to tens-of-thousands of years, (4) they can be precisely dated using U/Th methods, and (5) they can potentially record annual or seasonal climatic variations (Shopov, 2004; Guilfoyle, 2006; Banner et al., 2007).

Oxygen isotopes are useful as a paleoclimate proxy because the oxygen isotope composition of meteoric precipitation can exhibit systematic variation based on: (1) the ambient temperature at the time of precipitation, (2) the amount of precipitation that occurs, (3) storm paths, (4) the distance of a precipitation event from its moisture source region in the ocean, and (5) the ground surface elevation where precipitation occurs (Dansgaard, 1964; Clark and Fritz, 1997; Ingraham, 1998). In previous studies, cave drip waters have been found to represent a long-term weighted average of the

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oxygen isotope composition of precipitation (Yonge et al., 1985; Chapman et al., 1992; Williams and Fowler, 2002; Onac et al., 2008), demonstrate seasonal-scale temporal oxygen isotope variability similar to precipitation (Harmon, 1979; Li et al., 2000; van Beynan and Febbroriello, 2006; Johnson et al., 2007), or, in semi-arid regions, exhibit seasonal-scale variation based on changes between semiannual wet and dry seasons (Bar-Matthews et al., 1996).

Before robust conclusions about paleoclimate can be drawn from speleothem oxygen isotope records, it is important to establish the following criteria: (1) the climatic controls on the oxygen isotope composition of meteoric precipitation in the region where the caves are located, (2) the extent to which climatic signals in the oxygen isotope composition of meteoric precipitation above the caves are preserved in the drip waters that precipitate speleothem calcite, (3) how drip-water oxygen isotope compositions vary spatially among caves on a regional scale, and (4) whether the oxygen isotope signal of the cave drip waters is preserved in speleothem calcite that precipitates from those waters. The present study addresses the first three criteria through analysis of an eight-year time series of $\delta^{18}O$, rainfall amount, and temperature data for rainfall and cave drip waters from central Texas.

Controls on stable isotopes in precipitation

As a result of isotopic fractionation during the condensation of water vapor masses to form meteoric precipitation, the stable isotope composition of oxygen and hydrogen in precipitation is controlled by the following factors, or effects:

(1) *A temperature effect*, whereby vapor masses that evolve through rainout under cold conditions will experience an enhanced depletion in ^{18}O and ^{2}H compared to warmer conditions. This results from increased Rayleigh distillation of vapor masses and increased isotope fractionation at colder temperatures (e.g., Ingraham, 1998). The temperature effect is most pronounced at high latitudes with lower average annual temperatures (Dansgaard, 1964; Rozanski et al., 1992).

(2) *A continental effect*, whereby vapor masses that move progressively further inland from their original source in the ocean become increasingly depleted in ^{18}O and ^{2}H. The continental effect may vary for given regions based upon prevailing storm paths (Craig, 1961; Ingraham, 1998).

(3) *An elevation effect*, whereby water vapor masses become increasingly depleted in ^{18}O and ^{2}H over regions of increasing elevation as a result of increased rainout and larger fractionation factors that result from cooler average temperatures at higher elevations (Friedman and Smith, 1970; Clark and Fritz, 1997).

(4) Finally, in precipitation in monsoonal climates and tropical latitudes, an *amount effect* has been observed that results in precipitation that is increasingly depleted in ^{18}O and ^{2}H with increasing monthly or mean annual precipitation (Dansgaard, 1964; Rozanski et al., 1993; Jones and Banner, 2003). In detail, the causes of this effect are influenced by several factors. First, $H_2{}^{18}O$ has slightly lower vapor pressure than $H_2{}^{16}O$, leading to increasingly ^{18}O depleted vapor within a storm cloud, especially in high intensity, strongly convecting storms (Dansgaard, 1964; Lee and Fung, 2007). Also, high intensity rainfall tends to have greater numbers of relatively large raindrops that take longer to reach isotopic equilibrium with ambient vapor layers. These raindrops tend to preserve the isotopic signature of ambient water vapor higher in the atmosphere, which generally has lower $\delta^{18}O$ values. Because of interaction with these ^{18}O depleted raindrops, the $\delta^{18}O$ of water vapor below the cloud base becomes lower. This contributes to increasingly lower $\delta^{18}O$ values below the storm cloud because of continuous isotopic exchange with falling raindrops. Finally, the amount effect can be enhanced by decreased re-evaporation of falling raindrops in moister conditions (Stewart, 1975; Rozanski et al., 1993; Lee and Fung, 2007).

For temporal records from a single location, such as the one presented in this study from Austin, Texas, the stable isotopic composition of precipitation on a seasonal-scale commonly reflects a combination of influences including temperature, local evapotranspiration rates, and precipitation amount (Fricke and O'Neil, 1999).

Karst aquifers: diffuse vs. conduit flow

The flow paths through which meteoric waters percolate through the unsaturated zone into caves in karst aquifers are broadly characterized within the context of two end-members: diffuse flow and conduit flow. Diffuse flow occurs along centimeter-scale or smaller interconnected pores, whereas conduit flow occurs through localized centimeter- and meter-scale fractures or conduits (Shuster and White, 1971). Cave drip waters originating from diffuse flow paths are characterized by lower flow volumes as well as lower drip rate and geochemical variability. Conversely, drip waters originating from conduit flow paths exhibit higher flow volumes with higher drip rate and geochemical variability (Smart and Friedrich, 1987; Musgrove and Banner, 2004).

Study area

The precipitation collection site in Austin and five caverns – Caverns of Sonora (CS hereafter), Natural Bridge Caverns (NB), Inner Space Cavern (IS), Kickapoo Cavern (KP), and Devil's Sinkhole (DS) – are located across a 300 km regional extent on the Edwards Plateau of central Texas (Fig. 1). The plateau has a subtropical climate with a regional east–west subhumid to semi-arid gradient. The plateau is a well-developed karst region built in lower Cretaceous marine carbonates. It comprises parts of two regional aquifer systems, the Edwards–Trinity aquifer and the Trinity aquifer.

The average annual precipitation above CS is ~56 cm/year and the average annual precipitation above NB and IS is ~81 cm/year (Larkin and Bomar, 1983). CS formed in the thin to massively bedded limestone and dolomitic marls of the Segovia member of the Cretaceous Edwards Limestone Group (Kastning, 1983). Drip sites at CS are located at least 35 m from the nearest cavern entrance and between 15 and 40 m below the surface. NB is located in the alternating limestone and dolomite beds of the upper Glen Rose Formation (Elliott and Veni, 1994). The cave system consists of the disconnected Natural Bridge South and Natural Bridge North caverns. Drip sites at NB are located within both the north and south caverns at least 50 m from the nearest cavern entrance and between 42 and 45 m below the surface (Guilfoyle, 2006). IS was formed in the chert-rich limestone and dolostone beds of the Edwards Limestone. Drip sites at IS are at least 100 m from the cavern entrance and between 12 and 18 m below the surface (Guilfoyle, 2006). Stable isotope data for drip-water samples collected between 1995 and 1997 from NB, KP, and DS, described in Musgrove (2000), are included in this analysis. KP and DS are both located on the western portion of the Edwards Plateau (Elliott and Veni, 1994). KP is formed within the Devil's River Limestone; DS is largely within the Segovia Formation, although the lower part of the cave is within the Fort Terrett Formation (Elliott and Veni, 1994).

