

The geochemistry of cave calcite deposits as a record of past climate

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ABSTRACT

Cave calcite deposits, and stalagmites specifically, are proving to be critical recorders of paleoclimate. Stalagmites develop from the slow accumulation of calcite deposited after the degassing of carbon dioxide from percolation water in caves. Stalagmites are therefore theoretically capable of recording the hydrochemistry of every drip of water that impacts their surface, but complications involving hydrology, cave air PCO_2 variability, intra-aquifer processing, and petrography preclude straightforward interpretation. Nevertheless, stalagmite climate proxy records using stable isotopes, particularly of oxygen, are reconstructing the timing, structure, and in some cases magnitude of climate shifts worldwide. Trace element to calcium ratios in stalagmite are a promising new proxy for both independent reconstruction of climate and for supporting oxygen isotope ratios. Extensive monitoring of individual cave sites is required to most accurately interpret stalagmite proxy records.

INTRODUCTION

Speleothems are secondary sedimentary, usually monomineralic, cave deposits that may consist of any mineral and may take on any number of morphologies. Over 250 different minerals have been identified in caves, ranging from common species such as calcite and gypsum to much less common species, such as vanadate and organic minerals (Hill and Forti 1997). Despite this broad diversity of minerals, speleothems are predominantly composed of only three: calcite, aragonite, and gypsum, and of these the vast majority are composed of calcite. Of the different forms of speleothem (including stalagmites, stalactites, helictites, flowstones, and many more), calcite stalagmites are by far the most researched and provide the vast majority of important climate records (Fig 1) (McDermott 2004). Stalagmites are formed by the gradual accumulation of calcite from a drip emanating from the point where a water flowpath through the aquifer intersects a void space. Groundwater in karst aquifers typically has very high levels of dissolved carbon dioxide and calcium due to contact with the soil derived CO_2 (Murthy et al. 2003) and subsequent limestone dissolution (White 1988). When the drip enters the cave atmosphere, which almost always has a lower CO_2 partial pressure (PCO_2) than the soil zone with which the water has equilibrated with, CO_2 degassing occurs from the drip resulting in calcite deposition. Cave drips therefore typically become oversaturated with respect to calcite immediately upon exposure to the cave atmosphere, and deposit calcite first on

the ceiling of the cave, resulting in a stalactite. After the drip gains enough mass to overcome surface tension (Collister and Matthey 2008), it falls to the cave floor where it deposits calcite until it completes its equilibration with ambient PCO_2 . The relatively straightforward morphology of calcite stalagmites (Fig 2), combined with their occurrence worldwide and amenability to radiometric dating, means that they are excellent multi-proxy archives of climate, particularly in parts of the world where other easily-dated climate archives (e.g., ice cores, deep sea sediments cores) are scarce or nonexistent (Cruz et al. 2006; Hodge et al. 2008; McDermott et al. 2001).

This paper reviews how stalagmite geochemistry records climate, and discusses some case studies to demonstrate the ability of these sediments to provide both long-term and very highly resolved records. In addition, research aiming to better constrain how the climate signal is altered as groundwater passes through the soil, epikarst, and bedrock, until its discharge point in the cave is summarized. Finally, some future research problems, challenges, and applications of the technique will be introduced.

KARST HYDROLOGY

Karst landscapes are characterized by an abundance of caves, sinkholes (dolines), and lack of surface drainage. Karst aquifers are often problematic for hydrological studies because the basic rules of hydrogeology as defined by Darcy's Law sometime do not apply. Groundwater flow is often non-Darcian in karst aquifers; that is, it is more comparable to open channel flow and therefore often adheres more closely to the Manning Equation than Darcy's Law. Because stalagmites grow in the unsaturated zone of the aquifer, much of the relevant groundwater flow is vertical and may be affected by local anisotropic features such as bedding planes, fractures, and dissolutional features. However, abundant intragranular permeability may also exist, as well as smaller fractures that may store water for long time intervals. Some estimates suggest that the majority of water stored in the unsaturated zone of karst aquifers is stored in this 'diffuse' permeability reservoirs (Atkinson 1977). This leads to a situation where stalagmites may be fed by drips with vastly different water histories: *i*) water that have resided in the aquifer for decades or longer, *ii*) drips that have only recently percolated through the aquifer, or *iii*) any combination of the two. Recharge to growing stalagmites is therefore generally composed of diffuse and fracture-fed components and identifying the relative importance of both of these is critical for understanding how climate is conveyed from the atmosphere to the stalagmite.

