2010

LATEST QUATERNARY PALEOCLIMATE RECONSTRUCTION UTILIZING STABLE ISOTOPIC AND TRACE ELEMENT PROXIES IN A STALAGMITE FROM CULVERSON CREEK CAVE, WEST VIRGINIA

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ABSTRACT OF THESIS

LATEST QUATERNARY PALEOCLIMATE RECONSTRUCTION UTILIZING STABLE ISOTOPIC AND TRACE ELEMENT PROXIES IN A STALAGMITE FROM CULVERSON CREEK CAVE, WEST VIRGINIA

A reconstruction of regional climate variability in southern West Virginia that spans the last glacial/interglacial transition is presented. Paleoclimate interpretations obtained from the 50-cm long stalagmite provide key insights regarding the timing, magnitude, and forcing mechanisms responsible for past climate variability. Stable isotopic ($\delta^{18}O$ and $\delta^{13}C$) and trace element (Ba, Sr, Mg) signatures from samples contiguously milled along the growth-axis of a ^{230}Th-dated stalagmite which grew between approximately 20 and 5 thousand years before present (kyr BP) provide critical constraints for above-cave mean annual temperature, seasonality of moisture mean annual precipitation, and potential vegetation shifts. Specifically, the stalagmite record reveals subcentennial-scale variations in the proxy records, and strong multimillennial-scale features that correlate to well-known patterns of sea-surface variability in the North Atlantic Ocean (i.e., Bond cycles). The large-scale glacial/interglacial transition is sufficiently resolved to show that regional climate changes largely paralleled climatic transitions preserved in low-latitude (Chinese monsoon records; Cariaco Basin) and high-latitude (Greenland Ice Sheet) paleo-archives. However, the Younger Dryas interval in the south-central Appalachian Mountains is not as prominent a feature as in other records.

KEYWORDS: Stable Isotopes, Trace Elements, Paleoclimate, Paleohydrology, Karst

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THESIS

A thesis submitted in partial fulfillment of the
requirements for the degree of Master of Science in the
College of Arts and Sciences
at the University of Kentucky

By

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Lexington, Kentucky

Director: Dr. Harold D. Rowe, Assistant Professor of Geology

Lexington, Kentucky

2010

This thesis is dedicated to my grandmother, Nan, for sacrificing her “golden years” to help me get this far and to my son, August, for reminding me why I must continue.

ACKNOWLEDGMENTS

The following thesis benefited from the insights and direction of several people. First, my Thesis Chair, Dr. Harry Rowe, made the thesis possible by providing ongoing direction which included instructive comments and evaluations and by investing both time and personal faith in the research. In addition, Dr. Sue Rimmer brought patience and structure to the research which allowed me to complete this project effectively. Dr. J. Richard Bowersox contributed to the thesis process by providing critical reviews and constructive comments, for which I am grateful .Next, I wish to thank the complete Thesis Committee: Dr. Harry Rowe, Dr. J. Richard Bowersox, and Dr. Edward Woolery. Each individual contributed to the thesis in unique ways, substantially enriching the finished product.

I received equally important assistance from family and friends. My husband, Brian Lee Gilbert, provided on-going support throughout the thesis process along with patience, faith and encouragement. My parents, Madonna and Denver Williams, instilled in me from an early age the desire to obtain the Master's while my late grandmother, Fay Embry, provided the environment which allowed for the maturation of my goals. My brother, Corey Williams, has been quietly, my biggest supporter. In addition, the thesis would not have been possible without the technical assistance provided by my mother-in-law, Wilma Gilbert. Finally, I'd like to thank Dr. Andrew H. Wulff, who showed me what it felt like to aspire to be excellent which led me to strive for excellence in my life.

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1.0 Chapter 1.0 -INTRODUCTION

The overarching purpose of the present study is to demonstrate that the stable isotopic and geochemical records preserved along the growth axes of stalagmite samples from caves in southern West Virginia can be used to infer past climate changes. Throughout the development of the paleoclimate record, the working hypothesis was:

> *Given that high-resolution, low-latitude (i.e., the Cariaco Basin record of Haug et al., 2001) and high-latitude (i.e., the Greenland Ice Sheet Project record of Grootes et al., 1993) records of past global climate change reveal surprising synchrony, it is hypothesized that a mid-latitude paleoclimate record of similar time resolution will possess a high level of synchrony. Furthermore, differences between such records are the product of regional-scale climate variability and/or site-specific responses to environmental change.*

In addition to the above hypothesis, several questions were posed and evaluated:

1) *What was the timing, magnitude, and duration of climate changes in the study region during the period from ~20 to ~5 kyr BP?*
2) *What were the underlying mechanisms responsible for regional climate change?*
3) *Can the suite of analyses and subsequent interpretations provide sufficient foundation to establish an understanding of cave drip*

conditions during full glacial conditions, and are these conditions geochemically and isotopically distinct from interglacial and mild glacial conditions?

4) *What were environmental conditions (precipitation, temperature, soil cover) like during the following time periods?: Last Glacial Maximum, Heinrich Event 1, Bøling-Allerød, Younger Dryas, Pre-Boreal, early and middle Holocene?*
5) *Can the lead up to the middle Holocene warming (i.e., Holocene Climatic Optimum or Hypsithermal Episode) assist in defining how the modern climate might evolve under greenhouse warming conditions?*

The results and discussion portions of the thesis addresses the overarching hypothesis and the five questions in order to provide a more complete understanding of 1) past climate change in the south-central Appalachian region of eastern North America, and 2) how regional climate change is associated with larger-scale (global) climate shifts that have been inferred from other paleoarchives.

The remainder of the introduction focuses on 1) developing an understanding of how calcite cave deposits have been utilized to reconstruct climate and environmental change, and 2) developing an understanding of other records of global climate change that will ultimately be used to interpret and temporally relate the stalagmite record produced in this study.

1.1 Section 1.1-Speleothem Geochemistry Background

The forcing mechanisms behind climate variability on human timescales (years to centuries) remain elusive, and as such, the development of highly-resolved paleorecords is increasingly important in order to 1) validate predictive efforts put forth by the climate modeling community (Sundqvist et al., 2007), and 2) provide an understanding of the background climate variability on a planet that is, and will be, undergoing enhanced, anthropogenic-induced greenhouse warming (Rosenzweig et al., 2007). Geochemical and stable isotopic records preserved in *speleothems* – the generic term given to cave formations such as stalagmites, stalactites and flowstones (Hill and Forti, 1997), may provide critical evidence to evaluate climate forcing mechanisms in the past, including the intensity and duration of their associated climate shifts. Their occurrence in karstified regions of the planet, their ability to be precisely and accurately dated using radiometric methods, and their capacity for passively recording environmental shifts associated with changes in hydrology make speleothems, and specifically stalagmites, unique recorders of paleoclimate variability (i.e., Vaks et al., 2003; Fairchild et al., 2005).

1.1.1 $\delta^{18}O$ of Stalagmite Calcite

The oxygen isotopic signature preserved in speleothem calcite has been used to estimate relative changes in mean annual temperature during stalagmite growth (Dorale et al., 1998). The relationship between mean annual $\delta^{18}O$ of precipitation and mean annual air temperature is estimated to be ~0.6 ‰/°C

(Dansgaard, 1964; Friedman et al., 1977), thus speleothem calcite that grows in oxygen isotopic equilibrium with cave drip waters under stable ambient conditions has traditionally been inferred to preserve the mean annual air temperature (Moore and Sullivan, 1978). Assuming no or minimal kinetic effects, the equilibrium fractionation factor between calcite and water (-0.26 ‰/°C; O'Neil and Epstein, 1966) must still be considered when reconstructing above-cave air temperatures. The equilibrium isotopic offset must be added to the 0.6 ‰/°C, yielding a net linkage between $\delta^{18}O$ of mean annual precipitation and mean annual air temperature of ~0.35 ‰/°C (Dorale et al., 1998). Based upon new and developing research, the $\delta^{18}O$ signature of speleothem calcite is also linked to seasonality of moisture (Rowe, et al. in review). A poorly ventilated area far from a cave entrance is believed to provide the best environment for recording above-cave environmental changes (i.e., air temperature, precipitation, biogeochemical responses) and guarding against unwanted cave influences, in particular, evaporation and cave temperature variability, which induce kinetic fractionation of the stable isotopes (i.e., Mickler et al., 2006).

