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A global model for cave ventilation and seasonal bias in speleothem paleoclimate records

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Key Points:

- Seasonal CO_2 variations in caves cause variations in speleothem growth rates. This can bias speleothem environmental proxies
- Seasonal ventilation should be strongest in mid to high latitudes relative to low latitudes, and in continental relative to maritime settings

Supporting Information:

- Supporting Information S1

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Abstract Cave calcite deposits (speleothems) provide long and continuous records of paleoenvironmental conditions in terrestrial settings. Typical environmental proxy measurements include speleothem growth rate and variations in elemental and isotope geochemistry. Commonly the assumption is made that speleothems grow continuously and at a constant rate throughout the year. However, seasonal variation of growth rate may be the rule in many caves. Here we apply observations of modern calcite growth and cave-air CO_2 concentrations and a model of factors controlling cave ventilation to construct a global model predicting where cave calcite growth may be seasonal. Previous models and measurements of calcite precipitation in caves demonstrate the retardation of speleothem growth by high cave-air CO_2. Elevated CO_2 is commonly dissipated by ventilation driven by density differences between cave and surface air. Seasonal cycles in atmospheric temperature, pressure, and humidity commonly drive these density contrasts. Modeling these changes latitudinally and globally indicates a geographic control on seasonal cave ventilation and thus on a principal controlling factor of speleothem growth. The model predicts that given constant water, calcium, and CO_2 inputs, speleothems from temperate to boreal continental regions commonly accumulate more calcite in the cool season and less or none in the warm season. These models predict that proxies from temperate to boreal speleothems may be seasonally biased due to seasonal ventilation, whereas tropical and maritime records should not.

1. Introduction

Speleothem climate proxies provide valuable insights into past climates. Interpretation of these proxy results often assumes consistent growth throughout the year, providing an accurate depiction of mean annual climate. Recent studies of cave environments, however, suggest that this assumption may not be valid for many cave settings [*Banner et al.*, 2007; *Baldini*, 2010; *Cowan et al.*, 2013]. A comprehensive evaluation of the impacts of temperature-controlled density-driven ventilation can help distinguish regions that might be more prone to seasonal growth bias and help improve interpretation of paleoclimate records.

1.1. Controls on Growth Rate

The important equilibrium controls on precipitation of calcite include temperature [*Plummer and Busenberg*, 1982] and the chemical species in the calcite precipitation reaction

$$Ca^{2+}{}_{(aq)} + 2HCO_3^-{}_{(aq)} = CaCO_3 + CO_{2(gas)} + H_2O. \quad (1)$$

Increasing Ca^{2+} or decreasing CO_2 drives the reaction to the right, precipitating calcite. Increasing CO_2 or decreasing Ca^{2+} drives the reaction to the left, inhibiting precipitation. The equilibrium diagram for CO_2 and Ca concentrations shows the CO_2 contents required to allow or prohibit calcite precipitation (Figure 1). Although CO_2 levels of 2–5% have been measured in many caves, lower concentrations are the norm [*Ek and Gewelt*, 1985; *Banner et al.*, 2007; *Baldini*, 2010].

The kinetics of speleothem calcite growth are governed by the extent of calcite oversaturation, the thickness and fluid dynamics of the water film that is precipitating calcite, drip rate, a kinetic constant related to temperature, and cave-air CO_2 level [*Buhmann and Dreybrodt*, 1985; *Dreybrodt*, 1988; *Dreybrodt et al.*,

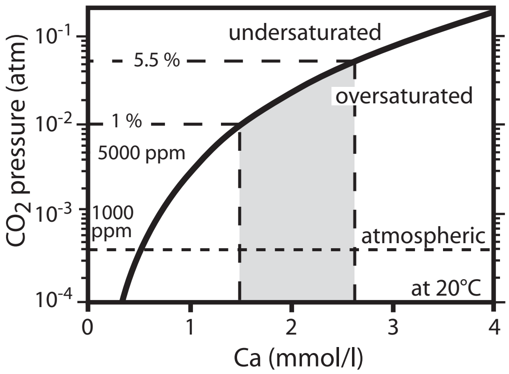

Figure 1. Saturation diagram for equation (1). Shaded area shows the typical range of Ca concentrations in central Texas cave waters. Corresponding CO_2 equilibrium concentrations are enclosed by the long-dashed lines at 1 and 5.5%.