OXYGEN ISOTOPE RATIOS

The majority of paleoclimatic records using stalagmites are based on the ratio of stable isotopes within the calcite, particularly the ratio of ^{18}O to ^{16}O , or the $\delta^{18}\text{O}$. Stalagmite $\delta^{18}\text{O}$ is derived from the drip water, which itself is rainwater processed within the karst aquifer and soil. Rainwater $\delta^{18}\text{O}$ is largely affected by temperature, the rainout amount, and the $\delta^{18}\text{O}$ of water from the moisture source region (itself often linked to climate), so stalagmites record changes in these parameters. Stalagmite growth occurs gradually from calcite precipitated directly from cave drip water; stalagmite geochemistry is therefore dependent on drip water hydrochemistry which in turn reflects rainwater chemistry and climate. Because drip water $\delta^{18}\text{O}$ reflects rainfall $\delta^{18}\text{O}$ (McDermott 2004), stalagmites preserve a record of past variability in rainfall $\delta^{18}\text{O}$. The initial focus of studies using $\delta^{18}\text{O}$ in stalagmites was paleotemperature reconstruction; if calcite and drip water $\delta^{18}\text{O}$



Figure 2. A cross-sectional view of stalagmite BA-99-2 from Ballynamindra Cave, Dungarvan, Ireland. The calcite is deposited as lens that drape over each previous lens. Typically analytical traverses run along the central growth axis of the stalagmite, as this is the location that experiences the least amount of kinetic fractionation and has the highest deposition rate and therefore the highest temporal resolution achievable using microanalytical techniques. The sample is approximately 30cm long.

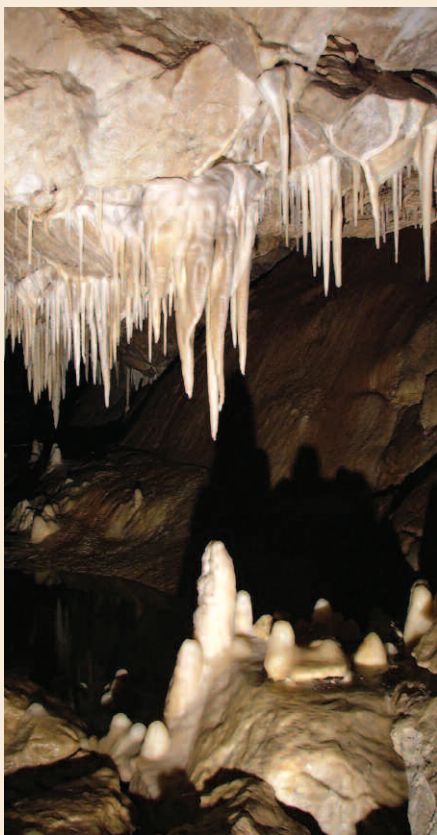


Figure 1. Calcite cave deposits in Niedzwiedzia Cave, Kletno, Poland. The stalagmites accumulate from the floor upwards and the stalactites from the roof downwards.

Recent research has demonstrated that different stalagmites record climate with differing resolution (Baldini et al. 2006a; Cruz et al. 2005) depending on the hydrochemical characteristics of the drip feeding the sample. Different stalagmites, even within the same cave, can record different aspects of the climate signal; some samples may retain a long-term averaged climate signal while others may record individual rain events. Overly responsive drips result in stalagmites yielding very 'noisy' records, can be subject to unpredictable flow rerouting, and may be seasonally undersaturated with respect to calcite, and should therefore be avoided for anything except very specialized applications. Conversely, diffuse drips result in stalagmites with an extremely 'averaged' climate signal that only encodes a small percentage of total rainfall isotope variability, and, while useful for determining longer-term climate, are unsuitable for reconstructing seasonal-scale or event-scale climate (Baldini et al. 2006b; McDermott et al. 2006). Morphological characteristics of stalagmites combined with drip monitoring using automated drip rate loggers (Mattey et al. 2008) and dripwater