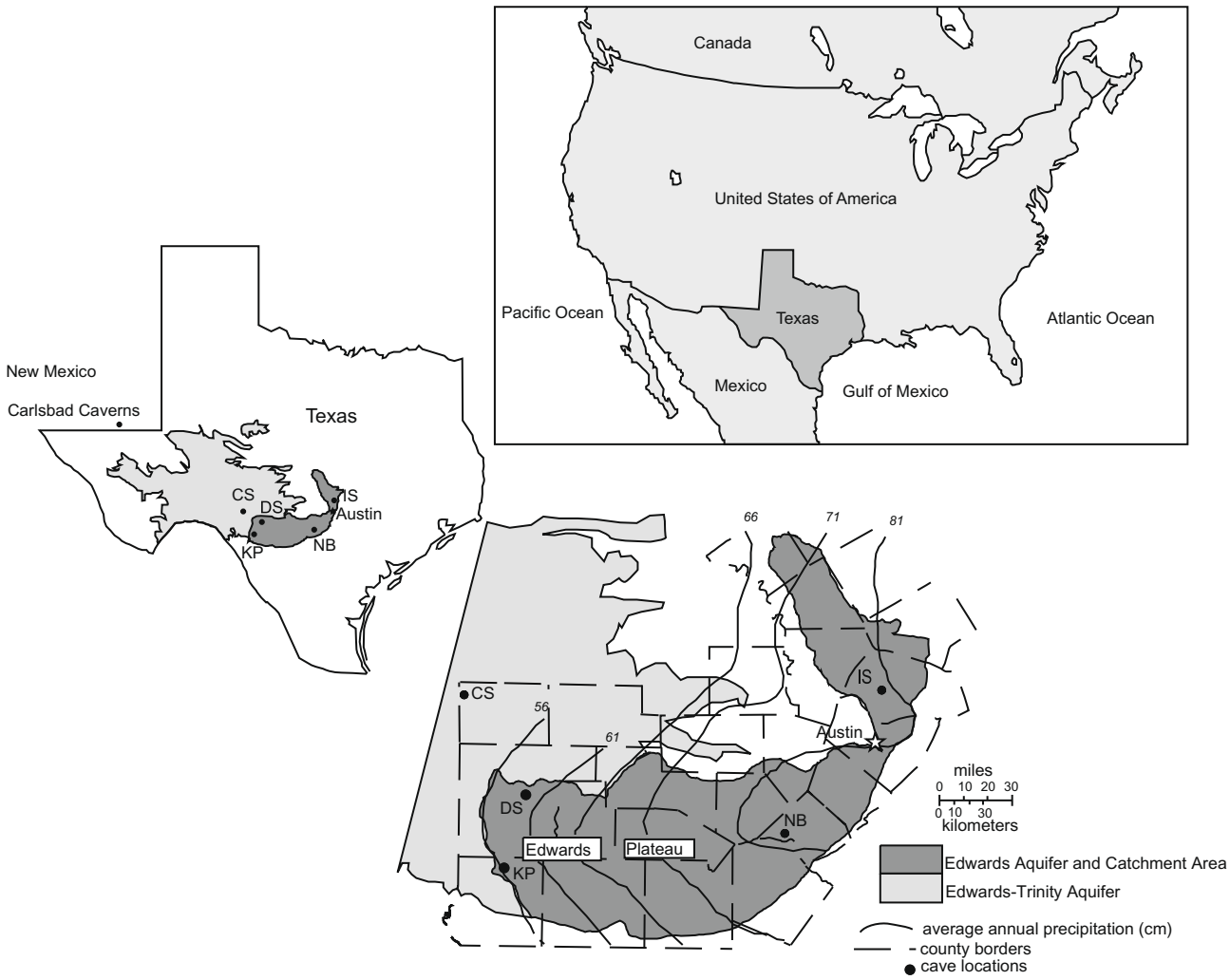

Fig. 1. Locations of Caverns of Sonora (CS), Natural Bridge Caverns (NB), and Innerspace Cavern (IS). Also shown are the locations of Kickapoo Cavern (KP) and Devil's Sinkhole (DS). Hydrologic zones of the Edwards aquifer and rainfall gradient of central Texas are also shown. Location of Carlsbad Caverns and extent Edwards–Trinity aquifer shown in upper left insert. Upper right insert shows location of Texas relative to the Pacific Ocean, Gulf of Mexico, and Continental United States. Modified from Musgrove and Banner (2004).

Previous workers have characterized the drip sites in this study as exhibiting a continuum of flow characteristics that vary from diffuse flow to conduit flow based on observation of drip rates and analysis of major and trace elements (Musgrove, 2000; Musgrove and Banner, 2004; Guilfoyle, 2006). Drip sites NBEL, ISHW, NBWS, and ISBH (Table 1) appear to largely exhibit conduit flow characteristics compared to the other drip sites studied, which appear to exhibit largely diffuse flow characteristics (Guilfoyle, 2006).

Methods

Sample collection

The daily precipitation and temperature data primarily used in this study were collected at a weather station operated by KVUE News Network and located on the rooftop of the Geography Building on the University of Texas campus. Daily precipitation and temperature data from the National Climatic Data Center (NCDC) archive collected at Bergstrom International Airport at Austin, Texas were also used to supplement the KVUE dataset (National Oceanic and Atmospheric Administration, 2008). Both NCDC and KVUE data yield similar daily precipitation and temperature trends when available over the same time interval.

Cumulative precipitation samples were collected at monthly to bimonthly intervals from the rooftop of the Jackson Geological Sciences Building on the University of Texas campus between 1999 and 2007. Rainwater samples were collected using glass bottles and mineral oil to minimize evaporation. These samples were filtered upon collection to remove the mineral oil. To minimize evaporation prior to analysis, all rain and drip-water samples were refrigerated in glass bottles with no head space (Guilfoyle, 2006).

Cave drip-water samples were collected at monthly intervals from IS and NB, and monthly to quarterly intervals from CS. Drip-water samples to be analyzed for H and O isotopes were collected directly from the drip sites and were not filtered. For slow-dripping sites (typically less than 0.01 ml s^{-1}), water was collected using a 1 L HPDE bottle that was left under the drip for approximately 2 h. H and O sample bottles were then filled with water from the 1 L bottle immediately after it was recovered from the drip site.

Six rainwater samples from a single rain event were collected on October 17th and 18th of 1998 in northwest Austin. These samples were collected over a period of approximately 24 h at 3–8 h intervals. These samples were unfiltered.

Table 1
Drip site names and average drip rates.

Cavern	Drip site name	Abbreviated name	Average drip rate (ml s^{-1})	Time range of drip-rate data collection
Inner Space	Press room	ISPR	0.023 (n = 21)	5/31/2000–7/7/2003
Inner Space	Lake of the moon	ISLM	0.009 (n = 86)	5/31/2000–10/25/2009
Inner Space	Lake of the moon right view	ISLM right view	0.387 (n = 55)	5/31/2000–8/30/2009
Inner Space	Hallway	ISHW	1.200 (n = 58)	5/31/2000–10/25/2009
Inner Space	Drapery column	ISDC	0.361 (n = 48)	5/31/2000–10/25/2009
Inner Space	Bore hole	ISBH	1.540 (n = 37)	5/31/2000–8/30/2009
Inner Space	Flowing stone of time	ISST	0.148 (n = 101)	5/31/2000–10/25/2009
Natural Bridge	Castle table top	NBCT	0.623 (n = 59)	8/31/2001–10/19/2009
Natural Bridge	Emerald lake	NBEL	3.36 (n = 34)	8/31/2001–10/19/2009
Natural Bridge	End of path	NBEP	0.030 (n = 72)	5/16/2001–10/19/2009
Natural Bridge	Fried egg	NBFE	0.072 (n = 67)	8/31/2001–10/19/2009
Natural Bridge	Switchback	NBSB	0.574 (n = 57)	8/31/2001–10/19/2009
Natural Bridge	Well shaft	NBWS	0.407 (n = 69)	5/16/2001–10/19/2009
Caverns of Sonora	Dracula's cape	CSDC	0.005 (n = 16)	1/5/2001–8/19/2006
Caverns of Sonora	Halo lake	CSHL	0.011 (n = 15)	6/28/2000–8/19/2006
Caverns of Sonora	Devil's pit	CSDP	0.008 (n = 16)	1/5/2001–8/19/2006
Caverns of Sonora	Seven falls	CSSF	0.017 (n = 7)	6/28/2000–11/7/2004
Caverns of Sonora	Dino lair	CSDL	0.031 (n = 7)	7/22/2003–8/19/2006
Caverns of Sonora	Righthand passage	CSRP	0.010 (n = 8)	6/28/2000–8/19/2006

Sample analysis

Fifty-six rainwater samples collected over the eight year period of the study were analyzed for oxygen isotope composition. Four of these samples likely experienced evaporative effects prior to analysis based on the presence of head space in their sample vials. Data from these samples are included in Table 2, but excluded from the graphs and statistical calculations of this study. Rainwater and cave drip-water samples were analyzed for their oxygen isotope composition on either a Prism II dual-inlet mass spectrometer at the University of Texas at Austin or on Finnigan MAT 251 and 252 mass spectrometers at Southern Methodist University. In both cases a method similar to that described by Epstein and Mayeda (1953) was used. A volume of 0.3–5 ml of sample water was equilibrated for at least eight hours with CO_2 gas, and the equilibrated CO_2 gas was sampled and analyzed against a reference gas of known isotopic composition. Replicate O isotope analyses for waters had a standard deviation of 0.024‰ (n = 5). Results from standard runs indicate an analytical uncertainty (2σ) of ±0.1‰ or better.

The October 1998 rain event precipitation samples were analyzed for O isotope compositions at the University of Arizona Environmental Isotope Laboratory using a Finnigan Delta *S* mass spectrometer. A method similar to that described by Craig (1957) was used in which water samples were equilibrated with CO_2 gas. Values were corrected based on the isotopic composition of the oxygen in the CO_2 used for equilibration. Replicate analyses had a standard deviation of 0.065‰ (n = 4), and reported values have an analytical precision (2σ) of ±0.1‰ or better.

Drip-water and precipitation samples were analyzed for hydrogen isotope compositions on Finnigan MAT 251 and 252 mass spectrometers at Southern Methodist University. A method similar to that described by Bigeleisen et al. (1952) was used for these analyses. Five microliters of cryogenically purified sample water was reduced to H_2 gas by passing it over depleted uranium metal at 800 °C. Results from the standard runs and from replicate analyses indicate an analytical precision (2σ) of ±1‰.

All hydrogen and oxygen isotope values obtained through mass spectrometric analysis are expressed in per mil (‰) deviations relative to Vienna Standard Mean Ocean Water (VSMOW). All statistical calculations referred to in this study are statistically significant with a p value of <0.05.

Results

Rainfall O and H isotope results

Cumulative Austin rainfall O and H isotope data are presented in Table 2. Rainfall $\delta^{18}O$ values for 56 samples collected between 1999 and 2007 range from −12.6‰ to −1.1‰, although the $\delta^{18}O$ values of all but one of the precipitation samples fall between −7.3‰ and −1.1‰ (Fig. 2a). Because these rainfall samples are cumulative, larger rainfall events exert a stronger influence on the $\delta^{18}O$ values of water collected during a given collection interval than smaller events. The oxygen isotope composition of Austin precipitation shows variability that does not appear to be related to seasonal temperature change (Fig. 2b), and when precipitation $\delta^{18}O$ values are compared with average temperature during each collection interval, there is no correlation. Rainfall $\delta^{18}O$ values from the entire dataset trend toward lower $\delta^{18}O$ values with increasing precipitation amount, but the correlation is not significant (Fig. 3a). Rainfall $\delta^{18}O$ values from the 10 warmest collection intervals (average temperatures range between 26.9 and 30.4 °C, vs. 9.7 to 30.4 °C for the entire data set) also trend toward lower $\delta^{18}O$ with increasing rainfall amount (Fig. 3b) and have a strong correlation (R^2 = 0.79).