1.1.2 $\delta^{13}C$ of Stalagmite Calcite

Down-axis variations in the carbon isotopic composition of speleothems have been used to infer changes in above-cave vegetation during the growth of the speleothem because cave drip waters first pass through the overlying soil, inheriting the stable isotopic characteristics of soil zone respiration (Dorale et al., 1998; Baker et al; 1998; Denniston et al., 1999) While a significant portion of geochemical modification of meteoric waters occurs in the soil zone, the subcutaneous zone—the zone directly beneath the soil--is also responsible for altering water chemistry before it reaches the drip site in a cave (Williams, 1983).

CO_2 concentrations in the atmosphere seem to be traceable by plant communities (Williams et al., 2002). There is a -2.0+/- 0.1 ‰ change in the $\delta^{13}C$ of plants for every 100 ppm increase in atmospheric CO_2 (Feng and Epstein, 1995; Hatte' et al., 2001 and Williams et al., 2002). The relative influences of C_3 (more depleted in ^{13}C) and C_4 (less depleted in ^{13}C) vegetation potentially define the $\delta^{13}C$ composition of soil zone dissolved inorganic carbon; however, the amount of carbon derived from bedrock materials in the subcutaneous zone also greatly influences the carbon isotopic composition of waters, along with CO_2 in the atmosphere and production of biogenic CO_2. Dreybrodt (1980) defined a relationship between $\delta^{13}C$ and vegetation type such that carbonate isotope values of $\delta^{13}C$ ranging from -14 to -6 ‰ are typical of C_3 vegetation and values of $\delta^{13}C$ ranging from -6 to +2‰ are typical of C_4 vegetation. Without additional information, (i.e., trace element concentrations), it is difficult to define the relative influences contributing to the carbon isotopic composition of speleothem calcite (Williams et al., 2002). Similarly, a decrease in soil zone respiration may be linked to a depletion in the $\delta^{13}C$ signature and an increase in soil zone respiration may be linked to an enrichment of the $\delta^{13}C$ signature.

1.1.3 Trace Element Geochemistry of Stalagmite Calcite

Trace element analysis of speleothem calcite has proved useful for constraining hydrological variability in the epikarst zone above the drip-water site (Baker et al., 1997; Fairchild et al., 2001; Finch et al., 2001). More specifically, it is believed that speleothem trace element concentrations typically vary as a function of water-residence time in, and the overall solubility and biogeochemical activity of, the epikarst zone (i.e., Williams, 2008), which is here divided into the overlying soil and underlying subcutaneous zones. Storage in the soil and subcutaneous zones is determined by epikarst thickness, pore space, hydrologic head, and permeability/transmissibility. For the purpose of interpreting speleothem-based geochemical transects as records of paleoclimate change, one must initially make the assumption that epikarst characteristics, with the exception of the amount and timing of water through-flow, are invariant. Together, stable isotopic and trace element compositions of speleothem calcite constitute powerful tools for reconstructing regional paleohydrology and paleoclimate, and establishing linkages to global paleoclimate records.

1.2 Section 1.2- Global Paleoclimate Background

Records of paleoclimate variability spanning at least the last 20,000 years have been developed from multiple paleoarchives (i.e., ice-cores, marine/lacustrine sediments, speleothems) across all continents and ocean basins. However, there are only a handful of paleoarchives that preserve both long, continuous records, and records of sufficiently high resolution, defined here as subcentennial-scale resolution (i.e., resolving climate changes that occur at timescales less than a century). Developing paleorecords that preserve subcentennial-scale variability are critical because 1) they describe conditions at or near the timescales of human activity and response (years, decades), and 2) many of the climate mechanisms and oscillations of specific interest to climate modelers and climate-change experts occur at subcentennial timescales.

1.2.1 Ice- Cores

Atmospheric gasses which have homogeneously mixed at the global scale are often trapped in bubbles within ice (Sowers et al., 1995), and thus serve as a record of atmospheric chemistry. Paleorecords developed from ice-cores are of particular importance because the multiple isotopic and geochemical signatures preserved within the ice can be used to infer large-scale changes in atmospheric chemistry, circulation, and temperature (Alley, 2000). For understanding high-latitude paleoclimates spanning the last ~110,000 years, the Greenland Ice Sheet Project (GISP-2) (Figure 1.1) ice-core $\delta^{18}O$ record represents the most accepted reconstruction of atmospheric temperature (Grootes et al.,1993; Alley, 2000), showing highly variable late Pleistocene temperature fluctuations followed by relatively stable Holocene conditions. Some ice cores preserve annual layers which are able to be counted in order to determine an absolute age chronology (Alley et al., 1997; Thompson et al., 1998). However, ice flow may compact and disrupt layers previously deposited in which case, additional lines of evidence are needed to discern ice core chronology (Alley et al., 1995; Chappellaz et al., 1997). Radiometric dating is utilized in cores with sufficient material (i.e., Alley, 2000).

The down-core stable oxygen isotopic composition of ice has been used as a proxy record for atmospheric paleotemperature through time (Jouzel et al., 1997; Alley, 2000; Fluckiger et al., 2008). In addition to atmospheric gas concentrations and the isotopic composition of ice, climatic changes may also be inferred using aerosol concentrations within the ice (i.e., De Angelis et al., 1987; Biscaye et al., 1997) helping to not only correlate ages but also to reflect atmospheric composition during the time of deposition (Chappellaz et al., 1997; Anklin et al., 1997).

Changes in the formation of the North Atlantic Deep Water (NADW) are thought to account for some of the more defined climatic events in the ice core records with some shifts as dramatic as 8°C (Severinghaus et al., 1997; Severinghaus et al., 1998). Two dramatic climatic changes are shown by the Younger Dryas and the 8200 year event which are evidenced in the Greenland Ice-Core (Chapellaz et al., 1993).

Bond et al. (2001) proposed climatic forcing derived from solar output at centennial to millennial resolution which provides for advance of ice into the Northern Atlantic (Bond et al., 2001) on a Holocene “1500 year cycle”. This study of climate variability in the North Atlantic region provides insights to climatic instability throughout the Holocene. An earlier documentation provides further insights into climatic oscillations based upon $\delta^{18}O$ of Greenland ice which record Dansgaard-Oeschger cycles representing millennial timescale shifts of temperature (Bond et al., 1993). Each Dansgaard-Oeschger cycle is terminated by a Heinrich event (i.e., times of sea-surface cooling marked by ice-rafted carbonate debris) indicative of rapid and abrupt oceanic temperature changes, decadal in nature (Bond et al., 1992; Bond et al., 1993).

1.2.2 Marine Sediments

Marine sediments preserve records of paleoclimate variability, and more specifically, records of paleoceanographic variability (i.e., variability in sea-surface temperature, salinity, chemistry, sediment transport). However, due to generally low sedimentation rates, and the effects of bioturbation, most marine records do not preserve subcentennial-scale paleoceanographic variability. Fortunately, for understanding low-latitude (tropical) paleoclimate changes over the last glacial/interglacial cycle, the Cariaco Basin marine sediment record possesses a relatively high level of temporal resolution (subcentennial-scale resolution during the last 14,000 years) (Peterson et al., 2000; Haug et al., 2001; Hughen et al., 2004). The Cariaco Basin record is in a class of its own with regard to resolution and length of record, largely because of its unique environment of deposition, an isolated basin on the continental shelf of northern Venezuela (Figure 1.1) (Schubert, 1982; Dean and Piper, 1999).

The last 14.5 thousand years of Cariaco Basin sedimentation shows seasonal patterns of deposition which are preserved due to anoxic bottom waters (Peterson et al., 1991; Hughen et al., 1996; Haug et al., 2001). Resolution of the record is about 4 to 5 years. The geochemical record consists of down-core concentrations of Fe and Ti which are thought to reflect changes in terrigenous sediment input and thus, river volume and precipitation amounts with lack of diagenetic control (Peterson et al., 2000; Haug et al., 2001). Haug et al. (2001) have interpreted down-core changes in bulk geochemistry of the Cariaco Basin sediments to reflect changes in the latitudinal position if the Inter-Tropical Convergence Zone (ITCZ) (Haug et al., 2001). The ITCZ represents the zone of confluence of the southern and northern trade winds, and is marked by low pressure and high precipitation (Peterson and Haug, 2006).

