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Late Holocene Paleoenvironmental Reconstruction in Barbados

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LATE HOLOCENE PALEOENVIRONMENTAL RECONSTRUCTION IN BARBADOS

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By
Gilman Reno Ouellette

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LATE HOLOCENE PALEOENVIRONMENTAL RECONSTRUCTION IN BARBADOS

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LATE HOLOCENE PALEOENVIRONMENTAL RECONSTRUCTION IN BARBADOS

Gilman Reno Ouellette August 2013 70 Pages

Directed by: Jason Polk, John Andersland, Jennifer Cole, and Joshua Durkee

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Barbados is the easternmost island in the Caribbean region, and is uniquely situated between the Atlantic Ocean and Caribbean Sea. Being an isolated island with a karstified aquifer providing the majority of the nation's water resources, Barbados has found itself in water scarce situations in recent years. In order to better understand natural shifts in groundwater recharge (which is determined by shifts in precipitation), longer records of precipitation are needed than are available from modern measurements. This study presents a paleoclimate reconstruction for the late Holocene on Barbados using stable and radiogenic isotope ratios in speleothem lamina as proxies. In addition, it introduces the use of novel mineralogical analyses using Raman spectroscopy and large chamber-scanning electron microscopy to supplement the oxygen isotope record. For the past 1,500 years, the speleothem record indicates average δ^{18}O values near -4.1 $^{0}/_{00,}$ maximum δ^{18}O values around -3.2 $^{0}/_{00}$ that coincide with the Little Ice Age climate event, while minimum δ^{18}O values around -5.3 $^{0}/_{00}$ occur during the Medieval Climate Anomaly. Raman spectral analysis shows a recent period of increased Mg substitution, which potentially represents anthropogenic changes to the island's epikarst aquifer caused by European settlement and sugar cane cultivation on Barbados. Electron imaging revealed chemically distinct layers of detritus within the stalagmite sample, facilitating precise sampling for U-series dating while also providing some information on the nature of weathering on the island. Additionally, time series analysis of the isotope record indicates multidecadal and multicentennial periodicities that conform well to that of the Atlantic Multidecadal Oscillation exerting influence on rainfall variability at the decadal scale, and the Intertropical Convergance Zone modulating rainfall at the multicentennial scale. Collectively, these data provide a climate reconstruction for the island of Barbados that is useful for better understanding change in cyclic precipitation patterns, as well as non-destructive methods for speleothem analysis that complement the isotopic study, while allowing sample preservation.

Chapter 1: Introduction

As an isolated island in the Caribbean, water shortages are a very serious problem for the people who live in Barbados. Unlike continental nations, if a small island's limited surface and groundwater resources are depleted, there are few alternative sources and little infrastructure in place for easily importing water from other regions (Cashman et al. 2010). Throughout the spring of 2010, the island of Barbados experienced a severe water shortage due to persistent drought conditions, resulting in the implementation of an emergency drought management plan, and eventually a complete lack of potable water being available in several areas around Barbados over the course of several days (Farrell et al. 2011). The impacts of drought induced water shortages are even more pronounced because of the relatively small area of the island of Barbados, and the island's karst geology, which allows for rapid drainage, soil compaction from poor agricultural practices, rapid infiltration of pollutants, and impacts from land use changes, further exacerbating drought. Such drought events can be devastating, as water is a precious commodity even during favorable conditions (Cashman et al. 2010).

Precipitation and water resource issues are not limited to Barbados, as many islands in the Caribbean region face similar problems (Cashman et al. 2010). Though the islands in the Caribbean Sea are sensitive to significant shifts in precipitation patterns, there are still questions of how and to what extent different climatic features and/or teleconnections, which are large-scale atmospheric phenomena, influenced precipitation throughout the last few thousand years (known as the Late Holocene) leading up to the current climatic conditions (Mickler 2004). Barbados lies at the eastern edge of the Caribbean region; however, it is actually within the Atlantic Ocean (Fig. 1). Barbados' unique situation in between the Atlantic Ocean and the Caribbean Sea makes it a unique place for recording climate variability, as the island's climate is likely affected by both higher latitude and tropical climate mechanisms (Banner et al. 1996; Mangini et al. 2007). A better understanding of global climate change, as well as local climate variability, is essential in assessing potential climatic impacts on water resources in Barbados (Banner et al. 1996). To fully understand how changes in climate could affect Barbados, a longer-term record is necessary than contemporary meteorological records provide (Mickler et al. 2004). Unfortunately, the paleoclimate data that exist for the island of Barbados are few and far between (Banner et al. 1996; Mickler 2004; Mickler et al. 2004; Mangini et al. 2007). While there has been significant research into the geochemical and hydrogeological properties of the Barbadian aquifer, the robust climate data needed to assess the potential future of natural water resources for the country, and the region as a whole in the Caribbean, are sorely lacking (Cashman et al. 2010).

Research Overview

In order to address pressing issues of water resource management, a grasp of the nature and magnitude of past precipitation variability on Barbados is needed. Being an isolated carbonate island, the sole natural source of freshwater is from direct precipitation infiltration (Machel 1999). Thus, precipitation and the health of the Barbadian aquifer are intimately connected, and understanding changes in precipitation intensity over time also provides an understanding of how much water has been available to the hydrologic system on Barbados.

With the pressing issue of water management in mind, this study was conducted to answer three questions: (1) what are the local and regional fluctuations in precipitation, and thus potential water resources in Barbados throughout the late Holocene?; (2) can supplementary proxy information be extracted through non-destructive analysis employing Raman Spectroscopy (RS) and Large Chamber Scanning Electron Microscopy (LC-SEM)?; (3) are there distinguishable relationships between fluctuations in Barbadian precipitation and particular regional climate forcing mechanisms?

To answer these questions, this study uses a variety of well-established and novel analytical techniques for sampling of speleothems obtained from the island of Barbados. These speleothems are calcite formations that have precipitated in layers, or lamina, from carbonate rich dripwaters. Using oxygen isotope values of speleothem layers provides a snapshot of the oxygen isotope ratios in the dripwater from which the speleothem calcite was formed. These are representative of the isotopic values of the precipitation that percolated and became the dripwater. Over interannual to centennial periods, the major drivers of changes in rainfall patterns are usually atmospheric-oceanic teleconnections, which are periodic or quasi-periodic shifts in atmospheric conditions that result from changes in solar radiation, ocean conditions (e.g. ocean current variations), and global circulation patterns. Since Barbados is within the potential area of influence of the Atlantic Ocean, Pacific Ocean, Caribbean Sea, and the Gulf of Mexico, teleconnections that are driven by changes in these bodies of water are likely culprits for drivers of precipitation changes on the island (Fig. 1).

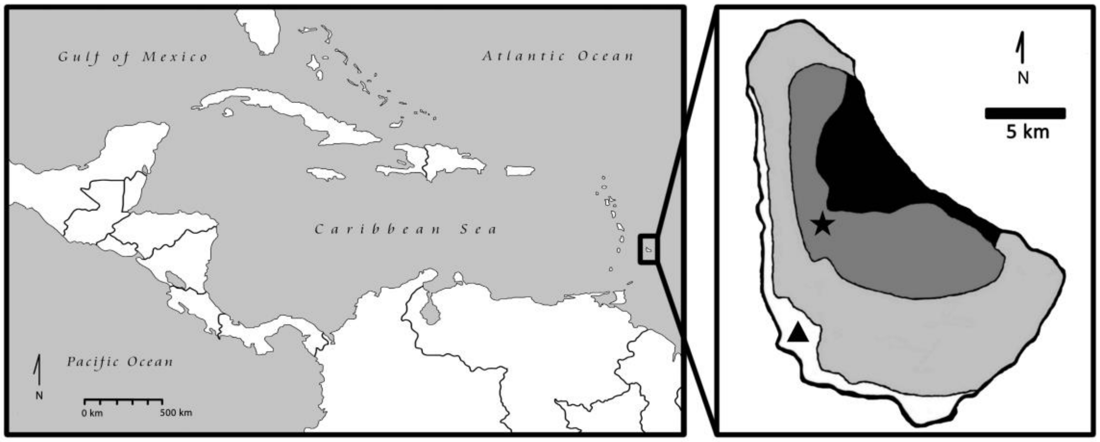


Figure 1: Map of the Caribbean region with major bodies of water labeled. Map of Barbados is inset, with the three coral terraces shown in grey scale from highest elevation and oldest age (dark grey) to closest to sea level and youngest (very light grey). The area in black is the Scotland district, comprised of siliciclastic materials. The capitol of Barbados, Bridgetown, is marked with a black triangle, the location of Harrison's Cave is marked with a black star.

While oxygen isotope records have been used to understand precipitation variation ad nauseum in studies that use samples such as cave formations, coral skeletons, or ice cores, and while it is a tried and true method, developing another method of assessing hydrologic change from a single speleothem sample, along with oxygen isotope analysis, would enable improved multiproxy reconstructions of paleohydrology from a single speleothem sample (Mann et al. 1999; Alley 2000; DeLong 2009). Identifying and developing an independent, quantitative proxy source within a speleothem sample, as well as identifying detrital and inclusion materials that lead to errors in chemical reconstructions, is instrumental in continuing to develop the use of speleothems as high-quality paleoclimate proxy data sources (Mann et al. 1999; Alley 2000; DeLong 2009).

Significance and Justification

The production of a multi-proxy Holocene paleoenvironmental reconstruction for Barbados, and frequency domain spectral analysis of the completed reconstruction provides a strong basis from which precipitation, and thus groundwater amount, patterns in the eastern Caribbean can be correlated to particular oceanic/atmospheric teleconnections that influence the region. As well as contributing to alleviate the relative lack of tropical paleoenvironmental records, this study also provides a unique opportunity to improve the quality of speleothem climate reconstructions through advancing minimally destructive methods of analyzing speleothem mineral growth patterns and their relationship with oxygen isotope ratios.

Study Area

Barbados is the easternmost island in the Lesser Antilles arc (Fig. 1). The island of Barbados covers an area of approximately 430 square kilometers, and is home to around 285,000 citizens as of 2009 (Donovan and Harper 2005; Speed 2013). One of the main economic contributors to Barbados' tourism economy is a government-owned show cave, Harrison's Cave, located within the center of the island. The cave was discovered previous to 1795, however, it was not widely explored until Tony Morrison and Ole Sorenson rediscovered, and subsequently began developing the cave for tours in 1974 (Hobbs 1994). Harrisons cave is comprised of at least 2.3 km of passage (Hobbs 1994). Stalagmite HC-1W was obtained from the Great Hall in Harrison's Cave. HC-1W was collected from the south side of the Great Hall, marked with a red star on the map adapted from Hobbs (1994) (Fig. 2).

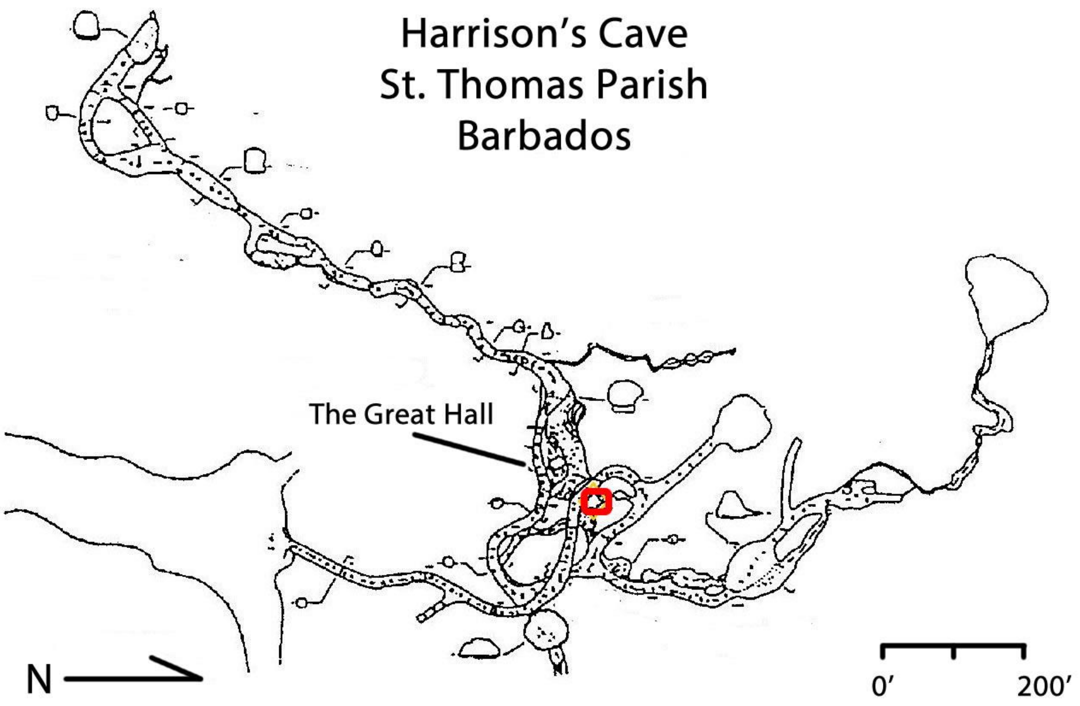


Figure 2: Map of Harrison's Cave, Barbados adapted from Hobbs (1994). Harrison's cave is located in the highest and oldest terrace of the coral rock formation on Barbados. Stalagmite sample HC-1W was obtained from eastern side of the tourist trail in the Great Hall. This site is indicated by the red rectangle.

Geology

The island of Barbados is part of an accretionary ridge, which has a base formed from sediment accumulated and uplifted through the subduction of the South American Plate under the Caribbean plate (Donovan and Harper 2005; Speed 2013). The majority of exposed rock on the island is Pleistocene coral limestones of the coral rock formation; the remaining exposed rock is comprised of tertiary marine sedimentary species of the oceanic formation (Machel 1999; Donovan and Harper 2005; Speed 2013). The extensive limestone deposits have facilitated the formation of significant karst aquifer, along with characteristic karst features around the island, including several other large caves and recent sinkhole collapses, as well as unique gully features (Machel 1999; Speed 2013).