1997; *Baker et al.*, 2014]. Theoretical growth rates (Figure 2) are approximately halved when the ambient CO_2 level is increased from atmospheric (390 ppm) to 2500 ppm in water containing 2 mmol/L Ca. Comparisons of measured CO_2 concentration and calcite growth rate in cave environments are consistent with these models (Figure 2, Table S1) [*Baker et al.*, 1998, 2014]. Note that cessation of calcite deposition occurs in several Texas caves when CO_2 concentrations are more than 5000 ppm [*Banner et al.*, 2007]. Calculated growth rates that differ from measured growth rates may be due to incomplete capture of precipitating calcite [*Banner et al.*, 2007], microbial mediation of calcite deposition [*Barton and Northup*, 2007], and uncertainties in the kinetic constant or in estimating water thickness [*Baker et al.*, 2014] or interfering trace elements (e.g., Mg). It is important to note that CO_2 is only part of the equation, as changes in the Ca concentration will change growth rate as well.

1.2. CO_2 Gains, Losses, and Accumulation

Given the importance of CO_2 in controlling speleothem growth, we consider the sources and sinks of cave-air CO_2. Microbial respiration in the unsaturated zone below the soil provides a CO_2-rich source of air in some settings [*Atkinson*, 1977; *Wood and Petraitis*, 1984; *Mattey et al.*, 2013]. In other caves, CO_2 inputs have been attributed to plant and microbial respiration in overlying soils [*Ek and Gewelt*, 1985; *Spötl et al.*, 2005; *Baldini et al.*, 2008; *Breecker et al.*, 2012]. Typically, soil CO_2 concentration correlates positively with soil temperature and water availability [*Harper et al.*, 2005]. Soil CO_2 concentrations are highest in midsummer in climates with sufficient effective precipitation year-round, but peaks in the spring to early summer in regions where soils dry out during the summer. In drips fed directly from soil water, these high-CO_2 periods should be periods of the highest dissolution of carbonate bedrock and thus the highest delivery of Ca and HCO_3^- (and ultimately CO_2) to caves. Although soil and unsaturated zone CO_2 flux to caves is an important variable controlling Ca and CO_2 delivery, the concentration of Ca in drip waters does not necessarily follow the seasonal cycling of CO_2 [*Tooth and Fairchild*, 2003; *Banner et al.*, 2007]. Calcium concentration and water availability are commonly influenced by independent variables such as water storage and transit time.

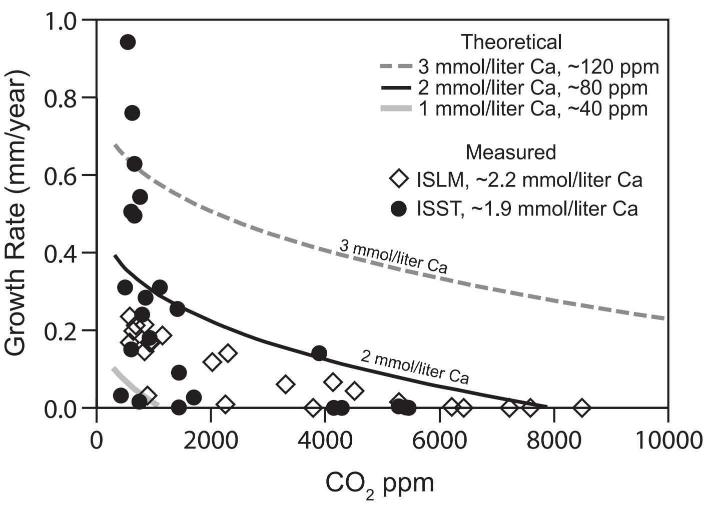

Figure 2. Calculated and measured growth rates of speleothems with respect to cave air CO_2 concentrations. Dashed, solid, and gray lines show calculated rates [*Buhmann and Dreybrodt*, 1985; *Dreybrodt*, 1988; *Dreybrodt et al.*, 1997] at three Ca concentrations. Conditions are 20°C, one drop per second, water film thickness of 0.5 mm, a kinetic constant of 2.6×10^{-5} cm/s, and apparent Ca equilibrium factor of 1.195. Diamonds and circles indicate measured growth rates and CO_2 concentrations from two drip water sites in Inner Space Cavern (ISST and ISLM) where calcite growth on artificial substrates is monitored, Table S1.

