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Temperature-driven seasonal calcite growth and drip water trace element variations in a well-ventilated Texas cave: Implications for speleothem paleoclimate studies

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ABSTRACT

A two-year cave monitoring study at Westcave Preserve in central Texas provides insight into the controls on the rate of calcite growth and drip water Mg/Ca, Sr/Ca, and Ba/Ca variations. The cave is shallow and has a large ratio of its opening area to its volume, which results in year-round ventilation of the cave. Unlike larger and deeper caves in the region that ventilate seasonally, cave-air temperature and CO_2 concentrations at Westcave are near atmospheric throughout the year and calcite growth is continuous. Changes in the rate of calcite growth positively correlate with seasonal temperature variations at all six drip sites studied ($r^2 = 0.12–0.76$; mean $r^2 = 0.47$).

Average monthly surface air temperature is positively correlated with drip-water Sr/Ca at five of six drip sites studied ($r^2 = 0.21–0.80$; mean $r^2 = 0.44$), and Ba/Ca at all six sites ($r^2 = 0.41–0.85$; mean $r^2 = 0.57$); whereas this correspondence is only seen in one of six drip sites for Mg/Ca. Applying geochemical modeling of mineral-solution reactions to the Sr/Ca and Ba/Ca time series at Westcave indicates that the evolution of drip-water Sr/Ca and Ba/Ca can be accounted for by two mechanisms: (1) prior calcite precipitation and/or incongruent calcite dissolution (PCP/ICD), which dominate drip-water evolution at one site; and (2) a combination of PCP/ICD and water–rock interaction (WRI) at the other five drip sites. The results suggest a possible seasonality in the operation of the mechanisms of drip-water evolution, whereby PCP/ICD plays a larger role than WRI during the warmer months of the year.

Understanding drip-water seasonal Sr/Ca and Ba/Ca variations has implications for paleoclimate studies using speleothems. It is important to first determine if seasonal geochemical variations in drip waters can be identified. One can then determine if these variations are preserved as geochemical laminae in speleothems, which may then provide seasonal temperature variations and thus seasonal age constraints for speleothems. Determining the proportional contributions of the mineral-solution reactions that drive drip-water trace element variations for different drip sites, as well as the extent to which trace element concentrations vary seasonally, will help inform speleothem sample selection and interpretation of geochemical data for paleoclimate study. Our results indicate that speleothems near the well-ventilated entrances of many larger and deeper caves may warrant further consideration for paleoclimate studies.

1. Introduction

Paleoclimate studies using cave calcite deposits (speleothems) have increased recently, as the controls on the incorporation of isotopes and trace-elements (e.g., Mg, Sr, and Ba) into speleothems have become better understood (e.g., Fairchild and Treble, 2009; Lachniet, 2009). Reconstructing paleoclimate is of importance to central Texas, as multi-year droughts and millennial-scale changes in moisture availability in the region are common but poorly understood (Musgrove et al., 2001; Banner et al., 2010). Dendrochronology for the region provides annual drought reconstructions that extend ~500 years into the past (Stahle and Cleaveland, 1988; Cleaveland et al., 2011). There are a number of other central Texas paleoclimate reconstructions using proxies with varying temporal resolutions (100s to 1000s of years) and temporal extents (1500 to 71,000 years before present; e.g., Toomey et al., 1993; Goodfriend and Ellis, 2000; Musgrove et al., 2001; Nordt et al., 1994; Ellwood and Gose, 2006). Thus, there is a need to extend and better resolve paleoclimate reconstructions in central Texas (and in other geographic regions around the world) on an annual to sub-annual time scale. Prior to applying geochemical proxies to speleothems, it is important to understand how surface climate signals are reflected in calcite growth rate as well as drip water and calcite geochemistry.

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Cave drip waters are an intermediary between changes in surface climate and speleothem geochemical composition and thus provide a means to ground truth paleoclimate reconstructions using speleothems. An understanding of the modern day drip-water geochemical response to climate is therefore essential for the most accurate interpretations of speleothem geochemistry. Many studies have provided evidence that surface climate can influence drip water/speleothem geochemistry. Oxygen isotopes have been widely used as climate proxies (see Lachniet, 2009) for variations in monsoonal intensity (Griffiths et al., 2010), tropical storm occurrences (Frappier et al., 2007), long term variations in rainfall source (Asmerom et al., 2010; Wagner et al., 2010), and seasonal temperature variations (Feng et al., 2014). Trace-element/Ca values (Mg/Ca, Sr/Ca, Ba/Ca) are less well understood, and thus less often used as paleoclimate proxies compared with oxygen isotopes, due to a large number of controlling factors on their incorporation into drip waters and calcite (Sinclair et al., 2012). Mg/Ca and Sr/Ca values have been interpreted to reflect variations in rainfall (Roberts et al., 1998; Johnson et al., 2006; Fairchild and McMillan, 2007; Fairchild and Treble, 2009; Wong et al., 2011) and cave-air CO_2 (Mattey et al., 2010; Wong et al., 2011). Among other factors, the extent of prior calcite precipitation (PCP), incongruent calcite dissolution (ICD), and water–rock interaction (WRI) are important factors influencing drip water trace-element/Ca values (e.g., Banner et al., 1996; Fairchild and Treble, 2009; Wong et al., 2011). PCP occurs as a unidirectional process whereby CO_2 degasses from drip water prior to dripping, thus driving calcite precipitation and depleting cave drip waters of Ca^{2+} while enriching the drip waters with respect to Mg, Sr, and Ba (Fairchild et al., 2000). ICD which occurs as trace elements are preferentially dissolved relative to Ca^{2+}, which enriches drip water trace-element/Ca values (McMillian and Fairchild, 2005). Processes that may drive ICD include dissolution of impurity-rich portions of a mineral, precipitation of secondary minerals, or preferential leaching of elements from mineral surfaces (Brantley, 2008). WRI is used here to encompass multiple processes of dissolution and recrystallization of carbonate minerals, exclusive of PCP and ICD, and can also increase trace-element/Ca values. Determining the specific mineral-solution processes involved in drip-water evolution will strengthen paleoclimate reconstructions. We thus apply quantitative assessment for distinguishing mineral-solution processes in the Westcave drip-water time series.

An area to advance in speleothem research is the ability to constrain the temporal resolution of speleothem paleoclimate data on annual to sub-annual timescales. U-series dating and C-14 dating have yet to independently provide annual age constraints. Dating by counting growth bands is not always reliable due to inconsistencies in the occurrence of seasonal or annual banding (e.g., Genty et al., 1998; Musgrove et al., 2001; Baker et al., 2008). The potential for geochemical laminae to serve as markers of seasonal cycles in speleothems has been identified through drip water and speleothem studies (e.g., Fairchild et al., 2000; Johnson et al., 2006; Mattey et al., 2010; Wong et al., 2011; Feng et al., 2014). Wong et al. (2011) demonstrated that variations in drip water geochemistry for multiple drips in the same cave can be the result of (1) rainfall variations and/or (2) seasonal cave-air CO_2 fluctuations that influence the PCP of cave drip waters and produce seasonal Mg/Ca and Sr/Ca cycles. This occurs as seasonal variations in CO_2 ventilation enhance calcite growth rate in cooler months and inhibit calcite growth rate in warmer months in deeper, seasonally ventilated caves in central Texas (e.g., Banner et al., 2007; Wong et al., 2011; Cowan et al., 2013).

The cave in this study, located at Westcave Preserve in central Texas ("Westcave" hereafter; Fig. 1), was selected for the study because it is well-ventilated, which drives cave air to have a similar composition and temperature to atmospheric air. We investigate the extent to which variations in cave air temperature effect calcite growth rates and cave drip water geochemistry at six drip sites. We find seasonal variations in external air temperature to be an overarching control on both calcite growth rate as well as drip water Sr/Ca and Ba/Ca values. The results of this study have significant bearing on understanding the processes and influence of temperature on calcite growth rate as well as trace element evolution in drip waters, all of which are important for interpreting speleothem climate proxies. The relationship between calcite growth rate, temperature, and cave drip water Sr/Ca and Ba/Ca values indicates the potential for speleothem calcite Sr/Ca and Ba/Ca values to serve as a proxy for relative variations in seasonal surface temperature. These results provide a framework for selecting speleothems for paleoclimate analysis in future studies of Westcave and of other caves in similar settings. Feng et al. (2014) also address the temperature control at Westcave by examining the seasonal variation of calcite $\delta^{18}O$ values.

2. Hydrogeologic setting

Westcave is located in central Texas on the eastern edge of the Edwards Plateau; approximately 50 km west of Austin, TX (Fig. 1). Westcave resides in the lower Cretaceous Cow Creek Limestone Formation (Caran, 2004). The preserve is in the Heinz Branch Watershed, which has a drainage area of 1.66 acres (LCRA, 2007). The regional climate ranges from subtropical/sub-humid to semi-arid (Larkin and Bomar, 1983), and is characterized by dry, hot summers, wet springs and falls, and dry, mild winters. Average annual rainfall at Westcave is 88.6 cm (1974–2011) while average monthly temperature ranges from 8 °C to 33 °C (2009–2011). Annual and monthly variability of central Texas rainfall is high with intermittent droughts dispersed among wetter periods (Larkin and Bomar, 1983). Soils of the watershed are thin (~20 cm deep), rocky, and composed of Volente Series (alluvial), Brackett Series (shallow gravelly clay loam), and Hensell Sand, all of which support pasture grasses, ashe juniper trees and shrubs, and oaks (LCRA, 2007).

Westcave has a large ratio of the area of its openings to the surface per volume of the cave of 0.02 m^{-1}, in comparison to other caves studied in the region that have ratios that range from 0.001 to 0.0003 m^{-1} (Cowan et al., 2013). This is a result of a small cave volume of ~2000 m^3 and multiple openings to the surface, including a large opening at one end and multiple smaller openings at the other end. Westcave is located in the sidewall of a canyon, approximately 7 m above the valley floor of a 30 m deep canyon (Reddell and Smith, 1961; Fieseler et al., 1972; Caran, 2004). These factors allow for Westcave to be well ventilated year-round and have an internal atmosphere similar to the surface atmosphere. The bedrock thickness above the cave is ~20–25 m. The drips feeding the stalagmites at sites WC-1, WC-3, WC-4, WC-5, and WC-7 flow through the karst overburden and emanate from soda straws (2.5–12.5 cm in length), whereas the drip for WC-6 flows down a 30-cm long drapery prior to dripping.