Climate and Water Resources

Barbados experiences a tropical monsoonal climate, which results in the island's wet and dry seasons. The island receives an average of 1.4 meters of rainfall annually, with most of it falling during the island's wet season (June to December) (Schomburgk 2001). The seasonality in Barbados precipitation regime is dominantly the result of the migration of the Intertropical Convergence Zone (ITCZ) throughout the year; previous research suggests that annual precipitation variability is affected by the phase of the El Niño-Southern Oscillation (Banner and Jones 2004). As an island, the only natural inputs of freshwater to the country are through rainwater. Groundwater refreshed by meteoric waters accounts for approximately 90% of the natural water resources available on the island of Barbados, with surface reservoirs and streams accounting for the remaining 10% (Schomburgk 2001; Cashman et al. 2010; Speed 2013).

Discrete groundwater withdrawals have yet to be thoroughly quantified on Barbados. This makes calculations of overall groundwater flux unreliable. While human use of ground water resources dramatically affects how much groundwater is within the island's karst aquifer at any given time, the total groundwater that can possibly be used is modulated by precipitation (Jones and Banner 2003). Recent drought in 2010 resulted in problematic issues of water resource availability. With a growing population, and expanding tourism and industry, the natural groundwater resources of Barbados already are beginning to show signs of economic and environmental strain (Cashman et al. 2010).

Karst Geology

The island of Barbados is dominated by karst landforms. Karst landscapes are defined by the distinctive hydrologic and geomorphic characteristics that arise from the unique combination of highly soluble rock with sufficient secondary porosity (Ford and Williams 1989). The range of landforms and hydrologic patterns that arise when portions of bedrock dissolve is wide; however, one of the most common features of such landscapes is the ubiquitous presence of subterranean conduits for water and material transport, including humanly traversable cave systems (Palmer 2007). These subterranean systems facilitate the transportation not only of water, but dissolved chemicals as well (Ford and Williams 1989). Deposits can be formed from these chemical sediments when they can no longer be held in solution with the water they are being transported in (e.g. calcite commonly deposits due to CO_2 degassing of drip-water exposed to the cave atmosphere). Under favorable circumstances, these deposits can serve as records of paleoenvironmental information (White 2007).

Speleothem Proxies

Speleothems have become the dominant karst-borne source of paleoclimate information (White 2007). Speleothems form through the buildup of many fine layers (or lamina) of calcite as it precipitates out of cave dripwater (Jennings 1971). Using speleothems to understand paleoclimatic conditions has amassed a large following since the proliferation of labs capable of advanced mass spectrometry (Gascoyne 1992; White 2007; Lachniet 2009). The benefit of advanced mass spectrometry is in the relative ease of determining the isotopic components of very small material samples, which is necessary when dealing with very fine layers of material deposited in cave formations (Gascoyne 1992; Li 2006). Generally, the best specimens are “broom handle” stalagmites that have formed more or less cylindrical formations (White 2007; Frappier 2009).

The basic technique for using speleothems as paleoclimate proxies is fairly uniform for all such studies; a speleothem is selected and sampled (either by coring or it is completely removed). The sampled speleothem is generally microsampled at each lamina, or to as fine a resolution as possible (Gascoyne 1992; White 2007). Depending on the geochemical context, individual lamina can resolve anywhere from hundreds of years to sub-annual variations in cave drip-water, and hence past environmental conditions (Xiaoyan 2006). The actual methods for deriving paleoenvironmental data from speleothem laminae vary; however, analyzing stable isotope ratios is among the most effective methods (Li 1998). Oxygen and hydrogen ratios are commonly used in paleoenvironmental studies, due to the favorable abundances of the light and heavy isotope of each ($^{18}O/^{16}O$ and $^{2}H/^{1}H$), their ready inclusion within speleothems, and their strong modulation by environmental conditions (Gascoyne 1992; White 2007; Lachniet 2009). When used in this context, the ratios of heavier isotope to lighter isotope are measured, rather than raw numbers of isotopes. These measurements are then used to calculate a difference from a standard (often the Vienna Standard Mean Ocean Water (VSMOW), or the Vienna Peedee Belemnite (VPDB) standards) (White 2007). The results of stable isotope ratio calculations are reported as “δ” values (Fairchild 2001; Sharp 2007; Lachniet 2009). The δ value calculation for O is shown as an example (Eq.1).

$$\delta^{18}O = \left(\frac{\left(\frac{^{18}O}{^{16}O}\right) sample}{\left(\frac{^{18}O}{^{16}O}\right) standard} - 1 \right) * 1000\ {}^{o}/_{oo}$$

Equation 1: Formula for the calculation of $\delta^{18}O$ values.

The relationship of sampled stable isotope ratios of oxygen and hydrogen to the standard ratios is related to environmental effects that shift the ratios toward a more positive or negative value. These effects influence the initial isotopic signature of water as it falls as precipitation, and include the continental effect, which is a systematic depletion of heavier isotopes as precipitation moves over land; the altitudinal effect, which is the systematic depletion of heavier isotopes in precipitation at higher altitudes; the temperature effect, which is a systematic depletion of heavy isotopes with decreasing temperature; and the amount effect, which is a systematic depletion of heavy isotopes with increasing precipitation amount (Daansgard 1964; Dorale et al. 1998; Lachniet 2009; Fensterer et al. 2012). After precipitation makes it to the ground, isotopic signals from these effects can be further altered through mechanisms within the soil and ground water system, and changes in the cave environment (Lachniet 2009).

In order to link δ values to actual periods in time, decay chains of radiogenic isotopes are often used to absolutely date laminae within a speleothem. The most common chain used to date speleothems is the ^{230}Th/^{234}U (Uranium) series (Ford and Williams 1989). The U-series is commonly used to date speleothems because the initial value of the daughter isotope thorium can be assumed to be approximately zero thanks to the water solubility of the uranyl ion (which is found in some quantity in most natural waters) and the virtual insolubility of thorium in water (Schwarcz 1989; Edwards et al. 2003). Like most radiogenic dating methods, U-series dates are obtained through the measurement of the ratio of the parent isotope to its daughter isotope (Schwarcz 1989; Polyak et al. 1998; Edwards et al. 2003; White 2007). Rather than calculate a date based off of the accumulation of the daughter versus the parent, U-series dates are obtained by calculating the ratio of parent of isotopic decay chains and comparing it to the time frame to reach secular equilibrium (Schwarcz 1989; Polyak et al. 1998; Edwards et al. 2003). Thanks to improvements in mass spectrometry technology, the use and accuracy of speleothems in climate reconstruction is evolving (Edwards et al. 2003). Continued improvement and geographic expansion of speleothem climate reconstructions could prove to be at least as valuable as deep-sea sediment and glacial ice cores (Mann et al. 1999; Alley 2000; White 2007).

In order to produce a precise paleoenvironmental reconstruction and ensure that speleothem proxies are recording isotopic signals in a uniform manner, the nature of speleothem deposition must be determined (Hendy 1971). When speleothem laminae are deposited under equilibrium conditions, they precisely record isotopic signals in a uniform manner; however, if laminae are deposited under non-equilibrium conditions, there is the potential for error in the proxy from other fractionation mechanisms (Hendy 1971). In order to ensure speleothem proxies were deposited under equilibrium conditions, several isotopic samples can be compared along a single speleothem lamina, with uniform isotopic signatures verifying equilibrium deposition, and dissimilar signatures identifying non-equilibrium deposition (Hendy 1971). This method is known as the “Hendy Test,” and while theoretically useful, the applied utility of the method has been criticized (Dorale and Liu 2009). Currently employed methods of ensuring equilibrium deposition include independent replication of speleothem isotope values, as well as observing a lack of correlation between oxygen and carbon isotope ratios within speleothem laminae (Mickler et al. 2004; Dorale and Ziu 2009; Polk et al. 2012). If multiple coeval speleothem proxies are sampled, and the isotopic signatures of their corresponding lamina share isotopic signatures, equilibrium deposition is verified (Dorale and Ziu 2009).

Determining whether speleothem laminae were deposited in equilibrium is necessary to verify the precision of isotopic reconstructions produced from them. One must be careful however, to not confuse precision with accuracy. While verifying equilibrium deposition is necessary to ensure isotopic signatures of speleothem lamina are uniformly recorded, it says nothing about how the actual environmental signal(s) of interest change before being recorded in the proxy. In order to ensure accuracy in reconstructions based on speleothem lamina, a thorough understanding of how the source of dripwater changes throughout the environmental system and screening for diagenesis in samples is ideal (Mickler et al. 2004; Polk et al. 2012). Layers of speleothem calcite do not necessarily retain the original isotopic signature of precipitation, and an understanding of how local hydrology as well as speleothem calcite changes from initial speleothem formation to isotopic analysis is necessary to provide confidence in the results of isotopic analysis (Mickler 2004; Mickler et al. 2004; Dorale 2009; Polk et al. 2012).

Other proxies

Thanks to the unique environment in the tropics, contemporary shallow marine environments facilitate assemblages of coral colonies. Coral colonies, which grow uniquely in the tropics, have become a popular proxy for reconstructing paleo-ocean and paleoclimate conditions (Fairbanks & Matthews 1978; Cole & Fairbanks 1990; Gagan et al. 2000). While no coral proxies are used in this study, the limestone bedrock of Barbados is comprised of former coral colonies. Additionally, what paleoclimate information is available for the eastern Caribbean is dominantly derived from coral proxies (Broecker et al. 1968; Matthews 1968; Fairbanks & Matthews 1978). Coral based reconstructions from the Caribbean, and particularly from the coral communities in and around the island of Barbados have been instrumental in isolating long-term Milankovitch orbital cycles through isotopic shifts recorded in aragonitic growth layers in coral skeletons, and in identifying shifts in sea level though subaerial exposure or subaqueous drowning of coral colonies due to rapid sea level changes (Broecker et al. 1968; Matthews 1968; Fairbanks & Matthews 1978). While invaluable tools in understanding past climate, coral proxies have hitherto been unable to resolve quasi-annual scale changes in precipitation on Barbados, which this study aims to elucidate; while not useful in this particular project, the utility of coral proxies in past and future studies of tropical paleoclimate and paleoceanography cannot be overstated.

Previous Stalagmite and Groundwater Studies on Barbados

Paleoclimate reconstructions are still minimal within the tropical latitudes; however; relevant research has been carried out in these regions. There are limited research efforts relevant to speleothem climate reconstructions from the island of Barbados (Mickler 2004; Mickler et al. 2004; Mangini et al. 2007). The most prominent was a speleothem climate reconstruction for Barbados also from Harrison’s Cave (Mangini et al. 2007). Unfortunately, this reconstruction was based on a single ancient stalagmite sample; this stalagmite record does not contain the last several thousand years before present, which this study seeks to analyze (Mangini et al. 2007). Another set of studies focused on the geochemical and isotopic characteristics of the Barbadian Aquifer (Banner et al. 1996; Jones et al. 1998; Mickler 2004; Mickler et al. 2004). Mickler (2004) analyzed samples for stable isotopes of O and H, as well as for radiogenic isotopes to build growth chronologies. While this study successfully produced a reconstruction of stable isotope shifts in several samples, isotopic values were not uses to interpret paleoenvironmental conditions. Banner et al. (1996) focused on examining the evolution of the Barbadian aquifer through strontium isotope signatures in several speleothem samples, while Jones et al. (1998) constrained the timing and amount of precipitation, which actually recharged the aquifer. The results of these previous research endeavors are of direct relevance to this research, and the most useful information gained from these works includes the determination that the "amount effect" dominates the O isotope signatures in Barbadian precipitation, and thus the predisposition of Barbadian stalagmite records to capture the precipitation amount signal through hydrologic recharge that feeds cave dripwaters (Dansgaard 1964; Banner et al. 1996; Jones et al. 1998; Jones and Banner 2003; Mickler 2004; Mickler et al. 2004; Mangini et al. 2007; Lachniet et al. 2009). The dominance of the amount effect on oxygen isotope signatures in tropical precipitation generally, and on Barbados specifically is the underlying basis from which meaningful precipitation reconstructions could be made, and so ensuring that the amount effect is indeed responsible for the shifts in oxygen isotope ratios in precipitation and ultimately cave drip water is essential (Lachniet 2009; Jones and Banner 2003; Mangini et al. 2007; Risi et al. 2008; Polk et al. 2012)What this study provides beyond previous research is a high-resolution record of precipitation, an attribution of the teleconnection drivers of Barbadian precipitation patterns, and a novel implementation of Raman spectroscopy and large chamber scanning electron microscopy to mineralogic examination of speleothem proxies.

Atmospheric/Oceanic Teleconnections

Simply knowing how hydrologic conditions on Barbados have changed throughout the Holocene is a worthy scientific endeavor; however, understanding what mechanisms produced those changes provides insight into what conditions can be expected as the mechanisms that drive them change. The climate of the Caribbean is affected by several oceanic-atmospheric teleconnections, which act to modulate precipitation in the region (Enfield and Eric 1999, Alessandra et al. 2001). Teleconnections are interrelated phases of atmospheric and oceanic conditions, which shift phase at quasi-regular intervals (Barry and Chorley 2010). Understanding the interactions of teleconnections and climate can be accomplished through a variety of mathematical methods focused around extracting cyclical patterns from climate data, and then statistically linking it with records of teleconnection phase (Ghil et al. 2001; Wang 2007; Delong 2009; Barry and Chorley 2010).

Since Barbados is located between the Caribbean and Atlantic regions, it is intuitive that the island's climate would be affected by teleconnection end-members from each region (Barry and Chorley 2010). Due to the potential complexity of teleconnection influences on Barbados precipitation, teleconnections acting upon both the Caribbean and the Atlantic regions could potentially contribute significantly to Barbados' climate, and so this study compares its results with previously reconstructed teleconnections that are demonstrated to act in the Caribbean and Atlantic regions. The major teleconnections that are geographically likely to affect precipitation patterns on Barbados include the El Nino-Southern Oscillation (ENSO), the North Atlantic Oscillation (NAO), the Atlantic Multidecadal Oscillation (AMO), and shifts in the Intertropical Convergence Zone (ITCZ) (Enfield and Eric 1999; Barry and Chorley 2010; Hidore et al. 2010).