If caves are closed to the atmosphere, then CO_2 should accumulate until calcite precipitation stops [*Moore and Nicholas*, 1964, p. 34]. Few caves, if any, are gas-tight systems. We emphasize the importance of seasonal cave ventilation, which is commonly a consequence of density differences between air inside and

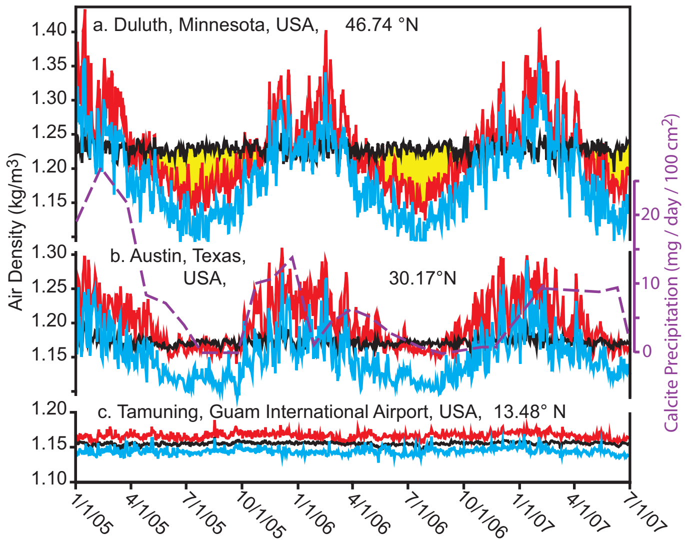

Figure 3. Modeled seasonal air densities in caves and at the surface for three locations: Minnesota, Texas, and Guam. Daily minimum (blue line) and maximum (red) surface air densities compared to cave air density estimated from average yearly temperature, daily barometric pressure, and 95% RH (black) for each location [*NOAA*, 2010]. When the maximum daily surface air density (red) is below the cave air density (black), there is no density-driven exchange of air between cave and surface. This period of potential CO_2 accumulation is highlighted in yellow in Figure 3a. When surface air density is above cave air density, there is density-driven flow of outside air into the cave, flushing the cave with ~390 ppm CO_2 air. (c) In tropical settings the diurnal density range (red to blue lines) brackets cave air density, suggesting diurnal ventilation that would prevent CO_2 accumulation due to air stagnation. Note that the duration and magnitude of summer density differences are greatest at (a) the highest latitude site. Purple line in Figure 3b shows seasonal changes in calcite precipitation rate for site ISST, Table S1.

outside a cave, as one important cause of seasonal cycling of cave CO_2 concentrations [*Wigley and Brown*, 1976; *Buecher*, 1999]. Air density is a function of temperature (T), pressure (P), relative humidity (RH), and gas composition. For nontropical latitudes, temperature is the most important of these variables over a seasonal cycle. A change from 25 to 0°C at 65% humidity results in approximately an 11% increase in air density. A 3 kPa increase in P at 20°C, by contrast, yields only a 3.2% increase in density. A change from 100% RH to 0% at 20°C increases density by less than 1%. An increase in the CO_2 concentration from 400 ppm to 1% at 20°C and 100% RH increases air density by just over 0.5% [*Sánchez-Cañete et al.*, 2013]. Outside T and RH are progressively damped as one moves into a cave [*Wigley and Brown*, 1976] and at sufficient depth cave temperature represents the local average yearly temperature [*Moore and Nicholas*, 1964]. Additionally, RH in the deep parts of most caves, particularly those containing growing speleothems, is high and does not vary substantially with surface RH [*Wigley and Brown*, 1976]. It can be assumed that cave air pressure typically adjusts to surface pressure within a matter of hours. Surface T, P, and RH cycle seasonally, synoptically, and diurnally. The combination of relatively constant cave temperature approximating the local annual mean with the variation of local surface temperatures above and below this mean commonly results in predictable seasonal airflow. Thus, differences in T, P, RH, and composition between cave air and surface air create differences in density that can (1) stratify cave and surface air (2) mix cave and surface air, or (3) force less dense air out of a cave through the primary entrance, secondary entrances, or fracture systems.