3. Methods

Six drip sites were sampled and monitored (WC-1, WC-3, WC-4, WC-5, WC-6, and WC-7; Fig. 1) every 4–5 weeks from July 2009 to December 2011. Sampling included measurement of air parameters (cave and surface air temperature, cave and surface CO_2 concentration, cave-air relative humidity), cave water drip rates, cave drip water temperature, collection of drip water for geochemical analysis (cations, anions, alkalinity, and pH), and collection of calcite on glass plate substrates. Rainfall was measured daily at Westcave by staff using a rain gauge and surface air temperature was measured at the closest weather station in Lago Vista, Texas, 11 km northeast of Westcave (NOAA station ID: GHCND: US1TXTV0019). Cave air temperatures are spot measurements taken at each sampling trip until 4/27/10, at which time a temperature logger was installed in the cave to record temperature at hourly intervals. Drip water temperature measurements are spot measurements taken at each sampling trip, approximately every 4–5 weeks. Field data collection and sample preparation methods follow those developed over a 12-year period of cave monitoring (Musgrove and Banner, 2004; Banner et al., 2007; Wong et al., 2011). Specifics of

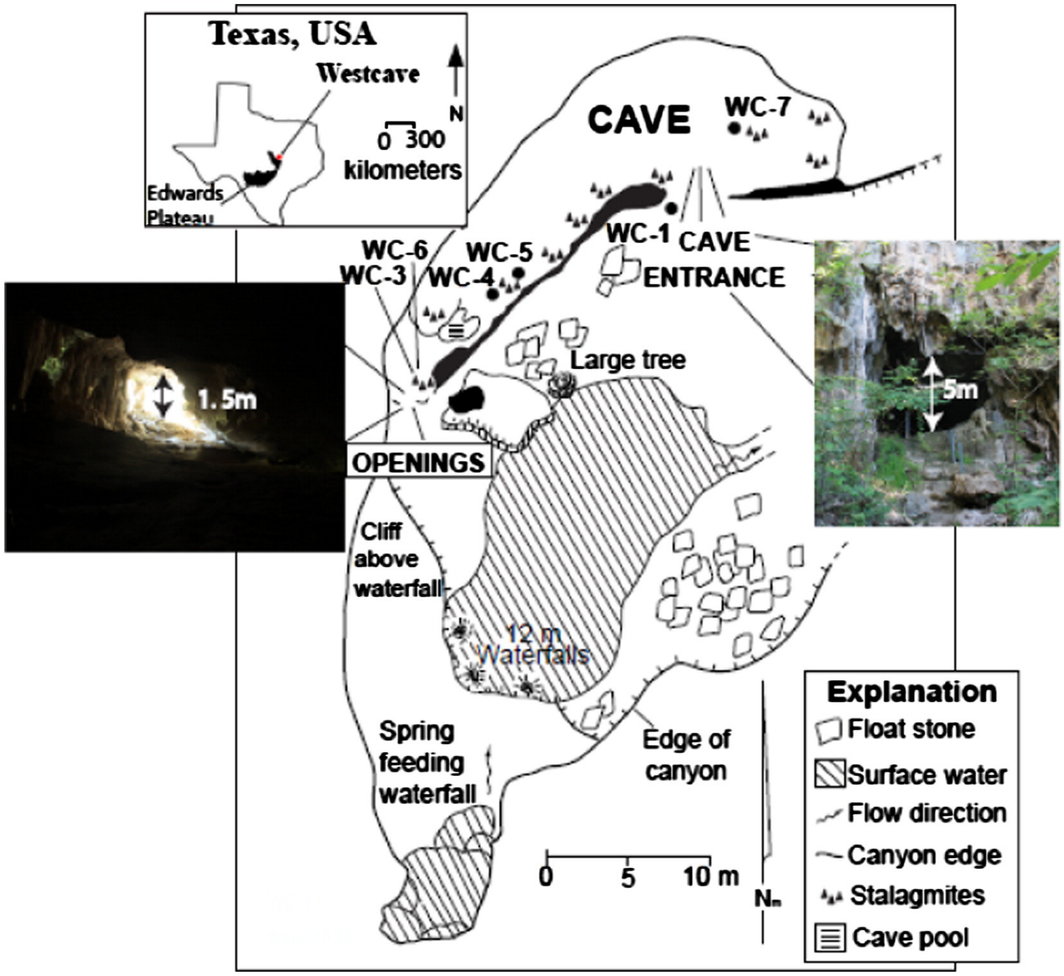

Fig. 1. Smaller map: Regional location of Westcave on the eastern edge of the Edwards Plateau in central Texas. Larger map: Map of Westcave with drip sites WC-1, WC-3, WC-4, WC-5, WC-6, and WC-7 labeled.
Modified from Reddell and Smith, 1961; Fieseler et al., 1972; Feng et al., 2014.

the sampling methods can be found in Casteel (2011). All analyzed geochemical samples were collected at Westcave (Latitude/Longitude: 30.338361/−98.142929).

Our initial monitoring revealed that surface temperature is higher than cave-air temperature in the warmer months by a maximum of ~5 °C, whereas surface and cave-air temperatures are similar during the remainder of the year. This is likely due to a combination of effects from the cave being shaded and evaporative cooling from a nearby pool (Feng et al., 2014). Following Feng et al. (2014), we choose to use surface air temperatures in our analysis because it is a key paleoclimate variable. We do not use cave drip water temperature because these are spot measurements taken during each sampling trip and thus do not reflect the variability inherent within the time period between sampling trips.

Cation analyses were performed at The University of Texas at Austin using an Agilent 7500ce quadruple ICP-MS in the Department of Geological Sciences. NIST 1643e was used as an external standard (measured three times throughout each run) and reveals an accuracy of 3.8% for Ca, 2.8% for Mg, 2.9% for Sr, and 6.1% for Ba. This accuracy was determined by measuring the NIST 1643e standard and comparing the measurement difference to the known value. Each unknown sample was measured three times during a run (i.e., duplicate analyses) and the relative standard deviation between measurements reveals an analytical precision of 1.7% for Ca, 1.0% for Mg, 1.4% for Sr, and 3.4% for Ba, 1.8%. Replicate analyses (i.e., splits of the same water sample followed by dilution) on 10 unknown samples reveal an average percent difference between a sample and its replicate of 2.3% for Ca, 3.6% for Mg, 1.9% for Sr, 3.4% for Ba, 3.6% for Mg/Ca, 0.80% for Sr/Ca, and 1.5% for Ba/Ca. Field blanks for Ca, Mg, Sr, and Ba are below the detection limits of 1.8, 0.83, 0.012, and 0.011 ppb, respectively. Anion analyses were conducted at the Bureau of Economic Geology at The University of Texas at Austin using a Dionex Ion Chromotography System-2000. The RSD for eight internal standards are as follows: F = 7%, Cl = 2%, Br = 8%, NO_2 = 4%, NO_3 = 4%, SO_4 = 4%, and PO_4 = 9%. The RSD values are calculated by dividing the standard deviation of internal anion instrument standards (1–10 ppm), measured eight times throughout the run, by the average of the standard measurements. Three unknown replicates reveal an average percent difference as follows: F = 0.56%, Cl = 0.62%, Br = 0.57%, NO_2 = 0.51%, NO_3 = 0.51%, SO_4 = 0.59%, and PO_4 = below detection limit. Spike recovery for the anions is as follows: F = 106%, Cl = 100%, Br = 98%, NO_2 = 99%, NO_3 = 92%, SO_4 = 99%, and PO_4 = 94%. Charge balances of five of six samples for which there was sufficient volume to permit anion and alkalinity analyses were <5% and there was no bias towards positive or negative charges. One sample had a charge balance of 5.9%. Alkalinity samples were analyzed less than 24 h after collection. The difference between replicate alkalinity analyses was less than 4.8% (n = 3). Cation, anion, and alkalinity data were used as inputs in PHREEQC (Parkhurst and Appelo, 1999) to calculate calcite saturation indices ($SI_{calcite} = IAP/K_{sp}$; where equilibrium = 1).

Calcite was collected by placing 10 × 10 cm glass plates under each drip site and collecting them during the subsequent cave trip. In order to measure monthly calcite growth (expressed in units of mg/day), plates were weighed prior to deployment and after collection. A standard plate was repeatedly weighed and reveals a standard deviation of 0.0002 g. This approach follows the methods described in Banner et al. (2007). X-ray diffraction (XRD) analyses were conducted at Southern Methodist University using a Rigaku Ultima III X-ray diffraction system to determine the mineralogy of the precipitates on the glass plates. The detection limit for the non-calcite phases is 1% of the sample weight, which ranged from 22.5 to 30 mg. Predicted calcite growth rates were modeled for each Westcave drip site using the equations of Kaufmann (2003) and Kaufmann and Dreybrodt (2004) where:

$$\begin{aligned}\text{Growth rate}\left(\text{mmol/cm}^2\ \text{s}\right) &= [(\text{Ca concentration–equilibrium Ca concentration})\\ &\quad\times(\text{film thickness (cm)/drip interval (s)}]\\ &\quad\times 1\text{–}e^{(-\alpha(\text{cm/s})/\text{film thickness}\times\text{drip interval})}.\end{aligned}$$

Growth rate expressed as mmol/cm^2 s was then converted to mg/day:

$$\begin{aligned}\text{Growth rate (mg/day)} &= \left(\text{mmol/cm}^2\ \text{s}\right)\times(40.08\ \text{g/mol Ca})\\ &\quad\times(24\ \text{h/day})\times(60\ \text{min/h})\\ &\quad\times(60\ \text{s/min})\\ &\quad\times\left(100\ \text{cm}^2\ \text{plate surface area}\right).\end{aligned}$$

Measured Ca^{2+} concentration, drip interval, and average surface air temperature were used as input parameters. The model assumes that supersaturated drip waters precipitate calcite onto the stalagmite surface until the water is no longer supersaturated (Kaufmann and Dreybrodt, 2004). A water film thickness of 0.01 cm was assumed to be constant for each drip site, based on Baker et al. (1998). The equation for α (the kinetic rate constant) from Table 1 in Romanov et al. (2008) was used. The spreadsheet used to calculate predicted calcite growth rates can be found in Appendix B. The predicted amount of calcite growth for each drip site was then compared to the measured amount of calcite growth at each drip site. PHREEQC (Parkhurst and Appelo, 1999) modeling was performed to determine the $SI_{calcite}$ of the drip waters for the two drip sites for which alkalinity was analyzed, WC-1 and WC-6. Input variables were monthly measured drip water temperature, pH, cation concentrations, and anion concentrations for each site, respectively.

Using mathematical derivations, Sinclair (2011) and Sinclair et al. (2012) concluded that the formula $(K_{D\text{-}Sr} - 1) / (K_{D\text{-}Mg} - 1)$ will yield slopes on plots of ln (Mg/Ca) vs. ln (Sr/Ca) that allow differentiation between the processes of PCP/ICD and WRI. We applied this approach first to plots of Westcave drip water ln (Mg/Ca) vs. ln (Sr/Ca) using: $(K_{D\text{-}Sr} - 1) / (K_{D\text{-}Mg} - 1)$, following Sinclair et al. (2012), and then to plots of ln (Sr/Ca) vs. ln (Ba/Ca) using: $(K_{D\text{-}Ba} - 1) / (K_{D\text{-}Sr} - 1)$. Published K_D values were used for Sr/Ca and Ba/Ca (i.e., Tesoriero and Pankow, 1996; Terakado and Taniguchi, 2006). The ln (Sr/Ca) and ln (Ba/Ca) data were then divided into two groups to determine if seasonal differences in the slope of ln (Sr/Ca) vs. ln (Ba/Ca) exist: (1) time periods when temperatures were >22.3 °C represent the summer/warm season and (2) time periods when temperatures were <22.3 °C represent the winter/cool season. The temperature of 22.3 °C was chosen as a divider as it is the average surface temperature during the study period. The slopes of these two groups were then compared using a *Wilcoxon signed-rank* test to determine if significant differences existed between the warm and cool season trace element results. The *Wilcoxon signed-rank* test is a non-parametric test useful for small data sets (Wilcoxon, 1945).

4. Results

The average yearly rainfall for Westcave Preserve over the period 1974–2011 was 88.6 cm. The range of average surface air temperature during the study period was 8.3–33.1 °C (mean = 22.3 °C; Fig. 2), while the range of average cave-air temperatures was 8.8 °C to 25.6 °C. Average cave air and surface air temperatures are averaged for the time period between sampling trips using hourly data. Average monthly cave-air relative humidity ranged from 77% to 98% (mean = 95%). Cave drip water temperature (measured monthly) ranged from 8.3 °C to 28.4 °C (Appendix A). The ranges in drip water temperature and cave-air temperature are much larger than those for typical caves, such as found in central Texas (~19–22 °C; Cowan et al., 2013).

Cave-air CO_2 concentrations are near atmospheric throughout the year (390–510 ppm; Fig. 2). By comparison, other central Texas caves, both tourist and undeveloped caves, have CO_2 ranges of 370–38,000 ppm (Table 1; Banner et al., 2007; Wong et al., 2011; Cowan et al., 2013). In these caves CO_2 peaks in the summer and calcite growth is inhibited in the summer due to the lack of ventilation and build-up of cave air CO_2 (Banner et al., 2007; Cowan et al., 2013). At Westcave the rate of calcite growth on the glass plate substrates ranges from 2.8 to 67 mg/day with an average growth rate of 18 mg/day (Appendix A). Calcite is deposited continuously throughout the year. On average, calcite growth is highest in August, ~25 mg/day, and lowest in January, ~6 mg/day, and shows a pronounced seasonality at all sites. Calcite is the only phase precipitated on the glass plates, as determined by XRD analysis. At Westcave the average rate of calcite growth at all sites is not correlated with cave-air CO_2 concentrations; $r^2 = 0.003$; $p = 0.40$ (Fig. 2). The average calcite growth rate for all sites is significantly correlated to average monthly surface temperature, $r^2 = 0.62$; $p < 0.001$. Calcite growth rate is also significantly correlated with temperature at each individual drip site; $r^2 = 0.12$–0.76, mean = 0.62 (Table 2; Fig. 2). Predicted calcite growth rates (using equations from Kaufmann, 2003; Kaufmann and Dreybrodt, 2004) were significantly related to measured calcite growth rates at all six Westcave drip sites: r = 0.61–0. 89; mean = 0.73.