The ENSO is a quasi-periodic bi-decadal teleconnection, which is the result of the interaction of zonal shifts in the pacific warm pool and its effects on walker circulation over the pacific, resulting in alternating periods of warm wet periods (El Nino-positive phase) and cool dry periods (La Nina-negative phase) (Enfield and Eric 1999; Wang 2007; Hidore et al. 2010). The ENSO has been correlated to annual precipitation variation on the island of Barbados in the literature, and there is little doubt that this teleconnection affects annual scale precipitation variability on Barbados (Jones et al. 1996; Jones and Banner 2003) The NAO is a quasi-periodic teleconnection, which results from the balance of the Azores high and the Icelandic low. This teleconnection often changes phase at random intervals (Cook et al. 2002). This teleconnection modulates the mid-latitude jet, and affects temperature and weather patterns in the North-Atlantic (Cook et al. 2002). The AMO is a quasi-periodic teleconnection potentially driven by shifts in sea surface temperatures in the North-Atlantic. The AMO has a cycle ~50-80 years long, its warm phase causes drought in central and northern- North America, and enhances rainfall in southeastern North America (Mann et al. 2009; Enfield and Cid-Serrano 2010). The ITCZ is the band of convective activity that circles the globe roughly at the thermal equator. This zonal band fluctuates interanually with the migration of the thermal equator due to the Earth’s axial parallelism, as well as to changes in solar activity; however there is also evidence that the ITCZ migrates over longer periods of time as the astrophysical conditions of solar activity and the earths orbital characteristics shift through various Milankovitch cycles (Haug et al. 2001; Asmerom et al. 2007; Fairbanks & Matthews 1978). The ITCZ is responsible for many tropical regions bi-seasonality, and long term changes in the ITCZ can result in extensive precipitation or drought depending on an areas location in relationship to the ITCZ (Haug et al. 2001).

Time-series Analysis

It is possible that several teleconnections are jointly responsible for affecting precipitation patterns on Barbados. Discerning the teleconnections that are most influential on the Barbadian climate end member is not straightforward. In order to match paleoprecipitation data with teleconnection cyclicity, it is useful to deconvolve the precipitation time signal into a frequency resolved signal. Transforming the time series into a frequency, or frequency resolved time series, allows for periodic oscillations, such as teleconnection phase to be easily and robustly identified (Thompson 1990; Ghil et al. 2001; Asmerom et al. 2007; DeLong et al. 2009). Entire fields of study have emerged around the mathematical methods of signal processing and time series analysis, with perhaps the most frequently used time series analysis method being Fourier frequency analysis; this method transforms a function of time as a function of frequency via the component sinusoidal functions within the time series data (Priestly, 1991; Mudelsee 2001), and while Fourier analysis is quite popular among many sciences it suffers from shortcomings that other methods of spectral analysis overcome (Mudelsee 2001; Ghil et al. 2002).

Understanding which teleconnections have modulated the precipitation regime of Barbados provides additional data to bolster the tropical paleoclimate record over the Late Holocene. Additionally, it provides valuable insight into the mechanisms modulating precipitation amount, and is useful information for climate forecasters and water resource managers.

Speleothem Mineralogy

Due to the unique features of carbonate minerals, there exists the possibility to exploit the unique features of speleothem proxies to improve the scientific understanding of lamina-climate relationships, as well as potentially producing a synergistic proxy methodology from the mineralogical character of speleothem laminae.

Speleothems have been characterized by their mineralogy for decades; however, there exists a distinct gap between the identification and record of cave minerals, and a robust understanding of speleothem ontogeny (White 2012). Over 250 cave minerals are known to exist; however; just three minerals make up the vast majority of speleothems (Hill and Forti 1997). The majority of speleothems are comprised of calcite, aragonite, or gypsum (Hill and Forti 1997; Self and Hill 2003). In moist tropical environments, the majority of speleothems are comprised only of calcite or aragonite, or both (Hill and Forti 1997). The significant homogeneity of speleothem mineral constituents does not necessarily result in mineralogical uniformity between discrete lamina. Individual speleothems may host unique mineralogical differences between lamina, which formed under different environmental conditions (Railsback et al. 1994; Self and Hill 2003; Hill and Forti 1997).

While research into the complexities of environmental conditions and changes in speleothem mineralogy are relatively underdeveloped, there seems to be significant potential to exploit variations in mineralogical properties of speleothem lamina as a paleoenvironmental proxy by elucidating the relationship between environmental conditions and mineralogical characteristics of speleothems (Railsback et al. 1994; Brooks et al. 1995; White 2012). In addition to the application of mineralogical analysis as an independent proxy, there is robust evidence supporting its utility in identifying diagenetic processes that can cause significant issues for isotopic analysis through post-depositional alteration of speleothem isotope content (Railsback et al. 1997; Railsback et al. 2002; Frisia et al. 2005; Onac & Forti 2011). Improving the understanding of inter-speleothem mineralogical change provides not only a potential independent climate proxy, but a means to reduce error in radiogenic dating, and stable isotope reconstructions from speleothems.

Nondestructive Mineralogical Analysis Tools

Two methods used in mineralogy in general, and that are used to some extent on cave formations, are Raman Spectroscopy (RS) and Scanning Electron Microscopy (SEM) (White 2012). RS employs focused monochromatic light (in most cases laser radiation) to interact with the molecules of a material (White 2006). Most of the incident light will be Rayleigh scattering, however, in molecules that exhibit shifts in polarization potential with regards to vibrational mode some of the photons will inelastically interact with the molecule (White 2006; White 2012). This inelastic interaction results in an excitation of the molecule from its ground state to a virtual energy state, and upon the molecules relaxation, the emission of photons of a different wavelength than the initial monochromatic light source (White 2006). The shifts in wavelength caused by these interactions are a function of the vibrational frequencies of the chemical bonds in the sample, and they produce spectra unique to the mineral under observation (White 2006). These unique spectra (known as a Raman spectrum) can be used to characterize the material being observed, and provides information on the presence and arrangement of chemical bonds within the analyzed material (White 2006). This makes RS especially useful for mineral identification and analysis due to the unique ability of RS to characterize molecular characteristics within a sampled material (Urmos 1991; White 2006).

SEM employs a focused electron beams to interact with the surface of a sample. With different detectors, different properties of the material being analyzed can be discerned (Self and Hill 2003). Two common capabilities of SEM include secondary electron imaging (SEI), and backscatter electron imaging (BSE). SEI produces very high magnification (> 100,000x magnification) topographic information about a sample (Railsback et al. 1994). BSE acquires information on the bulk chemical constitution of a sample through the detection of electrons elastically scattered by the atoms in a sample; the intensity of this scattering is directly related to the atomic number of the materials constituent atoms (Railsback et al. 1994, Self and Hill 2003).

Both LC-SEM and RS provide potential bases for non-destructive mineralogical analysis of speleothem proxy samples, and exploring the capabilities and realistic utility of these technologies in tandem provides a unique system to improve the accuracy and precision of paleoenvironmental reconstructions based on speleothem proxies.

Chapter 2: Non-destructive mineralogical analysis; assessing Large Chamber Scanning Electron Microscopy and Raman spectroscopy for speleothem material analysis and independent proxy verification

Introduction

Speleothems are diverse mineral assemblages that often contain chemical and biologic proxies of paleoenvironmental conditions. Speleothems, primarily stalagmites, often contain sedimentary laminae that resolve inter-annual to semi-annual changes in the local hydrological system (Railsback et al. 1994; White 2007; White 2012). As a result, studies of lamina characteristics, such as layer width, isotopic composition, organic luminescence, and mineral composition are all used to elucidate past environmental conditions (Brook et al. 1995; Railsback et al. 1997; Railsback et al. 2002; Ford and Williams 2007). Various analytical techniques are used to identify cave-borne minerals, and approximately 250 unique minerals have been identified as occurring naturally in the cave environment (Hill and Forti 1997; Hill 1999). While there has been much effort put into identifying the occurrence and distribution of cave minerals, there is a shortage of concerted studies regarding quantifiable mineralogical change along sedimentary mineral structures like stalagmite growth axes, and the existing data are primarily qualitative in nature (Onac and Forti 2011; White 2012). A thorough understanding of fine scale mineralogical change along the growth axis of a stalagmite would allow for much greater confidence in paleoenvironmental reconstructions derived from geochemical or detrital proxies (Railsback et al. 2002). Such mineralogical information could potentially provide additional information about past environmental conditions to corroborate, or enhance, other types of proxy data, such as isotopes of oxygen, within the calcite (Mickler et al. 2004).

Background

This study seeks to provide additional complimentary information to a $\delta^{18}O$ record derived from a speleothem from Harrison's Cave, Barbados. The record from this formation spans ~1,500 years; constraining its error and perhaps an independent mineralogical proxy to use along with the oxygen isotope record are the goals non-destructive analyses using LC-SEM and RS. Speleothem mineralogy is often studied as an application to paleoenvironmental reconstructions derived from speleothems; this is due to the well quantified effects environmental variables such as temperature, drip rate, drip amount, chemical, and isotopic changes in drip water affect the growth rate and chemical nature of speleothem calcite (Dreybolt 1988; Railsback 2002; Dreybolt 2008; Lachniet 2009). Understanding the mineralogical changes associated with these variables is of the utmost importance when using speleothem samples as proxy records, as changes in calcite growth rate throughout a sample will often lead to significant errors in age models that assume a constant growth rate, as well as exposing recrystallization and diagenesis in speleothem materials that can suggest base assumptions of isotopic analysis are violated (Asmerom et al. 2007; Dreybolt 2008).

While understanding mineralogical changes in growth layers is important in assuring the accuracy of speleothem proxies, contemporary mineralogical and petrological analysis of speleothems tends to rely heavily upon traditional optical mineralogical techniques including polarized light microscopy of thin sections, as well as X-ray diffraction (XRD) methods (Brook et al. 1995; Railsback et al. 1997; Railsback et al. 2002; White 2012). While these techniques are useful staples of mineralogical analysis, producing thin sections that result in the loss of the speleothem as an integrated sample, and XRD frequently requires modest amounts of powdered material for analysis (Mickler 2004; White 2012). These destructive qualities make traditional mineralogical techniques less desirable for speleothem samples. While it is often impossible to avoid all damage during preparation if a speleothem is intended for robust chemical analysis, reducing that damage and preserving unique speleothem samples is a must if samples are to be used for multiple analyses and archived, or preferably restored back to the cave from which they were collected for the sake of conservation (Mickler 2004; Frisia et al. 2005). Other studies have already explored several promising technologies that have displayed clear utility in providing useful chemical or structural information on a speleothem sample with minimal damage. Some studies have used magnetic resonance imaging and x-ray tomography to assess speleothems for usability as a chemical proxy, identify structural flaws, and analyze chemical inclusions; thus producing non-destructive methods to identify problem samples, or provide independent proxy information from a single speleothem (Mickler 2004; Zhang et al. 2006; Frappier 2009).

Speleothems are inherently unique formations, and while they provide excellent sources of proxy data for paleoenvironmental reconstructions, reducing the damage caused to them during analysis is essential in maintaining a speleothem sample for continued and varied analysis (Mickler 2004; Frappier 2009; White 2012). Expanding the non-destructive analyses possible on speleothem samples only increases the utility and potential of speleothem proxies, particularly if they supplement, or even replace, traditional isotopic and trace element analytical methods (Mickler 2004).

This study examined backscatter scanning electron microscopy (BSE) and Raman Spectroscopy (RS) to derive useful mineralogical information from the Harrison's Cave stalagmite (HC-1W; see Chapter 1). Observations using the Large Chamber Scanning Electron Microscope at the WKU NOVA center and the Thermo DXR Raman microscope at the WKU Crystal Kinetics laboratory were made to assess mineralogical change throughout the sample. The main data sets were put into mineralogical and chemical context with X-ray Diffraction (XRD) analysis and Energy Dispersive X-ray Spectroscopy on characteristic materials within HC-1W. The results of these observations were combined with a stable oxygen isotope record derived from HC-1W. Comparing the BSE analysis (which would elucidate bulk chemical change along and within calcite layers) and the RS analysis (which would elucidate changes in the carbonate molecules within and along calcite layers) analysis with a stable isotope record was used to assess the utility of interpreting a common paleoenvironmental proxy with high-resolution mineralogical information.

Isotope Record Preparation and Analysis

Speleothem HC-1W was obtained with permission from Harrison's Cave on the island of Barbados. Harrison's Cave is a government-owned show cave located in the third coral terrace of Barbados (Fig. 2). Sample HC-1W was cut in half and slabbed, and cut again to produce a thin (~1-2 cm thick) sample slice. The slice was polished along the exposed growth axis using an MK-Diamond wet polisher with successively increasing grit up to 8,500 grit; a final polish was applied by hand with 0.3µm alumina polish. One half of the slabbed stalagmite was sampled with a hand held dremel tool for large calcite powder samples (~150 mg), which were sent to the University of New Mexico's Radiogenic Isotope lab for absolute U-series dating. The other half of the slabbed stalagmite was micromilled at a 0.1mm resolution along the primary growth axis, and a sub sample of 210 samples were isotopically analyzed using the gas bench isotope ratio mass spectrometer (IRMS) at the University of Kentucky's Environmental Research Training Laboratory. Next to this transect, non-destructive analyses were conducted using the methods described below to be able to compare the techniques along the same growth axis transect.

Electron Microscopy and Raman Spectroscopy Preparation

Many conventional RS systems are amenable to modest speleothem sample sizes, however the Thermo DXR Raman microscope at the Western Kentucky University (WKU) Crystal Kinetics laboratory required some preparation to fit sample HC-1W under the Raman microscope. The sample preparations made for RS in this study were minimal, and involved only reducing the height of one half of the slabbed HC-1Wsample. This was done only to fit HC-1W under the aperture of the Thermo DXR Raman microscope system in the WKU Crystal Kinetics laboratory, and would not be necessary with a Raman Microscope or Spectroscope system that was designed for larger samples. Besides any pre-analysis preparation, the sample as a whole remains intact after RS analysis as long as reasonable laser intensities are employed; it should be noted however that it is possible to ablate the sample at high laser intensities. While many RS systems are flexible to sample size, conventional SEM analysis is very often limited by the chamber size of the electron microscope. This limitation is a result of the need for a vacuum or partial vacuum environment, which is required for electron imaging. Most conventional SEM systems have chambers limiting sample sizes to no more than several centimeters in any given dimension due to the generally small sample chamber sizes. The issue of chamber size often requires extensive processing and ultimately the disassociation of a continuous speleothem sample in order to conduct SEM analyses (Railsback et al. 1994). Employing a LC-SEM system eliminates the need to destroy large speleothem samples for SEM analysis. The LC-SEM at the WKU NOVA center has a chamber capacity of several cubic meters; chamber size was not an issue for sample HC-1W, which was 30 cm long by 10 cm wide at maximum.