1.3. The Effects of Seasonal Temperature Cycles

As the year progresses into fall, daily minimum surface temperatures decrease and drop below the temperature of the cave air. At this time, air density outside the cave becomes greater than that inside the cave. The denser, cooler outside air flows into the cave as the warmer, lighter cave air flows out. High CO_2 air is flushed out of the cave and replaced by low CO_2 air (~390 ppm). The comparatively low CO_2 content of the outside air allows faster calcite precipitation. At some time in the spring, daily low temperatures rise above the cave air temperature and cave and surface air stratify due to density differences. CO_2 concentrations in the cave will begin to build and rise through the summer, bolstered by increasing supply from the warming soil.

This yearly cycle of cave-air CO_2 concentrations can be modeled for most caves using local weather data [*NOAA*, 2010], T, P, and RH, to calculate outside air densities (Figure 3). The density of cave air can be calculated if T, P, and RH have been measured or can be approximated with annual average temperature, an approximated RH (80–100%), and measured outside atmospheric pressure. At mid to high latitudes this yields a surface air density versus time record with diurnal density variations superimposed on a yearly surface-air density cycle. This yearly cycle has a density minimum in the summer and a maximum in winter

(Figures 3a and 3b). In comparison, cave air density is relatively constant throughout the year. The yearly surface air density cycle crosses the cave air density curve in the spring and the fall. The period in the summer when cave air density is greater than surface air density typically becomes longer and the density difference more profound with increasing latitude of the site (Figure 3).

When the surface air density is less than the cave air density, caves with chambers below the entrance should experience CO_2 buildup during these periods. This seasonal cyclicity in CO_2 has been observed in caves in many regions, including southwestern USA [*Buecher*, 1999; *Banner et al*., 2007; *Cowan et al*., 2013] (Figure 3a), southeastern USA [*Kowalczk and Froelich*, 2010], and Europe [*Spötl et al*., 2005; *Bourges et al*., 2006; *Liñán et al*., 2008; *Baldini*, 2010]. This summer CO_2 buildup (Figure 3) and the inhibition of calcite precipitation by elevated CO_2 levels (Figure 2) can cause a seasonal bias in speleothem growth. There will be more cool-season calcite precipitation than warm-season calcite precipitation [*Banner et al*., 2007; *Baldini et al*., 2008; *Baldini*, 2010]. Additionally, speleothem growth rate changes, caused by ventilation, can cause seasonal differences in C and O isotope compositions of calcite [*Spotl et al*., 2005; *Scholz et al*., 2009; *Baldini*, 2010; *Feng et al*., 2012]. Because seasonal growth in most speleothems commonly eludes observation or sampling resolution, such biases can be significant. Proxy measurements from speleothems that grew in caves where summer CO_2 is elevated will yield measurements biased toward winter conditions in proportion to winter versus summer calcite growth. However, if these seasonal variations can be observed they become a chronologic tool.

1.4. Exceptions to Warm Season CO_2 Accumulation

We expect that this type of cyclicity in CO_2 concentration is common, but certainly not universal. If the cave entrance is at a lower elevation than the cave itself, summer and winter ventilation regimes will be reversed. The large class of caves with multiple openings has complex ventilation patterns [e.g., *Bourges et al*., 2006; *Spötl et al*., 2005]. Those with openings at different elevations may change ventilation direction seasonally due to a "chimney effect," whereby air enters and exits at different openings [*Wigley and Brown*, 1976; *Atkinson et al*., 1983]. In some settings, seasonal winds may cause summer ventilation. This is governed by wind direction and the orientation of the cave and its entrances [*Kowalczk and Froelich*, 2010]. Flowing water in caves can influence local T, RH, and pCO_2 significantly. CO_2 ventilation is less efficient in caves with tortuous or narrow passages and in very deep caves [*Moore and Nicholas*, 1964; *Wigley and Brown*, 1976]. Low effective moisture in summer may limit CO_2 production and transportation, and climates with strong winter vegetation growth may supply more CO_2 to caves in winter. In the tropics, the diurnal temperature range, and thus density difference, is greater than seasonal density fluctuations and therefore the temperature-driven ventilation model does not predict a seasonal cycle (Figure 3c).

