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# SEASONAL VARIATIONS IN MODERN SPELEOTHEM CALCITE GROWTH IN CENTRAL TEXAS, U.S.A.

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ABSTRACT: Variations in growth rates of speleothem calcite have been hypothesized to reflect changes in a range of paleoenvironmental variables, including atmospheric temperature and precipitation, drip-water composition, and the rate of soil CO<sub>2</sub> delivery to the subsurface. To test these hypotheses, we quantified growth rates of modern speleothem calcite on artificial substrates and monitored concurrent environmental conditions in three caves across the Edwards Plateau in central Texas. Within each of two caves, different drip sites exhibit similar annual cycles in calcite growth rates, even though there are large differences between the mean growth rates at the sites. The growth-rate cycles inversely correlate to seasonal changes in regional air temperature outside the caves, with near-zero growth rates during the warmest summer months, and peak growth rates in fall through spring. Drip sites from caves 130 km apart exhibit similar temporal patterns in calcite growth rate, indicating a controlling mechanism on at least this distance. The seasonal variations in calcite growth rate can be accounted for by a primary control by regional temperature effects on ventilation of cave-air CO<sub>2</sub> concentrations and/or drip-water CO<sub>2</sub> contents. In contrast, site-to-site differences in the magnitude of calcite growth rates within an individual cave appear to be controlled principally by differences in drip rate. A secondary control by drip rate on the growth rate temporal variations is suggested by interannual variations. No calcite growth was observed in the third cave, which has relatively high values of and small seasonal changes in cave-air CO<sub>2</sub>. These results indicate that growth-rate variations in ancient speleothems may serve as a paleoenvironmental proxy with seasonal resolution. By applying this approach of monitoring the modern system, speleothem growth rate and geochemical proxies for paleoenvironmental change may be evaluated and calibrated.

# INTRODUCTION

Use of the growth rate and geochemistry of cave calcite deposits, or speleothems, as paleoenvironmental proxies has grown rapidly in the past decade, reflecting the great potential of speleothems as high-resolution records for late Pleistocene and Holocene environmental change. These applications typically postulate a correlation between speleothem calcite growth rates and paleoclimate but cannot directly investigate the relationship between surface climate and subsurface speleothem growth (Musgrove et al. 2001). Radiometric chronologies cannot resolve seasonal or annual timescales of ancient speleothems. For the relatively uncommon cases where speleothems contain seasonal growth laminae (Shopov et al. 1994; Genty and Quinif 1996), meteorological data and water samples for the same time intervals are rare. Records of speleothem growth rate have the potential to address key paleoclimate questions during time intervals where other proxies have limitations (e.g., Smith et al. 2006). Of further interest, growth rates may control the extent to which geochemical proxies record equilibrium processes during speleothem growth (e.g., Huang and Fairchild 2001; Mickler et al. 2006).

We evaluate the application of the growth rate of speleothem calcite (referred to as "growth rate" hereafter) as a paleoenvironmental proxy by quantifying the growth rates of modern speleothem calcite. We placed

artificial substrates under active drip-water sites in three caves across the Edwards Plateau of central Texas. Environmental measurements taken at the drip-water sites and at the surface allow direct comparison between growth rates on the substrates and the local and regional factors that may control the growth rates. Advancing the approach of Mickler et al. (2006), sampling intervals were designed to determine subseasonal variations in growth rates, meteorological parameters, and water chemistry. Our results over six years demonstrate consistent seasonal changes in growth rates between two caves 130 km apart. We examine the roles of temperature, rainfall, drip rates, drip-water composition, and cave-air composition in controlling speleothem growth.

### HYDROGEOLOGIC SETTING AND CAVE DEVELOPMENT

The study sites span part of the Edwards Plateau (Fig. 1), which has a subhumid to semiarid subtropical climate. The plateau is a well-developed karst region built in lower Cretaceous marine carbonates, and contains caves with active speleothem deposition. It comprises parts of two regional aquifer systems, the Edwards–Trinity aquifer (Plateau aquifer) and the Trinity aquifer. The plateau also encompasses the contributing and recharge zones and is adjacent to the artesian zone of the Edwards aquifer (Balcones Fault Zone aquifer) along the plateau's southern and eastern margins. The geomorphology and hydrogeology of the plateau and the caves of this study are described by Eliot and Veni (1994), Musgrove et al. (2001), and Musgrove and Banner (2004). Caves of this study are formed below gentle slopes with thin, rocky soils supporting oak and juniper savannah. The drip waters of the caves are

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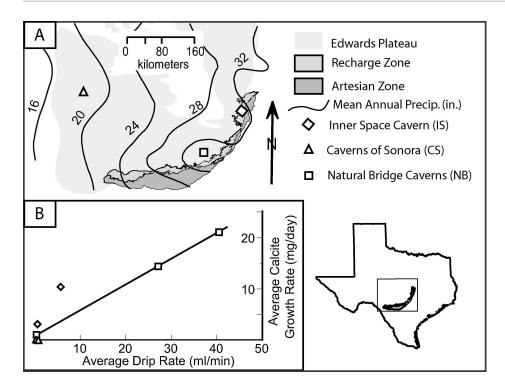


Fig. 1.—A) Maps of the Edwards Plateau and its location in central Texas, and locations of caves in which calcite growth rates were studied. The plateau comprises lower Cretaceous marine carbonate strata. Average annual precipitation in inches shown as contours (from Larkin and Bomar 1983). Different zones of the Edwards (Balcones Fault Zone) aquifer are indicated by shading. B) Average growth rate for speleothem plate calcite vs. average drip rate for eight drip sites in three caves (three sites at cave CS plot on top of each other). Regression for three sites at cave NB yields  $r^2 > 0.99$ .