chemical analyses (Baldini et al. 2006a; Tooth and Fairchild 2003) help identify samples that may yield the climate signal most suitable for specific project goals. For example, several drip sites in Crag Cave, Castleisland, Ireland, were evaluated and compared to rainfall amounts to better understand the different hydrologies that could occur within one cave (Fig 3). Diffuse, responsive, and overly responsive drip sites were identified, and it was determined that only stalagmites underneath the diffuse and responsive drips would be suitable for a climate reconstruction study (Baldini et al., *unpublished data*).

CAVE ATMOSPHERE CONTROLS ON CALCITE DEPOSITION

Although hydrological controls on stalagmite growth and climate signal emplacement have been very well researched recently, a less well quantified variable critical to stalagmite growth is the differential between soil and cave air PCO_2 . Because research (Baldini et al. 2008; Banner et al. 2007) has demonstrated that cave air PCO_2 greatly affects the rate of calcite deposition, characterization of cave air PCO_2 variability is required to aid in interpretation of any climate records produced. There are numerous ways that the CO_2 may enter cave systems, but in most temperate limestone caves the CO_2 is derived from the soil zone, either as direct percolation of gaseous CO_2 through fractures or indirectly dissolved in drip water. Without any ventilation, the cave would eventually reach the same PCO_2 as the soil zone and no degassing, and no calcite deposition, would occur. Cave ventilation, controlled by changes in temperature, air density, barometric pressure, or wind direction, is known to modulate cave air PCO_2 . Because drip equilibration with ambient PCO_2 results in the deposition of calcite, elevated cave air PCO_2 results in less calcite deposition than low cave air PCO_2 . For example, New St. Michael's Cave in Gibraltar ventilates in the summer (Mattey et al. 2008), so, assuming other growth determining variables remain constant, more calcite deposition during the summer months would be expected. This would skew annually averaged climate reconstructions towards summer recharge, and thus impacting the net climate signal (Baldini et al. 2008). To assess the seasonality of calcite deposition, loggers are often used to record cave air PCO_2 , thus facilitating the interpretation of any proxy records generated. New studies are attempting to measure all growth determining variables while simultaneously collecting stalagmite calcite to test the concepts outlined above (Fig 4).