Peterson and Haug (2006) provide evidence to suggest that when north Atlantic sea-surface temperatures are below-average, detrital input from nearby rivers is below-average—indicating that the ITCZ is anomalously to the south of its average position. Similarly, when the north Atlantic sea surface temperature is above-average, an increase in detrital material is observed, indicative of a more northerly location of the ITCZ. It is believed that the input of terrestrial detritus provides a more definitive history of ITCZ movements than does reconstruction of past upwelling and biological input as has been previously documented.

A recent contribution by LoDico and others (2006) illustrates decadal- to centennial-scale climatic change from about 10.5 kyr BP to 7 kyr BP in the Gulf of Mexico (GOM) (Figure 1.1) with an overall warming of about 1.5 ^{0}C and six major climatic oscillations. This is documented with Mg/Ca, $\delta^{18}O_{calcite}$ (which in this study is utilized as a proxy for temperature) and inferred $\delta^{18}O_{sw}$ (a function of ice volume and salinity) by utilizing foraminifera calcite. The 8200 year event which signifies a dramatic climatic cooling is evidenced in this record by a change in salinity and biotic communities preceded by major freshwater input from about 8.6 kyr BP to 8.3 kyr BP (LoDico et al., 2006). Another freshwater input is evidenced by planktonic foraminifera as melt water from the Laurentide ice sheet between 14 kyr BP and 10.2 kyr BP (Poore et al., 2003). The GOM reached optimum temperatures between 9 kyr BP and 7 kyr BP although low latitudes show this warming earlier. This may be explained by a lingering influence of the Laurentide Ice Sheet affecting the continent of North America during the early Holocene. (Mitchell et al., 1988).

A correlation to the Cariaco Basin and the ITCZ position may be evidenced by the movement of Caribbean waters into the GOM. The ITCZ moves north of the equator during the North American Summer, an effect of which is the transport of moisture into northern Mexico and the southwestern United States (i.e., the North American Monsoon) (Poore et al., 2003). The maximum movement of Caribbean waters into the GOM occurred between 6.5 kyr BP and 4.5 kyr BP (Poore et al., 2003).

1.2.3 China Speleothems

For understanding subtropical to mid-latitude climate variability, the speleothem records from the monsoon-sensitive regions (China and Oman) have yielded the most highly-resolved paleoclimate reconstructions, and they correlate with the GISP-2 record (Wang et al., 2001; Fleitmann et al., 2003). Speleothem $\delta^{18}O$ records from Hulu Cave and Dongge Cave, China (Figure 1.2), document changes in East Asian Monsoon intensity, which has been attributed to changes in solar insolation, shifts in sea level and internal climatic circulation (Wang et al., 2001). Asian Monsoons are important heat and moisture transporters from the Western Pacific Warm Pool (WPWP) to the northern hemisphere. Indian Ocean Monsoon (IOM) records reveal that increasing air temperatures in the northern Atlantic region correlate with an increase in IOM precipitation and that a decrease in monsoon precipitation correlates with cooling events recorded in the GISP-2 ice-core (Neff et al., 2001; Fleitmann et al., 2003). The Q5 speleothem record from Fleitmann et al. (2003) obtained from Qunf Cave is unique because it reveals that the transport of heat and moisture to higher latitudes by the IOM is variable, and that it is dictated by glacial boundaries. This comparative study suggests that modern precipitation in the northern tropics is affected by the weakening of monsoons on a global scale, the driving force of which is summer insolation (Fleitmann et al. 2003).

Wang and others (2001) document a Pleistocene record of paleoclimate from Hulu Cave, China, resembling Greenland ice-core records, implying that East Asian Monsoon intensity was dictated by the same processes dictating Greenland temperatures. Changes in the NADW (or changing heat transport to the Atlantic) have been used to explain shifts in the Greenland temperature and paleoclimatic changes (Broeker, 1994*).* Atmospheric and oceanic circulation as well as solar insolation may be responsible for the observable paleoclimate changes in the Hulu Cave record (Porter and An, 1995).

Dongge Cave, China, is located 1200 Km to the WSW of Hulu Cave (Yuan et al. 2004). The Dongge record is important as it is also affected by the Asian

Monsoon and is longer than is the Hulu Cave record. Like the Hulu Cave record, however, Dongge speleothems record variations in paleoclimate and precipitation which correspond to the temperature changes reflected in the Northern hemisphere as has been preserved in the Greenland Ice Core records.

1.3 Section 1.3- Brief Geologic Setting and the Regi onal Late Quaternary Paleoclimate Record of the South-Central Appalachians

Speleothem CCC-001 was recovered from Culverson Creek Cave, located in Greenbrier County, West Virginia (Figure 1.3). The cave is formed in the Mississippian-age Greenbrier Limestone, named for its exposure along the Greenbrier River. The limestone is massive, dark gray-blue, containing chert, and is characterized by abundant caves, underground streams and other karst-related features and also contains many ox-bow river channels (Springer et al., 2003). The Greenbrier Limestone is exposed from southern Pennsylvania to Maryland, Virginia and West Virginia. Wynn and Read (2006) illustrate the extent of shallow-water carbonates with siliclastic units in the Greenbrier limestone, and provide a detailed stratigraphic column of regional extent, determined by well cuttings.

A study conducted at Colonial Acres Cave, West Virginia (Figure 1.3), utilized stable isotope climate data from a stalagmite collected in Buckeye Creek Cave located in the Greenbrier watershed (Springer et al., in review). Buckeye Creek Cave is located 10 Km NE of Culverson Creek Cave., Stable carbon and oxygen isotopes obtained from the stalagmite reveal regional climatic changes that occurred during the last ~7000 years (Springer et al., in review). Mid to late Holocene temperatures, interpreted from published pollen data, were warmer and drier relative to the rest of the record during a time that $\delta^{18}O$ of stalagmite BCC-002 were heavy. For the purposes of this study, $\delta^{18}O$ was assumed to reflect past changes in above-cave air temperature and that $\delta^{13}C$ of calcite largely reflected floral and soil composition, productivity and moisture (Kirby et al., 2002; McDermott, 2004).

A study conducted at Buckeye Creek Cave, West Virginia utilized a stalagmite, BCC-002 to reveal six centennial scale droughts in the study region (Springer et al., 2008). Buckeye Creek Cave, 10 Km NE of Culverson Creek Cave, is affected by low level jets and moist air masses from the Gulf of Mexico and is sensitive to the North/South contrast of pressure over the Northern and Eastern Atlantic Ocean. Droughts were believed to be caused by a weakening of moisture transport over the North Atlantic in response to the cooling of the Pacific and Atlantic Oceans. Geochemical proxies for drought were $\delta^{13}C$ and Sr/Ca, or the amount of water/rock interaction and relative moisture abundance in the overlying soils. The geochemical proxies were more depleted when the region was moist and less depleted when dry due to an increase/decrease in soil zone respiration. (Springer et al., 2008). This study links the relationship of moisture transport from the North Atlantic to the Gulf of Mexico.

