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The potential of near-entrance stalagmites as high-resolution terrestrial paleoclimate proxies: Application of isotope and trace-element geochemistry to seasonally-resolved chronology

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Abstract

Sub-annually resolved environmental proxies can be valuable archives of climate change, but they are rare in terrestrial settings, and it can be difficult to verify their annual nature. We suggest that speleothems that grow in well-ventilated zones of caves may preserve such high-resolution records. Near-entrance cave environments are characterized by year-round, near-atmospheric CO_2 concentrations and are significantly influenced by surface air temperature fluctuations, particularly in temperate latitudes. Previous monitoring studies of a well-ventilated, temperate-latitude cave (Westcave Preserve, central Texas) have documented seasonal variations in the oxygen isotope composition of calcite grown on glass substrates (with winter $\delta^{18}O$ maxima and summer $\delta^{18}O$ minima) as well as seasonal variations in drip water trace element compositions. Extending this work to a stalagmite (WC-3) from the same drip site, we find that stalagmite $\delta^{18}O$ variations are similar in magnitude to the seasonal $\delta^{18}O$ variations previously observed for calcite grown on glass substrates, that stalagmite [Mg] variations have a similar seasonal period with winter minima and summer maxima, and that geochemical variations follow stalagmite growth fabric as mm-scale couplets comprising thin, slow-growing, compact sparry calcite laminae (winters) and thicker, fast-growing, porous-elongate columnar calcite laminae (summers). We interpret a high-resolution (weekly to monthly) 52-year record of $\delta^{18}O$, Mg, Sr, and Ba in WC-3, and report new monthly measurements of drip water and associated calcite grown on glass substrates. We find drip water $\delta^{18}O$ and [Mg]/[Ca] are essentially invariant and that seasonal variations in WC-3 calcite $\delta^{18}O$ and Mg concentration agree well with predicted temperature-dependent fractionation between water and calcite. WC-3 calcite Sr and Ba also vary, but with higher and more variable frequencies compared to $\delta^{18}O$ and [Mg]. The annual nature of $\delta^{18}O$ and [Mg] cycles is supported by monitoring and ^{14}C bomb-peak chronology. We suggest that stalagmite $\delta^{18}O$ and [Mg] vary primarily in response to large seasonal temperature changes in this setting, allowing for unambiguous differentiation between summer and winter calcite growth. From such $\delta^{18}O$- and [Mg]- derived sub-annual chronologies, the timing of enrichments in other geochemical species that are less directly coupled to external cave temperature (e.g., calcite Sr and Ba) can be considered as proxies of other important processes such as water-rock interaction in the epikarst, precipitation events, or subsurface respiration rates. The potential for this kind of multi-proxy, seasonally-resolved dating may add near-entrance stalagmites to the list (ice cores, lake varves, tree rings) of high-resolution terrestrial proxies available for paleoclimate studies.

Keywords: Sub-annual chronology; Near-entrance speleothem; Trace elements; Oxygen isotopes

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1. INTRODUCTION

Paleoclimate reconstructions endeavor to interpret the nature and history of climate change over a range of scales in both time and space. The temporal resolution of paleoclimate reconstructions depends upon the precision and accuracy of available age control available from natural records. In this regard, proxies that reliably encode environmental seasonality are of particular value, potentially offering chronologies capable of sub-annual resolution. In terrestrial settings, the list of environmental proxies capable of recording seasonality is short, and these proxies are often limited in geographic occurrence or difficult to validate their annual nature. Karst systems span a wide latitudinal range, covering ~15% of Earth's ice-free land (Stevanović, 2018), however, and laminated speleothems from regions influenced by strong seasonal contrasts may also offer seasonally-resolved proxy records (Boch et al., 2011). Provided the age and annual timing of lamina development can be constrained, the derived lamina chronologies can facilitate a wide range of high-resolution studies (e.g., seasonality of rainfall, temperature, soil productivity, and water resource management, Wolter et al., 1999; Raich et al., 2002; Weiss et al., 2009; Dong et al., 2010; growth and retreat of glaciers, Rupper et al., 2009; geographic distribution of C_3 and C_4 plants, Schwartz et al., 2006; and refined U-series-based age models, Shen et al., 2013). Speleothems may also encode variations in and above the cave environment that are non-periodic or stochastic in nature. Coupled with annually-resolved chronologies, the nature of these variations can be compared to historical or instrumental meteorological records to evaluate potential controls and achieve a better understanding of karst system processes.