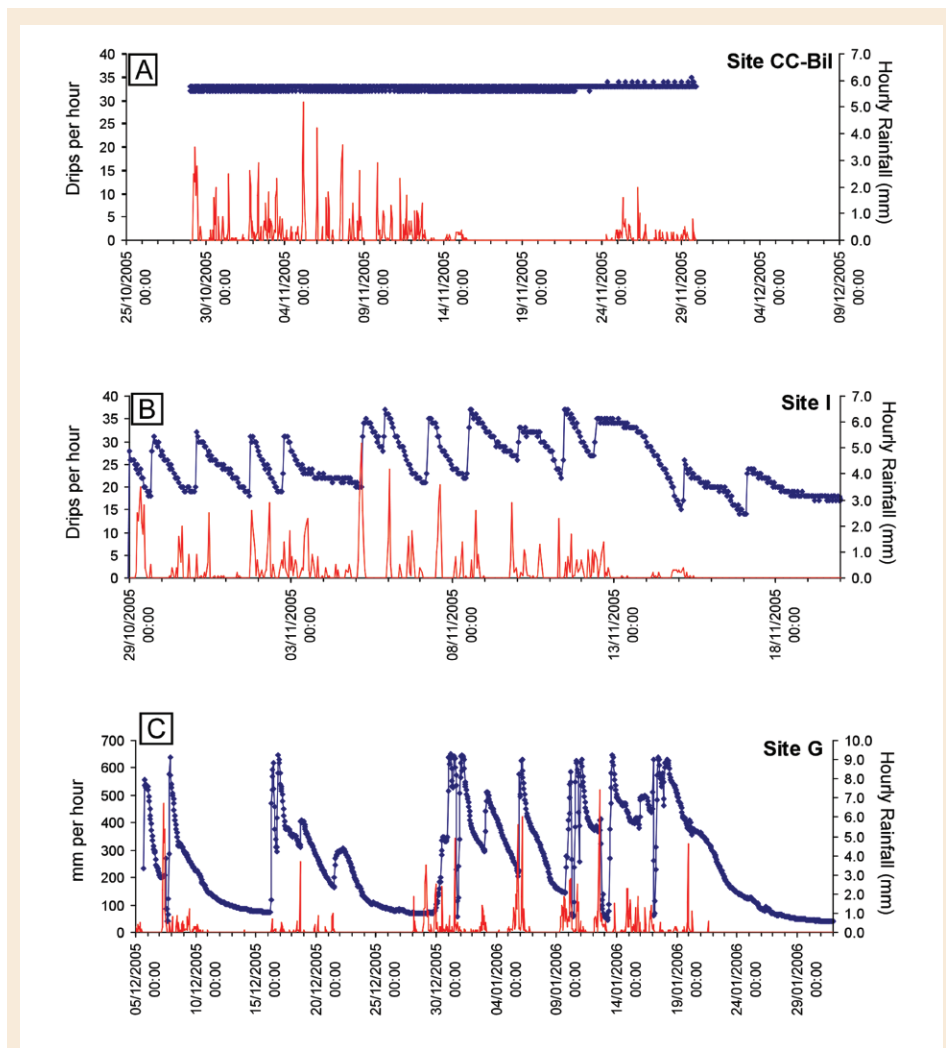


Figure 3. Automatically logged drip rates for three drip sites in Crag Cave, Ireland. *A) An example of a diffuse flow drip. Note the static drip rate and lack of response to rainfall events. B) An intermediate 'responsive' drip site. Note how large rainfall events result in a rapid increase in drip rate followed by a more gradual decrease. A diffuse flow component is also present, demonstrated by the asymptotic behaviour of the recession limb of the storm hydrographs. C) An example of an overly responsive drip site. The water responds to nearly all rain events within hours and is often undersaturated with respect to calcite.*

are known, the temperature that the calcite was deposited at can be calculated, because the water-calcite fractionation factor for oxygen isotopes is temperature dependent (Craig 1965). Although this undoubtedly does affect calcite $\delta^{18}\text{O}$, external climate exerts a much stronger influence on the drip water $\delta^{18}\text{O}$ than cave air temperature, therefore stalagmite $\delta^{18}\text{O}$ records are now generally interpreted as reflecting shifts in rainwater $\delta^{18}\text{O}$. Some of the most important climate records are derived from regions that experience extremely variable amounts or types of rainfall. Because rainwater derived from different sources, occurring at different times of year, or that is impacted by the 'amount effect' (Rozanski et al. 1993), can have vastly different $\delta^{18}\text{O}$ values, shifts in any of these parameters can be manifest in stalagmite records. Southeast Asia

experiences a strongly monsoonal climate, and thus stalagmites from the region record variations in monsoonal strength through time (Wang et al. 2001). Monsoonal rainfall is characterized by extremely low $\delta^{18}\text{O}$ values compared to non-monsoon rainfall, so changing proportions of monsoonal recharge compared to non-monsoonal rainfall results in fluctuations in groundwater recharge $\delta^{18}\text{O}$. Increased monsoonal strength causes lower $\delta^{18}\text{O}$ values of groundwater and stalagmite calcite. Combined with the excellent chronological control afforded by U-series techniques, this permits extraordinarily long records of monsoonal variability to be constructed for this region, which can then be compared with incoming solar radiation to achieve a better understating of the timing of major shifts in the Earth's climate on both

orbital and suborbital timescales (Cheng et al. 2009; Cheng et al. 2006; Henderson 2006).