Chapter One Figures

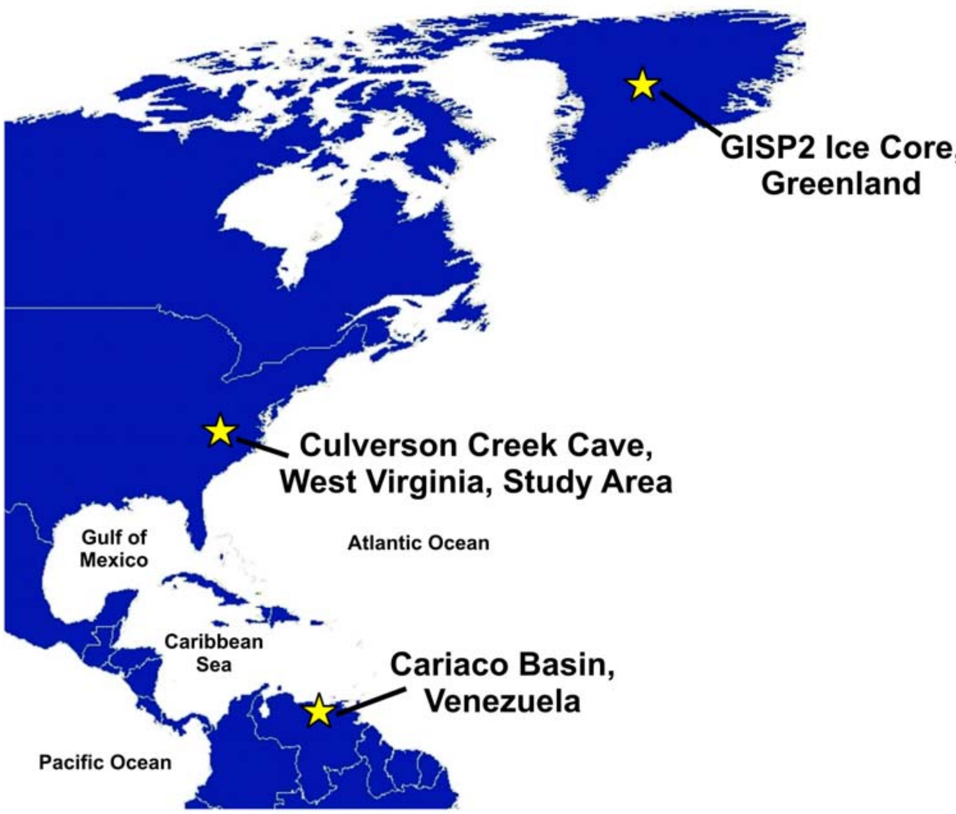

Figure 1.1- Location Map for GISP2 (Greenland), Culverson Creek Cave (West Virginia-US), the Gulf of Mexico and the Cariaco Basin (Venezuela). J. Richard Bowersox, 2010.

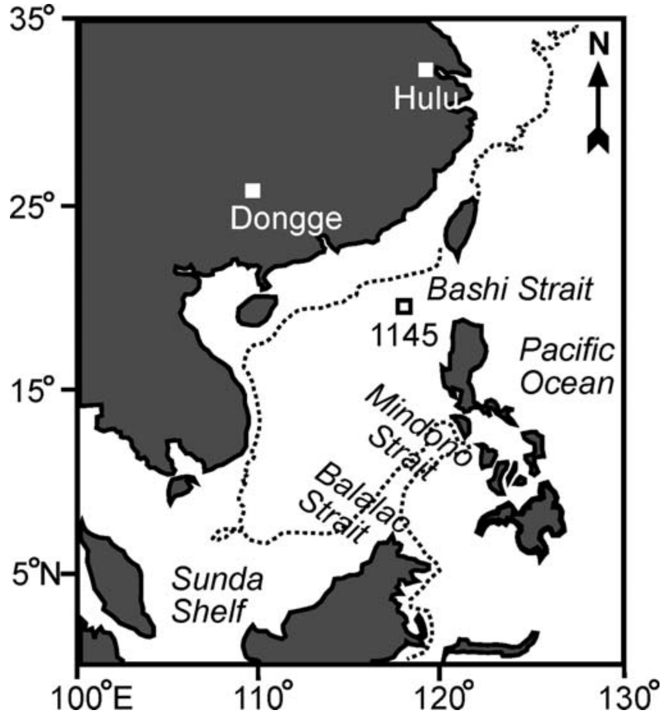

Figure 1.2- Location Map of Hulu and Dongge Caves, China
GSA Publications

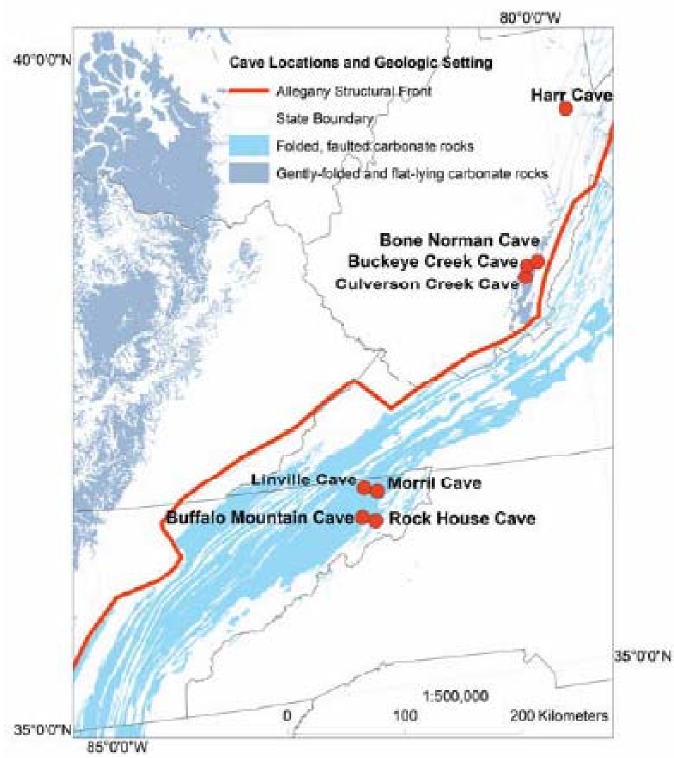

Figure 1.3- Location Map of Culverson Creek Cave and Buckeye Creek Caves, West Virginia (Rowe et al., 2008).

2.0 Chapter 2.0- METHODS

2.1 Section 2.1-Collection, Preparation, and Sampling

CCC-001 was collected from Culverson Creek Cave, Greenbrier County, West Virginia. While the speleothem was wet during collection, subsequent ^{230}Th-dating revealed that growth ceased ~5500 years BP. The speleothem was deposited in a chamber less than 10 m below the surface and >0.5 km away from the entrance. The stalagmite is 50 cm in length, and its dense, white/tan-colored calcite is fibrous (Figure 2.1). The speleothem was wet-sawed perpendicular to the growth axis with a continuous-rimmed diamond blade and polished with a hand-held, water-spray polisher. The speleothem was sampled contiguously at a 0.5-mm resolution along the central growth axis using a hand held milling tool (DREMEL, 400-XPR) equipped with a dental burr (Brasseler USA, Lot #12050, US#1/4). Sample powders were stored in labeled micro-centrifuge tubes.

2.2 Section 2.2- Stable Isotopic Analysis

Sample powders were weighed (range = 370-450 μg) using a Sartorius microbalance and individual weighed samples were placed into LABCO Exetainer vials. The sealed Exetainers were helium-purged, manually acidified using phosphoric acid, and equilibrated at 50ºC for 12 hours. Samples were analyzed using a GasBench II with GC-PAL auto-sampler and Delta*Plus* XP ThermoFinnigan isotope ratio mass spectrometer (IRMS). Isotopic values (δ^{13}C and δ^{18}O) were standardized using NBS-19. Approximately 3% of the dataset was analyzed in duplicate. For the period of analysis, the average standard and unknown measurement precisions were 0.03‰ and 0.09‰ for $\delta^{13}C$ and $\delta^{18}O$, respectively. Isotopic values are expressed in per mil (‰) according to the following equations:

$$\delta^{13}C = [((^{13}C/^{12}C)_{SAMPLE} - (^{13}C/^{12}C)_{STANDARD}) / (^{13}C/^{12}C)_{STANDARD}] \times 1000$$

$$\delta^{18}O = [((^{18}O/^{16}O)_{SAMPLE} - (^{18}O/^{16}O)_{STANDARD}) / (^{18}O/^{16}O)_{STANDARD}] \times 1000$$

2.3 Section 2.3- Trace Element Analysis

Sample powders were weighed using a Sartorius microbalance (range = 1.400-1.600 mg) and transferred into polycarbonate test tubes, to which 3 ml of 5% nitric acid were pipetted. The tubes were shaken using a vortex shaker immediately after acidification, and again twelve hours later, just prior to ICP-OES (inductively-coupled plasma optical emission spectrometer) analysis. Mixed element ICP-OES calibration standards (Ca, Mg, Ba, Sr) were created using calibrated single element standards (CPI, Inc.). All samples were analyzed using a Thermo JarrelAsh Corporation IRIS Advantage ICP-OES with auto-sampler, under the following conditions:

Flow: 2.03 ml/min

RF Power: 1150 watts

Polypro Nebulizer flow rate: 0.75 l/min (Argon gas)

Auxiliary gas cooling: 1 l/min (liquid Nitrogen).