Non-Destructive Analytical Methods

In this study, sample HC-1W was analyzed using the BSE mode of the LC-SEM. Continuous BSE imagery was captured of stalagmite HC-1W along its growth axis at 50x magnification. Along with the BSE imagery, EDS data was captured from pristine calcite as well as detrital and inclusion features within lamina to inform the chemical nature of inclusions. EDS was conducted while HC-1W was in the LC-SEM with the NOVA center's integrated X-ray Spectroscopy system. The LC-SEM was running at 15kV with a working distance between 20 and 30mm in BSE mode. Once images were captured, a binary signal was produced indicating pristine calcite layers (0) and detrital layers (1) along the growth axis. Detrital layers were defined as discrete laminae containing greater than 10% detrital material by surface area.

After the BSE transect was complete, sample HC-1W was analyzed on the Raman microscope in the crystal kinetics laboratory. Raman spectra were obtained along a two part transect coinciding with the isotope record and U-series dates obtained from HC-1W. This transect was comprised of three lateral points of Raman spectra, obtained along the growth axis of HC-1W every 50 μm. The Raman spectra obtained from this analysis were examined with particular attention to the most intense carbonate spectral peak, located at approximately 1086 cm^{-1}. This peak results from vibrational mode attributed to the symmetric stretch of the carbonate molecule, and shifts in the position and full width half maximum of this peak result from changes in mineralogy (e.g. calcite to aragonite) or substitution of magnesium ions for calcium in the carbonate molecule (Rividi et al. 2010). Differences in the peak width half maximum and peak center shift of the ~1086 cm^{-1} peak were recorded, and the peak shift was mapped around several distinct lamina transition zones. Mapping the shifts in peak position was a first look at the potential variability between speleothem lamina that could be resolved using features of their Raman spectra. After identifying the nature of spectral variability between the distinct layer materials in the spectral maps, Raman spectra were taken along the growth axis of HC-1W from 0 to 19 cm in two runs. The first run captured 9-19 cm, while the second captured 0-12 cm. X-ray diffraction (XRD) analysis was conducted on the two apparent mineral phases present in HC-1W (pristine crystalline calcite, and amorphous carbonate cement matrix in detrital layers) in order to validate the nature of the Raman spectral changes observed in the sample. XRD analysis was conducted using the WKU Crystal Kinetics laboratory's Rigaku Miniflex II X-ray Diffractometer. The BSE transect and Raman spectral transect were both compared to each other, as well as the stable isotope record derived from sample HC-1W. The spectral data from the Raman transect was used to calculate a record of magnesium substitution in speleothem calcite. Magnesium ions can substitute themselves for calcium ions in speleothem calcite; this substitution is modulated by environmental conditions at the time of calcite formation, making Mg a potentially useful trace element in interpreting past environmental conditions (Huang et al. 2001). In this study, the peak position and peak width half maximums of the carbonate peak (~ 1086 cm^{-1}) were used to calculate the mole percent of $MgCO_3$ throughout HC-

1W using Rividi et al.'s (2010) model. The $MgCO_3$ end-member from these models represents the pure stoichiometric component created by Mg substitution in the carbonate molecule as a mole percentage of the solid calcite solution. The mole percent of $MgCO_3$ in this study represents only a useful stoichiometric reference for Mg substitution in the solid solution of speleothem calcite, and should not be confused for an indication of inclusions of dolomite or magnesite minerals within speleothem HC-1W structure. Positive results from this modeling effort would indicate a strong potential for developing independent paleoenvironmental proxies using RS with calcite speleothems, as Mg incorporation into speleothems, and its related mineralogic characteristics have been studied extensively as a proxy of paleohydrologic conditions (Railsback 1994; Huang et al. 2001; White 2007; Palmer 2010; Onac and Forti 2011; Baker and Fairchild 2012). The $MgCO_3$ mol% record modeled from the RS analysis was compared to a $\delta^{18}O$ isotope ratio record derived from sample HC-1W. Oxygen isotope ratios in speleothem calcite have been well established as paleoenvironmental proxies (Gascoyne 1992; White 2007; Frappier 2009; Lachniet 2009). In sample HC-1W, oxygen isotope ratios have been ascribed to shifts in the average amount of rainfall on the island via the "amount effect," effectively making the $\delta^{18}O$ values from HC-1W indicators of wet (more negative values) and dry (more positive values) conditions. Due to the much higher spatial resolution of the RS data than the oxygen isotope record, the raw spectral data and subsequent $MgCO_3$ mol% record was smoothed using a running mean algorithm, which transformed the data to an amenable resolution for comparison with the isotope record. The oxygen isotopes were used to calculate oxygen isotope ratio values in $\delta^{18}O$ notation (Eq.1). These two data series were plotted with the binary BSE detritus signal and compared.

Results and Discussion

The U-series dates were plotted and polynomial and non-linear regression was applied to the corrected dates to obtain an age model. The best model was a 1st order polynomial equation, and the age model is a virtually linear chronology (Tab.1). The age model suggests that HC-1W is approximately 2,000 years old, and grew on top of a precursor speleothem that is approximately 20,000 years old after an extended hiatus (Fig. 3). The age model also suggests that HC-1W's growth rate has remained very steady throughout at least the past ~1,500 years.

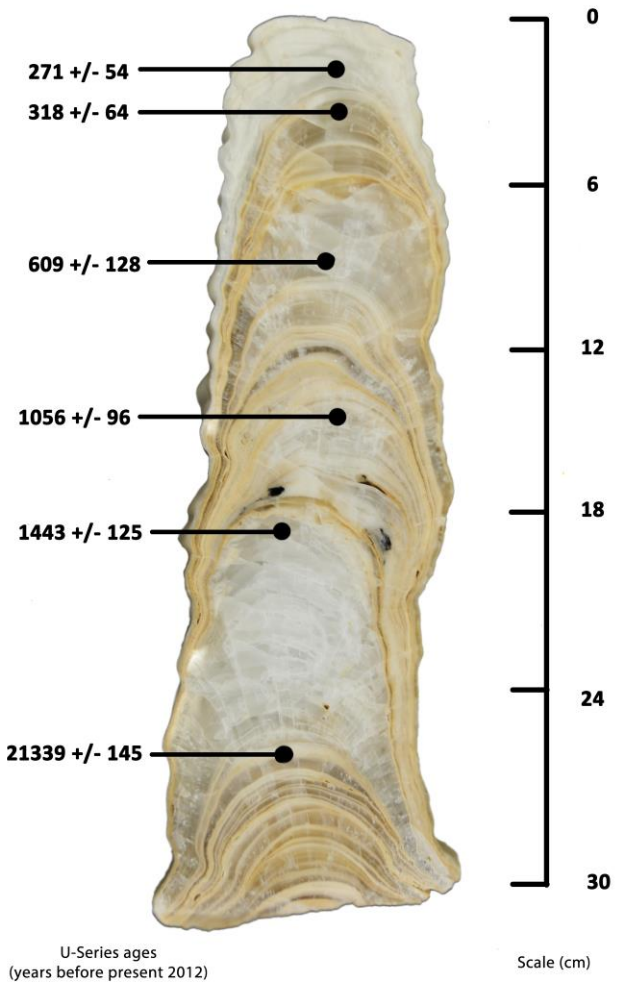


Figure 3: Image of stalagmite HC-1W with U/Th series dates and scale in centimeters.

The BSE transect was taken at a low magnification (50x) for the intended purpose of identifying broad, chemically distinct inclusions and detrital materials within the sample. In that respect, the LC-SEM provided excellent results, with detrital layers being easily discerned against the speleothem calcite. Even layers that did not appear to be detrital based on optical examination were shown to contain silica inclusions. The ability to identify inclusions and detritus based on atomic composition rather than optical character is integral when examining large or delicate speleothem samples where producing thin sections for polarized light microscopy is undesirable or impractical. The binary signal that was coded from the BSE transect facilitated rapid comparison between the oxygen and magnesium records and potential areas of error introduced to analyses by detrital materials. The Raman spectral maps were matched with their corresponding BSE imagery (Fig. 4). Low to no peak shift was observed in the detrital layers cement, while large variation in the primary carbonate peak was seen in the crystalline calcite, especially directly following a detrital layer (Fig. 4).

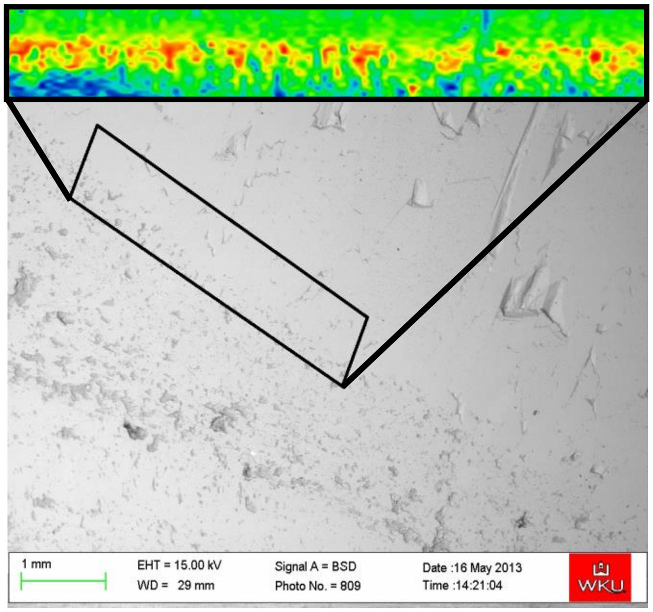


Figure 4: Bakscattered electron image at the boundary between a detrital layer and a pristine calcite layer in HC-1W. Inset is a Raman spectral peak shift map, visualizing shifts in the ~1086 cm^{-1} carbonate peak position across the boundary zone. Blues represent little peak shift, while reds represent significant peak shifts. The peak map shows an increase in peak shift beginning after the boundary, and continuingwell into the pristine calcite.

XRD analysis confirmed that both the carbonate cement holding together detrital layers, and the pristine crystalline calcite were 100% calcite within analytical error; EDS results agreed with XRD results, and additionally identified two different types of detrital inclusions throughout HC-1W along with the pristine crystalline calcite layers (Fig. 5). Results suggested that the nature of Raman spectral shifts observed in HC-1W were due to inclusion of larger ions (e.g. Mg^{2+}) into the calcite crystal lattice, rather than shifts from calcite to aragonite. This was necessary to build confidence that calculated $MgCO_3$ mol% were in fact indicative of real changes in Mg ion substitution into speleothem calcite.

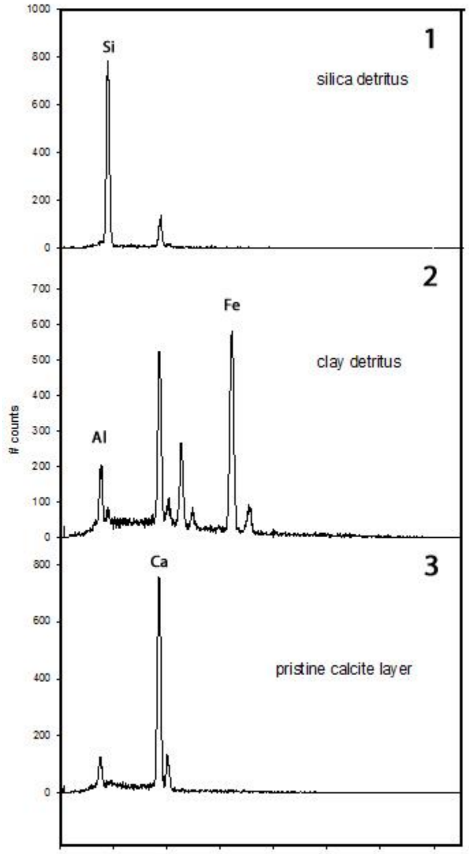


Figure 5: Energy Dispersive X-ray Spectroscopy (EDS) results from the WKU NOVA center's LC-SEM. EDS spectra show three distinct materials present in HC-1W; (1) calcite matrix with silica inclusions, (2) calcite matrix with iron bearing clay minerals, (3) pristine crystalline calcite. The major element peaks present in each material are labeled.

The two types of detrital materials observed in HC-1W include silica-based inclusions, which resemble calcite under optical observation, and clay inclusions, which contain varying amounts of Al, Fe, and disaggregated clay minerals. The clay inclusions are not Raman active, so the BSE analysis is ideally suited for identifying them in the calcite sample, as the Raman microscope is unable to resolve them. However, silica molecules are Raman active, and could potentially be identified using RS in a hyperspectral mode. The results of the XRD suggested that rather than a mineralogical transition perhaps from calcite to aragonite, the greater shifts observed in the primary carbonate peak were the results of greater inclusion of Mg into the calcite lattice. The $MgCO_3$ mol% values derived from modeling the Raman transect were compared to the oxygen isotope record derived from HC-1W, along with the BSE detrital signal (Fig.6)

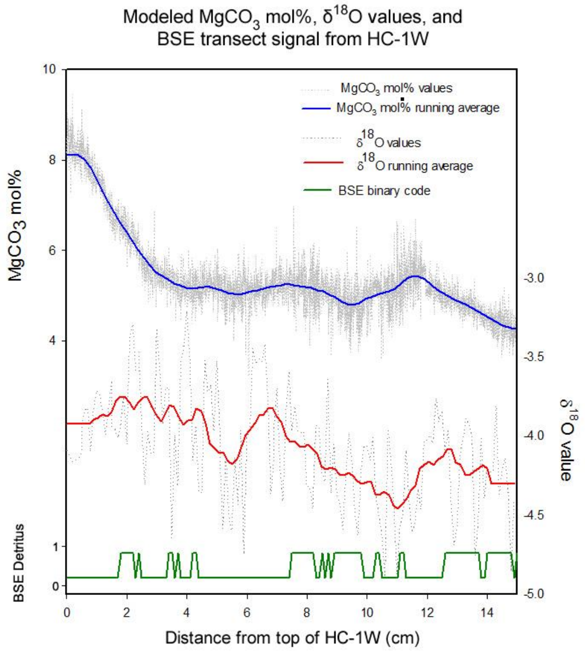


Figure 6: Comparison of the oxygen isotope record and the magnesium record (0 – 15 cm from top of HC-1W). The oxygen record and magnesium record display coinciding trends. The BSE pristine calcite (0) and detrital inclusions (1) signal is shown at the bottom of the graph.