Some speleothems have been shown to record annual variations, including: laminations caused by seasonal variations in calcite growth (Genty, 1992, 1993; Baker et al., 1993; Railsback et al., 1994; Genty and Quinif, 1996; Genty et al., 1997; Johnson et al., 2006; Baker et al., 2008), laminations caused by seasonal deposition of organic matter or detrital material (e.g., Allison, 1926; Baker et al., 1993; Shopov et al., 1994; McGarry and Baker, 2000), and trace element concentrations following seasonal changes in drip water chemistry (Kuczumow et al., 2003; Treble et al., 2003; Borsato et al., 2007; Mattey et al., 2010). In general, speleothems are useful terrestrial paleoclimate indicators because of their long and continuous growth histories, their widespread geographic distribution, and the wide applicability of high-precision U-series geochronology for constraining high-temporal-resolution proxy records (Schwarcz, 1986; Gascoyne, 1992; Wang et al., 2001; McDermott, 2004). When present, regular annual variations in speleothem growth and geochemical composition provide inherent age constraints on the timing and duration of important karst processes, but visible laminations and geochemical cycles in a stalagmite may not be reliably annual in nature. Some stalagmite records that are otherwise annually-laminated often include some years recording no cycles or laminations, and some years recording multiple cycles or laminations (Treble et al., 2005; Baker et al., 2008). The annual nature of these signals must therefore be confirmed by other age-constraint methods, such as radiometric dates and known events observed in the stalagmite record (e.g., Smith et al., 2009; Nagra et al., 2017), by a comprehensive understanding of karst processes through cave monitoring (e.g., Frisia et al., 2000) or through stalagmite growth modeling (e.g., Genty et al., 2001a,b).

For the few speleothem studies that achieve annual or sub-annual resolution, high resolution variations in oxygen isotope composition ($\delta^{18}O$) and trace elements (especially Mg, Sr, and Ba) in the speleothem calcite are interpreted as markers of environmental change. Variations in oxygen isotope compositions are often attributed to annual variation in rainfall oxygen isotope composition (e.g., Treble et al., 2005; Johnson et al., 2006; Orland et al., 2015), and Mg variations are often interpreted as a proxy for seasonal variations of groundwater flux and its interactions with the host rock (e.g., Fairchild et al., 2001; Treble et al., 2003; Borsato et al., 2007; Orland et al., 2014; Rutlidge et al., 2014). Both oxygen isotope fractionation and Mg partitioning between water and calcite are temperature-dependent processes (Mucci, 1987; Rosenthal et al., 1997; Kim and O'Neil, 1997; Huang and Fairchild, 2001), but speleothems are typically selected from environmentally stable, deep cave settings, where cave-air temperatures remain near mean annual temperature year-round (Davies, 1953).

The entrances of caves often experience significantly more temperature variation than deep within the cave (Davies, 1953; Spötl et al., 2005). With notable exceptions (e.g., Allison, 1926; Railsback et al., 1994; Roberts et al., 1998; Johnson et al., 2006; Couchoud et al., 2009), however, sites near the entrances of caves are typically avoided for paleoclimate studies owing to concerns about the high variability of temperature, relative humidity, rates of CO_2 degassing and calcium carbonate growth, biological activity, and uncertainties about how these variations impact the geochemical composition of drip waters and speleothem calcium carbonate (Hendy, 1971; Goede et al., 1990; Gascoyne, 1992; Lauritzen and Lundberg, 1999; White, 2007). The large seasonal variations in temperature that occur near cave entrances, however, could be useful as seasonal chronometers if recorded in near-entrance stalagmites. In near-entrance settings, if the $\delta^{18}O$ value of drip water does not significantly vary at a seasonal scale, temperature could be a primary control on speleothem $\delta^{18}O$ variations. Similarly, if drip water [Mg]/[Ca] are relatively invariant on a seasonal scale in a near-entrance cave setting, temperature may be a primary control on speleothem Mg variations. While temperature estimates based on either speleothem oxygen isotope values or Mg concentrations are subject to significant potential error, near-entrance cave environments in temperate regions may see enough seasonal variation in temperature that these temperature-sensitive proxies may act as useful annual chronometers.

At Westcave Preserve, the site of the current study, Feng et al. (2014) found that the $\delta^{18}O$ values of calcite grown on glass substrates (substrate calcite, hereafter; collected monthly, $n = 16$, October 2009 to March 2011) systematically fluctuated over a 2–3‰ range, following seasonal cave air temperature variations, with $\delta^{18}O$ minima