Emission wavelengths used: Ca (430.253 nm), Ba (493.408 nm), Mg (279.553 nm), Sr (421.552 nm

2.4 Section 2.4- Geochronology of Stalagmite CCC-001

The geochronology of CCC-001 is based on 14 age estimations determined using the ^{230}Th radiometric dating technique (Edwards et al., 1987). The calcite powder drilled with carbide dental burrs was dissolved in nitric acid, mixed with a $^{229}Th/^{233}U/^{236}U$ tracer and then dried down. An iron chloride solution was added, followed by NH_4OH until the iron precipitated. The supernatant was decanted. Columns containing anion resin were utilized to separate the Th and U. HCl was added to elute the Th and water to elute the U. Each separated sample was dried down and dilute nitric acid was added.

An inductively coupled plasma spectrometer at the University of Minnesota was utilized for analysis of the samples. The instrument was operated at low resolution and in electrostatic peak hopping mode. Combined ionization plus transmission efficiency of 2.5 to 3% was measured for uranium and 1.5 to 2% was measured for thorium (Dykoski et al., 2005) Error on ages +/-100 years.

Chapter Two Figures

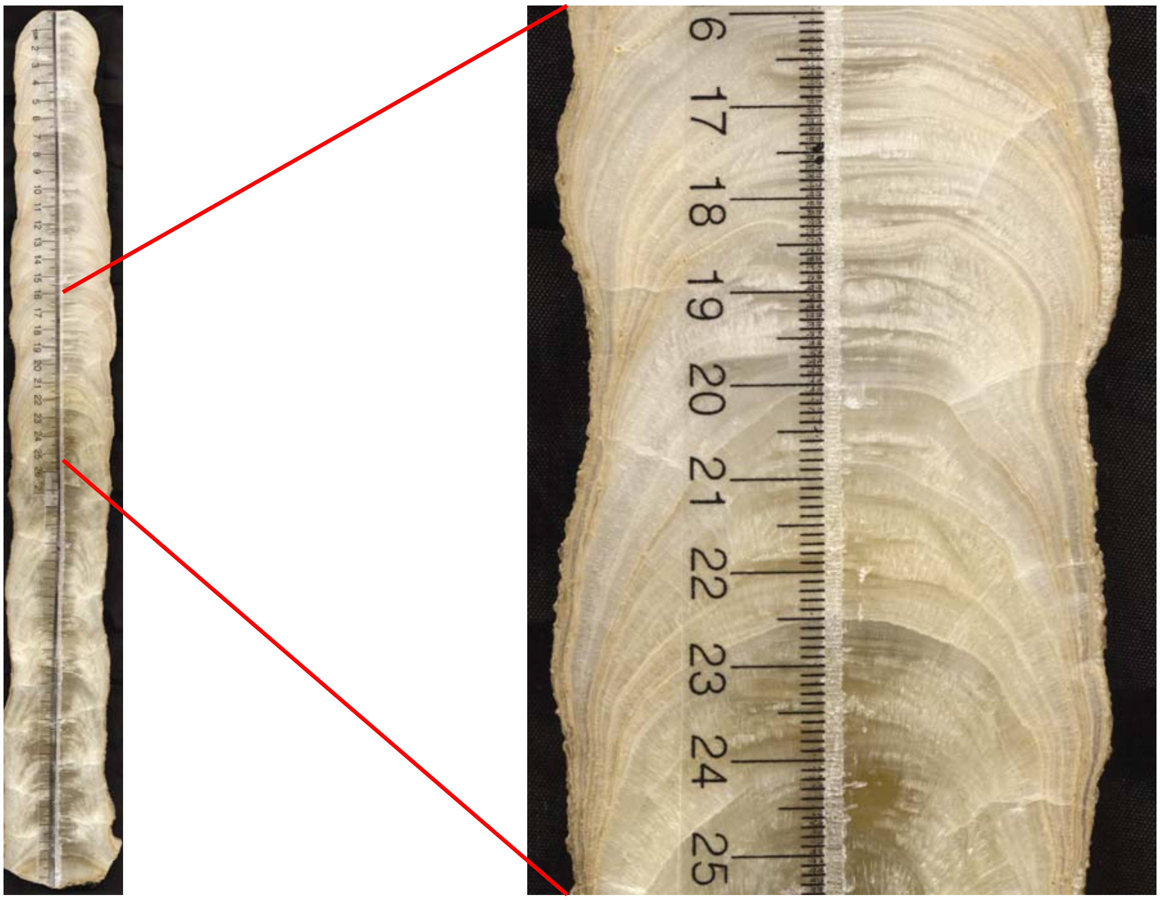

Figure 2.1- Speleothem CCC-001. 50 cm, milled at 0.5 mm resolution. Enlarged to show detail.

3.0 Chapter 3.0-RESULTS

3.1 Section 3.1- CCC-001 $\delta^{18}O$ Record

From the beginning of the record at ~20 kyr BP, through 12 kyr BP, $\delta^{18}O$ ranges from -6.0‰ to -3.5‰, an overall range of 2.5‰. The record exhibits a decreasing trend during this interval, punctuated by six major episodes of enrichment/depletion (Figure 3.1 A-K). A depletion of 1.5‰ occurred gradually at 19 kyr BP, followed by an abrupt 1.5‰ enrichment at 18 kyr BP (Figure 3.1 A-C). At 17 kyr BP, a gradual 2‰ depletion is followed by two gradual 1.5‰ depletions before another 1.5‰ shift toward more negative values at about 15.5 kyr BP (Figure 3.1 D-G). The 2‰ enrichment in $\delta^{18}O$ between 14.5 and 13 kyr BP initiated at an abrupt increase in speleothem growth (Figure 3.1 H-J). Another 2‰ depletion and immediate 2‰ enrichment followed until approximately 12 kyr BP. (Figure 3.1 J-K).

Between 12 kyr BP and 5.5 kyr BP, when growth ceased, $\delta^{18}O$ values range from -5.7‰ to -4.2‰, an overall change of 1.5‰. Six major episodes are observed during this interval (Figure 3.1 L-W). Between 12 and 11 kyr BP an abrupt 1‰ depletion, followed by a more gradual 1.25‰ enrichment occurred, with a subsequent ~0.8‰ depletion (Figure 3.1 L-N). At about 11.5 to 10.8 kyr BP, a 1‰ enrichment is detectible, then at about 10.8 kyr BP a 1‰ enrichment occurred followed by a gradual decrease of 1‰ until just before 9.2 kyr BP (Figure 3.1 O-Q). At 9.2 kyr BP an abrupt 1.5‰ depletion occurred (Figure 3.1 R). At 8.4 kyr BP growth rate quickened and a gradual 1‰ depletion is observed

(Figure 3.1 S-T). At about 8 kyr BP the growth rate of CCC-001 was constant with fewer major isotopic shifts observable with the exception of a 0.8‰ depletion at 6400 years BP, recovering gradually at about 6200 years BP(Figure 3.1 U-V). At about 6600 yrs BP the growth rate of CCC-001 quickened. While the isotopic signature of the sample remained relatively constant, the deposition was remarkably faster. The speleothem remained inactive after ~5.5 kyr BP. (Figure 3.1 W)

3.2 Section 3.2- CCC-001 δ^{13}C Record

From 20 to 12 kyr BP δ^{13}C ranges from -6.8‰ to -0.5‰, an overall range of 6.3‰. In general, there is a decreasing trend in δ^{13}C during this interval, with six major episodes approximating the δ^{18}O signature but which can be farther divided into seventeen climatic events on a regional scale (Figure 3.1 column 2). At about 18.5 kyr BP a 0.5‰ depletion and subsequent recovery is observed before becoming depleted by 4.5‰ at 18.2 kyr BP and abruptly recovering only 2.5‰ at about 17.8 kyr BP. At 17.8 kyr BP a depletion of 2.5‰ occurred, denoted by a series of three abrupt events before gradually becoming enriched by about 4.5‰ at around 15.9 kyr BP. At 15 kyr BP, δ^{13}C became more enriched and growth rate increased. At about 14 kyr BP, a gradual enrichment of about 1‰ occurred and remained relatively constant until 12 kyr BP. (Figure 3.1 Column 2)