Ca-HCO<sub>3</sub> waters, and were sampled at depths of 17–45 m. Inner Space Cavern (IS) is formed within the Edwards Limestone, which contains minor dolostone. Natural Bridge Caverns was divided by collapse into two caverns known as the North and South Caverns (NB North and NB South), which are formed in the interbedded limestone, marly limestone, and dolostone of the upper Glen Rose Formation and lower Walnut Formation. The Caverns of Sonora (CS) are formed in the Segovia Member of the Edwards Limestone. Land use change has occurred above each cave, most extensively above cave IS via urban development in the 1960s and establishment of a visitors center, and above NB North via a visitors center. At IS, a man-made tunnel entrance remains open to air exchange, whereas at both NB North and CS, the natural entrances are no longer open and visitors enter and exit through glass doors, normally kept closed to limit air exchange. During development of each cave, several conduits were constructed from the surface into the cave for various purposes, including running electrical cables, controlling air exchange, and surveying. Some of these conduits remained open during the course of the present study. Relative to the natural setting prior to cave development, the total cross sectional area of openings to the surface increased at caves IS and NB South, decreased at cave CS, and remained approximately the same at cave NB North.

# METHODS

Modern speleothem calcite was collected by placing  $10~\rm cm \times 10~\rm cm$  glass plates horizontally under active drip sites in the three caves. Sites chosen were previously characterized for drip-rate and geochemical variability (Musgrove and Banner 2004). Plates were retrieved at 4–8 week intervals, except at CS, where they were retrieved at 5–16 week intervals. The amount of calcite growth during a given time interval was determined by weighing each plate before and after its deployment. Precise weights are obtained using multiple calibrations. Glass plates were sandblasted, cleaned, weighed, and mounted horizontally on a clay or plastic support placed on cave formations, which are protected with a polyethylene bag. The weights of plates, before and after calcite growth, were determined using a Sartorius MC1 RC 210P electronic balance. The

balance is calibrated internally prior to each use and externally on a periodic basis. An active ionized air generator is used to control static charging during weighing. Repeated measurements of the weight of an inhouse standard glass plate are interspersed with measurements of the glass sample collection plates and are used to adjust sample weights for drift in the balance. Prior to the use of the ionized air generator, reproducibility of the weight of the standard plate yielded a standard deviation of 0.0165 g. Use of the ionizing system starting in January of 2003 improved reproducibility substantially, yielding a standard deviation of 0.0003 g, with an average standard deviation for a given day's measurements of the standard plate of 0.00007 g.

Drip-water pH, conductivity, and temperature were measured in the field. In situ pH measurements on small-volume water films on plates and natural speleothems were made using an IQ solid-state pH probe. Ion concentrations were measured by ICP–MS, ion chromatography, and titration. Cave-air relative humidity, temperature, and  $CO_2$  concentration were measured during each cave visit with portable meters. Relative humidity was measured using a Vaisala HM34 and an Omega RH85 (+/–5% above 90% RH), and  $CO_2$  concentrations and temperature were measured using a Telaire 7001 meter.  $CO_2$  data are reported as concentrations (Table 1). Discussions in the text refer to cave-air  $P_{CO_2}$  for comparison with drip-water  $P_{CO_2}$ . Conversion from concentration to  $P_{CO_2}$  requires measurements of barometric pressure, which are not available, but the conversion would result in differences of less than the measurement uncertainty of +/– 5%. Surface meteorological data are from NOAA's National Climatic Data Center database.

### RESULTS

Results for calcite growth rates, drip-water chemistry, and cave meteorology are given in Table 1. Eight drip sites were monitored from 2001 through 2006, during which time calcite growth rates ranged from 0 to 107 mg/day (within measurement uncertainty, see Table 1), with mean growth rates at each site ranging from 0 to 21 mg/day (Table 1, Fig. 1B). Calcite grown on the plates occurs mainly as isolated to intergrown crystals of low-Mg calcite, 10 to 500 microns in length. Calcite