Eight hydrogen isotope samples were also analyzed for collection periods between 7/20/2004 and 5/17/2005 with δD values ranging from −42‰ to −7‰ VSMOW (Table 2). Precipitation hydrogen isotope samples are a subset of the oxygen isotope database. The δD and $\delta^{18}O$ values of these samples are included with rainfall and meteoric water available from other studies in central Texas (Oetting, 1995; Fahlquist and Ardis, 2004; IAEA/WMO, 2006; Otero, 2007; Slattery et al., 2006; US Geological Survey, 2008) to establish a Local Meteoric Water Line (LMWL; Fig. 4). The equation of this LMWL is $\delta D = 7.1 * \delta^{18}O + 6.7$ compared to the Global Meteoric Water Line which is defined by the equation $\delta D = (8.17 \pm 0.06) * \delta^{18}O + (10.35 \pm 0.65)$ (Rozanski et al., 1993).

Cave drip-water O and H isotope results

Drip-water oxygen and hydrogen isotope data are presented in Tables 3–5. Drip-water oxygen isotope data are also presented for selected drip sites in Fig. 5. Seventy-five water samples from six separate drip sites at Cave CS were collected between May of 2000 and November of 2004 and have $\delta^{18}O$ values ranging from

Table 2
Oxygen and hydrogen isotopic composition of Austin rainfall with mean temperature and normalized mean monthly rainfall during each collection interval.

Collection interval midpoint	$\delta^{18}O$	δD	T (°C)	Normalized mean monthly rainfall (cm)
3/18/1999	−2.4		16.6	10.5
4/17/1999	−2.9		22.1	2.0
5/19/1999	−3.3		25.2	2.0
6/21/1999	−3.3		27.8	9.0
7/21/1999	−3.7		27.8	10.8
8/19/1999	−3.6[a]		31.6	2.6
10/18/1999	−5		19.1	4.0
11/21/1999	−1.5		15.8	0.7
12/23/1999	−4		10.6	7.8
1/20/2000	−3.8		11.4	1.8
2/17/2000	−3.3		15.9	9.4
3/23/2000	−4.1		18.8	4.8
5/22/2000	−3.5		26.1	6.0
6/23/2000	−2.4		28.9	1.9
7/22/2000	−1.8		30.4	0.5
8/21/2000	−6.2[a]		31.0	2.2
9/17/2000	−3.4		27.2	1.7
11/2/2000	−4.6		17.4	11.9
1/6/2001	−4.4		9.6	8.1
3/21/2001	−3.8		17.0	7.3
6/16/2001	−3.1		28.1	4.3
8/19/2001	−7.3		29.5	22.2
9/24/2001	−4.3		24.2	8.2
10/28/2001	−3.2		20.7	2.6
11/27/2001	−4.2[a]		15.8	33.4
12/26/2001	−4		10.5	8.9
1/24/2002	−3		13.2	3.3
5/21/2002	−1.1		26.3	10.4
9/5/2002	−3.2		25.6	8.9
1/18/2003	−5.8		13.1	6.0
4/23/2003	−1.6		23.7	1.5
5/30/2003	−4.9		26.9	14.1
7/14/2003	−3.1		29.7	2.9
9/9/2003	−6.2		26.8	4.9
11/23/2003	−3.4		17.1	2.4
2/4/2004	−4.6		12.0	11.2
5/20/2004	−3		19.4	8.7
7/20/2004	−4.3	−28	25.2	13.0
9/8/2004	−2.5	−9	28.7	11.4
10/30/2004	−4.5	−28	26.5	3.8
12/27/2004	−2	−9	19.9	22.2
2/12/2005	−6.3	−42	11.2	1.6
3/15/2005	−3.4	−17	13.6	9.6
4/14/2005	−1.7	−7	17.0	8.5
5/17/2005	−3.4	−20	20.8	4.3
7/18/2005	−2.7		25.1	9.3
4/14/2006	−2.8		29.8	12.4
8/29/2006	−12.6		22.6	12.8
11/7/2006	−3.8		18.7	3.8
3/25/2007	−3.1		18.4	7.8
5/10/2007	−2.8		23.5	9.1
6/9/2007	−1.7[a]		27.6	15.6
7/27/2007	−3.8		28.2	14.2
9/20/2007	−5.8		28.1	10.1

Isotope data in per mil (‰) relative to VSMOW.
[a] Samples had large bubbles in vial prior to analysis and data have been omitted from figures and averages.

−5.5‰ to −4.0‰. Two-hundred and five water samples from seven separate drip sites at IS were collected between April of 1999 and January of 2005 and analyzed for oxygen isotopes with $\delta^{18}O$ values ranging from −5.5‰ to −2.3‰ VSMOW. One hundred and eighty-five water samples from six separate drip sites at NB were collected between December of 1998 and September of 2007 and analyzed for oxygen isotopes. NB drip-water samples have $\delta^{18}O$ values ranging from −5.1‰ to −0.6‰. Additional data for NB drip waters collected between 1995 and 1997 ($n = 14$) have $\delta^{18}O$ values that fall within this range (Musgrove, 2000). Oxygen isotope values for KP ($n = 2$) and DS ($n = 3$) have average values of −5.4‰ and −4.9‰, respectively (Musgrove, 2000).

Compared to Austin rainfall (Fig. 2a), drip waters in all three caverns have little variation in their $\delta^{18}O$ values – generally within 1‰ of their average values (Fig. 5, Tables 3–5). All collected and analyzed drip-water $\delta^{18}O$ averages and standard deviations from each drip site in the three caverns are compared with the weighted average of all collected Austin precipitation $\delta^{18}O$ values (Fig. 6). The weighted average of Austin precipitation $\delta^{18}O$ values lies within the range of the average values and standard deviations for most NB sites. The average $\delta^{18}O$ values for IS drip sites are intermediate between NB and CS, and the average $\delta^{18}O$ values of CS drip waters are generally lower than the weighted average of Austin precipitation as well as the drip waters from the other two caves.

A strong negative correlation between distance from the Gulf of Mexico, and mean drip-water $\delta^{18}O$ values is observed (Fig. 7a, $R^2 = 0.95$). A positive trend is also observed between average annual local surface temperature above the caves and mean drip-water $\delta^{18}O$ values, although it is not a statistically significant correlation There is a positive correlation between cave entrance elevation and mean drip-water $\delta^{18}O$ values (Fig. 7c, $R^2 = 0.90$). Drip-water samples generally plot on or near the LMWL, with the exception of two samples from drip site ISST that plot above it (Fig. 4).

Discussion

We first consider atmospheric processes that potentially control the oxygen isotope composition of central Texas precipitation. Next, we examine hydrologic processes that influence drip-water oxygen isotopes. We then note regional oxygen isotopic trends observed in-cave drip waters and conclude with the implications of these results for speleothem paleoclimatology.

Austin rainfall O isotope variation

The oxygen isotope composition of Austin rainfall varied from −12.6‰ to −1.1‰ VSMOW over the 8 year time period of the study (Fig. 2a; Table 2). Temporal $\delta^{18}O$ variations in meteoric precipitation at a specific location in middle latitudes can be controlled by a variety of factors including temperature, precipitation amount, the moisture source of individual rain events, the path those vapor masses traveled, and variations in kinetic effects during evaporation of the vapor mass in the marine source region (Dansgaard, 1964; van Beynan and Febbroriello, 2006).

Effects of moisture source

There is evidence that variability in the source of water vapor masses plays an important role in determining the oxygen isotope value of individual rain events in central Texas. The majority of moisture falling as precipitation in central Texas originates from the Gulf of Mexico (Bomar, 1995; Slade and Patton, 2003). Thus, it is likely that the weighted average $\delta^{18}O$ value of precipitation (−4.1‰) primarily reflects the composition of typical vapor masses that originate from the Gulf of Mexico. Over the eight year period of this study, the majority of monthly precipitation data varied within ~2‰ of this average value (Fig. 2a); however, there were at least two central Texas rain events that reached very low $\delta^{18}O$ values. The first such event occurred in Austin, Texas on October 17th and 18th of 1998. During these two days, moisture originating from Pacific Hurricanes Madeline and Lester, both of which occurred off the west coast of Mexico (Avila and Guiney, 2000), tracked northeast into Texas. Six instantaneous precipitation samples (Table 6) were collected over a period of ~24 h from this rain event and reached a minimum $\delta^{18}O$ value of −12.6‰, which is ~8‰ below the average value for cumulative samples of Austin precipitation over the 8 year study. The second rain event occurred

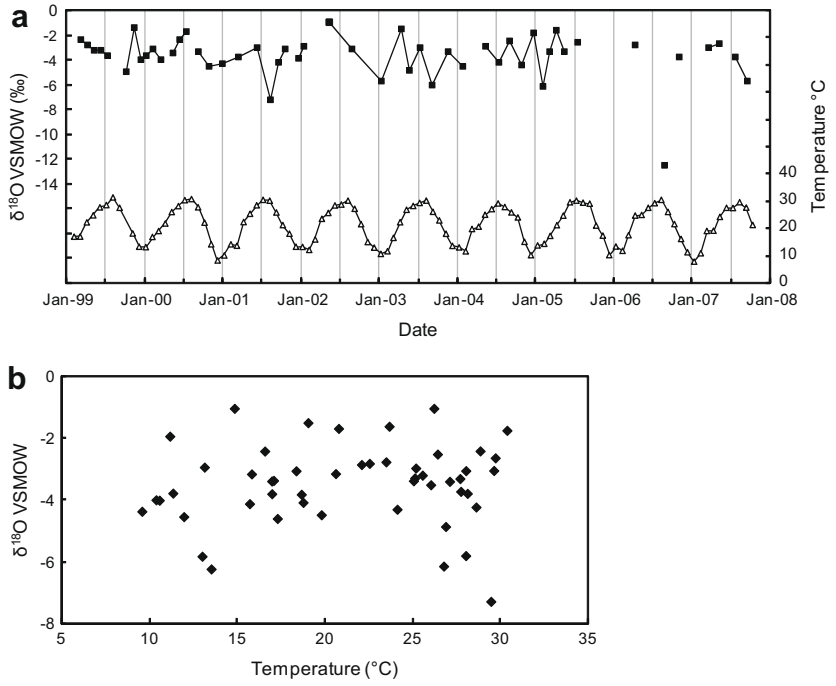

Fig. 2. (a) Upper curve: $\delta^{18}O$ values of cumulative precipitation samples collected on the rooftop of the Jackson Geological Sciences building on the UT Austin campus. Plotted points are located at the midpoint of each collection interval. Breaks in the curve connecting collection intervals indicate intervals without analyses for greater than 1 month. Analytical uncertainty of $\delta^{18}O$ values is +/−0.1 per mil, and is smaller than the size of the symbols shown. Lower curve: average monthly temperature for Austin Texas. (b) $\delta^{18}O$ values for Austin precipitation vs. average temperature during each collection interval.