At 12 kyr BP δ^{13}C became more enriched overall, with values ranging from -5.5‰ to -3.0‰, an overall range of 2.5‰ (Figure 3.1 column 2). This trend is observable until about 8.4 kyr BP when an abrupt depletion of about 2‰

occurred, followed by a more gradual decrease. and an enrichment from 8.4 kyr BP until 8.0 kyr BP. From 8.0 kyr BP until cessation of growth at ~5.5 kyr BP, $\delta^{13}C$ decreased overall, though the signal was considerably more stable than the previous ~13 kyr. (Figure 3.1 column 2)

3.3 Section 3.3- Trace Element (Mg, Sr and Ba) Record

Between 20 kyr BP and the cessation of speleothem growth, Mg was increasing overall with a range of about 8000 ppm. The record illustrates a large and abrupt increase in Mg at 17 kyr BP and again at 16 kyr BP, Values increase gradually until 8 kyr BP, then increase more dramatically until the cessation of speleothem growth (Figure 3.1 column 3).

Between 20 kyr BP and the cessation of speleothem growth, Sr was increasing overall with a range of about 900 ppm. Values increased until about 17 kyr BP and then began decreasing through 11 kyr BP. At 12 kyr BP an abrupt increase is observed which ended at about 11 kyr BP, after which the record was more constant and less oscillatory until 10 kyr BP. At 8 kyr BP, the record began to increase more dramatically with more oscillatory patterns and did so until the cessation of speleothem growth. (Figure 3.1 column 4)

Between 20 kyr BP and the cessation of speleothem growth, Ba was increasing overall with a range of about 60 ppt. Ba was increasing until 17 kyr BP, then began to gradually decrease until about 14 kyr BP. At 14 kyr BP the values increased abruptly, very gradually decreased until 11 kyr BP and then began to increase until about 8000 years BP. At 8000 years BP, the record became more constant, though still increasing, and remained this way until the end of the record (Figure 3.1 column 5).

Chapter three figures

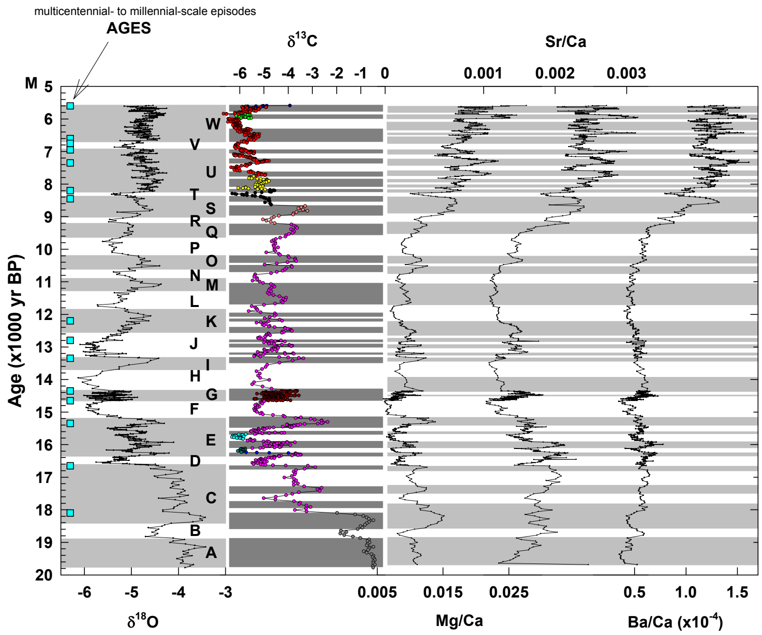

Figure 3.1- Multicentennial to millennial-scale episodes as recorded in CCC-001 and reflected in $\delta^{18}O$, $\delta^{13}C$ and trace elements Mg, Sr and Ba.

4.0 Chapter 4.0- Discussion

4.1Section 4.1- Combining the records

The $\delta^{13}C$ record has been subdivided into three distinct phases of $\delta^{13}C$ signatures (Figure 4.1). The first grouping from 20-18 kyrs BP may be termed "Post Glacial Vegetation Renewal Phase" (PGVR). From 20 to 18 kyrs BP, $\delta^{13}C$ is elevated relative to the rest of the CCC-001 record. One large depletion of approximately 1 ‰ is noticeable just after 17 kyrs BP. Trace elements were lower but gradually increasing over the 2 kyr period. This 2 kyr set of data is representative of a late-transitional phase coming out of the LGM. $\delta^{13}C$ was elevated as photosynthetic pathways were not being utilized. The lack of vegetation in the region due to glacial advances (resulting in less moisture availability) left the $\delta^{13}C$ signature primarily dependent upon carbon enriched bedrock leeching. Trace elements were in direct agreement, lowered due to the lack of soil zone respiration/lack of plant communities due to insufficient moisture.

A second grouping spanning from about 18 to 8.3 kyrs BP may be termed the "Vegetation Oscillation Phase" (V-O). From 18 to 15 kyrs BP, $\delta^{13}C$ decreased about 3-4 ‰ (fluctuating) with approximately 500 year quasi-periodic oscillations. Trace elements roughly co-vary with $\delta^{13}C$, indicative that controls on trace elements also controlled $\delta^{13}C$. It is hypothesized that during this interval conditions were warmer and possibly dryer, increasing the residence time of trace elements in the soil zone and allowing for more defined oscillations in direct co-variance with $\delta^{13}C$. Based upon these records, soil zone respiration during this interval oscillated at about a 500 year quasi-periodic cycle between an increase/decrease vegetation abundance.

From about 15 to 8.3 kyrs BP, the quasi periodic vegetation shifting continued, but with lesser intensities. The $\delta^{13}C$ signatures became more enriched. Trace elements, however, became less oscillatory and no longer co-varied with the intensity of the previous millennia. Drip rate was quickened and the trend was increasing overall. When compared to the $\delta^{18}O$ signature, which was stable to slightly increasing, it is plausible to conclude that while temperatures increased and warm season moisture moved into the region, less trees and shrubbery dominated the landscape. Trace elements ceased co-variance because as more moisture became readily available, leeching of the groundmass was kept at a minimum and waters were pushed through the epikarst zone more quickly.

A third phase which may be termed the Vegetation Stabilization Phase (V-S) is evidenced from about 8.3 to 5.5 kyrs BP. Just prior to the 8.2 kyr event, the $\delta^{18}O$ signature began to decrease and then to drop rapidly, when referencing the. Similarly, during the same time interval, the $\delta^{13}C$ record shows a dramatic and rapid depletion. It is during this time that vegetation in the region stabilized and became less oscillatory. While temperatures recovered from the 8.2 kyr event, the recovery for vegetation was more gradual and the aridity resultant of these shifts is seen in the trace elements data. The trace elements data is very oscillatory during this phase and varies inversely with $\delta^{13}C$. It is hypothesized that the trace elements signature is at this point, was less dependent upon vegetation, but rather on the stable temperatures of the mid-Holocene which allow waters to pass through the epikarst and record more sensitively, fluctuations in biogenic activity.

4.2 *Section 4.2- Correlation of major clim atic episodes with timing, m agnitude and dura tion evidenced in the CCC-001 record.*

Stalagmite CCC-001 shows features similar to deglacial features observed in both Greenland and China (Figure 4.2). This confirms that the relationship between Asian monsoons and Greenland temperature is maintained throughout the deglacial sequence (Dykoski et al., 2005; Cheng et al., 2009) and also that the climatic changes are present in the eastern United States.