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Site	Depth (m)	Water Temp (°C)	Drip rate (ml/min)	pН	S.I. <sub>calcite</sub>	Calcite growth rate (mg/day)	Ca (mg/L)	Cave-air CO <sub>2</sub> (ppm)	RH (%)
Inner Space C	'avern								
ISST	17	18.6-22.5	0.12 - 16.5	7.29-8.52	-0.33 - 1.06	0-36.5	62-92	450-7780	89-96
ISLM	20	20.7-23.4	0.13 - 0.94	6.75-8.42	-0.10 - 1.17	0-13	87-101	500-7670	90-98
Natural Bridge	e Caverns Nor	th Cavern							
NBCT	42	17.5-24.2	1.07-200	6.82-8.27	-0.04 - 1.02	0-107	52-99	380-7890	90-98
Natural Bridge	e Caverns Sou	th Cavern							
NBOP	45	ND	0-0.23	ND	ND	0-4.36	57-67	610-31,000	86-95
NBWS	45	17.5-24.2	2.4-300	6.77-8.15	-0.19 - 1.11	0-63.1	85-137	920-30,000	89–97
Caverns of So.	nora								
CSDP	30	19.8-25.1	0.21-1.77	7.39-8.15	0.15-0.61	0	68-74	3290-5640	85-93
CSDC	35	19.5-24.6	0.26-0.37	7.16-7.99	0.20-0.30	0	69-73	4530-6500	85-95

TABLE 1.—Ranges of cave drip site physical and chemical parameters.

S.I. calcite = log [IAP/K<sub>sp</sub>], where IAP = ion activity product [Ca<sup>2+</sup>]\*[CO<sub>3</sub><sup>2-</sup>]; K<sub>sp</sub> = solubility product constant of calcite at measured water temperature. S.I. values calculated using PHREEQC (Parkhurst and Appelo 1999). RH = relative humidity. ND, not determined due to slow drip rates. Calcite growth rates reported as zero are those below the detection limit of 0.37 mg/day prior to January 2003, and below 0.007 mg/day after this date, as described in the Methods section. Ranges given for the time period shown in Figures 3 and 4, except for Ca and S.I. calcite, for which ranges are for time period up to January 2006 for IS and NB sites, and up to October 2003 for CS sites.

0.20 - 0.40

6.95-7.84

morphology ranges from equant rhombohedra to complexly faceted crystals. Mean calcite growth rates over the study period at different drip sites correlate directly to mean drip rate (Fig. 1B). Within and between caves NB and IS, 130 km apart, different drip sites exhibit similar temporal cycles in growth rates, despite these sites having large differences in their mean growth rate (Figs. 2, 3). These cycles correspond to seasonal changes above the caves, with the lowest growth rates occurring during the summer, and peak growth rates occurring in fall through spring (Figs. 2, 3). In contrast, growth rates at all three drip sites at CS are within analytical uncertainty of zero year-round. Annual rainfall and effective precipitation are much lower, and cave-air  $P_{\rm CO2}$  is more constant at CS compared with NB and IS (Fig. 1; Table 1). Results for the five NB and IS drip sites, which exhibit significant temporal changes in growth rates, are described herein.

19.3-23.7

0.50 - 0.78

30

Temporal changes in growth rate are inversely correlated to outside air temperature at all five NB and IS sites (highly significant at p < 0.01), and also inversely correlated to changes in cave-air  $P_{\rm CO2}$  at all five sites (significant at p < 0.05; Table 2; Figs. 2, 3). Temporal growth rate changes are also inversely correlated to drip-water  $P_{\rm CO2}$  at three of four sites (p < 0.05). A weaker correspondence is found between temporal growth rate changes and both drip rate and effective precipitation, with three of five sites having a significant correlation (Table 2; Figs. 2, 3).

Near-zero growth rates occur at essentially the same time each year, in July-August at sites ISLM, ISST, and NBWS, and in June-August for sites NBOP and NBCT, coinciding with peak outside-air temperatures (~ 29°C; Figs. 2, 3). Within the uncertainty interval of the 4-8 week sampling periods of calcite growth, the slowest calcite growth rates each year coincide with the warmest outside air temperatures each year (vertical dashed lines in Figs. 2, 3). During all of the periods of near-zero calcite growth, drip rates do not fall to zero at any site (Figs. 2, 3). The rise in growth rates at site ISLM, which is located deeper in cave IS, consistently lags the growth rate rise at site ISST by one to four months each year (Fig. 3). Drip waters range from slightly undersaturated to supersaturated with respect to calcite, as indicated by saturation indices from -0.33 to 1.17, with the highest values typically occurring from November to March (Table 1; Guilfoyle 2006). In contrast, drip water Ca concentrations at a given site show limited variability (Table 1). During the fall-winter of 2005-2006, relatively low effective precipitation occurred above both caves, low drip rates occurred at all five IS and NB sites, and low calcite growth rates relative to other years occurred at three of the five sites (Figs. 2, 3).