Westcave drip waters are Ca-HCO_3 waters. Specific conductance ranges from 462 to 768 μS/cm, while pH ranges from 8.0 to 8.7. The range of HCO_3 is 359 to 434 ppm (Appendix A). Elemental concentrations are similar to previously published values for drip waters from other caves in the region (Musgrove and Banner, 2004; Guilfoyle, 2006; Wong et al., 2011). Ca values range from 67 to 118 ppm (median = 98 ppm) and do not vary seasonally; Mg values range from 29 to 53 ppm (median = 37 ppm); Sr values range from 0.26 to 1.1 ppm (median = 0.32 ppm); and Ba values range from 0.048 to 0.096 ppm (median = 0.07 ppm). Mg/Ca values range from 440 to 1070 mmol/mol; Sr/Ca values range from 1.18 to 6.7 mmol/mol; and Ba/Ca values range from 0.14 to 0.37 mmol/mol (Table 3). Soil cation values from two separate sampling sites with two samples each ranged from 55 to 130 mmol/mol for Mg/Ca, 0.38 to 0.42 mmol/mol for Sr/Ca, and 0.45 to 0.59 mmol/mol for Ba/Ca. Mg/Ca and Sr/Ca values are in agreement with previous Texas soil values while Ba/Ca values are higher (see Musgrove and Banner, 2004).

The majority of Sr/Ca and Ba/Ca values in drip waters follow a seasonal trend, with higher values in the warmer months and lower values in the cooler months (Fig. 2), whereas Mg/Ca values do not follow a clear seasonal trend. Average monthly surface temperature correlates significantly with Mg/Ca values at 1 of 6 drip sites ($r^2 = 0.19$), Sr/Ca values at 5 of 6 drip sites ($r^2 = 0.21$–0.80), and Ba/Ca values at 6 of 6 drip sites ($r^2 = 0.41$–0.85) at Westcave (Table 4; Fig. 2). The rate of calcite growth correlates significantly with Mg/Ca values at 1 of 6 drip sites ($r^2 = 0.13$), Sr/Ca values at 4 of 6 drip sites ($r^2 = 0.17$–0.36), and Ba/Ca values at 6 of 6 drip sites ($r^2 = 0.16$–0.48; Table 2; Fig. 2). The average rate of calcite growth from all sites and the average monthly surface temperature also correlate (Table 5; Fig. 2). In general, Westcave drip rates are not related to rainfall variability (Fig. 3; Appendix A). Trace-

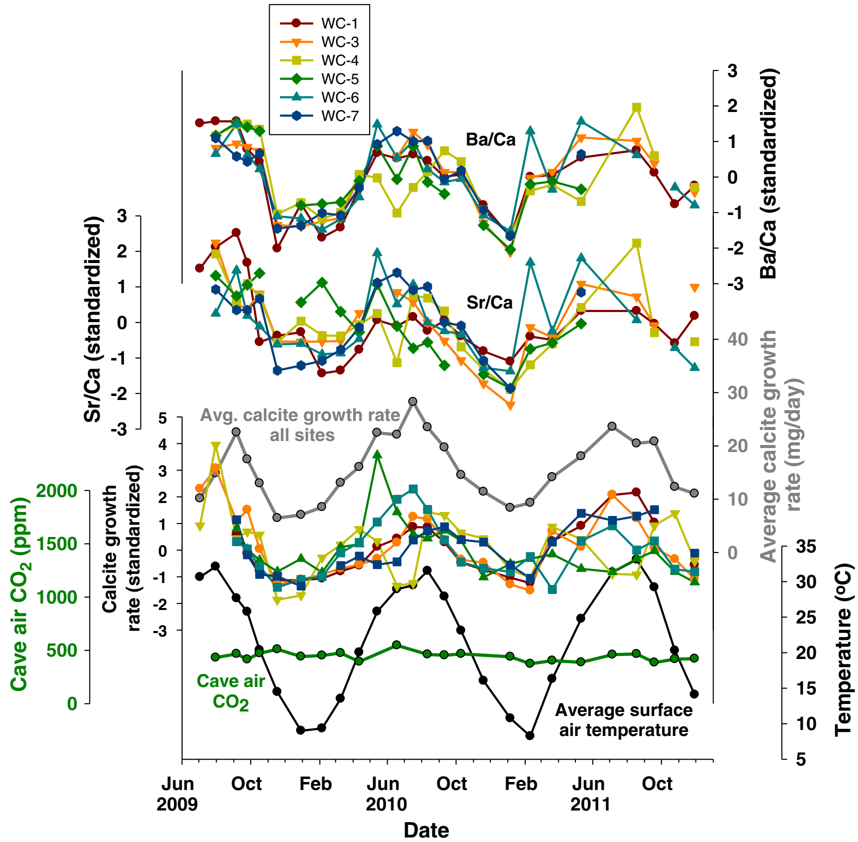

Fig. 2. Time series of average monthly surface temperature, cave-air CO_2, calcite growth rate for each drip site, the average amount of calcite growth for all drip sites, dripwater Sr/Ca values, and dripwater Ba/Ca values at Westcave. Calcite growth rates, Sr/Ca, and Ba/Ca were each standardized to their respective means for easier comparison between drip sites (i.e., z-scores). There are summer peaks and winter troughs for cave air temperature, calcite growth rate, Sr/Ca values, and Ba/Ca values.

element/Ca values and two measures of water flux, rainfall and drip rate, are generally not correlated (Appendix A). Trace-element/Ca, drip rate, and calcite growth rate data can be located in Appendix Table A.1.

Drip water data from two drip sites, WC-1 and WC-6, were used to determine the saturation index of calcite ($SI_{calcite}$). There was not enough water collected at the other drip sites for alkalinity to be measured, a necessary component for calculating mineral saturation indices. Data for both drip sites agree in that the waters are supersaturated with respect to calcite (Appendix A). Only drip site WC-6 provides enough data points to provide an indication of $SI_{calcite}$ seasonality. Given the uniformity among the drip sites of the seasonal pattern in the growth rate of calcite, we use the $SI_{calcite}$ of WC-6 as representative of the other drip sites. PHREEQC modeling indicates that at site WC-6 drip water $SI_{calcite}$ is supersaturated year round and ranges from 1.01 to 1.65; where $SI_{calcite} = IAP/K_{sp}$ and equilibrium = 1 (Appendix A; Table A.4). $SI_{calcite}$ peaks in the summer and there is a significant positive correlation between $SI_{calcite}$ for site WC-6 and average monthly temperature ($r^2 = 0.26$; $p < 0.05$; Table 5) as well as between $SI_{calcite}$ for site WC-6 and average monthly calcite growth rate from all sites ($r^2 = 0.34$; $p < 0.01$; Table 5). Drip water temperatures for site WC-6 are given in Appendix A, Table A.2.

Following the approach of Sinclair (2011) and Sinclair et al. (2012) the slopes of the Westcave drip water ln (Mg/Ca) vs. ln (Sr/Ca) plots range from 0.14 to 0.92 (median = 0.33) while the r^2 values range from 0.08 to 0.80 (median = 0.14). Because of the low correlation coefficients between ln (Mg/Ca) vs. ln (Sr/Ca), the lack of correlations between temperature and Mg/Ca, and the strong, consistently significant correlations between temperature and Sr/Ca and Ba/Ca, we examined the slopes of drip water data for ln (Sr/Ca) vs. ln (Ba/Ca) plots. The theoretically calculated slope for PCP/ICD-dominated evolution of cave drip waters ranges from 0.91 to 0.99, using the relation slope = $(K_{D,Sr} - 1)/(K_{D,Ba} - 1)$ and published K_D values for Sr and Ba (Table 6). Regression analyses reveal that the slopes of ln (Ba/Ca) vs. ln (Sr/Ca) for each drip

Table 1
Comparison of the variables that may affect central Texas speleothem calcite growth along with periods of maximum and minimum calcite growth and calcite growth ranges.

Cave	Ratio of opening/volume (m^{-1})	Number of openings to surface	Annual cave temperature range (°C)	Annual CO_2 range (ppm)	Season of peak calcite growth	Season of low calcite growth	Calcite growth range (mg/day)
Westcave	0.02	Multiple	8.8–25.6	400–510	Summer	Winter	3–67
Inner Space[1,3]	0.0004	1	20–22	450–11,900	Winter	Summer	0–36.5
Natural Bridge[2,3]	0.0003	1	19–22	380–37,000	Winter	Summer	0–107
Maple Run[3]	0.02	1	n/a	570–23,000	Winter	Summer	n/a
Whirlpool[3]	0.001	1	n/a	420–22,000	Winter	Summer	n/a
District Park[3]	0.05	1	n/a	500–31,000	Winter	Summer	n/a

[1] From Banner et al. (2007).
[2] From Wong et al. (2011).
[3] From Cowan et al. (2013).

Table 2
R^2 values for Westcave drip sites for the relationship between calcite growth rate and average surface air temperature (calculated between sampling periods) as well as trace-element/Ca values and calcite growth. All significant relationships are positively correlated.

Site	Calcite growth rate vs. temperature	Mg/Ca vs. calcite growth rate	Sr/Ca vs. calcite growth rate	Ba/Ca vs. calcite growth rate
WC-1	0.76*	0.13*	0.36*	0.48*
WC-3	0.66*	0.00	0.28*	0.44*
WC-4	0.12*	0.02	0.05	016*
WC-5	0.23*	0.05	0.003	0.19*
WC-6	0.61*	0.04	0.23*	0.35*
WC-7	0.46*	0.03	0.17*	0.20*

* Denotes statistically significant relationship at least $p < 0.05$.

Table 4
R^2 values for Westcave drip sites for the relationship between trace-element/Ca values and average surface air temperature. Average surface temperature is the average temperature between sampling trips. All significant relationships are positively correlated.

Site	Mg/Ca vs. average surface temperature	Sr/Ca vs. average surface temperature	Ba/Ca vs. average surface temperature
WC-1	0.08	0.39*	0.62*
WC-3	0.06	0.32*	0.69*
WC-4	0.19*	0.46*	0.43*
WC-5	0.003	0.03	0.41*
WC-6	0.06	0.21*	0.43*
WC-7	0.07	0.80*	0.85*

* Denotes statistically significant relationship at least $p < 0.05$.

site range from 0.25 to 0.73 (r^2: 0.41–0.84), which indicates a range from PCP/ICD-dominated to mixed WRI and PCP/ICD processes.

To determine if there are seasonal differences in PCP/ICD versus WRI processes the ln (Sr/Ca) vs. ln (Ba/Ca) drip water data from Westcave were divided into two groups; (1) time periods when temperatures were >22.3 °C to represent the warm season and (2) time periods when temperatures were <22.3 °C to represent the cool season (Table 7). The division of groups at a temperature of 22.3 °C was chosen as it is the average surface air temperature for the study period. Thus, any temperature value above/below 22.3 °C is considered to be warmer/cooler than average. This resulted in a small sample size of $n = 6$ (i.e., 6 paired summer and winter samples) in which a two-tailed *Wilcoxon signed-rank* test was used to determine if significant differences existed between the two groups. The results suggest that the two groups were significantly different ($p = 0.046$; $Z = -1.99$), where slopes are higher in the summer versus in the winter. However, there is a significant amount of uncertainty in slopes for some of the drip sites (Table 7).

5. Discussion

We discuss here the key results of the study: (1) the relationship between drip rate and effective rainfall is inconsistent; (2) the relationship between measures of water flux and trace-element/Ca variations is inconsistent; (3) calcite growth rate correlates with seasonal temperature variations at all six drip sites studied; (4) at most drip sites drip-water Sr/Ca and Ba/Ca vary on a seasonal time scale and positively correlate with average surface air temperature (hereafter referred to as 'temperature').