The entire $\delta^{18}O$ record of CCC-001 shows more variability than does the GISP2 record. The trace element records co-vary with $\delta^{18}O$ and vary inversely with $\delta^{13}C$. These episodes correlate with Greenland (GISP 2) and China within dating error as follows: The first episode occurred at approximately 16.8 kyrs BP with an increase in $\delta^{18}O$ in the GISP2 record. CCC-001 recorded this event with a 2‰ increase in $\delta^{18}O$, a 1‰ increase in $\delta^{13}C$, a spike in trace elements, and an increased growth rate before rapidly becoming depleted in $\delta^{18}O$ by about 1.5‰ , and in $\delta^{13}C$ by about 1‰ .The episode spanned a period of about 750 years. The episode is also evidenced in the $\delta^{18}O$ records of the China speleothems, though with a more gradual enrichment/depletion than what is shown in both the GISP2 and CCC-001 records. This event at 16.8 kyrs BP is likely Heinrich event 1(Bond et al., 1992). Heinrich events are times of sea-surface cooling marked by ice-rafted carbonate debris indicative of rapid and abrupt oceanic temperature changes, decadal in nature (Hulbe, 2010). However, another episode which overlaps or perhaps encompasses Heinrich event 1 is evidenced especially in the CCC-001 record and is termed the “Mystery Interval” or “Weak Monsoon Interval” (Cheng et al., 2006 and Denton et al., 2006).

The third episode occurred at about 14.5 kyrs BP in the GISP2, China speleothems and CCC-001 record. This event is also recorded in the Cariaco Basin Ti records (Figure 4.4). (Note: The Cariaco Basin sediment record, for purposes of this study, has been represented separately from the GISP2 and China speleothem records because while global events are able to be correlated, the record does not begin until approximately 14.0 kyrs BP which is after the end of the Mystery Interval, documentable in the other paleoclimate proxy records.Also, the Cariaco Basin sediment record correlates to regional events evidenced in CCC-001.) The 2‰ enrichment in $\delta^{18}O$ and 1‰ enrichment in $\delta^{13}C$ between 14.5 and 13 kyr BP followed an abrupt increase in speleothem growth at about 15.0 kyrs BP, during the Mystery Interval. This event, decidedly, the Böling-Allerod, led into the

Younger Dryas. The Younger Dryas was marked by an abrupt decrease or depletion in $\delta^{18}O$ of about 2 ‰, lasting less than 500 years in the CCC-001 record. The episode however, is not marked in the $\delta^{13}C$ or trace element records. China speleothems reflect a marked depletion in $\delta^{18}O$ during this time. At approximately 11.5 kyrs BP, or the end of the Younger Dryas, $\delta^{18}O$ in both the

GISP2 and China records were depleted along with the Cariaco Basin Ti deposits. In the CCC-001 record, however, $\delta^{18}O$ was gradually becoming more enriched. This is not reflected in the $\delta^{13}C$ or trace element records of CCC-001. While this signature was not as prevalent in the eastern United States as in higher latitudes, the Younger Dryas event is none the less evident in the $\delta^{18}O$ record of CCC-001.

At about 11.5 kyrs BP, an episode which was approximately 700 years in duration is reflected in CCC-001 along with the proxy records. $\delta^{18}O$ gradually increased with about 1‰ enrichment. $\delta^{13}C$ varied inversely with $\delta^{18}O$ and trace element signatures were relatively stable during this time. This episode has been termed the “Pre-Boreal” (Andreev and Klimanov, 1999).

At approximately 9200 years BP a brief yet dramatic depletion in $\delta^{18}O$ in the China records , the Cariaco Basin and in CCC-001 is evidenced. This event is reflected in $\delta^{13}C$ as well as trace element records in CCC-001.

Finally, a brief, yet abrupt event at 8200 years BP is evidenced in all four records, including a 2‰ depletion in $\delta^{13}C$ and trace element abundance for CCC-001. The $\delta^{18}O$ signature in CCC-001 reflects this excursion with a 1 ‰ enrichment just prior to the episode marked in the GISP2 core. The China speleothems also show an increased growth rate during this time (Cheng et.al, 2009).

Immediately following the Pre-Boreal period reflected in CCC-001, is a steady but gradual increase in all data through the cessation of speleothem growth. This reflects the Holocene Thermal Maximum or Hypisthermal.

4.3 Section 4.3- Non-correlative major climatic episodes with timing, magnitude and duration evidenced in the CCC-001 record (regionally evidenced).

CCC-001 shows at least six significant climatic episodes between 19.0 kyrs BP and the cessation of speleothem growth (Figure 4.3). The first of these episodes occurred at about 18.8 kyrs BP with a dramatic decrease in $\delta^{18}O$ of 1.5‰ lasting about 500 years. This episode is also reflected in the $\delta^{13}C$ record with a depletion of 4.5 ‰ and trace element records, though less dramatically and with a duration of less than 500 years. The second episode took place in the CCC-001 $\delta^{18}O$ record at about 18.0 kyrs BP. The episode shows two depletions in $\delta^{18}O$ of about 1‰ and a depletion in $\delta^{13}C$ of about 1.5 ‰ with only a slight decrease in trace element ppm. A third episode occurred at about 10.6 kyrs BP with an increase of about 1‰ in $\delta^{18}O$ followed by a decrease of the same magnitude. $\delta^{13}C$ was less variable while trace elements were gradually increasing. Between the 9.2 and 8.2 kyr events, an enrichment of $\delta^{18}O$ and $\delta^{13}C$ occurred followed by an abrupt depletion in $\delta^{13}C$. Trace elements were gradually increasing. An episode following the 8.2 kyr event is shown by fluctuating $\delta^{13}C$ which correlates with three dramatic depletions/enrichments in trace elements. The time frame encompassed from about 6.6 kyrs BP until the cessation of speleothem growth shows an increase in growth rate, gradually increasing $\delta^{13}C$ values and fluctuating trace element ppm. Note that all regional events, uncorrelated with the GISP2 and China Speleothem records are reflected in the Cariaco Basin Ti record.

4.4 Section 4.4- *Underlying mechanisms responsible for regional climate change*

Regional climate change is evidenced in the speleothem isotope record by down axis variations in $\delta^{13}C$. It is widely accepted that changes in this isotopic signature reflects above cave vegetation during the deposition of the speleothem calcite which is infiltrated into the system by way of slightly acidic ground water passing through the soil zone. The soil zone is of key importance to the given isotopic signature as it is here that microbial respiration occurs and causes the subsequent break down of organic materials comprising the soil zone. It is this signature which is recorded in the calcite $\delta^{13}C$ of speleothem CCC-001. It is speculated that other mechanisms governing the $\delta^{13}C$ signature preserved in speleothem calcite is also a function of water residence time in the epikarst zone. Given a long residence time, the isotopic signature of bedrock material may be incorporated into the groundwater and deposited into the speleothem. Degassing of groundwaters and degassing between stalactite and stalagmite may also affect the $\delta^{13}C$ signature recorded (Baker et al., 1997).

The Gulf of Mexico provides moisture to North America, particularly to the study region of West Virginia (LoDico et al., 2006). A change in the currents of the Gulf of Mexico (i.e. moving of Caribbean waters into the region) also affects air temperature over the study region, in turn affects vegetation and finally soil zone respiration, responsible for the $\delta^{13}C$ signature preserved in speleothem calcite from Culverson Creek Cave. Aharon (2003) illustrates post-glacial meltwater flooding events in the GOM which roughly correspond to signals recorded during the growth of speleothem CCC-001 (Figure 4.5). The Laurentide ice sheet has also been speculated to have played an important role in regional climate, along with the positioning of the ITCZ, widely known to be recorded in the sediments of the Cariaco Basin by way of Ti. All regional climatic events evidenced in the CCC-001 record correlate with the Ti sediment record of the Cariaco Basin. Therefore, it is plausible to speculate that factors affecting the Cariaco Basin climate also affect the climate in West Virginia and the study region. Meltwater flooding events also correlate to the regional events correlated in CCC-001 to the Cariaco Basin. Therefore, it is believed that an influx of meltwater into the GOM affects both the Eastern United States and the northern shelf of Venezuela.