Another good example of the applicability of stalagmites to reconstruct climate comes from the North Atlantic, where tropical cyclone (TC) rainfall is characterized by having anomalously low $\delta^{18}\text{O}$ values. Variability in TC activity is dependent on a vast number of natural and anthropogenic factors, so that definitively ascribing causality to global warming (or naturally occurring variability) is problematic. Recent statistical research attributes increasing TC intensity to increasing sea surface temperatures (SSTs) caused by global warming (Emanuel 2005; Hoyos et al. 2006; Webster et al. 2005), but uncertainty regarding data quality and the effects of natural decadal-scale climate oscillations have greatly complicated attribution (Landsea 2005; Pielke 2005). Furthermore, two recent climate model studies actually predict reductions in Atlantic TC frequency assuming predicted 21st Century global warming estimates (Knutson et al. 2008). No doubt exists that Atlantic TC activity has increased since 1995, but the 20th century record suggests that similarly elevated levels also existed from 1920-1969 (Goldenberg et al. 2001). Much of the contentiousness results from the brevity and questionable reliability of the available records. Accurate records of total Atlantic TC activity only extend back to the beginning of routine aircraft reconnaissance (1944-present), while somewhat reliable estimates extend back to the 1900s (Goldenberg et al. 2001), greatly reducing the statistical significance of correlations between Atlantic TC activity and climatic parameters. Rainfall in humid, low-latitude regions is characterised by elevated $\delta^{18}\text{O}$ values, typically ranging from 0 to -5‰ SMOW (Dansgaard 1964). Intense rainfall produced by TCs deviates from this trend, and is characterised by extremely negative $\delta^{18}\text{O}$ values (typically -8 to -14‰ SMOW) (Lawrence et al. 1998) and provides a substantial amount of groundwater recharge in areas affected by these storms. Simple calculations demonstrate that one TC alone can lower integrated annual groundwater $\delta^{18}\text{O}$ values by 1.5‰ in a localized area and by 0.5‰ over an area several hundreds of kilometres across (Fig 5). An even greater isotopic anomaly would result in a stalagmite if the stalagmite is analysed at subannual resolution. Because stalagmite $\delta^{18}\text{O}$ is correlated directly with unsaturated zone groundwater $\delta^{18}\text{O}$, stalagmites preserve a record of past variability in total rainfall amount derived from these seasonal, anomalously low $\delta^{18}\text{O}$ rainfall events. A recent

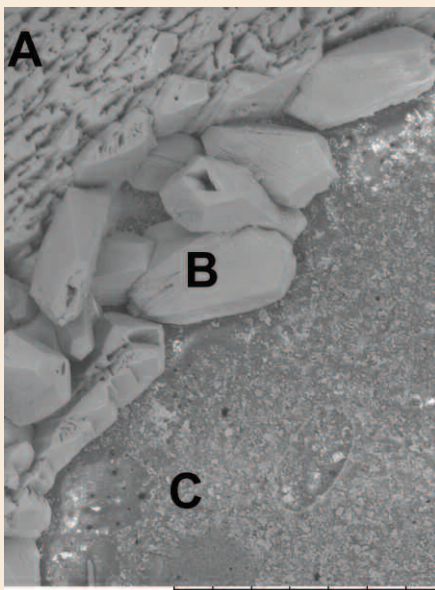


Figure 4. An SEM image of secondary calcite (A and B) deposited on an Iceland Spar (C) substrate placed underneath the drip CC-Bil (see figure 3). Well-developed columnar crystals are apparent (B). The calcite grew over the course of six months. All growth determining variables were measured simultaneously, so our understanding of calcite accumulation rates can be tested (Sherwin and Baldini, unpublished data). Scale bar division are 50 μ .

study from Belize used a very high-resolution $\delta^{18}\text{O}$ record from Actun Tunichil Muknal Cave in Belize to demonstrate that not only was the record a reflection of the El Niño-Southern Oscillation, but that brief isotopic excursions in the record coincided with hurricanes passing near the site (Frappier et al. 2007). The record only stretches back to 1977, but it clearly demonstrates the power and usefulness of this technique; the record consists of approximately one data point every month and detects every hurricane during the interval of calcite growth. Other research is trying to extend this record. For example, a \$1.6 million European Research Council-funded project (HURRICANE) based at the University of Durham (UK) aims to reconstruct TC activity throughout the Caribbean region using stalagmites. The principal goal of the HURRICANE Project is to reconstruct TC activity extending back at least 500 years, greatly lengthening existing records and helping to ascertain whether the current observed increases in TC activity are the result of anthropogenic global warming or part of a natural cycle.