5.1. Water flux

Previous research has identified variations in water flux and variations in the flow paths of infiltrating drip waters as controlling factors on the geochemistry of cave drip waters (e.g., Banner et al., 1996; Johnson et al., 2006; Fairchild and Treble, 2009; Wong et al., 2011). At Westcave, water flux does not appear to significantly affect drip rate as there is a lack of correlation between rainfall and drip rate (Fig. 3). This is consistent with previous karst research that suggests a complex network of flowpaths in the karst overburden and/or sizeable vadose zone storage above the cave (e.g., Baldini et al., 2006; Pape et al., 2010). Oxygen isotope drip water data from Westcave also suggest that the drip waters emanate from a well-mixed reservoir, where vadose zone water experiences residence times of at least a year (Feng et al., 2014). This is advantageous when examining drip water geochemistry as a function of temperature because variations in rainfall and thus drip rate have been shown to affect drip water geochemistry (e.g., Fairchild and Treble, 2009). At Westcave there is not a clear correlation between water flux and drip water geochemistry (Appendix A, Table A.3), and along with the well-mixed vadose reservoir here, enable the examination of the influence of temperature. The influence of temperature on growth rate appears to be the principal control, relative to water-flux, on drip water Sr/Ca and Ba/Ca variability at Westcave.

5.2. Calcite growth and cave ventilation

In deeper, seasonally-ventilated caves in central Texas cave-air CO_2 ventilation and build-up governs the seasonal growth of calcite, which is higher during cooler months and inhibited during warmer months (Banner et al., 2007; Wong et al., 2011; Cowan et al., 2013). This seasonal ventilation regime results from the greater depth, fewer openings to the surface, and a smaller ratio of the opening area to cave volume as compared to the well-ventilated system of Westcave (Table 1). Low cave-air CO_2 concentrations throughout the year (390–510 ppm; Fig. 2) lead to year-round growth at all six Westcave drip sites (Fig. 2), in contrast to the growth hiatuses observed in seasonally ventilated caves in the region (Banner et al., 2007; Wong et al., 2011). Westcave is also distinct from seasonally-ventilated caves in that calcite growth rate is highest in warmer months and lowest in cooler months (Table 1). Temperature explains the majority of the variance in calcite growth, as the calcite growth rate from all six drip sites and temperature are significantly related to each other ($r^2 = 0.12–0.76$; mean = 0.62; Fig. 2). We infer that the seasonal trends in calcite growth at Westcave are controlled by (1) seasonal soil zone CO_2 variations; and/or (2) the retrograde solubility of calcite and its effect on $SI_{calcite}$, whereby the calcite K_{sp} is lower, $SI_{calcite}$ is higher, and more calcite precipitates during the warmer months (Fig. 4).

We model calcite growth rates at Westcave drip sites using the equations of Kaufmann (2003) and Kaufmann and Dreybrodt (2004). The model growth rates are moderately to highly correlated with the measured calcite growth rates at individual sites ($r = 0.61–0.89$; mean = 0.73; Fig. 5). In general, the modeled growth rates approximate

Table 3
Ranges of elemental concentrations for Ca, Mg, Sr, and Ba as well as trace-element/Ca ratios for Mg/Ca, Sr/Ca, and Ba/Ca in drip waters at Westcave from July 2009 to December 2011.

Site	Ca (ppm)	Mg (ppm)	Sr (ppm)	Ba (ppm)	Mg/Ca (mmol/mol)	Sr/Ca (mmol/mol)	Ba/Ca (mmol/mol)
WC-1	104–118	29–37	0.28–0.33	0.058–0.073	440–538	1.18–1.41	0.16–0.20
WC-3	80–106	33–49	0.28–0.35	0.048–0.80	590–854	1.37–1.69	0.14–0.23
WC-4	77–109	36–43	0.26–0.36	0.047–0.079	600–811	1.32–1.64	0.15–0.22
WC-5	87–116	37–42	0.29–0.38	0.054–0.079	579–733	1.39–1.67	0.15–0.22
WC-6	73–104	32–42	0.30–0.34	0.055–0.072	602–815	1.38–1.95	0.17–0.25
WC-7	67–80	41–53	0.66–1.1	0.054–0.096	974–1070	5.2–6.7	0.21–0.37

Table 5
Correlations between average monthly surface air temperature, the $SI_{calcite}$ at WC-6, average calcite growth rate for all drip sites, and average drip-water Mg/Ca, Sr/Ca, and Ba/Ca for all drip sites. β (beta weight) indicates the direction of the relationship. All average values were standardized to allow for comparison.

	$SI_{calcite}$	Average calcite growth rate
Average surface temperature	$r^2 = 0.26$ $p < 0.05$ ($\beta = +$)	$r^2 = 0.79$ $p < 0.001$ ($\beta = +$)
$SI_{calcite}$		$r^2 = 0.34$ $p < 0.01$ ($\beta = +$)

the measured growth rates along a 1:1 line, with considerable scatter about the line (Fig. 5). This scatter is likely due to two factors. First is the inability of the glass plate substrates to capture all of the calcite that can be deposited by the drip water before it flows off the plate, whereas in the model calcite precipitates until the waters are no longer supersaturated. Second is that rapid CO_2 degassing driving rapid calcite precipitation that governs the measured calcite growth rates may engender departures from the equilibrium that constrains the model calculations. The first factor would produce an offset above the 1:1 line (i.e., higher model vs. measured calcite precipitation), which we observe for five of the six drip sites. In contrast, WC-6 is the only drip site that systematically falls below the 1:1 line (i.e., higher measured than predicted calcite growth rate). The results for WC-6 trend to the highest measured growth rates and exhibit an increasing departure from the 1:1 line with increasing growth rate. These results for WC-6 are consistent with the second factor above. In summary, the comparison between the measured and modeled calcite growth rates highlights the principal role of temperature in controlling calcite growth rates at Westcave.

Examination of the model input parameters (Ca^{2+} concentration, drip interval, and average surface air temperature) suggests that temperature variations are the primary controlling factor on calcite growth rate via the relationship between temperature and the K_{sp} of calcite. The largest variations in modeled calcite growth rate occur as a result of varying temperatures (i.e., the winter low temperature compared to the summer high temperature) and temperature is the only variable that changes seasonally. Drip-water Ca^{2+} concentration can exert a large control over calcite growth rate, but at Westcave Ca^{2+} concentration does not follow a seasonal trend and Ca^{2+} concentration at each drip site has a relatively low coefficient of variation that ranges between 3 and 9.7%. Thus, although the waters are sufficiently supersaturated to precipitate calcite year round, the Ca^{2+} concentration does not extensively vary. Drip interval is important in that water must be available to deliver calcite to a growing formation. Variations in drip interval do not significantly correlate with (1) seasonal temperature variations or (2) variations in calcite growth rate (Figs. 2, 3); thus, it does not appear that drip interval controls the seasonal growth of calcite. Temperature exerts the largest amount of control over variations in calcite growth. This is suggested by the correlation of temperature with measured calcite growth rates at Westcave and confirmed by the correlation between modeled calcite growth rates and measured calcite growth rates at all six drip sites studied. The role of temperature in driving calcite growth is evidenced through the positive correlation between $SI_{calcite}$ values and temperature as well as the positive correlation between $SI_{calcite}$ values and calcite growth rate (Fig. 4). Thus, when temperatures are highest, drip waters are at their highest value of supersaturation, and the rate of calcite precipitation is highest.

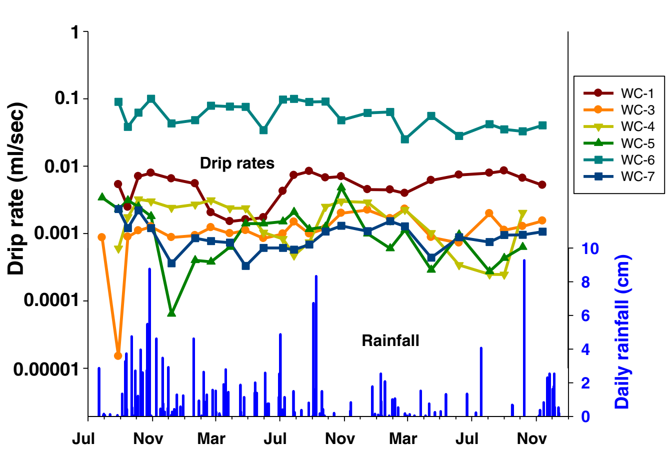

Fig. 3. Time series of daily rainfall collected at Westcave and drip rates at Westcave during the study period. There are weak and inconsistent relationships between drip rate and rainfall.

5.3. Seasonal Sr/Ca and Ba/Ca variations

At Westcave Sr/Ca and Ba/Ca values vary seasonally and correlate strongly with temperature variations (Fig. 2; Table 4), thus offering the opportunity to reconstruct past changes in seasonal temperature. Few studies have examined the relationship between drip-water Sr/Ca and/or Ba/Ca values, calcite growth rate, and temperature. Most of these studies are laboratory experiments carried out to determine the exchange reaction distribution coefficient (K_D) for elements such as Mg, Sr, and Ba (Lorens, 1981; Tesoriero and Pankow, 1996; Huang and Fairchild, 2001; Terakado and Taniguchi, 2006). The K_D values of Sr and Ba are less than one, indicating that these elements will prefer the aqueous phase relative to Ca. This has implications for the evolution and seasonal differences of the drip water Sr/Ca and Ba/Ca.

Numerous studies suggest that a positive correlation exists between Mg and Sr as the process of PCP influences their incorporation into drip water/calcite in a similar manner (e.g., Fairchild et al., 2000; Tooth and Fairchild, 2003). The correlation coefficients of Mg/Ca versus Sr/Ca are low at most drip sites (median $r^2 = 0.16$) whereas Sr/Ca versus Ba/Ca correlation coefficients are much higher at every drip site (median $r^2 = 0.63$). There is also a lack of correlation between Mg/Ca and temperature at all but one Westcave drip site, whereas there are strong correlations between temperature and Sr/Ca and Ba/Ca at nearly every drip site. This implies that Mg/Ca values are subject to different controls versus Sr/Ca and Ba/Ca values.

It seems problematic that there is a lack of correlation between temperature and drip water Mg/Ca values because Mg variations are thought to be temperature dependent (Gascoyne, 1983; Huang and Fairchild, 2001). However, these studies examine Mg with respect to calcite precipitation and do not examine drip-water Mg values. Another possible explanation is that drip water Mg is controlled by other variables such as water flux, as observed in other caves in this region (e.g., Wong et al., 2011).

Our working hypothesis is that the seasonal variations in dripwater Sr/Ca and Ba/Ca values (Fig. 2) are driven by calcite growth rates, which are driven by temperature variations. A scenario that can account for the results of our study is as follows: (1) higher temperatures lead to higher soil zone CO_2 (given sufficient moisture supply; see Wiant, 1967; Edwards, 1975; Rastogi et al., 2002; Kjelgaard et al., 2008), which increases the amount of calcite that infiltrating waters can dissolve, thus increasing the $SI_{calcite}$ values in the drip waters upon degassing; and/or (2) higher $SI_{calcite}$ values at higher temperatures due to the retrograde solubility of calcite will drive higher rates of calcite growth. Considering the components of $SI_{calcite}$, where $SI_{calcite} = IAP/K_{sp}$, we see that increased temperatures will favor more calcite precipitation by either factor (1) or (2). For IAP, increased drip water CO_2 at higher temperatures will increase vadose zone calcite dissolution and thus increase IAP upon drip water degassing. For the denominator, the K_{sp} value will decrease with higher temperatures. There are no discernible seasonal variations in drip water Ca, thus we infer that seasonal soil

Table 6
Experimentally derived K_d values for Sr and Ba as well as the growth rate and temperature of the experiment. The slope was calculated based on Sinclair (2011).