The comparison illustrates some periods where trends in the $\delta^{18}O$ values match with $MgCO_3$ mol% shifts. The $MgCO_3$ mol% record is precise to 0.5 mol%, and with data processing and slight beam variations during data acquisition the effective precision of the magnesium record is closer to 1 mol%. While not ideal, there are still trends in the data that exceed this margin of error; and the long-term trends can be identified with some confidence. The $\delta^{18}O$ record is precise to better than 0.05‰, which leaves little doubt in the significance of the trends observed in the oxygen isotope record. With the effective precision in mind, the comparison does prove valuable. Observing trends in both records from the older portion (right) of the record to the younger portion (left), a subtle match in trends can be observed, with $MgCO_3$ mol% following the $\delta^{18}O$ values throughout much of the stalagmite's growth. From 15 cm to a peak around 13 cm, $\delta^{18}O$ values increase, suggesting drier conditions based on the amount effect interpretation; $MgCO_3$ mol% appear to follow that trend, though they do not peak until approximately 12 cm. From 13 to 11 cm the $\delta^{18}O$ values decrease, suggesting increasingly wetter conditions; the $MgCO_3$ record follows suit from 12 to roughly 10 cm. The $\delta^{18}O$ values begin to increase until around 7 cm, with $MgCO_3$ mol% again following that trend from around 10 to 7 cm. The trends appear to match further until around 3cm; however, as these shifts in the $MgCO_3$ mol% record are below the effective precision it is difficult to draw significant conclusions from that period. From 3 cm on is perhaps the most interesting portion of the two records; $MgCO_3$ mol% increases dramatically, with little response in the oxygen isotope record. Given the confidence in this portion of both records being analytically sound, the best conclusion is that while both records apparently are recording similar paleoenvironmental signals, it is not the same signal. The $\delta^{18}O$

values from HC-1W are modulated by the isotopic amount effect, and record the amount of paleoprecipitation; however, the $MgCO_3$ signal appears to show greater mol%'s of $MgCO_3$ coinciding with drier conditions supported by the $\delta^{18}O$ record. This relationship suggests that the $MgCO_3$ record is modulated by changes in the dynamics and geochemisty of the soil and epikarstic aquifer that feeds dripwater to Harrison's Cave, rather than precipitation amounts directly. This interpretation is consistent with other studies of Mg variability in speleothem calcite, and provides a plausible physical basis for the changes observed in the modeled MgCO3 mol% record (Railsback et al. 1994; Fairchild et al. 2000; Fairchild et al. 2001; Huang et al. 2001; Self and Hill 2003; Baker and Fairchild 2012). It is reasonable then to interpret the portions of the Mg record which coincide with the $\delta^{18}O$ record as periods in which the geochemical dynamics of the soil and epikarst aquifer were influenced to a greater magnitude by the amount of precipitation on the island, though an exact attribution of the dominant mechanism by which this naturally occurs is difficult based on this analysis. If this interpretation is valid, then the large increase in $MgCO_3$ mol% observed from ~3 cm to 0 could be a result of European cotton, tobacco, and sugar cane cultivation altering the soil and epikarstic hydrology of the upper coral terrace Harrison's Cave is located within. Prior uranium series dating of HC-1W indicates that the beginning of the dramatic increase in $MgCO_3$ mol% just below 3 cm coincides with a U-series age of ~ 318 years before present (2012), or around the year 1690 AD. European colonization of Barbaos began with the English claiming the island in 1625. By 1640 cotton, tobacco and sugar cane were all grown on the island, and by the early 1700's sugar cane was the major Barbadian export (Schomburgk 2001). While an interesting possibility, substantiating that link would require more robust methods than covered by the scope of this study, however wide scale land cover changes as well as increased withdrawal of groundwater by English colonists provides a timely process that could reasonably have caused such a dramatic and rapid shift in the HC-1W magnesium record. What this comparison does illustrate well is a plausible connection between stalagmite calcite $MgCO_3$ Mol % derived from RS and past hydrologic conditions; though further work to validate this methodology and produce a truly robust method of obtaining paleoenvironmental information from calcite speleothems via RS is needed.

Comparing the BSE transect with the other data sets didn't reveal any major correlations or strong periodic shifts in detrital and pristine calcite layers. That being said, the lack of correlation with average rainfall and the magnesium record suggests that rather than regular environmental occurrences, these detrital layers represent perturbations to the hydrologic system of Barbados from relatively short (several years) periods of increased weathering on the island, and/or extreme events such as hurricane or tropical storm landfalls; or intense convective events. While it is very difficult to attribute individual detrital layers in HC-1W to specific types of storms, it is apparent that at least some of the detrital layers must have resulted from the influence of high energy extreme events, and the likely reality is a combination of periods of strong convective activity and tropical storm influence resulting in accelerated weathering on the island. While iron rich clays and weathered silica were the most frequent contents of these detrital layers, several fossilized planktonic foraminifera were also observed in detrital layers. The few foraminifera observed were well preserved, retaining even very fine calcium carbonate spines that covered their tests, suggesting that they may have been contemporary to the formation of the stalagmite layer they were observed in and were recently deposited into the epikarst aquifer through extreme convective activity. It should be noted that it is not impossible for fossil foraminifera from coralliferous limestones to be weathered out of the parent material and end up in another sedimentary formation such as a stalagmite, and so attribution to extreme events alone cannot be made with complete confidence.

The BSE transect using the LC-SEM was a great illustration of the technologies capabilities. While providing no new analytical techniques than what can already be found in most electron microscope systems, the major advantage lies in the LC-SEM's ability to analyze large samples with no need for destructive sample preparation to fit into small observation chambers. The ability to produce continuous imagery of bulk chemical change in the layers of a speleothem sample is also a major advantage, as the same exact setting's can be used for a full SEM transect, keeping the data consistent while also providing uninterrupted observations of chemical change along a speleothem sample. Other types of proxy samples could also benefit from analysis using a LC-SEM system, and the results from this study provide an indication of the strengths of the technology. Of course the major detraction from widespread use of LC-SEM analysis is the rarity of LC systems. Though few LC-SEM instruments are publicly available (or exist in general) in the US, increased collaborative efforts between private and government LC-SEM facilities would be of tremendous benefit in analyzing many differ types of physical climate proxies without having to damage the integrity of a sample in order to avoid having to produce thin-sections, or break up samples potentially hindering further analyses and reducing archival suitability of samples.

Conclusions

The Raman spectral analysis of HC-1W provides evidence that quantitative mineralogical analysis techniques can be applied to elucidate past environmental conditions to a similar resolution and as a supplement to contemporary stable isotope analysis. While it will take further study to develop a robust model of paleohydrologic conditions based on RS derived $MgCO_3$ mol% records, the nature of Raman spectroscopy is uniquely amenable to such an endeavor. The relative abundance of Raman systems, especially at institutions with strong material science facilities, makes the incorporation of Raman spectroscopy into speleothem studies a relatively straightforward proposition. Additionally, the potential for highly precise RS systems to resolve the oxygen isotope ratios of carbonate samples directly through the relationship between oxygen isotope ratios and the intensity of the ~1086 cm^{-1} peak has been demonstrated (McKay et al. 2013). While the accuracy of oxygen isotope analyses using RS has yet to reach levels necessary to resolve the natural isotopic variability in speleothems, future advances in the precision of RS systems could make the proposition a reality. That being said, in order to be confident that the results of RS analysis are due to any proposed mechanism, samples must be constrained and mechanisms validated through other analytical techniques such as XRD and inductively coupled plasma atomic emission spectroscopy. This makes the process of using both systems in tandem ideal, but both Raman spectroscopy and LC-SEM analysis offer individual benefits in speleothem analyses, and further applications of both types of systems should be explored. While speleothem HC-1W was uniquely suited for $MgCO_3$ mol% modeling via Raman spectroscopy, other samples, which might contain large volumes of non-carbonate materials, could have different information revealed through longitudinal studies using Raman spectroscopy. Each sample will need to be individually assessed for suitability, and care must be taken when interpreting Raman spectra of speleothem calcite. Properly treated BSE imagery can potentially shed light on extreme events in the past depending on speleothem site conditions, though it can always identify chemically distinct materials in speleothem lamina, as long as the chemical difference is on an order of magnitude that is within the detection capabilities of the SEM system in use; providing valuable guidance for precision chemical and isotopic analyses and assisting in identifying fine scale chemical heterogeneity within and along a speleothem sample. Whether used together, or separately, both RS and LC-SEM systems have a lot to offer speleothem studies of past environments.

Chapter 3: Stable isotope paleoprecipitation reconstruction and teleconnection attribution for Barbados

Introduction

The island of Barbados is the easternmost island in the Caribbean region, and though the country of Barbados is prosperous; serious issue of water resources are of increasing concern to the people who call Barbados home (Cashman et al. 2010). While issues of water resources often elicit an engineering response, the root of water resource issues on isolated carbonate islands like Barbados are a symptom of low groundwater supplies (Cashman et al. 2010; Speed 2013). On islands far from any upstream freshwater source, groundwater is often the major water resource; this is especially true of heavily karstified carbonate islands such as Barbados (Mylroie and Mylroie 2007; Speed 2013). In order to fundamentally address these water problems, a deeper understanding of the mechanisms of groundwater recharge are required, and in the case of Barbados those mechanisms are through the percolation of rainwater into the aquifer by diffuse and conduit flow (Jones et al. 1996; Machel 1999; Jones and Banner 2003; Mickler 2004; Mickler et al. 2004). While it is possible to monitor recharge directly at present, modern records only cover relatively short periods of time and longer records are desirable to tease out the mid and long term drivers of precipitation patterns on Barbados (Jones et al. 1996; Mickler 2004). Fortunately, the karst environment that has formed in the coral limestone of Barbados provides a means to understand past changes in precipitation patterns and their respective climate drivers (Mickler 2004).

Calcite formations in caves are often common to karst landscapes (Self and Hill 2003). These speleothems preserve the isotopic ratios of the drip waters that feed them

(Self and Hill 2003; Lachniet 2009; Polk et al. 2012). The preservation of these isotope ratios, especially using isotopes of oxygen, has been applied prolifically to elucidate past climate changes (Hendy 1971; Gascoyne 1992; Banner et al. 1996; Asmerom 2002; Bar-Matthews et al. 2003; Xiaoyan, 2006; Mangini et al. 2007; White 2007; Ford and Williams 2008; Lachniet 2009; Frappier 2009; Fensterer 2013). Shifts in the isotope ratios of elements like oxygen in water are affected by environmental conditions; when water precipitates speleothem calcite those isotopic ratios are preserved in speleothem calcite as long as the layers remain intact and unchanged (Lachniet 2009). Speleothems, specifically stalagmites, are additionally well-suited for resolving past climate changes due to the layered deposition of calcite in the formations, which provides a sedimentary record of isotope ratios in chronological order in successive speleothem lamina (Asmerom 2002). An added benefit in using stalagmite proxies is that good samples are very well preserved in relatively constant cave conditions (Asmerom 2002; Mickler 2004; Lachniet 2009; Frappier 2009). Prime speleothem samples display continuous or quasi-continuous deposition in regions that often have few alternative terrestrial climate proxies. Additionally, most speleothems can be absolutely dated using U/Th series dating methods. Absolute dating provides a high quality chronology to be produced and used in tandem with climatic information derived from a speleothem sample (Edwards et al. 1987). In prime samples, these traits permit the production of climate records at potentially sub-annual resolution (Asmerom 2002).

The $\delta^{18}O$ values of speleothem calcite adopt the character of the dripwaters from which they precipitate, reflecting the climatic and landscape processes occurring above the cave over time (Hendy 1971). Due to the crystallization kinetics of carbonate species however, the isotopic signature in speleothem carbonate is offset from its source by a factor dependent upon an equilibrium or non-equilibrium nature of deposition, which influences isotopic fractionation before and during calcite crystallization (Hendy 1971; Dorale and Liu 2009). It is established that if the fractionation extent between drip water δ^{18}O and speleothem calcite can be determined to be relatively stable, meaningful conclusions can be drawn about changes in temperature, geographic nature, or amount of rainfall experienced over the time a speleothem was deposited (Dansgaard 1964; Gascoyne 1992).

Issues with non-equilibrium deposition have prevented many promising speleothems from being used to produce meaningful, high-resolution paleoclimate records (Gascoyne 1992; Mickler et al. 2004; Mangini 2007). This study sought to overcome those issues through careful isotopic and mineralogical assessment and validation of the speleothem proxy to ensure that there was no significant non-equilibrium deposition or calcite diagenesis to add extra error to the analyses.

Here, a ~1,200 year record of changes in precipitation derived from oxygen isotope variability in speleothem calcite from Barbados is presented. The sample analyzed in this study was speleothem HC-1W, obtained with permission of the management from Harrison’s Cave, Barbados (Fig. 7). Using these isotope data, a reconstruction of past precipitation cyclicity and the driving teleconnections is possible in order to better understand water resource variability in the future.

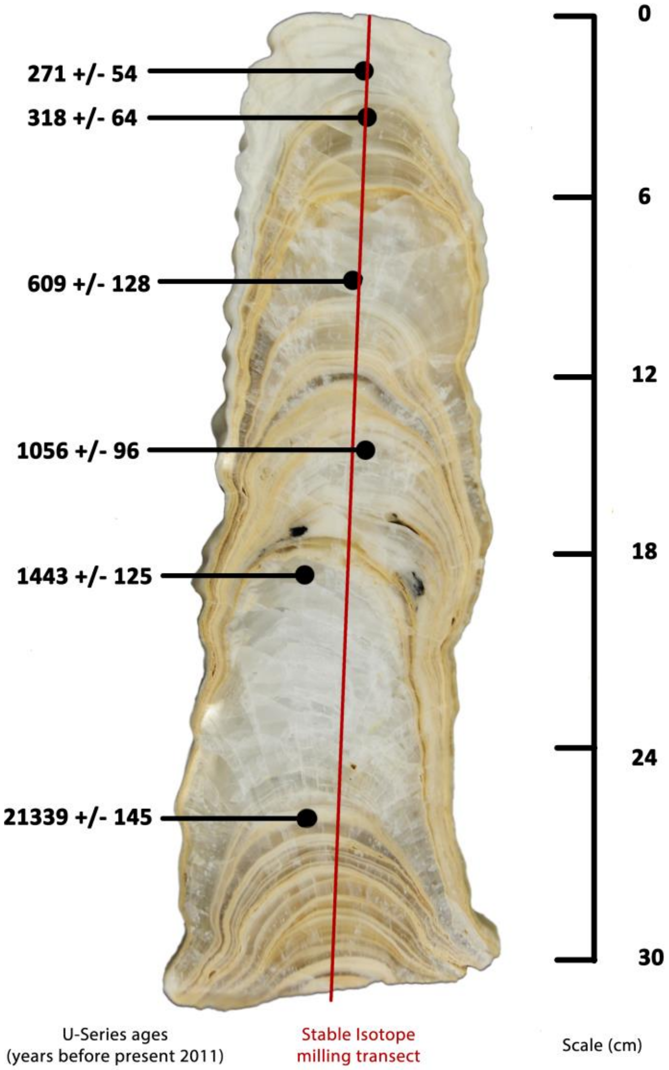


Figure 7: Image of stalagmite HC-1W with U-Series dates (black ovals), stable isotope milling transect (red line), and scale (cm).