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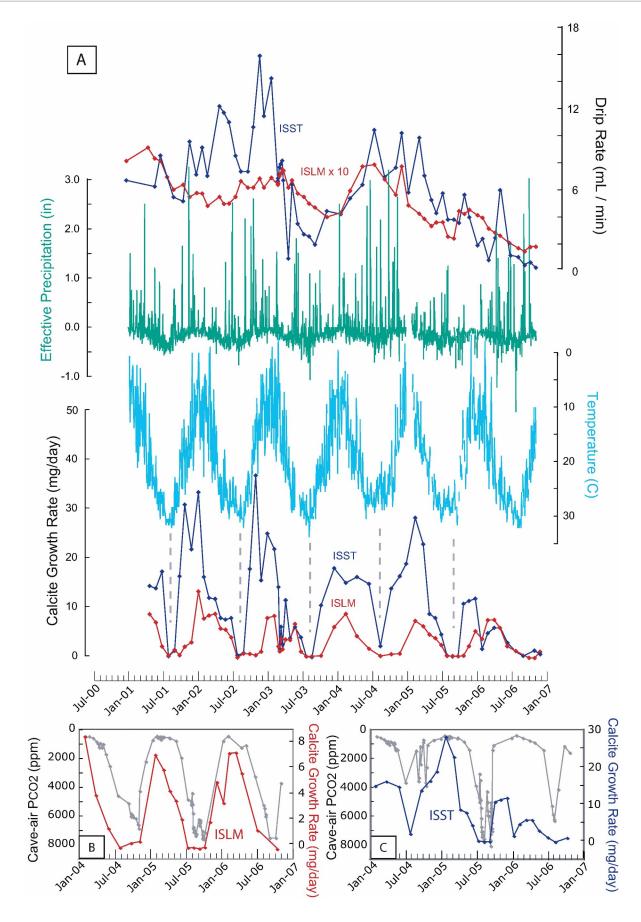
Cave-air  $P_{CO2}$  varies seasonally in caves IS and NB, with low, near-atmospheric levels in the winter, and higher values measured during summer months, coinciding with the periods of lowest growth rate (Figs. 2B, C, 3B, C). Similarly, high cave-air  $P_{CO2}$  in summer and low cave-air  $P_{CO2}$  in winter are found in caves from a variety of locations (e.g., Buecher 1999; Carrasco et al. 2002). Carbon dioxide levels in most caves are controlled by the balance between  $CO_2$  transport into the cave from overlying soil and removal of  $CO_2$  via cave ventilation. Ventilation is often seasonally driven by temperature and density contrasts between outside and cave air (Wigley and Brown 1976).

Spatial measurements of the pH of water films on the plates and natural substrates at site ISST in March and July 2005 reflect chemical evolution during water flow. For each time period, pH increased radially outward from the point of drip impact to the plate edge. In March, pH increased outward from 7.78 to 7.99, whereas in July pH increased outward from 7.59 to 7.61. Similar downstream pH gradients were observed in water films on a flowstone at this site. The higher pH and larger pH gradient occurred at this site in March, when cave-air  $P_{\rm CO2}$  was low (550 vs. 4800 ppm in March vs. July) and calcite growth rate was high (22.5 vs. 4.2 mg/day in March vs. July).

# DISCUSSION

# General Controls on Growth of Speleothem Calcite

Deposition of speleothem calcite is driven by the degassing of CO<sub>2</sub> from water entering a cave, which engenders, or increases, calcite supersaturation in the water (Holland et al. 1964). The controls on speleothem growth have been analyzed empirically in Pleistocene and Holocene speleothems, and by theoretical consideration of a range of physical and chemical controlling factors (Baker et al. 1993; Dreybrodt 1988). Modeled speleothem calcite precipitation is dependent on the interplay of a number of factors, including rainfall and amount of infiltration, drip rate, drip-water calcium concentration, water-film thickness, cave-air CO<sub>2</sub> concentration, soil and bedrock thickness, and temperature (Dreybrodt 1988). Temperature affects multiple factors that influence growth rate, including calcite solubility, soil CO<sub>2</sub> production, solubility of CO<sub>2</sub>, and effective precipitation, leading to both growth-



enhancing and growth-retarding effects (Dreybrodt 1988). Models also predict that drip-water Ca concentration and drip rate will positively correlate with speleothem growth, and studies of some Holocene speleothem growth rates support this prediction (Genty et al. 2001).

The specific relationship between speleothem growth rate and these factors, however, is complex and influenced by local differences. For example, a direct relationship between temperature and growth rate is attributed to the controls of surface temperature and soil moisture on soil CO<sub>2</sub> production, yet this relationship may break down for sites with little soil cover (Genty et al. 2001). Soil CO<sub>2</sub> production is correlated with soil temperature both geographically and temporally at specific locations, but soil moisture availability also affects soil respiration rates (Reichstein et al. 2003). While numerous factors may influence speleothem growth, two basic conditions must be met for speleothem growth to occur: (1) high CO<sub>2</sub> levels in the soil zone, which contribute to elevated P<sub>CO2</sub> of the infiltrating water, calcite dissolution, and subsequent CO<sub>2</sub> degassing in the cave, and (2) an availability of water for recharge (Baker et al. 1993).

## Controls on Central Texas Speleothem Growth Rates

We summarize here several key observations (from Figs. 1–3, and Tables 1 and 2) that constrain the mechanisms that control growth rates of calcite on glass plates at caves IS and NB: (1) the pronounced seasonal changes in growth rate; (2) the significant inverse correlation between growth rate and surface air temperature at all sites; (3) the similar temporal changes in growth rate from site-to-site within and between caves, including sites that differ by two orders of magnitude in their average growth rates; (4) the near-zero growth rates at each site during the warmest months of each year; (5) the positive correlation between average drip rate and average growth rate from site to site; and (6) the limited variability in drip-water Ca concentrations.

