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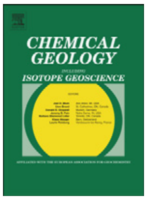

Temperature-driven seasonal calcite growth and drip water trace element variations in a well-ventilated Texas cave: Implications for speleothem paleoclimate studies

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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