Stalagmite HC-1W was collected from Harrison's Cave, Barbados, cut in half, and slabbed. The two halves were polished with an MK Diamond hand sander/ polisher using a succession of grit sizes (300-8500). The half intended for stable isotope analysis was then hand polished to a fine finish using 3µm Al oxide. Calcite from the speleothems was sampled from one half of the speleothem along layers of growth for U-series dating; the other half was sampled along the primary growth axis for oxygen and carbon isotope analysis ($\delta^{18}O$ values). Between 50 to 200 mg of calcite powder was sampled for radiogenic isotope analysis was extracted with a Dremel tool at the top and bottom of each speleothem, as well as above and below all potential growth hiatuses with a ~0.3-0.5 mm dental bit. The radiogenic isotope samples (U/Th) were analyzed using a Thermo-Neptune Inductively coupled plasma mass spectrometer (ICP-MS) at the University of New Mexico's Radiogenic Isotope Laboratory. Radiogenic isotope sample powder was be dissolved in acid and spiked with a mix of ^{236}U, ^{233}U, and ^{229}Th in order to prevent weighing error from affecting age error (Polyak and Asmerom 2001). U and Th were simultaneously precipitated via $FeOH_3$ and subsequently separated through anion exchange before ratios are measured on the ICP-MS (Polyak and Asmerom 2001).

Calcite powder samples for stable isotope analysis were ran on the gas bench - isotope ratio mass spectrometer (IRMS) at the University of Kentucky's Environmental Research Training Laboratory. Calcite powder was weighed to 150ug +/- 50ug, and placed in sealed exetainers with vulcanizing septa. Sealed exetainers were flushed with Helium for 30 minutes each, and then excess pressure was released via syringe. Depressurized He atmosphere exetainers were injected with H_3PO_4 to digest calcite powder; the reaction occurred at a controlled 25°C. After 12 hours of digestion CO_2 gas from the sealed exetainers was extracted and analyzed on the GB-IRMS. Results were corrected for fractionation due to the digestion reaction and delta values were calculated for oxygen isotope ratios in each sample (Sharp 2007). Due to cost limitations, a 1mm resolution subset of the full 100μm resolution sample set was run for this study.

In order to provide a chronology for HC-1W's oxygen isotope ratio variations, an age model was developed based on the U-series dates obtained from the UNM

Radiogenic Isotope lab. Dates and their distance from the top of HC-1W were modeled using multiple polynomial regression and non-linear regression in Sigmaplot, and the optimal model was accepted. This age model and the U-series dates were then used to run a Monte Carlo simulation to estimate the rate of accumulation of calcite in HC-1W over time, a necessary piece of information for running most time series analyses with confidence.

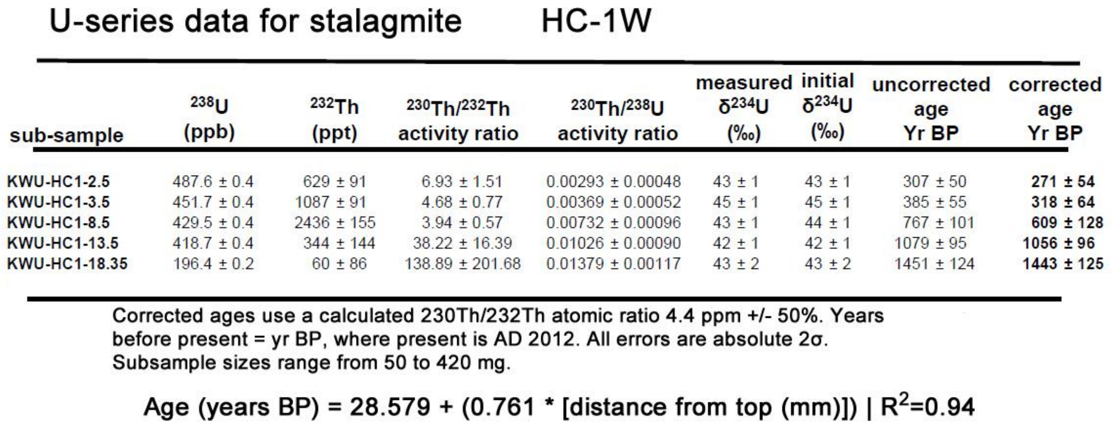
With the calcite accumulation rate estimated, four methods of time series analysis were implemented. A Fourier frequency analysis was performed as a first check of the precipitation signal in the frequency domain. Fourier transforms and analyses rely on fitting sinusoids to extract component periodicities in a signal. While Fourier based time series analysis is common among many scientific fields, it is not as useful for analyzing noisy geophysical data series (Mann et al. 1999). However, it is a simple first analysis to run that can be understood more easily by a broader range of professionals than more obscure methods. The second time series analysis preformed was a Lomb-Scargle frequency analysis. This method is similar to a traditional Fourier frequency analysis; however it uses a least squares algorithm to fit component periodicities to a time series (Mann et al. 1999; Ghil et al. 2002). The third time series analysis method preformed was spectral wavelet analysis, which fits data to a wavelet function (mother wavelet) in order to extract component periodicities at multiple resolutions and visualize them in time – frequency space (Ghil et al. 2002). The fourth method of spectral analysis was the Multi-Taper Method (MTM), which samples a time series with successive orthogonal data tapers, effectively producing an artificially large data set (Mann et al. 1999; Delong 2009; Polk et al. 2007). The MTM is exceptionally useful at extracting robust periodicity data out of time series that are otherwise too short to be robustly analyzed via other methods. Lomb-Scargle spectral analysis is also known as least squares spectral analysis. This method exploits the relationship between the Fourier transform and curve fitting with least squares sinusoidal functions (Ghil et al. 2002; Thompson 1990). While the Lomb-Scargle method is similar to Fourier analysis, it is much better at handling the discontinuous and uneven data spacing common to climate data sets (Priestly 1991; Mann et al. 1999).

MTM analysis is able to overcome the lack of data from small datasets (Mudelsee 2001; Ghil et al. 2002). MTM analysis achieves this through the production of a windowed trial set, based on orthogonal data tapers. This method produces multiple independent estimates from the same sample, effectively allowing small data sets to be treated as if they were larger (Mudelsee 2001). Spectral wavelet analysis uses wavelet functions, which are prescribed oscillations that have minimum amplitude of zero rather than sinusoids as Fourier analysis employs (Ghil et al. 2002). The benefit of using wavelets over sinusoids is the ease with which multi-scale signals can be decomposed (Thompson 1990; Mudelsee 2001; Ghil et al. 2002). Using wavelets rather than the sum of sinusoids as Fourier analysis does allows wavelet spectral analysis to analyze time series data at multiple resolutions (Ghil et al. 2002; Mudslee 2001). Wavelet analysis provides a useful summary of periodic components of time series at many time and frequency scales; these components can then be compared to published teleconnection reconstructions (Mudslee 2001).

Results and Discussion

The results of the U-series dating are displayed in Table 1. HC-1W was collected active in 2012 and the top date can be assumed to be modern referenced to that year. The effective date range for data analyzed in this study is from present (2012) to 1,500 years before present (BP). The corrected U-series dates were used to produce a modeled chronology. Multiple polynomial and non-linear regression were used to derive potential models. The most representative model was the linear model presented in Table 1.

Table 1: U-series chronology for HC-1W. Raw dates and data as well as the age model derived from them is provided. The optimal model was a first order polynomial model, with an R^2 value of 0.94.



U-series data for stalagmite HC-1W

sub-sample	^{238}U (ppb)	^{232}Th (ppt)	$^{230}Th/^{232}Th$ activity ratio	$^{230}Th/^{238}U$ activity ratio	measured $\delta^{234}U$ (‰)	initial $\delta^{234}U$ (‰)	uncorrected age Yr BP	corrected age Yr BP
KWU-HC1-2.5	487.6 ± 0.4	629 ± 91	6.93 ± 1.51	0.00293 ± 0.00048	43 ± 1	43 ± 1	307 ± 50	**271 ± 54**
KWU-HC1-3.5	451.7 ± 0.4	1087 ± 91	4.68 ± 0.77	0.00369 ± 0.00052	45 ± 1	45 ± 1	385 ± 55	**318 ± 64**
KWU-HC1-8.5	429.5 ± 0.4	2436 ± 155	3.94 ± 0.57	0.00732 ± 0.00096	43 ± 1	44 ± 1	767 ± 101	**609 ± 128**
KWU-HC1-13.5	418.7 ± 0.4	344 ± 144	38.22 ± 16.39	0.01026 ± 0.00090	42 ± 1	42 ± 1	1079 ± 95	**1056 ± 96**
KWU-HC1-18.35	196.4 ± 0.2	60 ± 86	138.89 ± 201.68	0.01379 ± 0.00117	43 ± 2	43 ± 2	1451 ± 124	**1443 ± 125**

Corrected ages use a calculated 230Th/232Th atomic ratio 4.4 ppm +/- 50%. Years before present = yr BP, where present is AD 2012. All errors are absolute 2σ. Subsample sizes range from 50 to 420 mg.

$$\text{Age (years BP)} = 28.579 + (0.761 * [\text{distance from top (mm)}]) \mid R^2=0.94$$

Oxygen isotope record and time-series analysis

Before the oxygen isotope record was analyzed, the effective sample interval needed to be determined. In order to do this, the U-series chronology was used along with the physical distance along the stalagmite to run a Monte Carlo simulation (Fig. 8). The simulation was iterated 10,000 times, and the results plotted as a histogram and with the average accumulation rate as a slope bounded by the total maxima and minima of the simulation (Fig. 8).

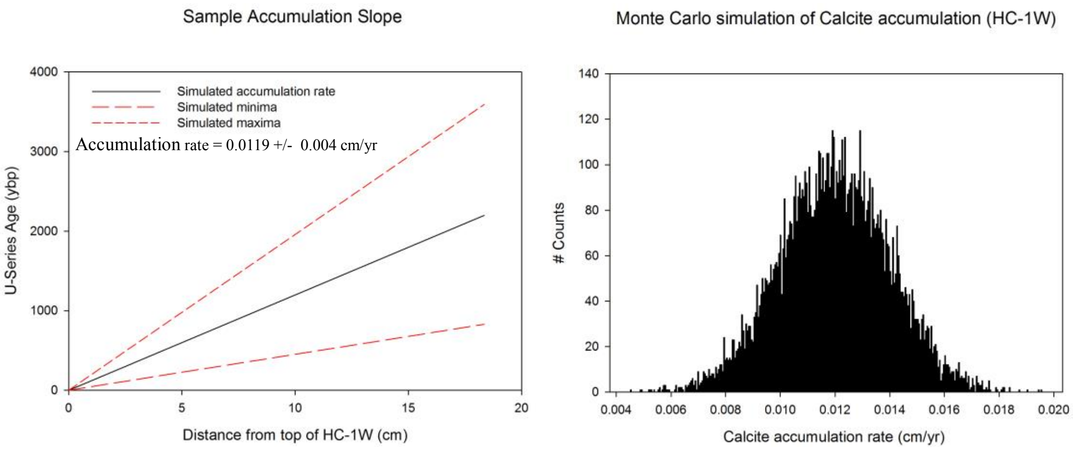


Figure 8: Monte Carlo simulation to estimate calcite accumulation rate. Accumulation rates were simulated. The histogram of simulation results to the right; the average accumulation rate is shown at left (red curve), grey curves demark the error bounds.

The simulation was necessary to estimate the effective temporal resolution of the proxy within the dating errors, rather than just the proxy sampling interval, which is needed for several of the time series analyses performed on the oxygen record. This simulation was used as the basis for all time steps used in time series analysis for stalagmite HC-1W.

Oxygen isotope ratios were derived from sample HC-1W (Fig. 9). Before interpretation, the oxygen isotope ratios were first compared to carbon isotope ratios obtained from the GB-IRMS analysis to identify correlation. Correlation between oxygen and carbon ratios within speleothem calcite is an indicator that the precipitation signal desired is being affected by kinetic fractionation between the drip point and the speleothem calcite end member (Hendy 1971; Mickler et al. 2004). No significant correlation between carbon and oxygen ratios was observed. In order to further ensure that kinetic effects were not significantly affecting oxygen isotope ratios in HC-1W, the temperature and relative humidity of the site HC-1W was sampled from has been monitored continuously with an Onset HOBO temp/RH probe. This monitoring is part of an ongoing complimentary study of the oxygen and carbon isotopic dynamics of precipitation on Barbados, though preliminary results suggest that the magnitude of kinetic effects at the HC-1W sample site is small. The amount effect has been identified on several occasions as the driving mechanism of oxygen isotope ratio shifts in Barbadian precipitation, meaning that shifts in the oxygen isotope ratios in rainfall on the island are representative of shifts in the average precipitation amount (Jones et al. 1996; Mickler 2004; Mickler et al. 2004). With considerations of the nature and magnitude of kinetic fractionation effects between cave drip water and speleothem calcite, the HC-1W oxygen isotope record is reasonably expected to show shifts in the average amount of precipitation on Barbados over the duration of the record, therefore the isotope record is interpreted as more negative (positive) δ^{18}O values indicate wetter (drier) conditions (Jones et al. 1996; Mickler 2004; Dreybolt, 2008). The oxygen isotope record from HC-1W for the past 1,500 years shows an average δ^{18}O value of -4.1‰. By the amount effect interpretation, the HC-1W oxygen isotope record illustrates a dry period from 1,500 years BP to roughly 1,300 years BP. This dry period is followed by increasingly wetter conditions from 1,300 to around 990 years BP. This wet period is followed by a short period of moderately dry conditions between 990 and 960 years BP with another slightly wetter period between 960 and around 700 years BP. The following period from 700 to around 200 years BP shows a considerable dry period, from which the period from 200 years BP to present appears to be recovering, trending towards wetter conditions. The wettest conditions in the record coincide with the Medieval Climate Anomaly (MCA) roughly 800-1,100 years BP, and the period of driest conditions coincides with the Little Ice Age (LIA) roughly 150-500 years BP (Fig. 9).