The consistent site-to-site and cave-to-cave seasonality in growth rate (observation 3) precludes mechanisms controlling growth rates that involve the particular evolution of flow paths or water chemistry at an individual drip site. The mechanism must operate on at least the 130-km distance between caves IS and NB. Temporal variations in growth rate in a given cave might be influenced by the changing delivery rate of supersaturated water, which would in turn be a function of effective precipitation, soil CO<sub>2</sub> output, and variations in water residence time in the vadose zone. Positive calcite saturation indices and non-zero drip rates throughout most of the year at caves IS and NB leads to the prediction that some deposition of calcite will take place during most of the year. A drip-rate control is also consistent with the site-to-site variability in growth rate (Fig. 1B), and some interannual variation in growth rate appears to correspond to changes in drip rate (e.g., low drip rate and growth rates during fall-winter of 2005-2006; see Results). However, the near-zero growth rates at all sites each summer, when drip rates are not zero, indicates a mechanism other than drip rate as the main control on the seasonal changes in growth rate. A process that can control growth rates in this manner is changes in  $P_{CO2}$  of the cave air.

The seasonal changes in cave-air CO<sub>2</sub> (Figs. 2B, C, 3B, C) is the likely mechanism controlling the low speleothem growth rate during summer months. The low cave-air CO<sub>2</sub> levels during the winter cause a large contrast in CO<sub>2</sub> concentration between cave air and drip water ("airwater CO<sub>2</sub> contrast" hereafter), which drives CO<sub>2</sub> degassing from the drip water (Spötl et al. 2005). This in turn would yield high levels of calcite supersaturation in the drips, and increase calcite precipitation rates.

Elevated summertime cave-air  $P_{\rm CO2}$  levels, on the other hand, would lower the air-water  ${\rm CO_2}$  contrast, which would inhibit degassing and reduce the rate of calcite growth. The lack of calcite growth at cave CS during any season is consistent with its relatively invariant and high levels of cave-air  ${\rm CO_2}$  (Table 1).

Two possible mechanisms can explain the observed seasonal variations in cave-air  $P_{CO2}$ . (1) First, many caves exhibit seasonal variations in caveair  $P_{CO2}$  that are a function of the temperature difference between cave air and outside air. During the winter, caves are often well ventilated as a consequence of relatively cold and dense outside air (with low, atmospheric CO2 levels) displacing warmer, high-CO2 cave air. This lowers cave-air P<sub>CO2</sub> and increases the air-water CO<sub>2</sub> contrast. During the summer, relatively warm outside air and relatively stable high-pressure weather systems create the opposite effect, leading to stagnant cave air with high P<sub>CO2</sub> (e.g., Kartchner Caverns, Arizona; Obir Cave, Austria; Buecher 1999; Spötl et al. 2005). The ventilation process will vary within a cave depending on location, and between caves and regions, depending on cave geomorphology, temperature seasonality, and water flow, among other factors. The decrease in cave-air P<sub>CO2</sub> at the onset of the cool season in Texas is closely followed each year by the increase in growth rate at site ISST, which in turn precedes the same changes at site ISLM. Because ISLM is deeper in cave IS, this cool-season sequence is consistent with the ventilation mechanism. (2) Alternatively, seasonal changes in cave-air CO<sub>2</sub> at caves IS and NB may be driven by drip-water delivery of higher levels of dissolved CO<sub>2</sub> to the cave in the summer. Low wintertime dripwater P<sub>CO2</sub> likely results from temperature control on soil respiration. Central Texas soil respiration rates are high during the spring through late summer, with a peak in late summer, and low during the fall and winter (Litvak et al., unpublished data). High summer temperatures, coupled with the plateau's thin soils, make soil moisture availability during the summer low except following intermittent, large rain events common to this region. Re-wetting of warm soils in such environments can induce rapid and large increases in soil respiration (Huxman et al. 2004), and recharge is also associated with these events. While a soil CO<sub>2</sub> production model can account for seasonal cave-air CO<sub>2</sub> changes, ventilation is also required to provide the air-water CO<sub>2</sub> contrast needed for driving seasonal changes in growth rate. The lack of both calcite growth and pronounced seasonal CO2 changes at cave CS suggest that relatively little ventilation occurs at this cave.

Cave-air CO<sub>2</sub> levels may also be affected by visitors, in as much as their respiration adds to CO2 levels (Ek and Gewelt 1985; Baker and Genty 1998; Baldini et al. 2006). This effect may be significant in show caves (Carrasco et al. 2002) such as IS, NB, and CS. Visitation at caves IS and NB reaches a maximum in the summer each year, suggesting an alternative mechanism to the outside air temperature or soil respiration control on the seasonal cave-air CO2 changes observed. Several observations, however, indicate that the contribution from visitor respiration is not the primary control on the seasonal cave-air CO<sub>2</sub> variations: (1) visitation rates peak in March and July each year at each cave, but cave-air CO<sub>2</sub> increases or maintains a relatively high level throughout the summer and through September at most sites each year (Figs. 2B, C, 3B, C); and (2) the highest CO<sub>2</sub> levels occur in the least visited cave (NB South, Fig. 3B). Regardless of the mechanism causing low cave-air CO2 levels during the fall-winter, it is the larger fall and winter air-water CO<sub>2</sub> contrast that likely drives greater degassing, resulting in higher calcite supersaturation and more growth.