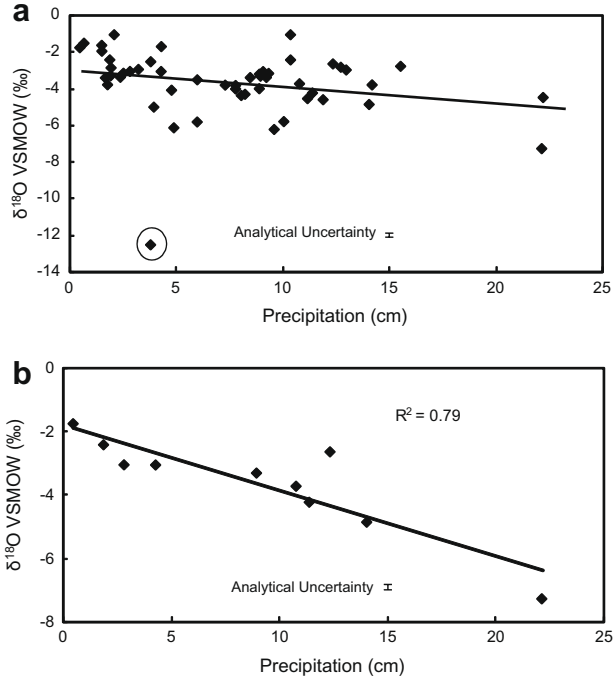

Fig. 3. (a) $\delta^{18}O$ values for Austin precipitation vs. normalized mean monthly precipitation for all collection intervals. $R^2 = 0.21$ and is statistically significant when the negative outlier from the collection interval from 8/9/2006 to 9/16/2006 that is reflective of Pacific moisture source (circled) is excluded. (b) $\delta^{18}O$ values for Austin precipitation vs. normalized mean monthly precipitation for 10 of the warmest collection intervals (collection interval average temperatures range between 26.9 °C and 30.4 °C). The data point from the collection interval from 8/9/2006 to 9/16/2006 is excluded because this sample primarily represents moisture from a Pacific Ocean source. This is elaborated on in detail in the discussion.

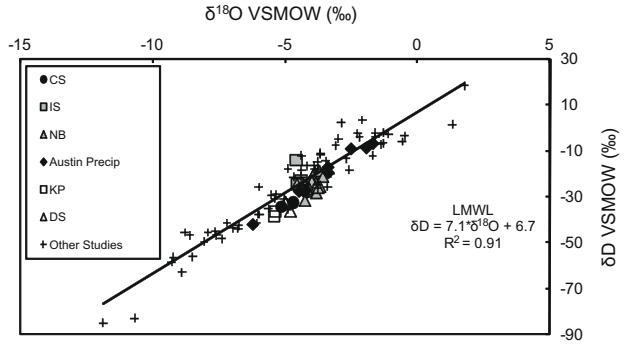

Fig. 4. $\delta^{18}O$ vs. δD for cave drip waters and precipitation. A Local Meteoric Water Line (LMWL) is established using $\delta^{18}O$ and δD results Austin precipitation reported in the present study, as well as isotopic data from precipitation and meteoric water available from other studies in central Texas (Oetting, 1995; Fahlquist and Ardis, 2004; IAEA/WMO, 2006; Otero, 2007; Slattery et al., 2006; US Geological Survey, 2008). Cave drip-water $\delta^{18}O$ and δD data for Kickapoo Cavern, Devil's Sinkhole, and additional data for Natural Bridge Caverns from Musgrove (2000).

on September 17th and 18th of 2006. This event was associated with a storm system originating from the Pacific Ocean off the west coast of Mexico. This rain event may also have been related to Pacific tropical cyclone activity as tropical storm Miriam was located off the coast of Northern Mexico prior to its occurrence. Water collected from this event was part of the cumulative rooftop precipitation sampling between 8/9/2006 and 9/19/2006 (Table 2). Based on NCDC rainfall data from Bergstrom International Airport, rain from this single event comprised ~80% of the cumulative sample collected during the 41 day collection interval. Thus, it can be assumed that the isotopic composition of the rain water collected during this interval is dominantly influenced by this single rain event. The $\delta^{18}O$ value of water collected during this interval was $-12.6 \pm 0.1‰$, which is within uncertainty of the isotopic composition of rain from the October 1998 rain event and, similarly, is very low compared to the average value for Austin.

Table 3
Caverns of Sonora: oxygen and hydrogen stable isotopic composition of drip-waters.

Sample collection date	CSDC	CSHL	CSDP	CSSF	CSDL	CSRP
5/29/2000			−4.4			
6/28/2000		−5.1				
6/29/2000	−5.2		−4.8			
7/27/2000	−5.1		−4.6			
9/30/2000	−5.3		−4.8			
10/28/2000	−5.1	−5.1	−4.8			
12/2/2000	−5.2	−5.2	−4.8			
1/6/2001	−5.3	−5.1	−4.8			
5/3/2001	−5.2	−4.6	−4.7			
7/7/2001	−5.2	−5.0	−4.0			
4/13/2002	−5.2	−5.0	−4.8			
7/20/2002	−5.2	−5.0	−4.8			
9/22/2002		−5.0	−4.8			
11/23/2002	−5.2	−5.0	−4.8			
6/9/2003	−5.2	−5.1	−4.8			
7/22/2003	−5.3	−5.1	−4.8			
8/25/2003	−5.1	−5.0	−4.8	−5.5	−4.9	−4.8
10/10/2003	−5.2	−5.1	−4.8	−5.2	−4.0	
1/15/2004	−4.7	−4.9	−4.6	−5.1	−4.2	−4.7
5/9/2004	−5.2	−4.8	−4.8	−5.1	−4.8	−5.0
7/29/2004	−5.2	−4.7	−4.8	−4.9	−4.5	−4.9
11/7/2004	−5.2 (−35)	−4.6 (−33)	−4.7 (−28)	−4.2 (−35)	−4.0 (−25)	−4.5 (−27)

All data in per mil (‰) relative to VSMOW; δD values in parentheses.

Two possible explanations can account for the very low $\delta^{18}O$ values recorded in these rain events. First, both of these events were potentially related to Pacific tropical cyclone activity. Tropical cyclones in the eastern Pacific can produce $\delta^{18}O$ values in precipitation that fall below −12‰ (Lawrence et al., 2002). Therefore, it is possible that the initial isotopic compositions of the vapor masses were strongly depleted in ^{18}O. Alternatively, since both of these rain events were associated with moisture sourced from the Pacific Ocean, the relatively long terrestrial transit distance for Pacific moisture to reach central Texas compared to that for moisture originating from the Gulf of Mexico may also account for the observed low $\delta^{18}O$ values of these rain events. Vapor masses originating in the Pacific Ocean travel at least 1000 km before reaching central Texas compared to ~250 km for Gulf of Mexico vapor masses, thereby experiencing increased Rayleigh distillation during transit. All other factors being equal, a Pacific vapor mass and any resulting precipitation will therefore have lower $\delta^{18}O$ values due to distillation of the parent vapor mass.

The data collected in this study are insufficient to conclusively determine whether the transit distance of Pacific sourced vapor masses or the influence of Pacific tropical cyclones is primarily responsible for the low $\delta^{18}O$ values observed in these two rain events. It is also important to note that precipitation from tropical cyclones in the Gulf of Mexico can have $\delta^{18}O$ values that are as low as −14.3‰ (Lawrence and Gedzelman, 1996). Thus, it can be concluded that, without prior knowledge of the source of the parent moisture mass, very low $\delta^{18}O$ values in central Texas precipitation most likely reflect the influence of tropical cyclones in the Gulf of Mexico or Pacific Ocean, increased vapor mass evolution related to the relatively long distance traveled by Pacific sourced moisture masses, or a combination of these factors.

Temperature and amount effects

If the temperature effect were a control on the temporal oxygen isotope composition of meteoric precipitation in Austin, one would expect to see a positive correlation between increasing local temperature and increasing $\delta^{18}O$ values in precipitation (Dansgaard, 1964). No such correlation exists for Austin precipitation (Fig. 2b) indicating that variation in temperature is not a primary factor influencing oxygen isotope composition in local precipitation.

Precipitation amount may also be a control on the oxygen isotope composition of Austin precipitation. If this is the case, $\delta^{18}O$ values in precipitation will correlate negatively with increasing precipitation amount, as commonly observed in tropical rainfall time series (Dansgaard, 1964; Jones and Banner, 2003). In regions outside of the tropics, the amount-effect correlation is often stronger during warmer periods (Dansgaard, 1964; Higgins and MacFadden, 2004). A comparison of mean monthly precipitation amount and $\delta^{18}O$ for the 10 warmest collection intervals from the Austin cumulative rainfall dataset (Fig. 3b) shows that an amount effect correlation is evident in Austin precipitation during the warmest time periods (average temperatures between 26.9 and 30.4 °C). The correlation decreases significantly when the entire dataset is considered (Fig. 3a). Although there is a trend of decreasing $\delta^{18}O$ values with increasing precipitation amount, an amount effect cannot account for most of the variation in the data.