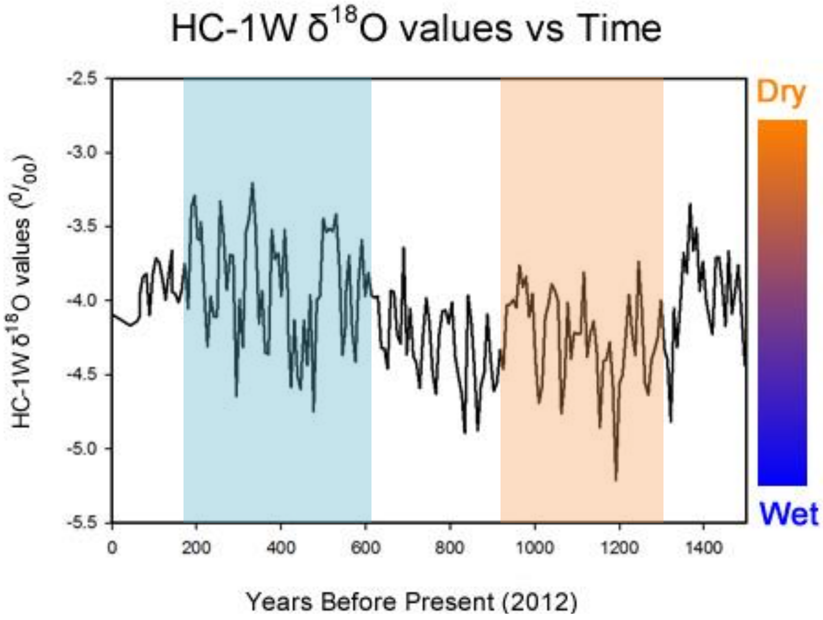


Figure 9: Record of oxygen isotope ratios from HC-1W. δ^{18}O values are representative of precipitation amount on the island of Barbados. More negative values indicate greater amounts of rainfall, and wetter conditions overall. Less negative values indicate lower amounts of rainfall, and drier conditions. The Medieval Climate Anomaly (MCA) is highlighted in red, and the Little Ice Age (LIA) is outlined in blue.

Oxygen isotope ratios from HC-1W were compared with the dominant teleconnection and climate influences operating at the sub-decadal to centennial scale (Fig. 10).

HC-1 δ^{18}O values vs Caribbean Teleconnection Reconstructions and Proxy Records

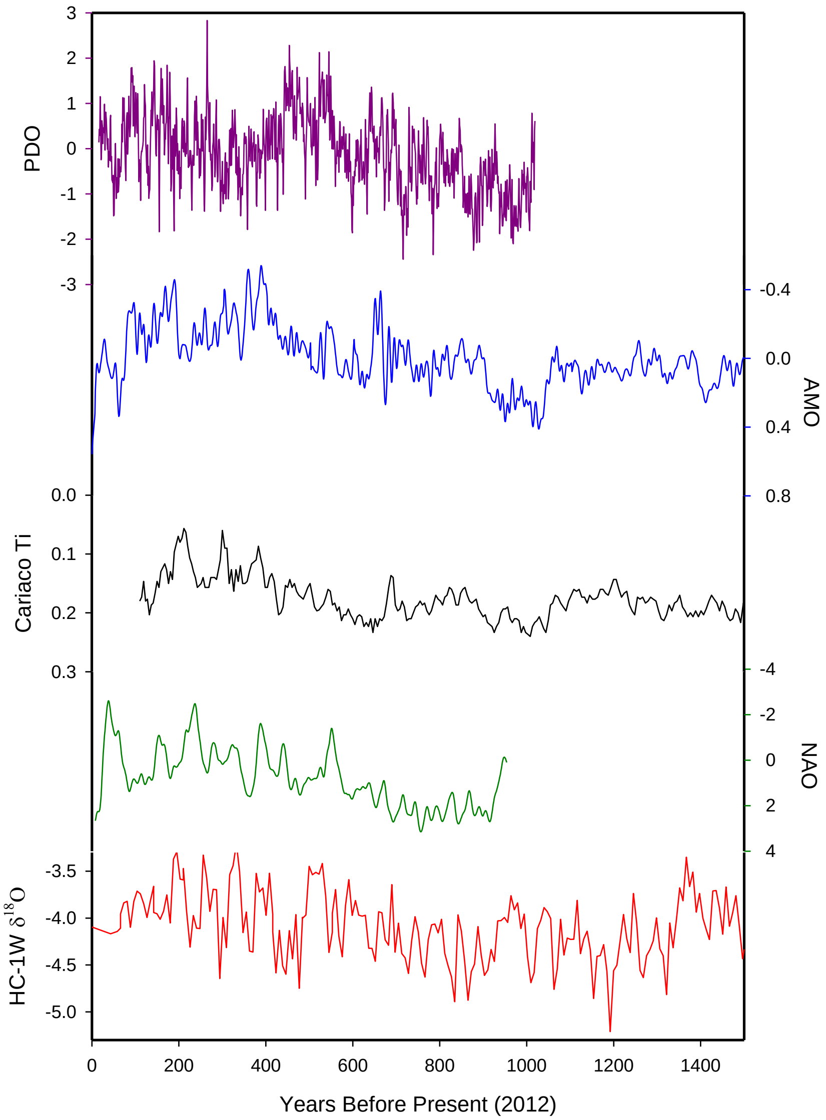


Figure 10: HC-1W oxygen isotope record (red curve) plotted along with reconstructions of the PDO (MacDonald and Case 2005), AMO (Mann et al. 2009), ITCZ shifts indicated by Ti levels in the Cariaco marine sediment core (Haug et al. 2001), and the NAO (Trouet et al. 2009).

When plotted together, both the HC-1W oxygen isotope signal and the AMO signal show the best match in both phasing and amplitude (Fig. 10). When compared to the Cariaco basin Ti record (which is interpreted to indicate migration of the ITCZ) we see a subtle relationship; this is expected as when the ITCZ is situated over the northern hemisphere portion of the tropics for longer periods of time, greater amounts of precipitation are expected. Comparison with the NAO shows a somewhat similar relationship as the AMO has with the HC-1W oxygen isotope record, however it is relatively muted, and is likely a result of connections between the drivers of Atlantic ocean/atmospheric circulation patterns that influence both the NAO and AMO (Wang 2007; Mann et al. 2009; Trouet et al. 2009) While overall the match is strong, there are two periods where the HC-1W and AMO signal are apparently out of phase; these periods occur during the periods of 150-500 years BP and 800-1,100 years BP, the Little Ice Age and Medieval Climate Anomaly, respectively (Mann et al. 1999; Mann et al. 2009). This could be explained by changes in the dominant teleconnections influencing the region, hence the AMO signal being more confounded by other influences.

Time series analysis was performed on the HC-1W oxygen isotope record in order to derive more meaningful information on the teleconnective drivers of Barbadian precipitation. Fourier Frequency analysis (Almedia 1994), the Multi-Taper Method (MTM) (Thompson 1990), Lomb-Scargle analysis (Lomb 1976; Scargle 1982), and wavelet analysis (Torrence and Compo 1998) were used to elucidate the dominant periodic oscillations present in the oxygen isotope record. While robust time series analysis is only possible on certain time series, the HC-1W oxygen isotope record meets these requirements (DeLong 2009). The requirements that must be met to ensure robust time series analysis include (1) roughly annual resolution, (2) adequate length of time captured (> 1,000 yrs), (3) an absolute chronology model, and (4) the desired variables must be coherent (DeLong 2009). That being said, it should be again noted that the oxygen isotope record presented here is a subset of the complete, annual sample set.

Wavelet analysis was performed in Systat Autosignal® using a Morlet mother wavelet, without spectral padding in order to display significant periodicities in time and frequency space (Fig. 11). Fourier Frequency analysis (Fig. 12) and Lomb-Scargle (Fig. 13) analysis resolve spectral power in the frequency domain, based on fitting sinusoids via the Fourier transform, and a least squares adaptation of the Fourier transform respectively. These analyses were performed in Systat Autosignal®. The Multi-Taper Method was performed in Systat Autosignal® using a detrended oxygen isotope record (Fig. 14). The time step used was advised by the average sample accumulation rate of 0.0119 cm/yr +/- 0.0041 cm/yr (Fig. 8; Ghil et al. 2002).

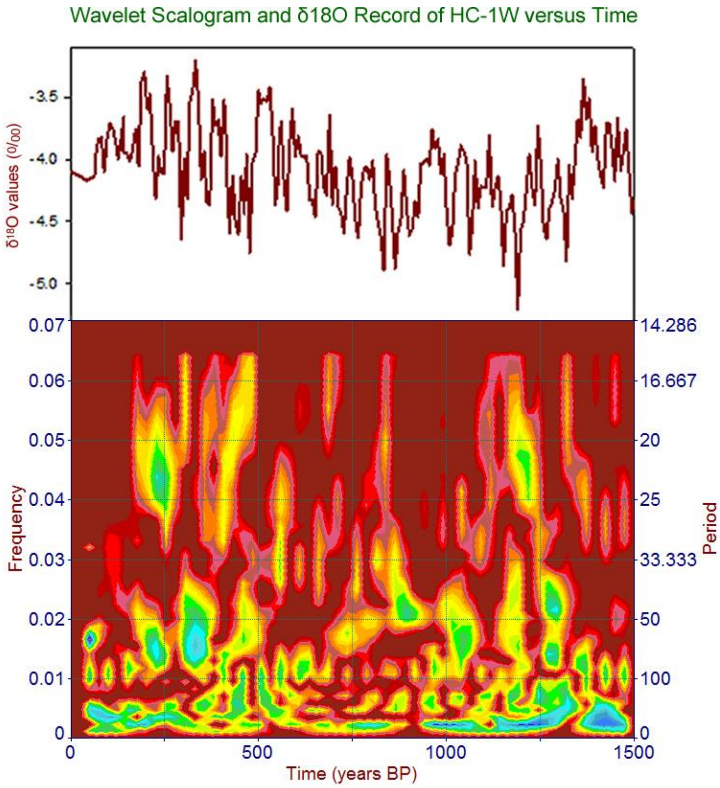


Figure 11: The HC-1W oxygen isotope record and wavelet scalogram. The wavelet analysis resolves spectral power (gradient from red – low to purple –high) in frequency & time space. Significant periodicity can be seen in the reoccurring spectral intensity peaks in the 50-90 year period.

The wavelet analysis shows significant periodicity around the 50-90 year period. Another apparent periodicity exists around ~200 years; however, periods greater than centennial scale are not significant in this wavelet analysis given the time series length

(Fig. 11).

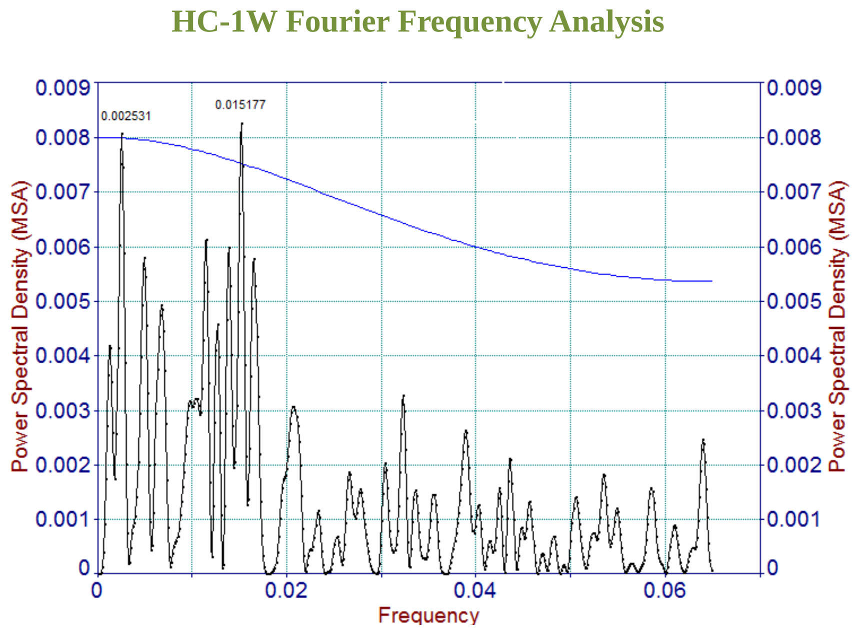


Figure 12: Fourier frequency analysis of HC-1W oxygen isotope record. The black curve illustrates the power spectral density of the HC-1W oxygen record in the frequency domain. The blue curve is the 50% significance boundary. Two periodic components at frequency 0.0151 and 0.0025 are significant at 50%.

Fourier frequency analysis of the HC-1W oxygen isotope record resolved two periodicities that were statistically significant. The significant periodicities occurred at frequencies of 0.0151 (period ~66 yrs), and 0.0025 (period ~400 yrs) (Fig. 12). The later frequency appears significant, however, due to the 1,500-year length of the time series, it must be considered with skepticism given the relatively short length of time covered by the HC-1W oxygen isotope reconstruction.

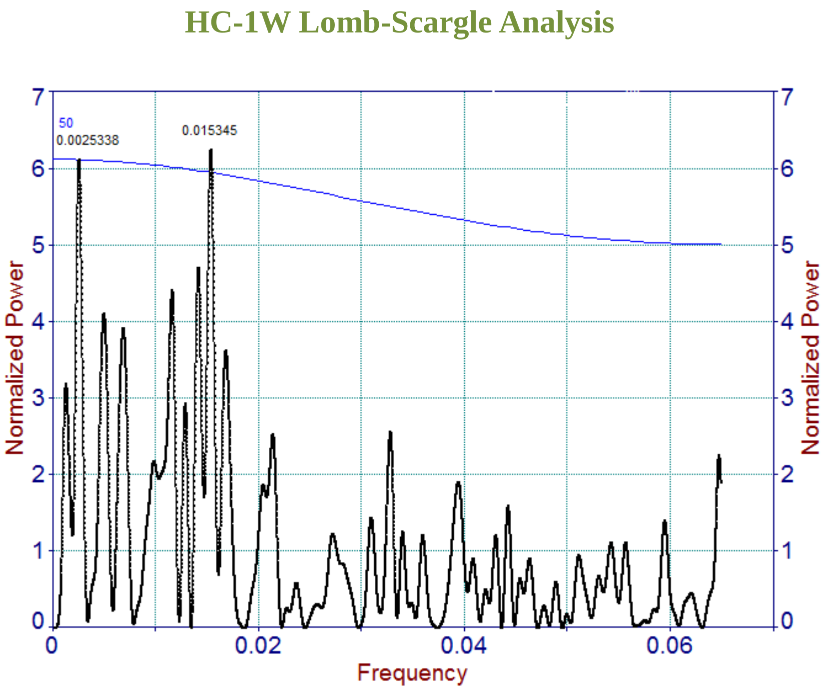


Figure 13: Lomb-Scargle analysis of HC-1W oxygen isotope record. The black curve illustrates the normalized power in the frequency domain. The blue curve is the 50% significance boundary. Two periodic components at frequency 0.0153 and 0.0025 are significant at 50%.