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Fig. 2.—A) Time series of modern speleothem plate calcite growth rate and drip rate for sites ISST and ISLM in cave IS, and outside air temperature (plotted inverse) and effective precipitation (= rainfall - evaporation). Vertical dashed gray lines indicate average midpoint of slowest growth period for the two sites each year. ISLM drip rates are multiplied by 10 for comparative purposes. B, C) Time series of cave-air P<sub>CO2</sub> (plotted inverse) and modern speleothem plate calcite growth rates for the same IS sites.

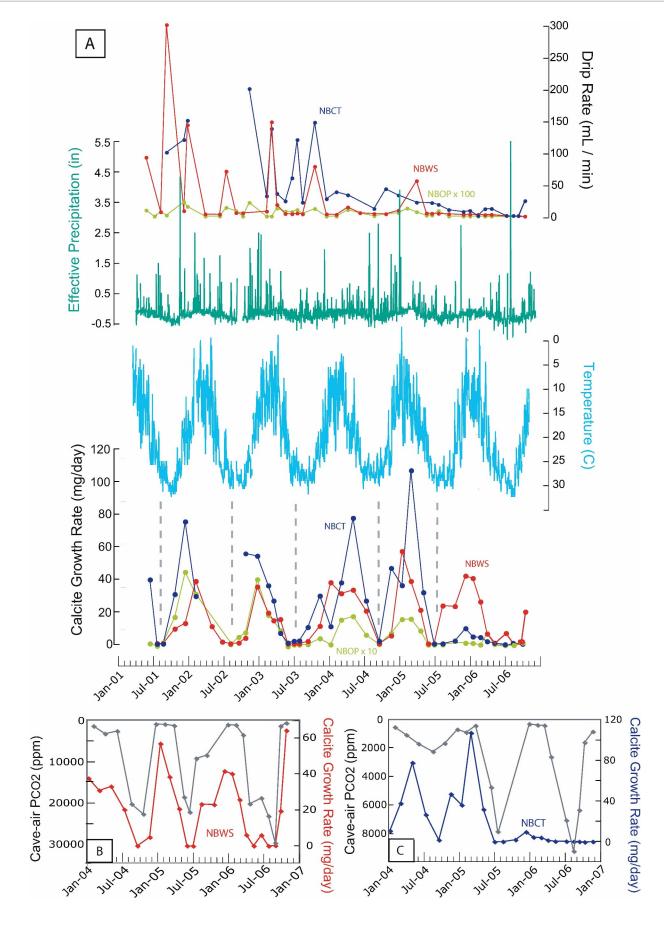


Table 2.—Significance of correlation between calcite growth rate and environmental characteristics at five NB and IS drip sites.

p value	Drip-water P <sub>CO2</sub>	Cave-air P <sub>CO2</sub>	Drip Rate	Effective Precip.	Surface Temp
NS	1	0	2	2	0
S	1	2	1	0	0
HS	2	3	2	3	5

Number of drip sites categorized as having non-significant (NS: p>0.05), significant (S: p<0.05), highly significant (HS: p<0.01) correlations are indicated for temporal variations at drip sites. Only four sites reported for dripwater  $P_{\rm CO2}$  due to slow drip rate at site NBOP. N ranges from 20–25 for cave-air  $P_{\rm CO2}$  and from 28–70 for all other parameters at a given drip site.

The higher pH and larger pH gradients in water films at site ISST during the cool season (see Results) are likely driven by higher extents of CO<sub>2</sub> degassing as water flows towards the edges of the plate and across the speleothems. Higher calcite growth across the glass plates at site ISST during the same time period is also consistent with more CO<sub>2</sub> degassing from these water films during cool seasons driving more calcite precipitation. Whereas the seasonal growth-rate cycles at a given site can be accounted for by temporal changes in the size of the air-water CO<sub>2</sub> contrast, site-to-site changes in the magnitude of growth rate are controlled principally by drip-rate variations (Fig. 1).

# Application to Ancient Speleothem Records

Pleistocene to Holocene growth rates of central Texas stalagmites have been interpreted as a function of century- to millennial-scale changes in effective precipitation (Musgrove et al. 2001). Growth rates of these stalagmites drop by nearly two orders of magnitude from the late Pleistocene to the Holocene. We consider here an alternative model for variations in stalagmite growth rate involving changes in both the airwater CO<sub>2</sub> contrast and moisture availability during these time periods. Long-term increases in the seasonality of temperature would likely enhance seasonality of cave-air CO2 levels both by promotion of seasonal cave ventilation and by enhancement of the seasonality of soil respiration. Such changes would affect the magnitude of the air-water CO<sub>2</sub> contrast. In addition, changes in the seasonal distribution of rainfall may affect the magnitude of drip rates during seasons when the air-water CO<sub>2</sub> contrast is favorable for speleothem growth. By this reasoning, time periods of high seasonality of temperature and rainfall, such as that inferred for the Holocene relative to the Pleistocene on the Edwards Plateau (Cooke et al. 2003), would lead to larger variability of Holocene growth rates. This seasonality model is inconsistent with the higher and more variable late Pleistocene stalagmite growth rates (Musgrove et al. 2001). This model does not take into account, however, the longer-term higher rainfall and cooler temperatures inferred for central Texas during the late Pleistocene relative to the Holocene, which would lead to higher effective precipitation during the late Pleistocene. A control on variations in ancient stalagmite growth rate by long-term changes in effective precipitation and, in turn, drip rate (Musgrove et al. 2001) is also consistent with the site-to-site correlation between drip rate and growth rate in the modern system (Fig. 1).