It should be noted that our ventilation model only addresses the seasonal output of CO_2 from caves; it does not take into account seasonal variations in CO_2 supply or the positive feedback between increasing CO_2 concentration and air density [*Sánchez-Cañete et al*., 2013]. However, both of these influences should act to amplify CO_2 accumulation in a seasonal time frame. CO_2 supply typically reflects soil productivity and is thus highest in spring and summer. Increasing cave CO_2 acts to increase cave air density, thus suppressing ventilation further. In some parts of the tropics, strong seasonality in rainfall and weak seasonality in temperature may result in soil CO_2 production producing seasonal cave-air CO_2 fluctuations, whereas our ventilation model does not predict a seasonal cycle.

2. Methods: Geographic Variation in Seasonal Cave Ventilation

To assess geographic variations in seasonal cave ventilation at the global scale, we construct a map (Figure 4) of the average yearly sum of the positive differences between average monthly minimum temperature and the annual mean temperature. These temperature differences (ΔT_m) are essentially the summer temperature contrast between the surface and a cave, which accounts for virtually all the density differences, as depicted in yellow highlight in Figure 3a.

ΔT_m is constructed using the sites in the Global Historical Climatology Network (GHCN) monthly data set v. 3 [*NOAA*, 2011], for which there were complete years (12 months) of temperature values from 1980 to 2010. An annual station mean was calculated for each year in the data set from 1980 to 2010 by taking the average of the monthly means weighted for the number of days in the month. The annual mean temperature