Study	$K_{D,Sr}$	$K_{D,Ba}$	Growth rate	Temperature	Slope of $(Kd_{Sr} - 1)/(Kd_{Ba} - 1)$
Tesoriero and Pankow (1996)	0.021	0.012	1 nmol/(mg−min)	25 °C	0.99
Tesoriero and Pankow (1996)	0.14	0.05	500, 300 nmol/(mg − min)	25 °C	0.91
Terakado and Taniguchi (2006)	0.0585	0.0302	152 μmol/m^2 ∗ h	25 °C	0.97
Terakado and Taniguchi (2006)	0.0546	0.0275	499 μmol/m^2 ∗ h	25 °C	0.97

zone CO_2 variations more likely drive seasonal IAP variations. While both factors (1) and (2) may play a role in governing drip-water $SI_{calcite}$ at Westcave, our model results indicate that the observed temperature variations alone (i.e., holding other parameters constant) can account for the seasonal $SI_{calcite}$ variations.

We conclude that (1) in the warmer months there are higher rates of PCP versus the cooler months; and (2) the K_D values of Sr and Ba are less than unity and dictate that each will prefer the aqueous phase compared to Ca, thus increased PCP along the flowpath will enrich drip water Sr/Ca and Ba/Ca. It is therefore hypothesized that in the warmer months the higher drip water Sr/Ca and Ba/Ca values are ultimately a result of higher temperatures producing higher $SI_{calcite}$ values and higher rates of PCP.

5.4. Evolution of drip water Sr/Ca and Ba/Ca

The enrichment in trace element ratios in cave drip waters via PCP, ICD, and WRI has been previously explored in other settings, where a cave-air CO_2 and/or water flux control is indicated (e.g., Fairchild et al., 2000; McMillan et al., 2005; Wong et al., 2011). In contrast, our results at Westcave support a temperature control on trace element ratio enrichment. One approach to evaluating the role of PCP in drip-water evolution is the comparison of modeled PCP geochemical evolution with measured drip-water variations, which is a common approximation used by researchers (e.g., Fairchild et al., 2000; Wong et al., 2011). Applying this approach to the Westcave drip waters suggests that PCP is a principal control, yet there is considerable scatter of the observations relative to the model results (Fig. 6). This discrepancy may be accounted for either by variations in starting fluid compositions or by the influence of other processes such as WRI on drip water evolution. To further delineate the relative roles of PCP and WRI in Westcave drip-water evolution, we use a model similar to Sinclair (2011) and Sinclair et al. (2012).

Sinclair (2011) and Sinclair et al. (2012) develop a mathematical proof to differentiate between the mechanisms (PCP/ICD and/or WRI) contributing to the evolution of Mg/Ca and Sr/Ca in cave drip water and speleothem calcite. This approach shows that slopes of ln (Mg/Ca) vs. ln (Sr/Ca) between 0.709 and 1.003 are indicative of PCP/ICD driven processes, whereas mixed WRI and PCP/ICD processes are indicated by slopes less than 0.709, with lower slopes reflecting more WRI (Sinclair, 2011; Sinclair et al., 2012). The model results imply that it is not possible to differentiate between PCP and ICD because the slopes are similar; therefore we group PCP/ICD in our discussion.

Because Mg/Ca values are not correlated to temperature, are not highly correlated to Sr/Ca, and are seemingly controlled by different processes than Sr/Ca and Ba/Ca values we apply this model approach to Sr/Ca and Ba/Ca values. Because the slopes calculated are based on K_D values, which indicate the propensity for a trace element to become incorporated into the solid or aqueous phase, theoretically any correlated elemental pair can be used. Therefore we modify here the Sinclair approach and use the formula $(K_{D,Ba} - 1)/(K_{D,Sr} - 1)$ to determine slopes for PCP/ICD and WRI.

The slope of ln (Sr/Ca) vs. ln (Ba/Ca) for one site, WC-6 (slope = 0.73; Fig. 7), falls within the range of calculated PCP/ICD-driven slopes, which indicates that WRI is not a dominant factor in drip water evolution. This is the only one of the six sites that has a relatively long flow path inside the cave, along a 30-cm drapery, compared to flow paths at the other sites that are along soda straws 2.5–12 cm in length. This longer in-cave flow path and larger surface area of the drapery over which the thin film of drip waters are exposed to the cave atmosphere prior to drip allows for PCP to be a more dominant factor, as degassing of CO_2 and thus calcite precipitation can more readily occur (e.g., Fairchild et al., 2000; Wong et al., 2011). This is also the only site that has a slope for ln (Mg/Ca) vs. ln (Sr/Ca) and ln (Sr/Ca) vs. ln (Ba/Ca) that falls within the defined range of PCP/ICD driven processes. The slopes for the other five sites that range from 0.25 to 0.52 (Fig. 7) are within the predicted range of a combination of PCP/ICD and WRI as the controlling processes. Two factors are hypothesized to limit PCP at these other drip sites: First, soda straws do not have an appreciable thin film of water exposed to the cave atmosphere prior to drip. Although soda straws do have water

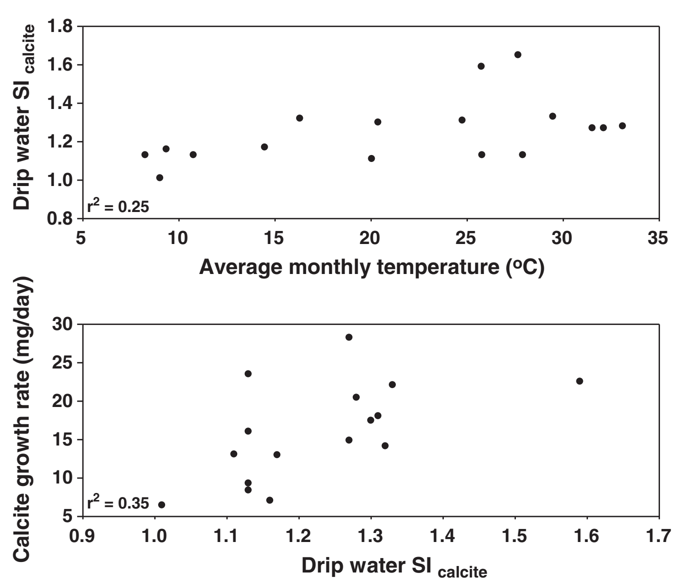

Fig. 4. The significant relationships between drip water $SI_{calcite}$ at site WC-6 and average monthly temperature (A) as well as between drip water $SI_{calcite}$ at site WC-6 and calcite growth rate (B). As drip water $SI_{calcite}$ increases both average monthly temperature and calcite growth rate increase. Only drip site WC-6 provides enough data points to provide an indication of $SI_{calcite}$ seasonality.

Table 7
Slopes of the ln (Sr/Ca) vs. ln (Ba/Ca) drip water data for (1) time periods when temperatures were >22.3 °C to represent the warm season and (2) time periods when temperatures were <22.3 °C to represent the cool season. A two-tailed Wilcoxon signed-rank test suggests that on average slopes are significantly higher in the warmer months versus the cooler months of the year, $p < 0.05$.

Site	Slopes of >22.3 °C ln (Sr/Ca) vs. ln (Ba/Ca)	Slopes of <22.3 °C ln (Sr/Ca) vs. ln (Ba/Ca)
WC1	0.91 (+/−0.04)	0.18 (+/−0.03)
WC3	0.34 (+/−0.05)	0.22 (+/−0.07)
WC4	0.32 (+/−0.08)	0.34 (+/−0.07)
WC5	0.60 (+/−0.06)	0.49 (+/−0.08)
WC6	1.20 (+/−0.10)	0.66 (+/−0.14)
WC7	0.46 (+/−0.19)	0.42 (+/−0.31)

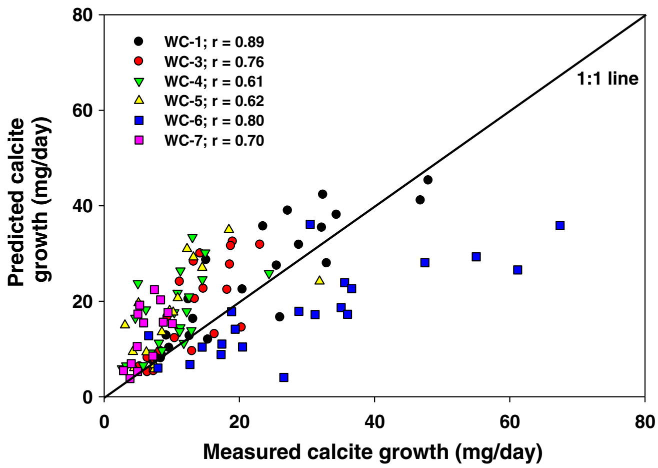

Fig. 5. Modeled calcite growth rates using a quantitative model based on Kaufmann (2003) and Kaufmann and Dreybrodt (2004) versus measured calcite growth rates at Westcave. There is a significant relationship at all six drip sites between predicted and measured calcite growth rates.

exposed to the atmosphere prior to drip, it is observed that the water emanates from inside the soda straw and appears at the tip of the soda straw as a large drop. Therefore it is inferred that there is less PCP due to a thicker, larger volume of water relative to surface area over which it flows, in contrast to a thinner film of water that flows down the larger surface area of a drapery. Secondly, the two fastest drip sites (WC-1 and WC-6) display the highest slopes (indicative of more PCP/ICD relative to WRI) while the slower dripping sites have lower slopes, which is indicative of more WRI. This is most likely a result of the slower dripping sites being more subject to diffuse flow, which allows for more WRI in the vadose zone versus faster dripping sites that experience more conduit flow and less WRI.

Based on the inference from the ln (Sr/Ca) vs. ln (Ba/Ca) variations that both PCP/ICD and WRI occur at five of the six Westcave drip sites we examine if the relative importance of these processes vary seasonally. We have already proposed that the seasonal enrichment of Sr/Ca and Ba/Ca at Westcave occurs because PCP occurs at higher rates in the warmer months relative to the cooler months. This is inferred through empirical observation of higher calcite growth rates in the summer and higher drip water $SI_{calcite}$ values in the summer. We explore the hypothesis of PCP/ICD being more dominant relative to WRI in the summer by comparing drip-water data from warmer months (>22.3 °C) with those from cooler months (<22.3 °C). We chose 22.3 °C as the division between the two groups as it is the average temperature during the study period; where values higher than average represent warmer time periods and values lower than average represent cooler time periods. We then compared the slopes of ln (Sr/Ca) vs. ln (Ba/Ca) for the two temperature groups using a *Wilcoxon signed-rank* test. The results suggest that the warmer temperature slope is significantly higher than the cooler temperature slope for five of six drip sites (see Fig. 8). This indicates the possibility that PCP/ICD plays a more significant role in drip-water evolution than WRI during the warm season. However, this result should be taken with caution as the data sets for each temperature group (+/−22.3 °C) have a small sample size (n < 14) and there is a large amount of uncertainty in the slopes of 4 of the 6 sites (Table 7). Therefore we can only conclude that there is a tendency for more PCP/