Uncertainties in applying our results from the modern to ancient speleothem records from this region include: (1) differences in the nature

of the glass plate substrate relative to stalagmites; (2) human development of the caves studied, which in other settings has changed ventilation patterns (Spötl et al. 2005); (3) lower temporal resolution in the ancient speleothem records, (4) evidence that central Texas soils were thicker and sinkholes more open at some times in the past (Cooke et al. 2003; Sansom and Lundelius 2005), which may have changed CO2 production and ventilation, and water infiltration paths relative to today; and (5) the hysteresis in drip rates common to karst systems (Baker et al. 1997). These uncertainties may be addressed through studies using: (1) automated, high-frequency drip-rate measurements, (2) other proxies with seasonal resolution, (3) different substrate materials, (4) soil CO<sub>2</sub> and respiration monitors, and (5) measurements in caves that (a) have been subject to minimal human impact, (b) underlie relatively thick soils, and (c) have a range of ventilation characteristics. The similarity in seasonal growth patterns at caves NB and IS and the lack of calcite growth at cave CS likely portray differences in geomorphology and human development between these caves. This suggests caution in generalizing conclusions regarding ventilation mechanisms across a re-

### IMPLICATIONS

These results indicate that growth-rate variations in ancient speleothems may serve as a paleoenvironmental proxy with seasonal resolution. Using the monitoring approach outlined in this study, speleothem growth rate and, moreover, geochemical proxies may be evaluated and calibrated. If growth rate variations driven by seasonal changes can be understood as a function of environmental change in modern settings, then the controls on such variations in ancient speleothems can be more rigorously interpreted. The effects of growth rate on isotopic and elemental variations in speleothems may be directly assessed using this framework (e.g., Mickler et al. 2006; Guilfoyle et al. 2006; Stern et al. 2005). We also note that such proxies will only record environmental conditions for the times of the year during which calcite growth occurs, and that temperature and seasonality effects on cave-air CO<sub>2</sub> should be explicitly included in models of speleothem growth.

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### REFERENCES

Baker, A., and Genty, D., 1998, Environmental pressures on conserving cave speleothems: effects of changing surface land use and increased cave tourism: Journal of Environmental Management, v. 53, p. 165–175.

BAKER, A., SMART, P.L., AND FORD, D.C., 1993, Northwest European palaeoclimate as indicated by growth frequency variations of secondary calcite deposits: Palaeogeography, Palaeoclimatology, Palaeoecology, v. 100, p. 291–301.

BAKER, A., BARNES, W.L., AND SMART, P.L., 1997, Variations in the discharge and organic matter content of stalagmite drip waters in Lower Cave, Bristol: Hydrological Processes, v. 11, p. 1541–1555.

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Fig. 3.—A) Time series of modern speleothem plate calcite growth rate and drip rate for sites NBWS and NBOP in cave NB South, and NBCT in cave NB North, and outside air temperature (plotted inverse) and effective precipitation. Vertical dashed gray lines indicate average midpoint of slowest growth period for the three sites. NBOP drip rates are multiplied by 100 and growth rates are multiplied by 10 for comparative purposes. Missing growth-rate data for site NBCT in part of 2002 are due to flooding at this site. B, C) Time series of cave-air  $P_{CO2}$  (plotted inverse) and modern speleothem plate calcite growth rates for the same NB sites.