Several effects may cause some Austin precipitation $\delta^{18}O$ values to plot off of the general amount-effect trend. During cold periods, the temperature effect can potentially produce negative outliers in the amount effect trend. For the Austin precipitation data, two negative outliers of −5.9‰ and −6.3‰ (Fig. 3a) occurred during periods when the average temperature was below 13 °C. Another likely cause of negative outliers in the data is variability in the source of water vapor masses. As noted above, moisture input from tropical cyclones in central Texas precipitation can have low $\delta^{18}O$ values, and meteoric waters originating from a Pacific moisture source could also have low $\delta^{18}O$ values due to their relatively long terrestrial transit distance. Thus, precipitation inputs in the monthly cumulative rain samples from Pacific Ocean sourced moisture and/or tropical cyclones will bias those samples toward low $\delta^{18}O$ values. Similarly, variability in the paths that individual vapor masses travel will also cause scatter in this amount-effect trend. Finally, kinetic effects that occur during vapor mass development via evaporation from the ocean in the marine source region will favor the preferential incorporation of lighter isotopic masses into vapor masses evaporating from the ocean. During evaporation from the ocean, kinetic effects occur to some extent because evaporation typically occurs under conditions of less than 100% relative humidity (Dansgaard, 1964; Ingraham, 1998). Thus, if greater than usual kinetic effects occur during evaporation from the Gulf of Mexico, this will produce initial vapor masses with lower $\delta^{18}O$ values, which will subsequently precipitate ^{18}O-depleted rainfall.

Table 4
Inner Space Cavern: oxygen and hydrogen isotopic composition of drip-waters.

Sample collection date	ISPR	ISLM (right view)	ISLM	ISHW	ISDC	ISBH	ISST
4/8/1999							
4/9/1999	−4.3						
5/19/1999	−4.3	−4.6					
5/20/1999			−4.7				
7/6/1999				−4.4			
7/7/1999	−4.3		−4.6				
8/19/1999				−4.4			−4.5
8/20/1999	−4.5		−4.5				
10/7/1999							−4.4
10/8/1999	−4.3		−4.6				
11/28/1999			−4.5				
1/31/2000	−4.3		−4.5				−4.4
3/3/2000							−4.3
3/4/2000			−4.5				
4/4/2000			−4.5	−4.5			−4.2
5/4/2000	−4.2			−4.3			−3.5
5/31/2000							−4.2
6/30/2000				−4.3			−4.3
7/1/2000	−4.2						
8/1/2000							−4.3
9/8/2000							
9/9/2000							−4.4
10/6/2000							
10/7/2000							−4.6
11/3/2000							−4.4
11/4/2000	−4.3						
12/8/2000							
12/9/2000	−4.3						−4.4
1/23/2001		−4.3		−4.4	−4.4	−4.6	
1/24/2001	−4.1						−4.4
2/27/2001		−4.4		−4.2			
2/28/2001	−4.2						−4.4
4/2/2001		−4.5		−4.3	−4.6	−4.7	
4/3/2001	−3.5						−4.4
5/8/2001		−4.4		−4.2			
5/9/2001	−4.1					−4.5	−4.4
6/7/2001	−4.1	−4.4		−2.3			−4.4
7/12/2001	−4.2			−4.3			−4.5
8/16/2001	−4.2						−4.5
9/13/2001	−4.4	−4.4		−4.4		−4.4	−4.4
10/5/2001	−4.3			−4.1			−4.5
10/7/2001			−4.5				
11/9/2001	−4.3			−4.4			−4.4
12/14/2001		−4.3		−4.3	−4.3	−4.3	−4.3
1/16/2002	−4.3	−4.4		−4.3			−4.4
2/11/2002	−4.3			−4.2		−4.5	−4.4
3/12/2002				−4.4			
4/15/2002	−4.1			−4.3			−4.4
5/9/2002				−4.4			
5/10/2002	−4.3						−4.4
6/6/2002							
6/7/2002	−4.2						−4.4
7/10/2002	−4.1	−4.4		−4.1	−4.3	−4.3	−4.2
8/7/2002	−4.2			−4.1		−4.4	−4.3
9/13/2002	−4		−4.3	−4.2		−4.3	−4.4
10/11/2002	−4.3		−4.3	−4.3			−4.4
11/15/2002		−4.4		−4.4		−4.5	
11/16/2002	−4.4		−4.4				−4.4
12/7/2002				−4.2		−4.4	−4.5 (−23)
12/8/2002			−4.5				
12/9/2002	−4.3						
1/16/2003		−4.4		−4.4		−4.6	−5.5
1/17/2003	−4.2		−4.4				
2/20/2003				−4.4		−4.6	−4.5
2/21/2003	−4.3		−4.4				
2/28/2003			−4.3				−4.6
3/6/2003			−4.4		−4.6		
3/14/2003			−4.4				−4.6
3/20/2003		−4.5	−4.4	−4.4		−4.6	−4.5 (−25)
3/21/2003	−4.3						
4/17/2003	−4.2		−4.3	−4.4			−4.5
5/6/2003							
5/7/2003	−4.3		−4.5				−4.5
6/5/2003			−4.4				−4.6 (−14)
7/7/2003	−4.3		−4.4				−4.5
8/4/2003							−4.5

Table 4 (*continued*)

Sample collection date	ISPR	ISLM (right view)	ISLM	ISHW	ISDC	ISBH	ISST
9/4/2003			−4.3				−4.6
11/6/2003			−4.3				−4.5
1/19/2004			−4.3			−4.6	−4.5
3/8/2004		−4.3	−4.2	−4.2	−4.3	−4.7	−4.6
5/13/2004		−4.5		−4.4			−4.6
7/15/2004		−4.4	−4.4	−4.5			−4.6
9/8/2004		−4.6	−4.5	−4.4			−4.6 (−14)
11/5/2004			−4.3	−4.3		−4.4	−4.5
12/7/2004		−4.5	−4.4	−4.3		−4.5	−4.6 (−25)
1/12/2005		−4.4	−4.5	−4.4		−4.5	−4.4

All data in per mil (‰) relative to VSMOW; δD values in parentheses.

Table 5
Natural Bridge Caverns: oxygen and hydrogen isotopic composition of drip-waters.

Sample collection date	NBCT	NBEL	NBEP	NBFE	NBSB	NBWS
12/14/1998				−4.5		−4.8
5/26/1999	−4.4	−4.6				
6/24/1999	−4.5	−4.6			−4.4	−4.4
8/2/1999		−4.8				−4.3
9/15/1999	−4.4	−4.6				−4.4
9/15/1999	−4.3					
10/14/1999	−4.3	−4.6				−4.5
5/25/2000	−4.1		−4.3		−3.3	−4.4
12/22/2000	−4.4	−4.6	−4.6		−4.8	−4.5
5/16/2001	−4.3		−4.5	−4.4	−3.8	−4.4
5/17/2001		−4.5				
6/28/2001	−4.4	−0.6	−4.4	−4.3	−3.6	−4.0
7/31/2001		−4.4	−4.4	−2.9		−3.9
8/31/2001	−4.4	−4.8	−4.3		−5.1	−4.5
11/30/2001	−4.5	−4.6	−3.6	−4.0	−4.4	−4.4
12/18/2001	−4.5	−4.7	−4.5	−4.4	−4.1	−4.4
3/22/2002	−4.3	−4.6	−4.5		−4	
6/5/2002	−4.3	−4.5	−4.5		−3.7	−4.4
7/9/2002		−4.3	−4.2	−4.1		−4.3
8/30/2002	−4.1	−4.3				
10/4/2002	−4.3	−4.6				−4.3
11/8/2002	−4.5	−4.7	−4.5	−4.4	−4.7	−4.6
2/6/2003	−4.3	−4.6	−4.4	−4.2	−4.6	−4.5
3/4/2003	−4.4	−4.5	−4.5	−4.3	−4.4	−4.5
4/1/2003	−4.4	−4.4	−4.5	−4.4	−4.6	−4.5
5/15/2003	−4.3	−4.6	−4.5	−4.4		−4.5
6/19/2003	−4.4	−4.6	−4.5	−4.3	−4.1	−4.4
7/17/2003	−4.4	−4.6	−4.5	−4.3	−4.1	−4.4
8/14/2003	−4.3	−4.6	−4.5	−4.2	−3.5	−4.3
10/16/2003	−4.5	−4.6			−4.7	−4.4
12/17/2003	−4.3	−4.6	−4.2	−4.1		−4.3
2/7/2004	−4.2	−4.5	−4.2	−4.2	−4.1	−4.2
4/7/2004	−4.2	−4.4	−4.3	−4.0	−3.8	−4.2
6/9/2004	−4.3	−4.4	−4.2	−3.9	−3.9	−4.2
8/23/2004	−4.2	−4.5	−4.2	−4.1	−3.9	−4.2
10/23/2004	−4.2	−4.6	−4.2	−4.0	−4.0	−2.6
12/28/2004	−4.2	−4.4	−4.2	−4.1	−4.0	−4.2
2/12/2005	−4.4		−4.4	−4.3	−4.6	−4.4
4/2/2005	−4.4	−4.5	−4.5	−4.3	−4.6	−4.4
4/22/2007					−3.9 (−20)	
5/16/2007					−4.0 (−21)	
6/14/2007					−4.1 (−23)	
7/17/2007					−3.7 (−19)	
9/19/2007					−4.5 (−25)	

All data in per mil (‰) relative to VSMOW; δD values in parentheses.