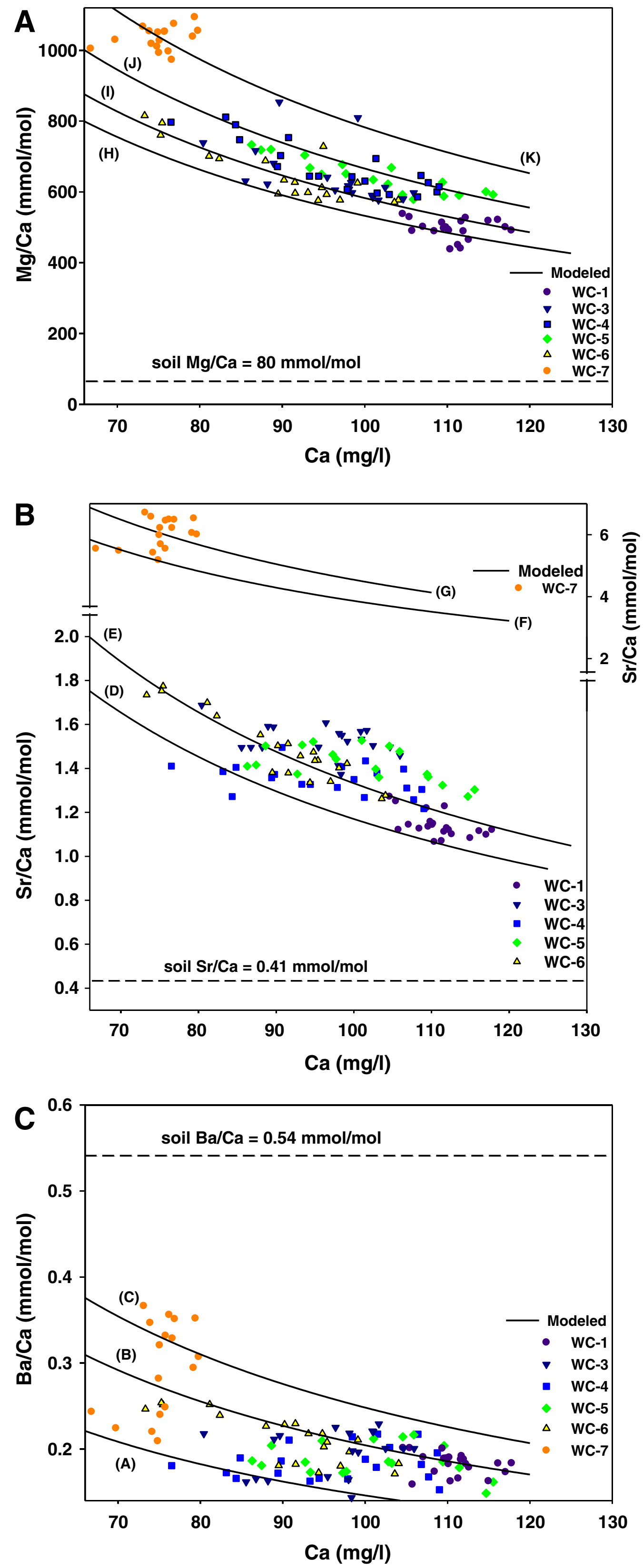

Fig. 6. Observed and modeled Westcave drip water (A) Mg/Ca, (B) Sr/Ca, and (C) Ba/Ca values for all drip sites. The modeled lines represent the evolution of cave drip waters via PCP for different initial compositions as given for each line. The starting compositions of the waters are as follows: (A) Ca = 120 ppm, Ba = 0.05 ppm; (B) Ca = 120 ppm, Ba = 0.07 ppm; (C) Ca = 120 ppm, Ba = 0.085 ppm; (D) Ca = 125 ppm, Sr = 0.28 pm; (E) Ca = 128 ppm, Sr = 0.33 ppm; (F) Ca = 120 ppm, Sr = 0.85 ppm; (G) Ca = 110 ppm, Sr = 1.0 ppm; (H) Ca = 125 ppm, Mg = 30 ppm; (I) Ca = 125 ppm, Mg = 35 ppm; (J) Ca = 125 ppm, Mg = 40 ppm; (K) Ca = 120 ppm, Mg = 47 ppm. Soil leachate values for Mg/Ca, Sr/Ca, and Ba/Ca are represented by a dashed line in each graph.

ICD in warmer months. A more statistically rigorous assessment of the data is needed.

The Sinclair (2011) and Sinclair et al. (2012) models do not provide a quantitative assessment of the extent to which PCP/ICD and/or WRI are influencing the evolution of cave drip waters. Nor do the mathematical models determine the factors that might cause PCP/ICD or WRI to be more of a dominant factor. Therefore our field measurement data become important as they can potentially add information and scenarios that move towards a more quantitative assessment of the extent to which drip waters evolve. We have shown plate calcite growth rates and drip water trace element values as evidence that PCP is the predominant mechanism driving evolution at one site, WC-6. This is expected based on the flow path over a drapery while the other sites reflect more WRI. We have also used field measurements to infer a possible seasonal temperature control over which PCP/ICD can be more of a factor in warmer months and used this to separate it from the effects of WRI. This is a step in better constraining the relationship between the processes driving drip water evolution. We also identified that temperature should be considered when accessing the extent to which PCP/ICD and/or WRI influences drip water evolution.

6. Implications for paleoclimate studies using speleothems

At Westcave, without assessment of the relationship between temperature and drip water trace-element/Ca values, it could have been

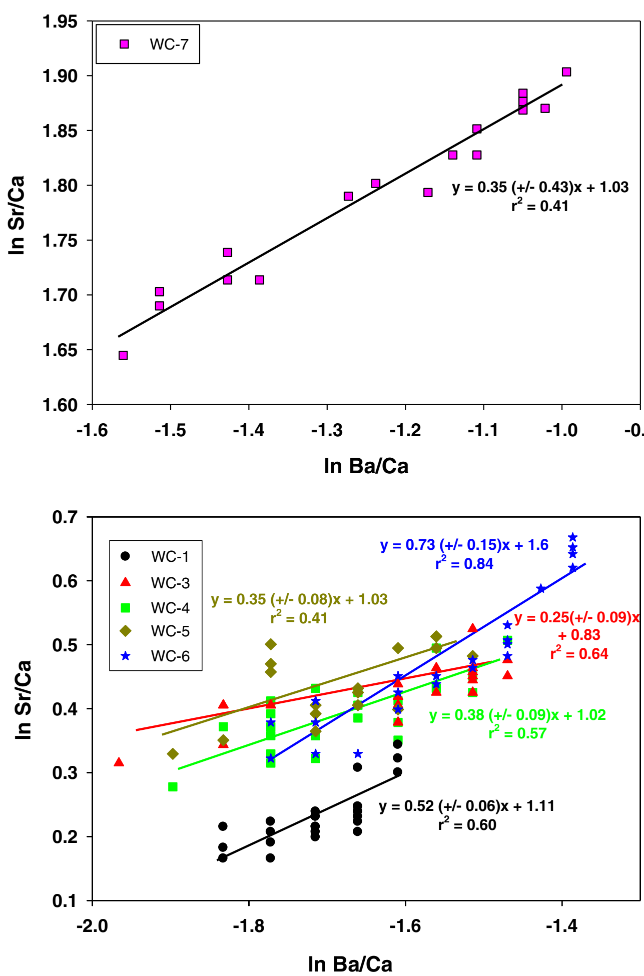

Fig. 7. Ln Sr/Ca vs. ln Ba/Ca variations for Westcave drip sites. Based on the methods of Sinclair et al. (2012) the slope of WC-6 (0.76) indicates that prior calcite precipitation and incongruent calcite dissolution (PCP/ICD) drive the evolution of drip waters at that site. The slopes of the other drip sites (0.25–0.55) reflect a mix between PCP/ICD and water–rock interaction (WRI).

possible to misinterpret speleothem Sr/Ca and Ba/Ca oscillations as a water flux proxy. Instead, we conclude that seasonal temperature variations, which influence calcite growth rate variations, drive variations in drip-water Sr/Ca and Ba/Ca values. This has implications for the use of trace-element/Ca values as a proxy for seasonal and interannual temperature variations.

One challenge with employing any geochemical proxy in speleothems is defining a timescale with which to construct a geochemical time series. Dating speleothems using growth bands is not a consistently reliable method for providing annual age constraints as banding is rare and the mechanisms are not well understood (Baker et al., 2008). Stalagmites in central Texas (and in many other regions of the world) do not generally have visible seasonal lamina nor is there evidence to suggest that when banding is present it is as consistently annual as laminae found in other paleoclimate proxies such as tree rings. As a consequence, age control relies on radiometric ages by U-series or C-14 methods, which have uncertainties of much greater than a year (Genty et al., 1998; Musgrove et al., 2001). But the radiometric methods may be used in conjunction with seasonal geochemical lamina, if they exist, to provide annual age constraints and independent tests of radiometric age determinations. The application of trace-element/Ca as a geochemical indicator of seasonal lamina has been demonstrated in a number of karst settings by Johnson et al. (2006), Mattey et al. (2010), and Wong et al. (2011). The summer peak and winter trough of cave drip water Sr/Ca and Ba/Ca values at Westcave indicate that there is a potential that speleothems can preserve geochemical laminae that may enable the constraining of relative ages at a seasonal resolution in speleothems.

Another approach to constrain ages at Westcave, beyond the trace element laminae approach described above, involves the seasonal pattern of calcite growth. It may be possible to use the bias towards higher summer growth rates as a complementary tool to Sr/Ca and Ba/Ca as a seasonal marker. For a sampling interval of constant stratigraphic thickness the summer season growth peaks would be reflected in a larger number of Sr/Ca and Ba/Ca data points relative to the number of winter season trough data points, as noted by Wong et al. (2011).

As well as providing age constraints, the relationship between temperature and Sr/Ca and Ba/Ca may provide an opportunity to reconstruct temperature, provided that some uncertainties can be addressed. For example, drip water Sr/Ca and Ba/Ca values at Westcave (compared to oxygen isotope values at Westcave; see Feng et al., 2014) are subject to higher frequency variations independent of temperature (e.g., heterogeneities of trace elements in the soil and karst overburden). At the least, there is the possibility that Sr/Ca and Ba/Ca can provide qualitative seasonal temperature reconstructions, if not quantitative temperature reconstructions, which would be an advancement in this realm of speleothem climate study. This also suggests that speleothem trace-element/Ca values may be used to reconstruct interannual temperature variations (Roberts et al., 1998).

Relative to a majority of caves studied, where drip water geochemistry is variable between drip sites, the seasonal variations in Sr/Ca and Ba/Ca at Westcave are a cave-wide phenomenon in that nearly every drip site studied follows the seasonal trend (5 of 6 for Sr/Ca and 6 of 6 for Ba/Ca). When the average Sr/Ca and Ba/Ca from every drip site are compared to the average growth rate from all drip sites there is a significant relationship ($r^2 = 0.73$). A noted difficulty in speleothem research has been the significant variation in geochemistry between drip sites within a single cave (e.g., Baldini et al., 2006; Wong et al., 2011). The strong temperature seasonality in Westcave, in contrast, may allow for more robust paleoclimate reconstructions via the replication of records from multiple stalagmites with similar geochemical signals. This approach is similar to dendrochronology studies where multiple samples are collected to statistically reduce the climate signal to noise relationship attributed to between-tree growth variability that is not related to climate variability. A caveat is that dendrochronology studies collect