- BALDINI, J.U.L., BALDINI, L.M., McDERMOTT, F., AND CLIPSON, N., 2006, Carbon dioxide sources, sinks, and spatial variability in shallow temperate zone caves: evidence from Ballynamintra Cave, Ireland: Journal of Cave and Karst Studies, v. 68, p. 4–11.
- BUECHER, R.H., 1999, Microclimate study of Kartchner Caverns, Arizona: Journal of Cave and Karst Studies, v. 61, p. 108–120.
- CARRASCO, F., VADILLO, I., LINÁN, C., ANDREO, B., AND DURÁN, J., 2002, Control of environmental parameters for management and conservation of Nerja Cave (Malaga, Spain): Acta Carsologica, v. 9, p. 105–122.
- COOKE, M.J., STERN, L.A., BANNER, J.B., MACK, L.E., STAFFORD, T., AND TOOMEY, R.S., 2003, Precise timing and rate of massive late Quaternary soil denudation: Geology, v. 31, p. 853–856.
- Dreybrodt, W., 1988. Processes in Karst Systems: Physics, Chemistry and Geology: Springer Series in Physical Environments 4, Berlin, Springer-Verlag, 288 p.
- EK, C., AND GEWELT, M., 1985, Carbon dioxide in cave atmospheres: new results in Belgium and comparison with some other countries: Earth Surface Processes and Landforms, v. 10, p. 173–187.
- ELIOT, W.R., AND VENI, G., 1994. The Caves and Karst of Texas: Huntsville, National Speleological Society, Convention Guidebook 342 p.
- GENTY, D., AND QUINIF, Y., 1996, Annually laminated sequences in the internal structure of some Belgian stalagmites—importance for paleoclimatology: Journal of Sedimentary Research, v. 66, p. 275–288.
- GENTY, D., BAKER, A., AND VOKAL, B., 2001, Intra- and inter-annual growth rate of modern stalagmites: Chemical Geology, v. 176, p. 191–212.
- GUILFOYLE, A.L., 2006. Temporal and spatial controls on cave water and speleothem calcite isotopic and elemental chemistry, central Texas [M.S. Thesis]: Austin, University of Texas, 337 p.
- Guilfoyle, A.L., Banner, J.L., and Stern, L.A., 2006, Spatial and temporal controls on the geochemical evolution of cave dripwaters and modern speleothem calcite (abstract): Geological Society of America, Annual Meeting, Abstracts with Programs, v. 38, 24 p.
- HOLLAND, H.D., KIRSIPU, T.W., HUEBNER, J.S., AND OXBURGH, U.M., 1964, On some aspects of the chemical evolution of cave waters: Journal of Geology, v. 72, p. 36–67. HUANG, Y., AND FAIRCHILD, I.J., 2001, Partitioning of Sr<sup>2+</sup> and Mg<sup>2+</sup> into calcite under
- karst-analogue experimental conditions: Geochimica et Cosmochimica Acta, v. 65, p. 47–62.
- HUXMAN, T.E., CABLE, J.M., IGNACE, D.D., EILTS, J.A., ENGLISH, N.B., WELTZIN, J., AND WILLIAMS, D.G., 2004, Response of net ecosystem gas exchange to a simulated precipitation pulse in a semi-arid grassland: the role of native versus non-native grasses and soil texture: Oecologia, v. 141, p. 295–305.

- LARKIN, T.J., AND BOMAR, G.W., 1983. Climatic Atlas of Texas: Austin, Texas Department of Water Resources.
- MICKLER, P., STERN, L.A., AND BANNER, J.L., 2006, Large kinetic isotope effects in modern speleothems: Geological Society of America, Bulletin, v. 118, p. 65–81.
- Musgrove, M., and Banner, J.L., 2004, Controls on the spatial and temporal variability of vadose dripwater geochemistry; Edwards aquifer, central Texas: Geochimica et Cosmochimica Acta, v. 68, p. 1007–1020.
- Musgrove, M., Banner, J.L., Mack, L.E., Combs, D.M., James, E.W., Cheng, H., and Edwards, R.L., 2001, Geochronology of late Pleistocene to Holocene speleothems from central Texas: implications for regional paleoclimate: Geological Society of America, Bulletin, v. 113, p. 1532–1543.
- PARKHURST, D.L., AND APPELO, C.A.J., 1999, User's guide to PHREEQC (Version 2) a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations U.S. Geological Survey, Water Investigations Report 99-4259, 312 p.
- REICHSTEIN, M., AND 26 OTHERS, 2003, Modeling temporal and large-scale spatial variability of soil respiration from soil water availability, temperature and vegetation productivity indices: Global Biogeochemical Cycles, v. 17, 1104 p.
- SANSOM, J.W, JR., AND LUNDELIUS, E., JR., 2005, Inner Space Cave: Discovery and geological and paleontological investigations: Austin Geological Society, Bulletin, v. 1, p. 53-69.
- Shopov, Y.Y., Ford, D.C., and Schwarcz, H.P., 1994, Luminescent microbanding in speleothems: high-resolution chronology and paleoclimate: Geology, v. 22, p. 407-410.
- SMITH, C.L., BAKER, A., FAIRCHILD, I.J., FRISIA, S., AND BORSATO, A., 2006, Reconstructing hemispheric-scale climates from multiple stalagmite records: International Journal of Climatology, v. 26, p. 1417–1424.SPÖTL, C., FAIRCHILD, I.J., AND TOOTH, A.F., 2005, Cave air control on dripwater
- SPÖTL, C., FAIRCHILD, I.J., AND TOOTH, A.F., 2005, Cave air control on dripwater geochemistry, Obir Caves (Austria): implications for speleothem deposition in dynamically ventilated caves: Geochimica et Cosmochimica Acta, v. 69, p. 2451–2468.
- STERN, L.A., BANNER, J.L., COWAN, B., COPELAND, E.A., MICKLER, P.J., JAMES, E., GUILFOYLE, A., MUSGROVE, M., AND MACK, L.E., 2005, Trace element variations in speleothem calcite: influence of non-environmental factors [abstract]: Geological Society of America, Annual Meeting, Abstracts with Programs, v. 37, 435 p. WIGLEY, T.M.L., AND BROWN, M.C., 1976, The physics of caves, *in* Ford, T.D., and
- WIGLEY, T.M.L., AND BROWN, M.C., 1976, The physics of caves, *in* Ford, T.D., and Cullingford, C.H.D., eds., The Science of Speleology: London, Academic Press, p. 329–345.

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