TRACE ELEMENTS

Whereas oxygen isotope ratios are used to reconstruct changes in the seasonal moisture balance, temperature, and moisture source $\delta^{18}\text{O}$; trace element ratios of stalagmite calcite are used to reconstruct paleohydrology, paleorainfall, and potentially paleo-bioproductivity of soils. Despite much promise and research, the controls on the trace element geochemistry of stalagmites remain somewhat enigmatic. Stalagmite calcite Mg and Sr concentrations may record paleo-recharge conditions due to a combination of incongruent dissolution, selective leaching, and residence time mechanisms (Fairchild et al. 2000; Huang et al. 2001; McDonald et al. 2004; McMillan et al. 2005; Roberts et al. 1998; Treble et al. 2003), and these trace elements have historically been the focus of most of the research output. Studies suggest that for karst aquifers without dolomite, groundwater residence time in the aquifer is a critical control on Mg and Sr concentrations in cave drip waters (Fairchild et al. 2000). A multi-year drip water study of an Australian cave system suggested that drip water Mg/Ca and Sr/Ca at this site increase dramatically during droughts (McDonald et al. 2004). This increase may reflect more CO_2 degassing in an increased volume of void spaces in the aquifer,

subsequently leading to increased calcite precipitation above the stalagmite. Because of low partition coefficients in calcite of Mg and Sr, this process reduces drip water $[\text{Ca}^{2+}]$ but does not impact drip water $[\text{Mg}^{2+}]$ and $[\text{Sr}^{2+}]$, resulting in elevated ratios. This 'prior calcite precipitation' (PCP) mechanism has been demonstrated to be an important influence on Mg and Sr concentrations in drip water in other studies as well' (Baldini et al. 2006a; Fairchild et al. 2000; Tooth and Fairchild 2003), and our recent unpublished work establishes the link between hydrology, cave air PCO_2 , and PCP. Long-term monitoring studies of a wide range of drip types show that PCP amounts vary according to site hydrological characteristics (Baldini et al. 2006a; Tooth and Fairchild 2003), and research in the Edwards aquifer of central Texas also suggests that increased groundwater residence times and fluid-rock interactions result in elevated drip water Mg/Ca and Sr/Ca, and that these trace elements are therefore good indicators of reduced recharge at these sites (Musgrove and Banner 2004). However, research has predominantly focused on using the trace elements Mg and Sr as paleoclimate proxies, either independently or to corroborate $\delta^{18}\text{O}$ based paleoclimatic interpretations.