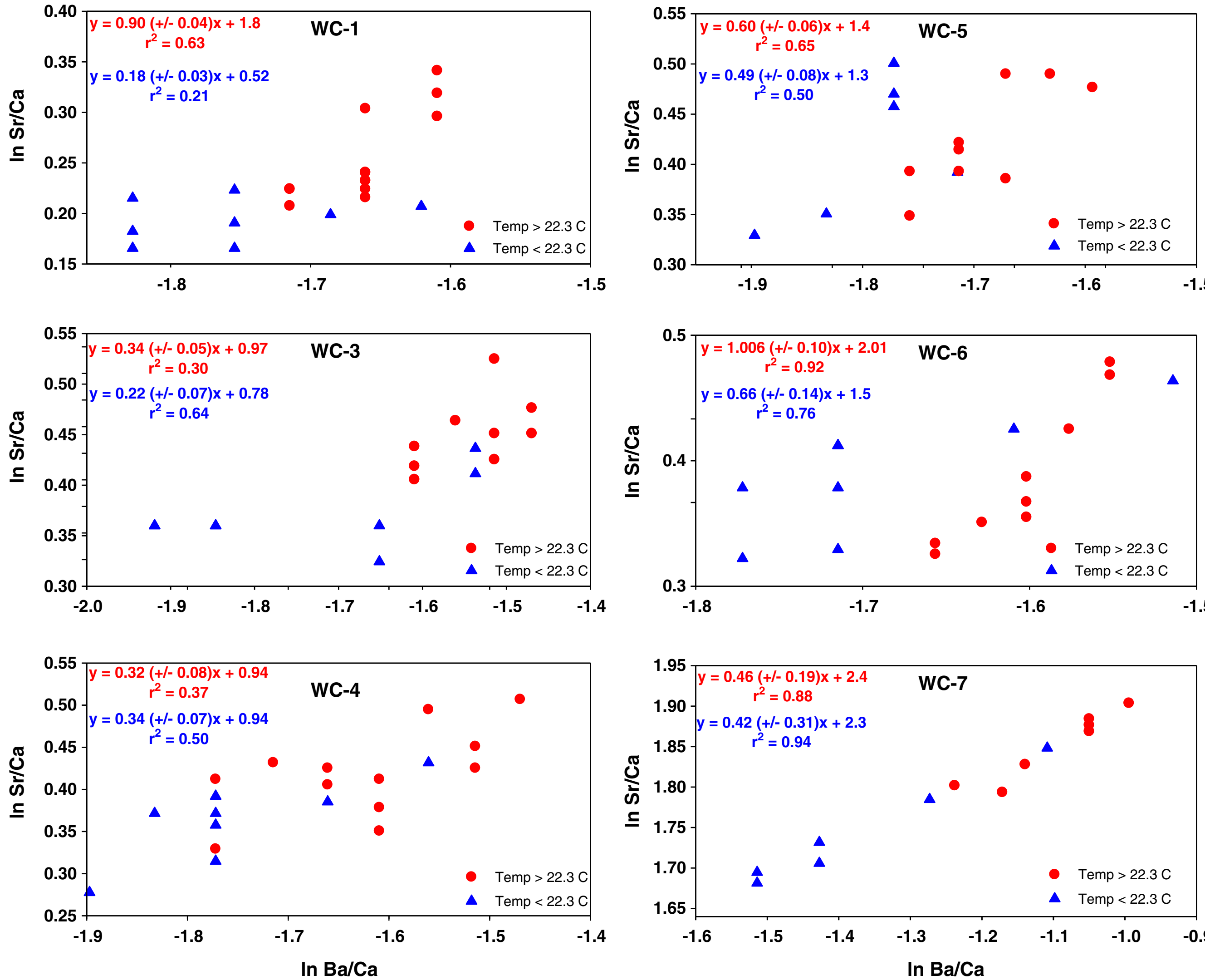

Fig. 8. ln Sr/Ca–ln Ba/Ca variations in Westcave drip waters for time periods when the average monthly temperature at Westcave Preserve was >17 °C (red circles) and for time periods when the average monthly temperature at Westcave Preserve was <17 °C (blue triangles). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

multiple samples from a large number of trees that respond to climate in a similar fashion. The significantly smaller number of available speleothems in a cave versus trees in a forest prevents collecting as many speleothem samples. It is encouraging, however, that the trace-element/Ca values of a large majority of drip sites studied respond to temperature variations in a similar manner. By contrast the drip sites at Natural Bridge Caverns in central Texas show three distinct groupings of drip-site geochemical response. These three groups are defined by drip waters being altered by seasonal cave air CO_2 variations, rainfall variations, or a combination of cave air CO_2 and rainfall variations (Wong et al., 2011). Additionally, oxygen isotopes vary with surface temperatures at Westcave as well (Feng et al., 2014) and can be used as a multi-proxy comparison with trace-element/Ca values of stalagmites.

Not only can the drip-water results at Westcave be applied to speleothems in the cave, these results are potentially applicable to other caves. It is possible that the methods of this study can be applied to reconstruct temperature variations at other caves with similar characteristics, including a relatively large opening area to cave volume ratio and/or a year-round ventilation regime producing a cave atmosphere that tracks surface conditions. There is evidence that other cave environments with relatively large temperature variations exist (Johnson et al., 2006). It can also be applied to the portions of many caves near the entrance, where cave-air CO_2 concentrations are closer to atmospheric year round and cave-air temperature varies seasonally. Speleothems near the entrance to caves have typically been avoided by previous paleoclimate studies owing to the instability of the cave atmosphere and low humidity near the entrances. It would be necessary to monitor cave drip-water geochemistry and cave-air characteristics prior to determining the utility of a drip site located near the entrance of a cave for this type of climate study (e.g., Feng et al., 2014). Speleothems near the entrances to caves may warrant further consideration for paleoclimate studies.

7. Conclusions

This study demonstrates the utility of a multi-year monitoring and assessment of a cave system in response to modern climate variations. We determine that water flux is not a key variable in drip water trace element variations at Westcave. The most significant findings are that Westcave Preserve calcite growth rates are controlled by seasonal temperature variations and that drip-water Sr/Ca and Ba/Ca values vary seasonally, corresponding with temperature and calcite growth rate at most drip sites studied. This is distinct from any cave studied in the region (e.g., Musgrove and Banner, 2004; Wong et al., 2011) and from many caves in other regions (e.g., Baldini et al., 2006; Karmann et al., 2007; McDonald et al., 2007). The shallow setting and small volume to large entrance ratio allow for the cave to be well-ventilated year round and have CO_2 concentrations and temperature similar to the surface atmosphere. We also have data to suggest that we might be able to differentiate the processes of PCP/ICD and WRI on a site by site basis using the mathematical approach of Sinclair (2011) and Sinclair et al. (2012); however a larger data set is needed prior to a definitive statement.

The data presented in this paper have implications for studying speleothems from near the entrances to caves, which have typically been avoided in speleothem studies. The control of temperature on processes at Westcave allows for future studies to (1) assess temperature proxies in speleothems from other caves in similar settings; and (2) compare multiple speleothem samples at Westcave to one another to increase statistical rigor when reconstructing climate.

Acknowledgments

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Appendix A

Table A.1
Drip rate, calcite growth rate, Ca, Mg, Sr, and Ba for all Westcave drip sites.

Site	Date	Drip rate (ml/s)	Calcite growth (mg/day on 100 cm^2 substrate)	Mg/Ca (mmol/mol)	Sr/Ca (mmol/mol)	Ba/Ca (mmol/mol)
WC1	7/3/2009	n/a	n/a	513	1.35	0.20
WC1	7/28/2009	n/a	n/a	n/a	n/a	n/a
WC1	8/28/2009	5.3e−3	n/a	529	1.38	0.20
WC1	9/15/2009	2.5e−3	n/a	538	1.41	0.20
WC1	10/5/2009	7.0e−3	28.8	517	1.36	0.19
WC1	10/29/2009	7.9e−3	20.5	441	1.23	0.19
WC1	12/7/2009	6.5e−3	12.7	490	1.24	0.16
WC1	1/21/2010	5.5e−3	8.4	489	1.25	0.17
WC1	2/20/2010	2.0e−3	8.5	438	1.18	0.16
WC1	3/28/2010	1.5e−3	9.2	450	1.18	0.17
WC1	4/27/2010	1.6e−3	12.5	465	1.22	0.18
WC1	5/31/2010	1.7e−3	15.1	502	1.27	0.19
WC1	7/6/2010	4.2e−3	23.5	497	1.26	0.19
WC1	7/28/2010	7.3e−3	27.2	491	1.27	0.19
WC1	8/26/2010	8.3e−3	32.4	489	1.25	0.19
WC1	9/26/2010	6.7e−3	32.2	494	1.26	0.18
WC1	10/24/2010	n/a	25.6	491	1.24	0.18
WC1	11/18/2010	n/a	16.4	n/a	n/a	n/a
WC1	12/15/2010	4.5e−3	13.2	501	1.21	0.17
WC1	1/27/2011	4.4e−3	9.6	519	1.20	0.16
WC1	2/24/2011	3.9e−3	7.1	527	1.24	0.18
WC1	4/15/2011	6.1e−3	26.0	521	1.23	0.18
WC1	6/7/2011	7.4e−3	32.9	500	1.28	0.19
WC1	8/4/2011	n/a	46.8	n/a	n/a	n/a
WC1	9/1/2011	8.5e−3	48.0	532	1.28	0.19
WC1	10/6/2011	6.6e−3	34.4	536	1.26	0.18
WC1	11/13/2011	5.2e−3	0.0	510	1.23	0.17
WC1	12/15/2011	n/a	15.4	541	1.27	0.18
WC3	7/3/2009	8.7e−4	n/a	n/a	n/a	n/a
WC3	8/28/2009	1.5e−5	28.1	738.95	1.69	.22
WC3	10/5/2009	1.1e−3	18.2	590.33	1.57	.22
WC3	10/29/2009	1.3e−3	20.3	607.42	1.56	.22
WC3	12/7/2009	8.7e−4	13.0	853.58	1.59	.22
WC3	1/21/2010	9.3e−4	6.4	622.06	1.50	.16
WC3	2/20/2010	1.2e−3	7.3	630.89	1.50	.16
WC3	3/28/2010	1.0e−3	8.3	716.41	1.50	.17
WC3	4/27/2010	1.1e−3	9.4	641.26	1.50	.17
WC3	7/6/2010	9.9e−4	11.2	597.81	1.55	.20
WC3	7/28/2010	1.5e−3	14.2	n/a	n/a	n/a
WC3	8/26/2010	9.9e−4	19.0	680.61	1.59	.21
WC3	9/26/2010	1.2e−3	18.6	576.79	1.57	.23
WC3	10/24/2010	n/a	14.7	584.88	1.53	.22
WC3	11/18/2010	n/a	11.0	580.22	1.50	.20
WC3	12/15/2010	2.2e−3	10.5	597.39	1.46	.20
WC3	1/27/2011	1.7e−3	6.4	n/a	n/a	n/a
WC3	2/24/2011	2.3e−3	5.3	617.31	1.41	.16
WC3	4/15/2011	8.8e−4	16.3	626.28	1.37	.14
WC3	6/7/2011	7.2e−4	13.4	809.63	1.52	.20
WC3	8/4/2011	2.0e−3	23.1	612.53	1.50	.20

Table A.1 (*continued*)