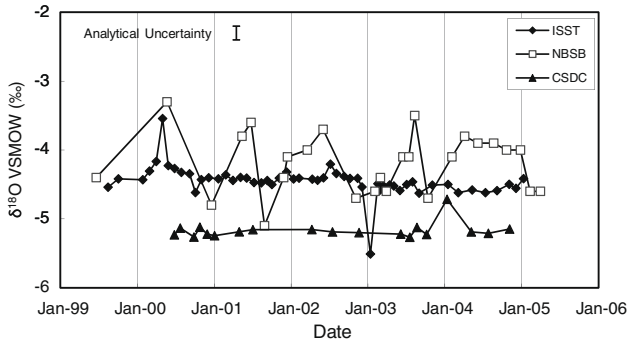

Fig. 5. $\delta^{18}O$ vs. time for a representative drip site from each cave. Temporal variations in drip site $\delta^{18}O$ values from the three caves are generally small relative to the range of Austin rainfall. NBSB experiences the greatest amount of $\delta^{18}O$ variation of all drip sites studied.

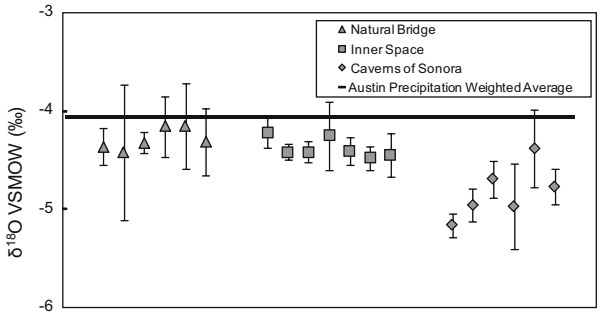

Fig. 6. Average $\delta^{18}O$ values with standard deviation of each drip site studied plotted with the average $\delta^{18}O$ value of Austin precipitation weighted to precipitation amount. Vertical bars indicate standard deviations of average values. The weighted average $\delta^{18}O$ value of Austin precipitation is shown by the bold line.

Relation of cave drip waters to meteoric waters

The stable isotope compositions of the majority of drip waters plot close to or slightly below the LMWL established from central Texas precipitation (Fig. 4). This implies that their oxygen isotopic compositions reflect the composition of meteoric waters above the caves. Cave drip waters plotting below the LMWL may have experienced evaporative effects prior to infiltrating into the unsaturated zone above the caves (Dansgaard, 1964). Three of five stable isotope values for drip site ISST (Table 2) plot on the LMWL, with values from two samples plotting well above this line. The three samples plotting near the LMWL were collected between late fall and spring, whereas the two samples that plot above the LMWL were both collected during warm periods in June of 2003 and early September of 2004 (Table 4). The timing of these deviations suggests a seasonal component to the observed variation. Cave drip-water samples could be displaced above the LMWL if they originate from precipitation that originally evaporated from the ocean under conditions of higher than average relative humidity.

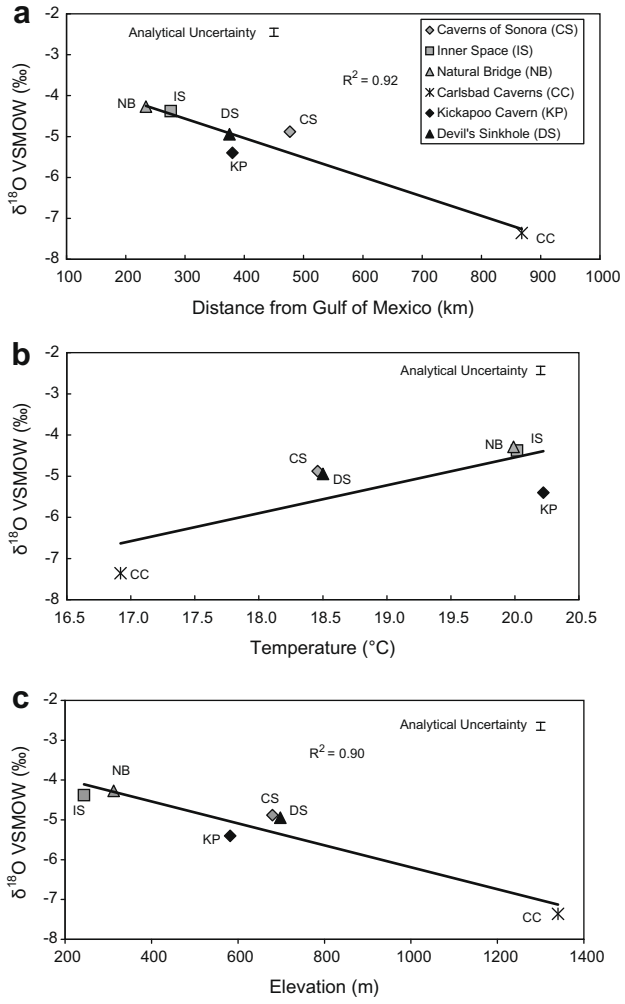

Fig. 7. (a) Mean cave drip-water $\delta^{18}O$ values vs. distance from the Gulf of Mexico. Data for Carlsbad Caverns drip waters from Chapman et al. (1992) (average value based on data from 12 drip sites). Additional cave drip-water $\delta^{18}O$ and δD data for Kickapoo Cavern and Devil's sinkhole from Musgrove (2000). (b) Mean cave drip-water $\delta^{18}O$ values plotted vs. mean annual surface temperature above caves. Mean annual surface temperatures calculated using data from the National Climatic Data Center archives (http://www.ncdc.noaa.gov) from the following stations: Carlsbad Caverns (COOP ID: 291480), Sonora (COOP ID: 418449), Canyon Dam (COOP ID: 411429), Georgetown Lake (COOP ID: 413507), Brackettville (COOP ID: 417706), and Rock Springs (COOP ID: 411007) (National Oceanic and Atmospheric Administration, 2008). (c) Mean cave drip-water $\delta^{18}O$ values vs. elevation of cave entrances.

Table 6
Oxygen isotopic composition of rainfall during single storm event, Austin, Texas.

Date	Time	$\delta^{18}O$
10/17/1998	2:37–3:30 PM	−7.4
10/17/1998	3:33–5:20 PM	−8.8
10/17/1998	5:20–8:20 PM	−9.9
10/17–18/1998	8:00 PM-1:00 AM	−10.5
10/18/1998	1:16–9:45 AM	−12.6
10/18/1998	9:45–4:00 PM	−8.9

All data in per mil (‰) relative to VSMOW.

However, this is probably not the case at ISST because ISST is a dominantly diffuse flow drip site (Guilfoyle, 2006) and has very consistent $\delta^{18}O$ values over time (Fig. 5). This implies that ISST drip waters originate from well-mixed reservoirs in the unsaturated zone and that the influence of individual precipitation events is dampened. Therefore, the isotopic composition of the drip waters at ISST should represent an annual or greater weighted average value of precipitation and plot near the LMWL. Thus, it seems more likely that processes occurring in the soil zone, unsaturated zone, or within the cave are responsible for the observed deviation of these two samples from ISST from the LMWL.

Cave drip waters at all of the drip sites in this study are saturated or supersaturated with respect to calcite (Musgrove, 2000; Musgrove and Banner, 2004; Guilfoyle, 2006; Banner et al., 2007). Water–rock interaction modeling of Edwards aquifer drip water and groundwater compositions indicates that $\delta^{18}O$ values have not been significantly altered toward equilibrium with host limestone and dolostone Compositions (Musgrove, 2000). Thus, it is unlikely that water–rock interaction has significantly altered the oxygen isotope ratio of the cave drip waters, and barring large evaporative effects, the oxygen isotope composition of the cave drip waters is representative of local precipitation (Bar-Matthews et al., 1996). This conclusion is also supported by drip waters with both δD and $\delta^{18}O$ values that fall along the LMWL (Fig. 4). Since there are no oxygen isotope data for local precipitation above the caves in this study, we compare cave drip-water values to the Austin precipitation oxygen-isotope dataset. Austin precipitation is probably an adequate representation of precipitation above both NB and IS because these caves are located within 90 km of Austin and have similar annual precipitation amounts and average temperatures. Precipitation above CS, which is located ~300 km inland of Austin, at a higher elevation, and has a ~1.5 °C lower average annual temperature, is likely to have lower average $\delta^{18}O$ values than Austin precipitation due to a combination of continental, elevation, and temperature effects.

Drip-water O isotope variation

The mean $\delta^{18}O$ value weighted to precipitation amount for Austin precipitation is -4.1 ± 2.0‰ (2σ), while the average $\delta^{18}O$ value and standard deviation for all drip sites in each cave are -4.9 ± 0.3‰ for CS, -4.3 ± 0.4‰ for NB, and -4.4 ± 0.2‰ for IS (Fig. 6). A single sample *t*-test was performed comparing the drip-water datasets from IS, NB, and CS to the single reference mean for the weighted rainwater $\delta^{18}O$ value (−4.1‰). All mean drip-water $\delta^{18}O$ values are statistically different from the reference mean. Two first-order observations can be made from these data: (1) the mean $\delta^{18}O$ values of the drip sites in each cave are lower than the weighted mean value of Austin precipitation, and (2) the cave drip waters experience significantly less variability in their $\delta^{18}O$ values than Austin precipitation. These observations are also consistent for the individual drip sites within each cave (Fig. 6).