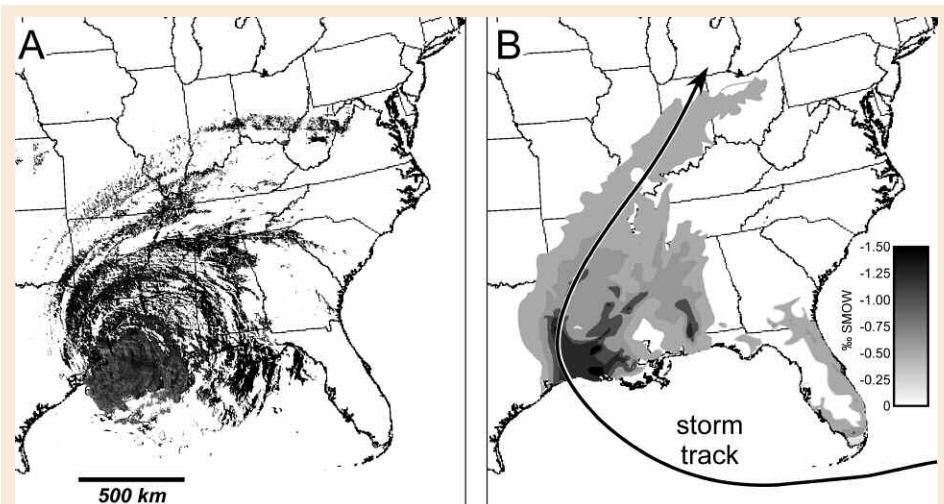


Figure 5. An example of the effects of a hurricane on regional isotope hydrology. (A) The geographic extent of Hurricane Rita at the moment of landfall September 24, 2005 (adapted from NOAA satellite data). The large size of tropical cyclones means that broad areas are affected by low $\delta^{18}\text{O}$ rainfall. (B) The estimated effect of Hurricane Rita on groundwater $\delta^{18}\text{O}$ values. The values shown are the per mil difference between hypothetical groundwater not affected by any hurricanes (calculated assuming all contributions to groundwater came from non-tropical rainfall) and hypothetical groundwater affected just by Hurricane Rita, which lowered integrated annual groundwater $\delta^{18}\text{O}$ by approximately 1.5 ‰ SMOW near the Texas/Louisiana border and by 0.5 ‰ over a much broader area. Stalagmite $\delta^{18}\text{O}$ values would be lowered by the same amount (Mickler et al. 2006). The values were calculated using measured Hurricane Rita rainfall amounts, mean annual rainfall for the area shown, and approximate $\delta^{18}\text{O}$ of hurricane (Lawrence et al. 1998) and non-hurricane rainfall (Dansgaard 1964).

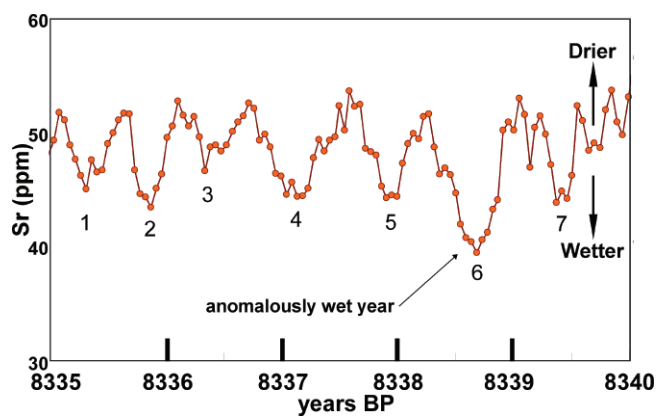


Figure 6. A very high-resolution strontium concentration transect through calcite that may have been deposited during the '8.2 ka' cold dry event from a stalagmite obtained from Crag Cave, Ireland (adapted from Baldini et al., 2002). Lower strontium values are representative of wetter conditions, and elevated values of drier conditions. Seven annual cycles are represented by the trace element data, which refines the uranium-series chronology used to define the x-axis that suggests just five years of growth. The lower growth rate suggested by the strontium data compared to the lower spatial resolution uranium series chronology is consistent with cold, dry conditions prevalent over this short time interval, which would have discouraged calcite deposition.

Microanalytical techniques have successfully resolved annual cycles in stalagmite trace element records (Baldini et al. 2002; Fairchild et al. 2001; Treble et al. 2003) at scales as low as 1 μm , providing a potentially powerful method of building annual-scale chronologies and reconstructing paleoseasonality (Fig 6). Borsato et al. (2007) used micro-X-ray fluorescence spectrometry ($\mu\text{-XRF}$) to study Pb, Zn, Fe, Sr, P, Br, Cu, and Y annual cycles at the micron-scale in a stalagmite from Grotta di Ernesto (northern Italy) and assessed the strength of the annual signal for these elements. A Secondary Ionization Mass Spectrometry (SIMS) of several different speleothems identified annual scale cycles in Mg, Sr, Ba, H, F, Na, and P (Fairchild et al. 2001), suggesting that annual trace element cycles are not uncommon. Of these, Fairchild et al. (2001) suggest that P may have the greatest potential as a paleoclimate proxy due to its role as a nutrient element. This was supported by a study of a modern Australian stalagmite that matched trace element cycles to the instrumental record and found that P, U, and Mg were the most reliable paleohydrological indicators at that site (Treble et al. 2003). However, the low soil retention capacity for P at that site may have increased the effectiveness of P as a paleohydrological proxy (Treble et al. 2003).