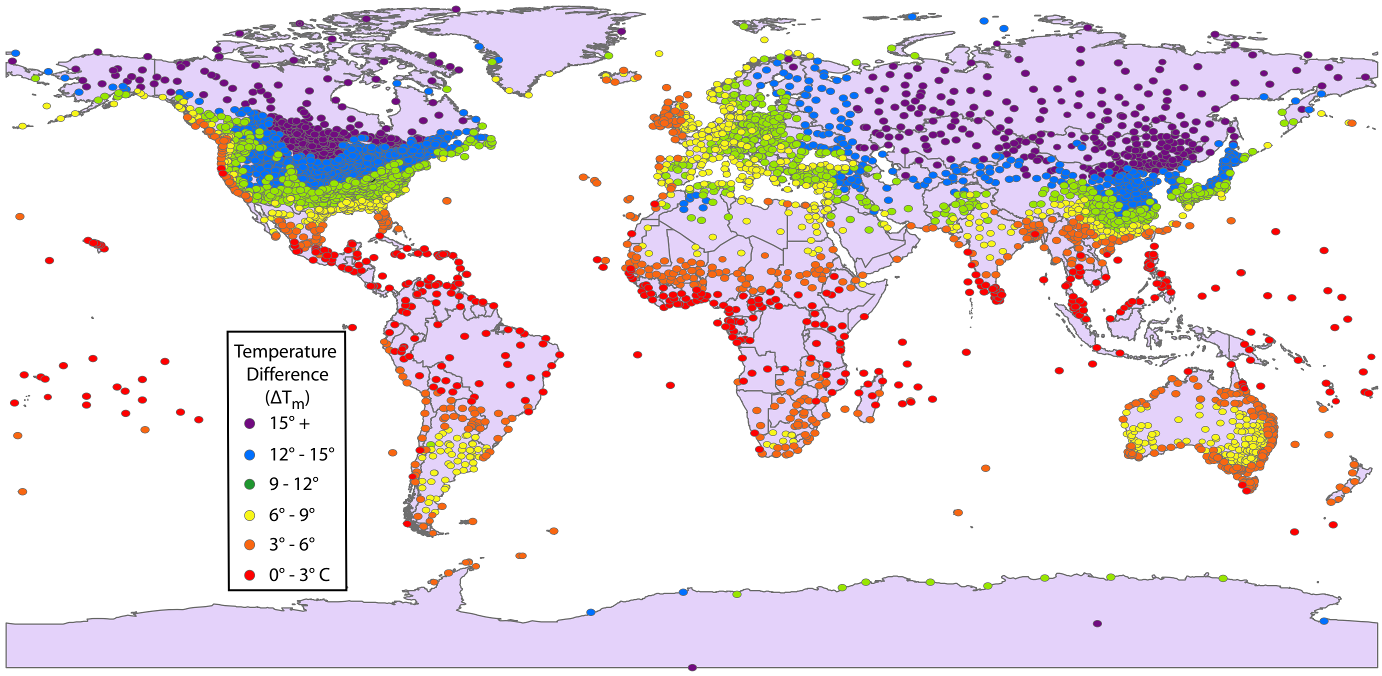

Figure 4. Map of temperature differences, ΔT_m, which represent the temperature contribution to air density contrasts (Figure 3a, yellow highlight), which typically drive cave ventilation. Because temperature is the major seasonally cyclic control of air density this is a first-order map of the seasonal differences between cave air densities and surface air densities. Cave atmospheres in regions with higher ΔT_m are more likely to stagnate seasonally and accumulate CO_2, which reduces calcite growth rates. ΔT_m is calculated as the average yearly sum of the positive differences between average monthly minimum temperature and the annual mean temperature for 1980–2010. No elevation corrections have been applied. Data are from GHCN [*NOAA*, 2011]. Data from Poland prior to 1995 are anomalously low and have been excluded.

for that year was subtracted from the average monthly minimum temperatures. These monthly differences were then averaged by station for all years. The annual number was determined by summing the differences for months when the average monthly minimum temperature exceeded the annual mean, giving the value ΔT_m. The units of ΔT_m are °C months.

3. Results

3.1. Latitudinal Structure

ΔT_m is a good representation of the temperature contribution to the density differences between cave air and surface air in the summer months, as highlighted in yellow in Figure 3a. Thus, Figure 4 provides a first-order approximation of the strength and duration of seasonal stagnation of cave air. This indicates regions where ventilation-controlled CO_2 accumulation in caves is potentially important in controlling speleothem growth. In areas where ΔT_m values are 0–3°C months (Figure 4, red symbols) the diurnal temperature range typically overlaps the annual temperature variation. This drives diurnal density changes in surface air that range above and below cave air density, suggesting daily ventilation, and thereby allowing year-round calcite growth. Moving poleward or toward continental interiors to orange to yellow to green ($\Delta T_m = 3–12$ ΔT_m), blues (12–15 ΔT_m), and indigo regions (>15 ΔT_m), there is an increasing likelihood that the hottest periods of the year will result in minimum surface temperatures that are above the mean annual temperature, which approximates local cave temperature. Without large surface versus subsurface differences in pressure or humidity affecting air densities, there will be little or no summer cave ventilation in these regions.

3.2. Local Geographic Structure

Figure 4 shows several significant deviations from a simple latitudinal trend. The first is where maritime climatic influences moderate annual temperature extremes. Coastal sites commonly have yearly air density curves that allow density-driven ventilation on shorter time spans than the seasons. For example, the temperature range above and below the yearly average is similar along the North American west coast and in the tropics to subtropics. Thus, in tropical and maritime settings CO_2 concentrations in caves are likely controlled by variations in supply from soil, diurnal temperature variation, synoptic pressure changes, and winds. CO_2 levels in soils commonly peak in summer in mid to high latitudes, paralleling ventilation-controlled cave CO_2 buildup. Other deviations from latitudinal control are in continental deserts and at high elevations, which typically have large diurnal temperature ranges that would drive diurnal ventilation and therefore limit seasonal effects.