At least two effects can cause the $\delta^{18}O$ values of cave drip waters to be negatively offset from Austin precipitation. First, as noted above, the local precipitation that feeds the drip sites at each of the caves can experience continental, temperature, and/or elevation effects that can drive it to lower average $\delta^{18}O$ values compared to the Austin dataset. This is likely the case for local precipitation at CS and may also occur at IS. The second possible effect is caused by infiltration thresholds in karst aquifers. Previous studies of karst aquifers in several tropical settings have found a precipitation amount threshold that must be exceeded for water to infiltrate into these aquifers (Jones et al., 2000; Jones and Banner, 2003) and previous work has proposed this for the Edwards aquifer (Musgrove, 2000). These recharge thresholds exist because small rain events do not generate enough runoff to transport water into the karst aquifer through discrete infiltration. Therefore, the resulting precipitation from small rain events is much more likely to be lost to evapotranspiration prior to infiltrating into the aquifer than precipitation from larger rain events. Because central Texas rainfall

has been shown to experience an amount effect during periods of warm weather (Fig. 3b), recharge thresholds that limit the infiltration of waters from smaller rain events with relatively high $\delta^{18}O$ values may contribute to the negative offset observed between the average values of cave drip waters and precipitation. Therefore, although the average $\delta^{18}O$ values of the drip waters at NB, IS, and CS are negatively offset from the weighted mean $\delta^{18}O$ value of Austin precipitation, it is likely that the average drip-water values at each cave reflect the weighted mean $\delta^{18}O$ value of local precipitation events that are above a recharge threshold.

Lack of variability of-cave drip-water $\delta^{18}O$ values compared to the meteoric precipitation feeding cave drips has been noted in many other studies on cave drip waters (Yonge et al., 1985; Chapman et al., 1992; Williams and Fowler, 2002; Onac et al., 2008). This lack of drip-water $\delta^{18}O$ variability is attributed to drip-water homogenization via mixing of meteoric waters in the matrix and/or fractures and conduits in the unsaturated zone above the caves. When this mixing occurs, drip-water $\delta^{18}O$ values are usually close to the annual weighted mean of precipitation. This mixing process can explain the lack of variation in the $\delta^{18}O$ values of the drip waters from CS, IS, and NB compared to Austin precipitation.

The extent of drip-water isotopic homogenization has implications for the residence time of drip waters within the unsaturated zone above the cave. Based on drip-rate data reported by Guilfoyle (2006), homogenization of the oxygen isotope composition of drip waters occurs for both responsive, fast-dripping sites closer to a conduit flow end-member such as NBEL (average drip rate = 3.36 ml/s; drip-rate range: <0.09–14 ml/s) and for consistent, slow-dripping, diffuse flow sites such as ISLM (average drip rate = 0.009 mL/s; drip-rate range = 0.003–0.020 ml/s). In fact, with the exception of NBSB, regular sub-annual variations in $\delta^{18}O$ values are not observed at any of the sampled drip sites, and drip sites generally vary within a range of less than 1‰ over the eight-year time period of the study. Some drip sites, most notably NBEL, display anomalous deviations from their average values, however such deviations are rare and occur inconsistently. Thus, if mixing of meteoric waters in the unsaturated zone above the caves is the cause of homogenization of cave drip waters, the residence time of meteoric waters in the unsaturated zone above the caves must be sufficient to damp out seasonal-scale variations in the $\delta^{18}O$ values of the meteoric waters feeding the drip sites. Therefore, with the possible exception of NBSB, residence time for drip waters at most sites must be on an approximately annual scale or greater.

Regional spatial $\delta^{18}O$ gradient recorded in-cave drip waters

If the drip waters in CS, NB, and IS are indeed reflective of the long-term average of local precipitation above each cave, one may reasonably expect that drip waters in these caves should have increasingly lower $\delta^{18}O$ values with increasing distance from the Gulf of Mexico reflective of the continental effect (Musgrove, 2000). Oxygen isotope variations for drip waters from six caves across the Edwards Plateau and into eastern New Mexico show a strong inverse correlation between distance from the Gulf of Mexico and average drip-water $\delta^{18}O$ (Fig. 7a). This provides evidence that the continental effect on local precipitation may be recorded by cave drip waters.

In addition to the continental effect, a temperature effect and an elevation effect could also create the observed spatial gradient in the average oxygen isotopic compositions of cave drip waters. Fig. 7b shows that the drip-water data trend toward decreasing average drip-water $\delta^{18}O$ with decreasing local average annual surface temperature above the caves. The correlation is not statistically significant; however, this is probably a factor of the limited cave drip-water data available for this study. Thus, it is likely that the temperature effect in local precipitation above the caves does contribute to the negative trend in average drip-water O isotope compositions moving inland from NB to Carlsbad Caverns (CC). A correlation between surface elevation and decreasing average drip-water $\delta^{18}O$ values also occurs for the caves (Fig. 7c). However, because the elevation effect relates to cooling of the vapor mass below the dew point through the process of orographic lift (Ingraham, 1998) it essentially reflects a temperature gradient as well.

It is difficult to determine the relative contributions of the continental and temperature effects in producing this gradient. Future studies involving regional climate models that incorporate O and H isotopes may be useful as a way to better understand how the observed spatial gradient among cave drip waters relates to climatic processes and regional changes in precipitation $\delta^{18}O$ values.

Implications for paleoclimate studies

The results of this study have a number of implications for the application of oxygen isotope composition of speleothems from these caves as a proxy for paleoclimate. Mixing of meteoric waters in the unsaturated zone above IS, NB, and CS caves caused drip waters to experience a large degree of oxygen isotopic homogenization such that they reflect a long-term weighted average composition of local precipitation above the caves. This homogenization occurred regardless of whether the drip sites from which the drip waters originated exhibited conduit flow or diffuse flow characteristics. Paleoclimate records based on oxygen isotopes in speleothems growing from such drip sites should reflect annual or greater scale variations in central Texas paleoclimate. Nonetheless, seasonal variability of cave atmosphere CO_2 levels can affect factors such as CO_2 degassing and calcite precipitation rates from drip waters, which, in turn, can alter the oxygen isotope composition of speleothem calcite (Mickler et al., 2006; Guilfoyle, 2006; Banner et al., 2007). Thus, seasonal-scale variations found in speleothem paleoclimate records originating from drip sites that have fairly constant drip-water $\delta^{18}O$ values may more likely reflect in-cave processes rather than short-term oxygen isotope variations in local rainfall.

Although the drip sites catalogued in this study have $\delta^{18}O$ values that appear to reflect a long-term weighted average of precipitation $\delta^{18}O$ values, other studies have found that cave drip waters can preserve seasonal-scale variations in the oxygen isotope composition of precipitation (Harmon, 1979; Li et al., 2000; van Beynan and Febbroriello, 2006; Johnson et al., 2007). It is possible that similar drip sites could be found in central Texas as have been identified in this region for seasonal C isotope and trace element variations (Guilfoyle, 2006; Wong et al., 2008). In this case, an oxygen isotope record of seasonal climate variation could be preserved in a speleothem precipitated from such a drip site, but seasonal controls on speleothem growth that occur in these caves would result in a seasonally-biased record (Banner et al., 2007). Negative excursions in the $\delta^{18}O$ values of such a detailed record has the potential to reflect inputs from moisture from Pacific Ocean or Gulf of Mexico tropical cyclones, or a shift in regional storm paths.

The regional spatial gradient observed in the cave drip waters may also be of use in paleoclimate studies. For example, a temporal change in the regional spatial gradient of cave drip-water $\delta^{18}O$ values inferred through speleothem paleoclimate records could indicate a major change in regional climatic factors, such as a shift in the relative contributions from vapor mass source regions. Moreover, the potential for preservation of a regional scale spatial gradient in the oxygen isotope composition of cave drip waters highlights the utility of speleothem paleoclimate studies that com-

pare speleothems from multiple, spatially distributed caves. Such studies may allow for the reconstruction of past weather patterns by using preserved temperature, elevation, and/or continental gradients in speleothem oxygen isotope compositions.

Conclusions

This study finds that precipitation in central Texas related to Pacific tropical cyclones has very low $\delta^{18}O$ values compared to the majority of central Texas precipitation that originates from the Gulf of Mexico. Tropical cyclones from the Gulf of Mexico can produce comparably low $\delta^{18}O$ values to those documented in this study from Pacific cyclones, such that very low $\delta^{18}O$ values in central Texas precipitation are not an independent indicator of storm source region. The amount effect appears to exert a strong control on the oxygen isotope composition of precipitation during periods of warm weather. However, during colder periods, the amount effect signal is likely damped by several variable factors that may include: (1) variability in the source of water vapor masses that produce precipitation in central Texas, (2) variable kinetic effects during initial evaporation of water vapor masses from the ocean, and (3) the temperature effect.

Drip-water $\delta^{18}O$ values from the three caves in this study are offset to lower values than the weighted average of Austin precipitation. This may reflect continental and temperature effects in local precipitation above the caves as well as the effects of recharge thresholds. Seasonal-scale stable isotopic variations in precipitation appear to be largely homogenized by mixing as meteoric waters percolate through the vadose zone above the caves. This homogenization implies a residence time on an approximately annual scale or greater for meteoric waters in the unsaturated zone above the caves. Drip waters have increasingly lower $\delta^{18}O$ values with increasing distance from the Gulf of Mexico. This spatial gradient most likely reflects a combination of the continental and temperature effects in the precipitation recharging the drip-water. Paleoclimate studies that examine speleothems from multiple, regionally distributed caves have the potential to reconstruct oxygen isotope gradients to constrain spatial paleoclimate patterns and vapor mass source regions.

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References

Avila, L.A., Guiney, J.L., 2000. Eastern north Pacific hurricane season of 1998. Monthly Weather Review 128 (8), 2990–3000.

Banner, J.L., Guilfoyle, A., James, E.W., Stern, L.A., Musgrove, M., 2007. Seasonal variations in modern speleothem calcite growth in central Texas, USA. Journal of Sedimentary Research 77, 615–622.

Bar-Matthews, M., Ayalon, A., Matthews, A., Sass, E., Halicz, L., 1996. Carbon and oxygen isotope study of the active water–carbonate system in a karstic mediterranean cave: implications for paleoclimate research in semiarid regions. Geochimica et Cosmochimica Acta 60 (2), 337–347.