Despite the potential importance of P as a paleoclimate indicator in stalagmite calcite,

techniques such as SIMS, $\mu\text{-XRF}$, excimer laser ablation inductively coupled plasma mass spectrometry (ELA-ICPMS), and micromilling. However, it is also apparent that drip water sampling studies have not matched the weekly- to monthly- scale temporal resolution possible through microanalytical analyses of speleothem samples, largely because of the logistical difficulties involved in collecting samples daily or even weekly. Automated drip rate loggers have produced very high resolution records of cave drip discharge rates (Collister and Mathey 2008; Hu et al. 2008; McDonald and Drysdale 2007; Sondag et al. 2003) and conductivity (Genty and Deflandre 1998), but long-term drip water trace element monitoring studies have remained at the monthly-scale. Consequently, high-resolution drip water trace element data are critical missing information that would help clarify the links between stalagmite trace element concentrations, climate, aquifer-related processes (e.g., residence time), and crystallographic mechanisms (e.g., calcite growth rate).

CONCLUSION AND FUTURE CHALLENGES

Stalagmites are proving to be exceptionally valuable repositories of climate information for low- to mid-latitude terrestrial settings where few other long-term, high-resolution, and accurately dateable climate proxies are found.

interpretations have largely depended on inferential relationships with other proxies and calcite petrography; very little information on P concentrations or seasonality in cave drip waters exists. Drip water geochemical work has suggested that several elements, not just P, may be transported bound to colloidal material (Borsato et al. 2007). However, no long term results on the P variability of a cave drip exist. Clearly the interest in applying trace element cycles to reconstruct paleoclimate stems largely from the very high resolution achievable using modern microanalytical

Although the initial promise of deriving absolute paleotemperatures from stalagmite calcite is currently unachievable, stable isotope ratios of oxygen and trace element-to-calcium ratios are proving to be excellent indicators of shifts in moisture availability, bioproductivity, and the strength of isotopically anomalous precipitation events such as hurricanes and monsoons. The excellent chronological controls achievable by using $\text{U-}^{230}\text{Th}$ dating techniques, combined with high precision multi-collector ICP-MS analyses, (McDermott 2004) means that, although stalagmite climate proxies may not typically permit quantification of the amplitude of environment change, climatic shifts can be identified and the timing, duration, and structure of climatic events can be reconstructed. Oxygen isotope ratios combined with complementary trace element data provide a powerful tool for unraveling past climates. Ongoing research using stalagmites is reconstructing climate on a variety of timescales, from the high-profile research on the Asian Monsoon that has repercussions for global paleoclimate on millennial to orbital timescales (Cheng et al. 2009; Johnson et al. 2006), to new research such as the HURRICANE Project that is attempting to reconstruct more recent paleoclimate variability on event scales. Despite the success of stalagmites in reconstructing global paleoclimate, a number of challenges still exist. It may yet be possible to use stalagmite calcite as a paleothermometer, and new techniques using clumped isotopes (Meckler et al. 2009) and fluid inclusions (Vonhof et al. 2006) are promising. Cave monitoring studies are critical for understanding how the climate signal is conveyed through the aquifer to the stalagmite calcite. The processes controlling the incorporation of many trace elements in stalagmite calcite are still poorly understood and these records are best interpreted after considerable monitoring and site characterization. It is becoming clear that every cave has a unique set of controls that modulate how the climate signal is recorded in stalagmite calcite, and a set protocol on how to best delineate these controls has yet to be established. Despite these challenges, stalagmites are providing key climate proxy records that are greatly improving our understanding of past climate fluctuations, which has important consequences for predicting future change.

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