4. Discussion

4.1. Geographic Variations in Ventilation

The exchange of cave air with surface air, along with variations in CO_2 input and water supply, are important controls on cave-air CO_2 and the therefore the growth of speleothem calcite. The principal driving force in cave ventilation is the density contrast between cave air and surface air, and this contrast is a function of air temperature, pressure, and relative humidity. Winter cave ventilation and summer cave-air stagnation are consistent with model results and observations from midlatitude sites of faster speleothem calcite growth in winter than in summer. These results yield a global model that predicts the potential for air exchange, cave-air CO_2 variation, and seasonal speleothem growth. The model predicts that caves in the tropics ventilate diurnally. Similarly, maritime climates dampen seasonal temperature extremes and, therefore, seasonal ventilation effects. Changes in CO_2 supply and subseasonal ventilation due to synoptic and subsynoptic scale weather are the likely controls of CO_2 levels in caves in tropical and maritime settings. In contrast, caves in temperate to boreal regions and in continental interiors are predicted to preferentially ventilate in the cool season.

4.2. Implications for Speleothem Paleoclimate Records

The global model predicts a lack of summer cave ventilation and consequent accumulation of CO_2 in caves at mid to high latitudes, which results in a summer slowing or cessation of speleothem growth. This prediction implies that paleoclimate reconstructions from speleothems from temperate to boreal regions and continental interiors are more likely to be seasonally biased toward recording cool season conditions, whereas those from tropical and maritime regions likely grow more continuously. The model yields a map (Figure 4) that can be used to predict this potential bias toward preservation of cool season conditions in speleothem proxies as a consequence of differences in density-driven cave ventilation. Comparisons of proxy records between caves in regions with different climates may be particularly problematic. Furthermore, even on a local scale the seasonality of ventilation may affect the geochemical parameters typically used as paleoclimate proxies at some drip sites more than at others [*Wong et al*., 2011]. In view of the exceptions to the general geographic pattern [e.g., *Spötl et al*., 2005; *Mattey et al*., 2008] (also see section 1.4) the seasonal airflow should be considered on a site-by-site basis.

4.3. Capture of Seasonal Information

Seasonal growth bias has both negative and positive consequences for speleothem climate proxies. An example of the potential for missing climatic data is illustrated by likely differences in the record of storm events in speleothems of tropical versus subtropical locations. *Frappier et al*. [2007] document the passing of individual tropical cyclones using the oxygen isotope records in fast-growing speleothems from Belize (Figure 4). However, data from central Texas caves (Figure 4) indicate that there is high CO_2 and little or no growth [*Banner et al*., 2007] in central Texas during the hurricane season. For example, in Inner Space Cavern, only 2% of the annual growth takes place from August through October [*Banner et al*., 2007] when 95% of major Atlantic hurricanes occur [*Landsea*, 1993]. The applicability of this paleotempestological technique is restricted to caves that allow the growth of summer and early fall calcite or in rare instances when large storms deliver a significant fraction of annual precipitation.

Seasonal patterns of growth are not exclusively an impediment to developing environmental proxy records. When recognized and understood, they are signal rather than noise. Speleothem calcite texture, trace element content, and stable isotopes values are controlled in part by cave air CO_2 concentration [*Stoll et al*., 2012; *Mattey et al*., 2008, 2010; *Feng et al*., 2012]. Additionally, seasonal growth can provide a basis for layer-counting to build multiyear chronologies and as a means of focusing on an interval within a year, increasing the proxy's resolution, albeit at the expense of knowledge about periods of less growth. The timing and duration of seasonal speleothem growth is a proxy for the intensity and duration of seasons (Figure 3). Measuring such differences is typically near the limit of analytical capabilities, but improved methods coupled with samples with fast growth rates may allow quantitative measures of seasonality.

5. Conclusions

Global-scale climate drives ventilation in many caves, and this seasonal ventilation is one control of speleothem growth rate. Seasonal ventilation should be strongest in mid to high latitudes relative to low latitudes, and in continental relative to maritime settings. In most caves, seasonal growth bias is toward the preservation of cooler season records. Furthermore, seasonal growth patterns in temperate to boreal latitudes may preclude the identification of events such as hurricanes that occur during a specific time of year. This model of cave air ventilation emphasizes the importance of understanding a cave system's ventilation dynamics prior to interpretation of paleoclimate records.

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