Site	Date	Drip rate (ml/s)	Calcite growth (mg/day on 100 cm^2 substrate)	Mg/Ca (mmol/mol)	Sr/Ca (mmol/mol)	Ba/Ca (mmol/mol)
WC3	9/1/2011	1.1e−3	18.8	605.26	1.61	.23
WC3	10/6/2011	1.3e−3	13.2	n/a	n/a	n/a
WC3	11/13/2011	1.5e−3	11.1	686.93	1.58	.22
WC3	12/15/2011	n/a	7.4	651.56	1.53	.21
WC4	8/28/2009	6.0e−4	24.4	753.58	1.64	.21
WC4	9/15/2009	1.8e−3	n/a	586.08	1.53	.22
WC4	10/5/2009	3.2e−3	11.3	596.61	1.57	.22
WC4	10/29/2009	3.0e−3	12.2	642.96	1.54	.21
WC4	12/7/2009	2.4e−3	11.8	607.01	1.43	.17
WC4	1/21/2010	2.7e−3	2.6	671.64	1.48	.17
WC4	2/20/2010	3.1e−3	3.3	644.52	1.45	.16
WC4	3/28/2010	2.4e−3	8.6	644.60	1.45	.17
WC4	4/27/2010	2.4e−3	10.4	630.46	1.47	.19
WC4	5/31/2010	1.0e−3	12.6	702.80	1.50	.19
WC4	7/6/2010	8.3e−4	10.9	789.85	1.39	.17
WC4	7/28/2010	4.7e−4	4.6	797.16	1.54	.18
WC4	8/26/2010	7.4e−4	5.0	747.63	1.53	.19
WC4	9/26/2010	2.5e−3	15.0	592.81	1.51	.20
WC4	10/24/2010	2.9e−3	14.5	600.20	1.42	.20
WC4	11/18/2010	1.6e−3	12.1	n/a	n/a	n/a
WC4	12/15/2010	2.2e−3	11.3	626.43	1.37	.17
WC4	1/27/2011	1.0e−3	6.9	614.73	1.32	.15
WC4	2/24/2011	3.4e−4	5.8	694.16	1.38	.18
WC4	4/15/2011	2.5e−4	12.9	646.38	1.43	.18
WC4	6/7/2011	2.5e−4	11.2	811.54	1.51	.17
WC4	8/4/2011	2.0e−3	6.3	n/a	n/a	n/a
WC4	9/1/2011	n/a	6.2	828.06	1.66	.23
WC4	10/6/2011	n/a	13.1	615.61	1.46	.20
WC4	11/13/2011	2.9e−3	14.8	n/a	n/a	n/a
WC4	12/15/2011	1.6e−3	8.1	656.47	1.43	.18
WC5	8/28/2009	2.3e−3	n/a	650.02	1.67	.21
WC5	9/15/2009	3.1e−3	n/a	579.02	1.62	.22
WC5	10/5/2009	2.5e−3	14.5	592.23	1.64	.21
WC5	10/29/2009	1.8e−3	9.7	634.54	1.67	.21
WC5	1/21/2010	4.0e−4	4.4	n/a	n/a	n/a
WC5	2/20/2010	3.8e−4	7.4	677.58	1.60	.17
WC5	3/28/2010	6.3e−4	4.2	668.03	1.65	.17
WC5	4/27/2010	1.4e−3	10.2	651.38	1.58	.17
WC5	5/31/2010	1.4e−3	10.9	622.29	1.53	.19
WC5	7/6/2010	1.5e−3	31.9	720.23	1.64	.20
WC5	7/28/2010	2.1e−3	18.5	733.32	1.54	.19
WC5	8/26/2010	1.2e−3	13.2	588.09	1.49	.20
WC5	9/28/2010	1.3e−3	12.3	703.96	1.50	.18
WC5	10/24/2010	n/a	14.1	590.73	1.44	.18
WC5	11/18/2010	n/a	11.7	n/a	n/a	n/a
WC5	12/15/2010	n/a	3.1	n/a	n/a	n/a
WC5	1/27/2011	9.9e−4	6.2	592.45	1.42	.16
WC5	2/24/2011	6.0e−4	7.4	600.81	1.39	.15
WC5	4/15/2011	1.1e−3	8.5	668.75	1.48	.18
WC5	6/7/2011	2.9e−4	5.1	627.56	1.50	.19
WC5	8/4/2011	9.6e−4	4.4	n/a	n/a	n/a
WC5	9/1/2011	2.7e−4	7.4	n/a	n/a	n/a
WC5	10/6/2011	4.3e−4	9.3	n/a	n/a	n/a
WC5	11/13/2011	6.3e−4	4.4	n/a	n/a	n/a
WC5	12/15/2011	no drip	1.9	n/a	n/a	n/a
WC6	8/28/2009	0.090	n/a	627.24	1.66	.23
WC6	9/15/2009	0.038	n/a	700.94	1.86	.25
WC6	10/5/2009	0.062	35.6	633.78	1.65	.23
WC6	10/29/2009	0.099	31.2	598.54	1.59	.22
WC6	12/7/2009	0.043	20.5	596.52	1.51	.18
WC6	1/21/2010	0.048	8.0	594.40	1.51	.18
WC6	2/20/2010	0.078	12.7	575.98	1.46	.17
WC6	3/28/2010	0.076	14.5	577.40	1.46	.18
WC6	4/27/2010	0.075	28.8	602.44	1.53	.20
WC6	5/31/2010	0.034	35.1	795.44	1.95	.25
WC6	7/6/2010	0.097	47.4	688.14	1.70	.23
WC6	7/28/2010	0.099	61.2	694.08	1.80	.24
WC6	8/26/2010	0.089	67.4	612.38	1.61	.22
WC6	9/26/2010	0.090	55.1	592.94	1.57	.21
WC6	10/24/2010	n/a	36.6	625.43	1.55	.21
WC6	11/18/2010	n/a	23.2	n/a	n/a	n/a
WC6	12/15/2010	0.062	19.4	577.20	1.39	.18
WC6	1/27/2011	0.064	17.3	570.96	1.38	.17
WC6	2/24/2011	0.025	26.6	815.66	1.90	.25

(continued on next page)

Table A.1 (*continued*)

Site	Date	Drip rate (ml/s)	Calcite growth (mg/day on 100 cm^2 substrate)	Mg/Ca (mmol/mol)	Sr/Ca (mmol/mol)	Ba/Ca (mmol/mol)
WC6	4/15/2011	0.056	6.6	728.62	1.57	.20
WC6	6/7/2011	0.028	36.0	760.58	1.92	.25
WC6	8/4/2011	0.042	45.2	n/a	n/a	n/a
WC6	9/1/2011	0.035	30.5	678.76	1.62	.23
WC6	10/6/2011	0.033	36.0	n/a	n/a	n/a
WC6	11/13/2011	0.040	18.8	616.39	1.49	.20
WC6	12/15/2011	n/a	17.4	587.29	1.39	.19
WC7	8/28/2009	2.3e−3	n/a	997.12	6.49	.36
WC7	9/15/2009	1.2e−3	n/a	973.58	6.22	.33
WC7	10/5/2009	2.2e−3	9.4	993.13	6.22	.32
WC7	10/29/2009	1.2e−3	6.0	n/a	6.37	.33
WC7	12/7/2009	3.6e−4	4.0	1018.63	5.42	.22
WC7	1/21/2010	8.5e−4	3.8	1030.09	5.49	.22
WC7	2/20/2010	7.7e−4	2.9	1004.89	5.55	.24
WC7	3/28/2010	7.3e−4	n/a	1027.88	5.69	.24
WC7	4/27/2010	3.3e−4	4.9	1050.66	5.99	.28
WC7	5/31/2010	6.1e−4	5.8	1054.21	6.58	.35
WC7	7/6/2010	6.1e−4	5.0	1067.22	6.71	.37
WC7	7/28/2010	5.7e−4	5.3	1074.99	6.48	.35
WC7	8/26/2010	6.8e−4	7.4	1094.05	6.53	.35
WC7	9/26/2010	1.1e−3	8.4	1039.04	6.06	.29
WC7	10/24/2010	1.3e−3	8.7	1055.31	6.01	.31
WC7	11/18/2010	n/a	7.5	n/a	n/a	n/a
WC7	12/15/2010	1.1e−3	7.2	1052.73	5.55	.25
WC7	1/27/2011	1.5e−3	4.9	1010.74	5.18	.21
WC7	2/24/2011	1.3e−3	3.6	n/a	n/a	n/a
WC7	4/15/2011	4.4e−4	7.2	n/a	n/a	n/a
WC7	6/7/2011	8.8e−4	10.1	n/a	n/a	n/a
WC7	8/4/2011	7.4e−4	9.4	n/a	n/a	n/a
WC7	9/1/2011	9.5e−4	9.8	n/a	n/a	n/a
WC7	10/6/2011	9.5e−4	10.4	n/a	n/a	n/a
WC7	11/13/2011	1.1e−3	0.0	n/a	n/a	n/a
WC7	12/15/2011	n/a	6.1	n/a	n/a	n/a

Table A.2
Average monthly surface temperature, average monthly cave air temperature, cave drip water temperature, and cave air relative humidity at Westcave. Drip water temperatures are monthly spot measurements from site WC-6. Average air temperatures are calculated based on the temperatures between sampling trips.

Date	Average surface temperature (°C)	Average cave air temperature (°C)	Cave drip water temperature from site WC-6 (°C)	Cave air relative humidity (%)
7/3/2009	30.7	n/a	n/a	n/a
7/28/2009	32.3	n/a	n/a	n/a
8/28/2009	32.1	n/a	28.4	n/a
9/15/2009	27.7	n/a	22.3	n/a
10/5/2009	25.8	n/a	22.8	n/a
10/29/2009	20.4	n/a	23.4	n/a
12/7/2009	14.5	n/a	15.4	n/a
1/21/2010	9.0	n/a	17.6	n/a
2/20/2010	9.4	n/a	17.8	n/a
3/28/2010	13.5	n/a	16.3	n/a
4/27/2010	20.0	n/a	17.0	n/a
5/31/2010	25.8	21.6	24.7	96.7
7/6/2010	28.9	24.0	24.7	98.1
7/28/2010	29.5	24.7	23.6	98.3
8/26/2010	31.5	25.0	23.6	97.2
9/26/2010	27.9	23.7	16.8	97.2
10/24/2010	23.1	17.9	21.3	72.8
11/18/2010	17.9	n/a	n/a	n/a
12/15/2010	16.0	12.8	12.9	67.0
1/27/2011	10.8	8.8	8.3	64.3
2/24/2011	8.2	9.0	17.7	61.4
4/15/2011	16.3	15.8	17.5	68.6
6/7/2011	24.8	20.3	21.9	68.0
8/4/2011	31.3	24.7	24.2	66.9
9/1/2011	33.1	25.6	23.8	66.3
10/6/2011	29.2	21.2	20.9	66.7
11/13/2011	20.3	16.9	17.3	68.5
12/15/2011	14.1	12.9	14.9	68.9

Table A.3
Statistical relationships between trace element ratios, drip rate, and effective precipitation. The +/− of β represents the direction of the relationship.

Site	Sr/Ca vs. drip rate	Sr/Ca vs. effective rainfall	Mg/Ca vs. drip rate	Mg/Ca vs. effective rainfall
WC-1	$r^2 = 0.03, p = 0.28$	$r^2 = 0.03, p = 0.28$	$r^2 = 0.02, p = 0.32$	$r^2 = 0.27, p < 0.05$ ($\beta = -0.52$)
WC-3	$r^2 = 0.30, p < 0.05$	$r^2 = 0.04, p = 0.27$	$r^2 = 0.04, p = 0.26$	$r^2 = 0.16, p = 0.09$
WC-4	$r^2 = 0.04, p = 0.24$	$r^2 = 0.07, p = 0.18$	$r^2 = 0.68, p < 0.001$ ($\beta = -0.82$)	$r^2 = 0.52, p < 0.005$ ($\beta = -0.72$)
WC-5	$r^2 = 0.07, p = 0.24$	$r^2 = 0.09, p = 0.40$	$r^2 = 0.33, p = 0.05$ ($\beta = -0.58$)	$r^2 = 0.006, p = 0.44$
WC-6	$r^2 = 0.06, p = 0.19$	$r^2 = 0.03, p = 0.28$	$r^2 = 0.11, p = 0.13$	$r^2 = 0.05, p = 0.28$
WC-7	$r^2 = 0.14, p = 0.13$	$r^2 = 0.005, p = 0.42$	$r^2 = 0.42, p < 0.05$ ($\beta = -0.65$)	$r^2 = 0.002, p = 0.46$

Site	Ba/Ca vs. drip rate	Ba/Ca vs. effective rainfall	Drip rate vs. effective rainfall
WC-1	$r^2 = 0.04, p = 0.25$	$r^2 = 0.23, p < 0.05$ ($\beta = -0.48$)	$r^2 = 0.05, p = 0.28$
WC-3	$r^2 = 0.00, p = 0.50$	$r^2 = 0.006, p = 0.40$	$r^2 = 0.32, p < 0.05$ ($\beta = -0.57$)
WC-4	$r^2 = 0.002, p = 0.45$	$r^2 = 0.03, p = 0.27$	$r^2 = 0.74, p < 0.001$ ($\beta = -0.48$)
WC-5	$r^2 = 0.84, p < 0.001$ ($\beta = 0.92$)	$r^2 = 0.04, p = 0.30$	$r^2 = 0.02, p = 0.30$
WC-6	$r^2 = 0.001, p = 0.46$	$r^2 = 0.01, p = 0.37$	$r^2 = 0.01, p = 0.35$
WC-7	$r^2 = 0.21, p = 0.09$	$r^2 = 0.003, p = 0.43$	$r^2 = 0.00, p = 0.48$

Table A.4
Alkalinity, pH, and saturation index (SI) data for drip sites WC-1 and WC-6.

Site	Date	Alkalinity	pH	SI
WC1	10/29/2009	414	8.16	1.33
WC1	12/7/2009	434	8.16	1.25
WC1	8/26/2010	447	8.14	1.35
WC1	9/28/2010	424	8.13	1.25
WC6	8/28/2009	381	8.01	1.27
WC6	9/15/2009	374	8.73	1.65
WC6	10/5/2009	392	8.57	1.59
WC6	10/29/2009	386	8.22	1.30
WC6	12/7/2009	372	8.22	1.17
WC6	1/21/2010	389	8.10	1.01
WC6	2/20/2010	361	8.17	1.16
WC6	4/27/2010	428	8.28	1.11
WC6	5/31/2010	359	8.19	1.13
WC6	7/28/2010	455	8.12	1.33
WC6	8/26/2010	420	8.15	1.27
WC6	9/28/2010	412	8.10	1.13
WC6	1/27/2011	407	8.11	1.13
WC6	2/24/2011	317	8.26	1.13
WC6	4/15/2011	384	8.30	1.32
WC6	6/7/2011	355	8.26	1.31
WC6	9/1/2011	427	8.24	1.28

Appendix B. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.chemgeo.2014.11.002.

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