Bigeleisen, J., Perlman, M.L., Prosser, H.C., 1952. Conversion of hydrogenic materials for isotopic analysis. Analytical Chemistry 24, 1356.

Bomar, G.W., 1995. Texas Weather. University of Texas Press, Austin.

Chapman, J.B., Ingraham, N.L., Hess, J.W., 1992. Isotopic investigation of infiltration and unsaturated zone flow processes at Carlsbad Cavern, New Mexico. Journal of Hydrology 133, 343–363.

Clark, I.D., Fritz, P., 1997. Environmental Isotopes in Hydrology. Lewis Publishers, Boca Raton, NY. 328pp.

Craig, H., 1957. Isotopic standards for carbon and oxygen and correction factors for mass spectrometric analysis of carbon dioxide. Geochimica et Cosmochimica Acta 12, 133–149.

Craig, H., 1961. Isotope variations in meteoric waters. Science 133, 1702–1703.

Dansgaard, W., 1964. Stable isotopes in precipitation. Tellus 16, 436–468.

Dorale, J.A. et al., 1992. A high-resolution record of holocene climate change in speleothem calcite from cold water cave, northeast Iowa. Science 258, 1626–1630.

Elliott, W.R., Veni, G., 1994. The Caves and Karst of Texas – 1994 NSS Convention Guidebook. National Speleological Society, Huntsville, AL.

Epstein, S., Mayeda, T.K., 1953. Variations of O^{18} content of waters from natural sources. Geochimica et Cosmochimica Acta 4, 213–224.

Fahlquist, L., Ardis, A.F., 2004. Quality of water in the trinity and edwards aquifers, South-Central Texas, 1996–98. US Geological Survey Scientific Investigations Report 2004-5201. 17p.

Fleitmann, D., Burns, S.J., Mudelsee, M., Neff, U., Kramers, J., Mangini, A., Matter, A., 2003. Holocene forcing of the Indian monsoon recorded in a stalagmite from southern Oman. Science 300, 1737–1739.

Frappier, A.B., Sahagian, D., Carpenter, S.J., González, L.A., Frappier, B.R., 2007. Stalagmite stable isotope record of recent tropical cyclone events. Geology 35, 111–114.

Fricke, H.C., O'Neil, J.R., 1999. The correlation between $^{18}O/^{16}O$ ratios of meteoric water and surface temperature: its use in investigating terrestrial climate change over geologic time. Earth and Planetary Science Letters 170, 181–196.

Friedman, I., Smith, G.I., 1970. Deuterium content of snow cores from Sierra Nevada area. Science 169, 467–470.

Guilfoyle, A.L., 2006. Temporal and spatial controls on cave water and speleothem calcite isotopic and elemental chemistry, Central Texas. Master's Thesis, University of Texas at Austin, Austin, Texas.

Harmon, R.S., 1979. An isotopic study of groundwater seepage in the central Kentucky karst. Water Resources Research 15, 476–480.

Higgins, P., MacFadden, B.J., 2004. "Amount Effect" recorded in oxygen isotopes of late glacial horse (Equus) and bison (Bison) teeth from the Sonoran and Chihuahuan deserts, southwestern United States. Palaeogeography, Palaeoclimatology, Palaeoecology 206, 337–353.

Hu, C., Henderson, G.M., Huang, J., Xie, S., Sun, Y., Johnson, K.R., 2008. Quantification of holocene Asian monsoon rainfall from spatially separated cave records. Earth and Planetary Science Letters 266, 221–232.

IAEA/WMO, 2006. Global network of isotopes in precipitation. The GNIP Database. Historical rainfall data for station 7225600, Waco, TX, 1961–1986. <http://isohis.iaea.org>.

Ingraham, N.L., 1998. Isotopic variations in precipitation. In: Kendall, C., McDonnell, J. (Eds.), Isotope Tracers in Catchment Hydrology. Elsevier, Amsterdam, pp. 87–118.

Johnson, K.R., Hu, C., Henderson, G., 2007. Modern stable isotope systematics in Heshang cave, China: implications for speleothem based paleoclimate reconstructions. AGU Fall Meeting Abstracts (abstract #PP34A-03).

Jones, I.C., Banner, J.L., 2003. Estimating recharge thresholds in tropical karst island aquifers: barbados, puerto rico and guam. Journal of Hydrology 278, 131–143.

Jones, I.C., Banner, J.L., Humphrey, J.D., 2000. Estimating recharge in a tropical karst aquifer. Water Resources Research 36, 1289–1299.

Kastning, E.H., 1983. Relict caves as evidence of landscape and aquifer evolution in a deeply dissected carbonate terrain – Southwest Edwards Plateau, Texas. USA Journal of Hydrology 61, 89–112.

Larkin, T.J., Bomar, G.W., 1983. Climatic Atlas of Texas. Texas Department of Water Resources, Austin, Texas.

Lawrence, J.R., Gedzelman, S.D., 1996. Low stable isotope ratios of tropical cyclone rains. Geophysical Research Letters 23, 527–530.

Lawrence, J.R., Gedzelman, S.D., Gamache, J., Black, M., 2002. Stable isotope ratios: Hurricane Olivia. Journal of Atmospheric Chemistry 41, 67–82.

Lee, J.E., Fung, I., 2007. "Amount effect" of water isotopes and quantitative analysis of post-condensation processes. Hydrological Processes 22, 1–8.

Li, B., Yuan, D., Qin, J., Lin, Y., Zhang, M., 2000. Oxygen and carbon isotopic characteristics of rainwater, drip water and present speleothems in a cave in Guilin area, and their environmental meanings. Science in China Series D: Earth Sciences 43, 277–285.

Mickler, P.J., Stern, L.A., Banner, J.L., 2006. Large kinetic isotope effects in modern speleothems. GSA Bulletin 118, 65–81.

Musgrove, M., 2000. Temporal links between climate and hydrology: insights from central Texas cave deposits and groundwater. Unpublished Ph.D. Dissertation, The University of Texas at Austin, Austin, TX. 432pp.

Musgrove, M., Banner, J.L., 2004. Controls on the spatial and temporal variability of vadose dripwater geochemistry: Edwards Aquifer, central Texas. Geochimica et Cosmochimica Acta 68, 1007–1020.

National Oceanic and Atmospheric Administration, 2008. National Climatic Data Center. Data from stations 291480, 410429, 418449, 411429, 411013, 417706, 411007, and 413507. Austin, TX. 1988–2007. <http://www.ncdc.noaa.gov/oa/ncdc.html>.

Oetting, G.C., 1995. Evolution of fresh and saline groundwaters in the edwards aquifer: geochemical and Sr isotopic evidence for regional fluid mixing and fluid–rock interaction, unpublished M.A Thesis. The University of Texas at Austin, Austin, TX, 204pp.

Onac, B.P., Pace-Graczyk, K., Atudirei, V., 2008. Stable isotope study of precipitation and cave drip water in Florida (USA): implications for speleothem-based paleoclimate studies. Isotopes in Environmental and Health Studies 44, 149–161.

Otero, C.L., 2007. Geologic, hydrologic, and geochemical identification of flow paths in the Edwards aquifer, northwestern Bexar and southern Comal Counties Texas. US Geological Survey Scientific Investigations Report 2007-5285. 48pp.

Rozanski, K., Araguas-Araguas, L., Gonfiantini, R., 1992. Relation between long term trends of oxygen-18 isotope composition of precipitation and climate. Science 258, 981–985.

Rozanski, K., Araguas-Araguas, L., Gonfiantini, R., 1993. Isotopic patterns in modern global precipitation. Geophysical Monograph 78, 1–36.

Shopov, Y.Y., 2004. 20 years of speleothem paleoluminescence records of environmental changes: an overview. International Journal of Speleology 33, 5–17.

Shuster, E.T., White, W.B., 1971. Seasonal fluctuations in the chemistry of limestone springs: a possible means for characterizing carbonate aquifers. Journal of Hydrology 14, 93–128.

Slade, R.M., Patton, J., 2003. Major and catastrophic storms and floods in Texas. Open-File Report – US Geological Survey, OF 03-0193.

Slattery, R.N., Furlow, A.L., Ockerman, D.J., 2006. Hydrologic and water-quality data, Honey Creek State Natural Area, Comal County, Texas, August 2001–September 2003. US Geological Survey Data Series 200, 27p.

Smart, P.L., Friedrich, H., 1987. Water movement and storage in the unsaturated zone of a maturely karstified aquifer, Mendip Hills, England. In: Proceedings of the Environmental Problems in Karst Terrains and Their Solutions Conference. NWWA, Bowling Green, KY, pp. 57–87.

Stewart, M.K., 1975. Stable isotope fractionation due to evaporation and isotopic-exchange of falling waterdrops – applications to atmospheric processes and evaporation of lakes. Journal of Geophysical Research 80, 1133–1146.

US Geological Survey, 2008. National Water Information System (NWIS Web). <http://waterdata.usgs.gov/tx/nwis/nwis> (accessed 2008).

van Beynan, P., Febbroriello, P., 2006. Seasonal isotopic variability of precipitation and cave drip-water at Indian Oven Cave, New York. Hydrological Processes 20, 1793–1803.

Williams, P.W., Fowler, A., 2002. Relationship between oxygen isotopes in rainfall, cave percolation waters and speleothem calcite at Waitomo, New Zealand. Journal of Hydrology (New Zealand) 41, 53–70.

Wong, C., Banner, J., Musgrove, M., 2008. Seasonal variations of cave dripwater trace element ratios in central Texas: implications for speleothem geochemical records. Geological Society of America Abstracts with Programs 40, 196.

Yonge, C.J., Ford, D.C., Gray, J., Schwarz, H.P., 1985. Stable isotope hydrology: deuterium and oxygen-18 in the water cycle. Chemical Geology 58, 97–105.