Lomb-Scargle analysis of the HC-1W oxygen isotope record resolved two periodicities that were statistically significant. The significant periodicities occurred at frequencies of 0.0153 (period ~65 yrs), and 0.0025 (period ~400 yrs) (Fig. 13). The later frequency should be considered with skepticism given the relatively short length of time covered by the HC-1W oxygen isotope reconstruction.

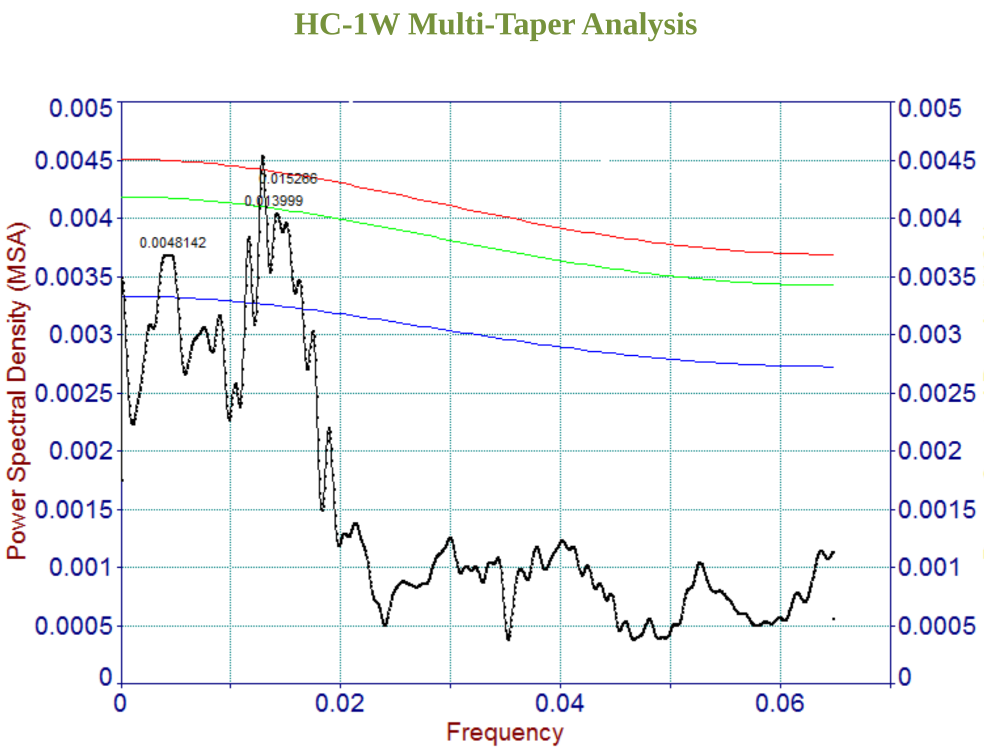


Figure 14: Multi-Taper analysis of HC-1W oxygen isotope record. The black curve illustrates the normalized power in the frequency domain. The blue curve is the 50% significance boundary, the green curve is the 90% significance boundary, and the red curve is the 95% significance boundary. One periodic component at frequency 0.0152 is significant at 95%, one periodic component at frequency 0.0139 is significant at 90% and a unique periodic component at frequency 0.0048 is significant at 50%.

Multi-Taper analysis of the HC-1W oxygen isotope record resolved one periodicity that was statistically significant at the 95% level. This periodicity occurred at a frequency of 0.0152 (period ~65 yrs). Two other periodic components occurred around frequencies of 0.0139 (period ~71 yrs) and 0.0048 (period ~208 yrs); both are significant above the 50% level (Fig. 14).

The periodicity of the HC-1W oxygen isotope record was compared to periodicities of the published records it was compared to. The same time series analysis preformed on the HC-1W oxygen isotope record was performed on the other records to identify their characteristic periodicities (Tab. 2). Conclusions of periodicity from the literature, as well as the results of this time series analysis were used, with the periods derived from this studies analysis taking precedence over significantly different periods in the literature. All periods used were above the 95% confidence interval of their respective records MTM analysis (Tab. 2). The average periodicity used for the PDO in this study was 76-100 years; this was based primarily on this studies' time series analysis of MacDonald and Case's (2005) record, as the periodicity identified by the authors only appears strongly in the most recent portion of their record. The average periodicity for the AMO used in this study was 60-80 years, consistent with an average 70 year quasi-period and ~50-90 year period proposed in the literature (Mann et al. 2009; Enfield et al. 2010), as well as this studies' time series analysis. The average periods used for the NAO were 6, 20, and 40 years respectively; these were taken primarily from this study's time series analysis along with Trouet et al.'s (2009) paper. The average period used for the Cariaco Ti ITCZ record was 450 years; a period of 1000 years was identified above the 95% confidence interval of the Cariaco record as well, but due to the short length of the record, the 1,000 year period was not used for comparison purposes.

Table 2: Calculated and average periods used to compare teleconnections, climate features, and HC-1W oxygen isotope record.

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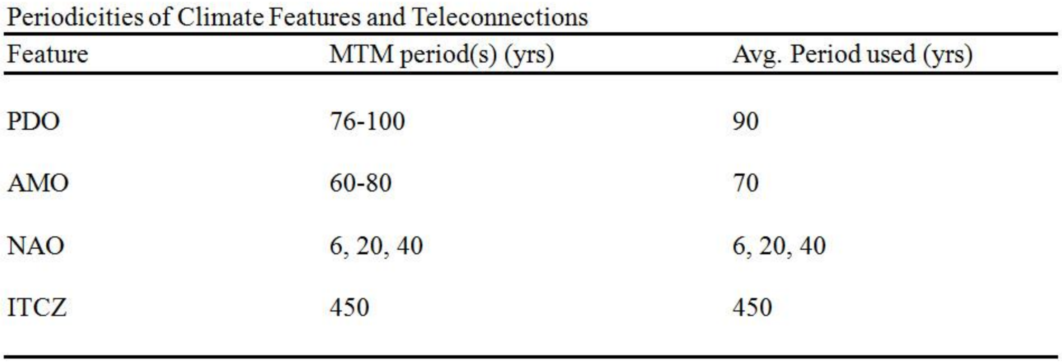

Periodicities of Climate Features and Teleconnections

Feature	MTM period(s) (yrs)	Avg. Period used (yrs)
PDO	76-100	90
AMO	60-80	70
NAO	6, 20, 40	6, 20, 40
ITCZ	450	450

The oxygen isotope ratios derived from HC-1W reasonably represent shifts in rainfall amount on the island of Barbados. While problems with variable kinetic fractionation effects have been noted in speleothem calcite derived from dripwaters in Harrisons cave, sample HC-1W displayed no significant correlation between carbon and oxygen isotope values, dating and sample accumulation modeling suggests that calcite growth rates did not change appreciably over the 1,500 year period in this study, and contemporary monitoring has verified that relative humidity remains above 99.9% year round, and temperature at the site has changed by less than 0.1°C between January 2012 and July 2013. While this suggests strongly that variable kinetic fractionation is not occurring dramatically at the particular sample site HC-1W was taken from, a replication test is forthcoming based on other samples obtained from the island. With consideration of kinetic effects, the patterns of lower δ^{18}O values in the HC-1W record are representative of periods of greater precipitation amounts, while higher δ^{18}O values indicate lower precipitation amounts as per the "amount effect," which is proposed to modulate isotope ratios in precipitation of Barbados, and often dominates the isotopic signal of rainfall in the tropics (Dansgaard 1964; Jones et al. 1996; Jones et al. 2000; Mickler et al. 2004; Mangini et al. 2007; Lachniet 2009)

Examination and comparison of the HC-1W δ^{18}O values reveals an interesting relationship between precipitation amount on the island of Barbados and climate influences of Atlantic origin. The influence of the ITCZ is clearly visible given the ~400 year period identified in the HC-1W oxygen isotope record. While the ~400 year period should be cautiously considered given the short length of this record, it is a decent match to the ITCZ migration period from the Cariaco Ti record, and the influence of the ITCZ on tropical precipitation is robustly supported (Enfield et al. 1999; Alessandra et al. 2000; Haug et al. 2001; Asmerom et al. 2007; Barry and Chorley 2010). While it is no surprise that long tern shifts in the ITCZ affect Barbadian precipitation, the more interesting relationship identified in this study is the strong link between the AMO and Barbadian precipitation. The $\delta^{18}O$ values derived from HC-1W, when compared with Mann et al.'s (2009) reconstruction of the AMO, produces a close match over the Late Holocene period. Slight disagreement between both records occurs only during the Medieval Climate Anomaly (MCA) and Little Ice Age (LIA) events, periods of regionally variable warm/wet and cool/dry conditions, respectively (Thompson 1990; Asmerom et al. 2007; Mann et al. 2009). These brief periods of disagreement aligned with these two climate anomalies suggests a potential overprint of other climatic forcing during these periods, most likely due to the astrophysical variations in solar activity and the Earth's orbit that are believed to have been behind the LIA and MWP events themselves. These results suggest that while the ITCZ may affect precipitation amounts occurring on Barbados on the multicentennial scale, the AMO is dominantly responsible for decadal scale changes in precipitation amount on the island of Barbados. The strong match in both frequency and timing between the HC-1W oxygen isotope record and Mann et al.'s (2009) AMO record suggests a dominant role of the AMO specifically, and Atlantic climate influences broadly, on the variability of precipitation in Barbados. While the physical basis of the AMO has yet to be confirmed definitively, and the teleconnection itself is still under discussion and interpretation regarding its long-term climate influences, this study clearly illustrates precipitation fluctuation concordant with the reconstructed phases of the AMO from Mann et al. (2009). This suggests that not only are shifts in circulation patterns in the Atlantic largely responsible for changes in precipitation amounts in the Eastern Caribbean, but it also provides further evidence that the proposed AMO represents real changes in Atlantic Ocean circulation patterns, and further concerted study should be aimed at solidifying the physical basis of the AMO (Enfield et al. 2001).

The implications from this study in light of anthropogenic and natural climate changes show that the AMO, and North Atlantic conditions, are the primary modulators of decadal precipitation in the region. Potential changes to dynamics in the Atlantic should be modeled and monitored into the future, as these will be the strongest contributors to precipitation change on Barbados on the decadal scale. When this study is viewed in a regional context along with other rainfall reconstructions from the Caribbean region, a consistent influence of the AMO on precipitation amounts can be observed in other regions of the Caribbean (Hetzinger et al. 2008; Fensterer et al. 2012). As the effects of natural and anthropogenic climate change on Atlantic circulation patterns and sea surface temperatures become better understood, so too does the understanding of expected precipitation amounts in the Caribbean region. This study provides a attribution of precipitation amounts on Barbados at the decadal scale, however in order to complete the understanding of precipitation shifts in the eastern Caribbean an improved understanding of the physical basis of the AMO, and a higher resolution reconstruction should be considered as next steps in improving the ability to forecast decadal precipitation shifts and to do the same for annual to sub annual of rainfall patterns in the Eastern Caribbean.

Agencies responsible for resource management in the Eastern Caribbean should include projections of AMO phase and Atlantic sea surface temperature shifts when planning for rainfall and subsequent recharge to island aquifers. Due to the heavily karst nature of Barbados, and the subsequent lack of major surface water bodies particular care should be taken in planning their water use specifically against accurate projections of aquifer recharge. Further research should be aimed at higher resolution studies to tease out the potential annual to sub annual shifts in Barbados' precipitation; attribution will likely be too subtle shifts in Atlantic SST's and circulation activity; however, that remains to be demonstrated at an annual to sub-annual scale thus far.

Chapter 4: Conclusions

This study sought to explore the nature and drivers of precipitation on the island of Barbados over the late Holocene, as well as to expand the proxy information that can be derived from a single speleothem sample. While each of these questions has led to more questions than definitive answers, this study reports dynamic shifts in precipitation on Barbados over the past 1,500 years, which are primarily modulated by the ITCZ at the multicentennial scale, and the AMO at the decadal scale. As the understanding of the AMO improves, it could be feasible to produce a useful predictive model of decadal precipitation patterns in the Eastern Caribbean based on projections of future changes in Atlantic atmospheric and oceanic circulation patterns. More work needs to be done to better understand the physical nature of the AMO, especially given the increasingly clear picture of its wide spread influence in the Caribbean region, a region particularly at risk from adverse effects due to anthropogenic climate change.

While elucidating the decadal and multicentennial drivers of precipitation on Barbados, this study also provides a first step towards a novel method to derive paleohydrologic information from calcite speleothems using Raman spectroscopy to model Mg incorporation into calcite speleothem proxies. Further research and application of Raman spectroscopy to high resolution longitudinal studies of speleothem proxies is warranted given the increasing capabilities of RS systems to resolve independent proxy information from speleothem samples, and the potential to identify particularly extreme changes in the hydrologic system feeding stalagmite dripwaters. With both the potential for high resolution trace magnesium analysis, and potentially as an eventual means to measure oxygen isotope ratios in carbonate speleothems, Raman spectroscopy should be embraced by the speleothem reconstruction community.

Examining the functionality LC-SEM systems in speleothem proxy analysis resulted in a unique method to easily identify detrital materials through BSE imagery and EDS analysis without destructive sample preparation for moderately sized speleothems. While less useful as an independent proxy source in this study, many speleothem samples, especially those including multiple non-carbonate materials (e.g. mud layers from extreme events, pollen, volcanic dust, etc) would benefit even more from using a LC-SEM system in their analyses. While few LC-SEM systems are widely available, increased academic collaboration with private and government facilities housing Large Chamber SEMs for studies of many different types of physical climate proxies can only benefit the quality and integrity of paleoenvironmental reconstructions.

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