While it has been suggested that shifts in $\delta^{13}C$ may be interpreted as oscillatory C_3/C_4 vegetation, there is no evidence that C_4 vegetation existed in West Virginia during the growth of speleothem CCC-001 (Watts, 1979). For purposes of this study, the $\delta^{13}C$ signature is interpreted to reflect more or less biogenic respiration. The trace element signatures are interpreted to reflect wet/dry conditions. When co-variance is seen among the records is it assumed that controls governing the two are one in the same. When the signatures vary inversely, it is assumed that what controls the one does not control the other. A factor which may affect these signatures is bedrock leeching (in reference to drought/cold aridity) which is a function of moisture availabili.

4.5 Section 4.5- *Cave drip conditions evidenced by growth rate*

Growth rate of CCC-001 between about 19 and 16.5 kyrs BP was minimal, yet constant at about 0.01mm/yr. At 16.5 kyrs BP at Heinrich Event 1,growth rate increased to about 0.05mm/yr and remained constant until 15.0 kyrs BP when a dramatic increase in growth of 0.15mm/yr briefly occurred. Growth decreased to about 0.08mm/yr and was constant until about 14.0 kyrs BP. At 14.0 kyrs BP, growth decreased to 0.01mm/yr. During the Younger Dryas, growth was taking place at about 0.03mm/yr. until about 12.0kyrs BP when it returned to 0.01mm/yr and remained throughout the 9.2 kyr event. Near the 8.2 kyr event, growth rate increased to 0.05mm/yr and then again at about 7.3 kyrs BP to 0.08mm/yr. A brief, but dramatic decrease in growth is evidenced at around 6.6 kyrs BP, preceding an increase to 0.95mm/yr at 6.5 kyrs BP until the cessation of speleothem growth. (Figure 4.6).

It does not seem as though growth rate was affected by enrichments or depletions in the isotopic or trace element records. For example, during the Pre-Boreal and the 9200 year growth rate was constant. Heinrich Event 1 and the Younger Dryas are both marked by a decrease in growth rate and the 8.2 kyr event is marked by an increase. Therefore, either drip conditions were affected by sources other than climatic oscillations or growth rate of the speleothem was affected by sources other than drip conditions. Calcite deposition is dictated by not only the infiltration rate of CO_2 saturated waters , but also on the amount of available CO_2 in the soil zone, the variables of temperature and aridity, the amount of water-rock interaction, the amount of biogenic activity in the soil zone and the CO_2 of the cave atmosphere (Sundqvist et al., 2007).

Despite changes in growth rate, growth was continuous throughout the deposition of the speleothem. While several cold events in the CCC-001 record are evidenced, full glacial conditions are not observable before the last glacial maximum (LGM) at about 21 kyrs BP, which is beyond the scope of this climate record. Therefore, based upon this suite of analysis it is difficult to determine that glacial verses interglacial conditions are isotopically or geochemically distinct. The record of CCC-001 began at about 19.8 kyrs BP. Prior to this date conditions were too arid for calcite precipitation. The enriched $\delta^{18}O$ and $\delta^{13}C$ records are characteristic of a signature coming out of a full glacial sequence, or in this case, the LGM. Due to a lack of infiltrating waters, an increase in isotopic values is achieved. Lower than expected trace elements data is evidence of a lack in soil zone respiration, another line of evidence for a declining glacial maximum in the eastern United States.

Typically, trace element records indicative of drought, stay in the epikarst zone longer than in wetter conditions. The lack of water infiltrating the system is a direct cause for a longer residence time which gives the opportunity for continued leeching of Sr, Mg and Ba and thus, enrich the ppm of the trace elements record. The opposite affect is observable when conditions are wetter and residence time in the epikarst is abbreviated. More waters are flushed through the system, giving little time for ground mass leeching of trace elements and thus, reflect a lowered or more depleted trace elements signature in the subsequent calcium carbonate deposition. It should also be noted that many of the drip rates recorded may be less constrained than is plausible due to a lack of age determinations. Given better age constraints at crucial intervals of the record, better drip conditions more specifically observed in correlation with climatic fluctuations may be labeled. In referencing proxy records, however, a geochemical and isotopic distinction does seem to be prevalent between glacial and interglacial times. For the CCC-001 record, it is assumed that glacial and interglacial signatures are geochemically distinct and that cold events similar in nature to glacial cycles are discernable based upon those parameters, such as the 8.2 and 9.2 kyr events.

Based upon this distinction in proxy records and the trace element record seen in CCC-001, several inferences can be made about the climatic fluctuations between approximately 20 and 5.5 kyrs BP. For example, when coming out of the 8.2 kyr event and also the 9.2 kyr event, there was an increase in drip rate. It is speculated that a lowered trace elements signature during these intervals should be observable, contingent on the fact that no other outside influences were obscuring the data such as a lack of soil zone respiration due to ice/temperature conditions or a lack of vegetation above the cave.

At about 6.5 kyrs BP an increase in drip rate is observable in the CCC-001 record until the cessation of speleothem growth. The $\delta^{18}O$ record is relatively stable reflecting a lack of a temperature increase. Given this signature alone the climatic record from 6.5 kyrs BP on is of no consequence. However, considering the $\delta^{13}C$ record, which shows a gradual increase toward less negative values, a shift toward increased vegetation and lowered trace element ppm, it is hypothesized that this region was being affected by the North American Monsoon (Poore et al., 2003) which brings warm air and moisture to the Western United States and to Mexico. Poore et al. (2003) shows evidence of warm Caribbean waters moving into the Gulf of Mexico at approximately 4.5 to 6.5 kyrs BP. Is it plausible and possible, that this increase in moisture was also affecting the eastern United States, particularly affecting vegetation and moisture. There are three rhythmic spikes in the trace elements data, perhaps indicative of a very sensitive adjustment to warm season moisture as evidenced by soil zone respiration in the epikarst zone. Meltwater pulses, while correlative to most climatic events on both a regional and global scale, do not seem to affect the growth rate of speleothem CCC-001.

4.6 Section 4.6- *Environmental Conditions (p recipitation, tem perature, soil cover) during significant climatic time periods:* "The Story of CCC-001"

Based upon the climate record of CCC-001 and of the proxy records, climate over the last 20 kyrs has been varied and fluctuating between periods of wet, warm/dry warm and wet, cold/dry, cold conditions. Multiple inferences based upon $\delta^{18}O$, $\delta^{13}C$ and trace elements in the CCC-001 record and Ti fluctuations, planktonic foraminifera records and monsoon intensity from proxy records, make it possible to reconstruct environmental conditions throughout the study region.

Prior to 19.8 kyrs BP, climatic conditions were too cold and arid for the infiltration of CO_2 saturated waters, but rather remained locked away in the cold atmosphere and soil zone. At 19.8 kyrs BP in the study region of West Virginia in the Eastern United States, the climate had recovered enough from the cold of the LGM to begin the slow precipitation of calcium carbonate into the form of what would eventually become the stalagmite, CCC-001. Vegetation and soil cover were recovering as well, soil zone respiration was minimal and yielded an elevated $\delta^{13}C$ and lowered trace elements record.

At about 19 kyrs BP the eastern United States was affected by a cooling which was not recovered from for 1000 years. At 18 kyrs BP, the local temperature raised to equal temperatures 1000 years prior. This fluctuation of $\delta^{18}O$ may be a result of oscillating winter/summer precipitation.

From 18 kyrs up to Heinrich event 1, at 16.5 kyr BP the climate fluctuated around a warm/cool cycle. Precipitation was minimal.

Culverson Creek Cave was not alone in the climatic event of Heinrich event 1. As temperatures shifted cooler/ winter precipitation increased in the eastern United States, similar shifts were seen in the high northern, southern and middle latitudes as ice rafted carbonate debris was taxied into the ocean, propagated by the plummeting temperatures over about a 200 year time frame. It would take another 200 years for temperatures to recover to that of pre-Heinrich event temperatures. Vegetation shifted twice and trace elements dropped significantly in response to vegetation swings. Soil cover and precipitation were both minimal in the study region. The Heinrich event 1 was encompassed in the

“Mystery Interval”, for purposes of this study lying within Vegetation Oscillation Stage B_1, which is characterized overall by warmer and dryer conditions with the exception of Heinrich Event 1. Heinrich Event 1 allows for part of the quasi-periodic shifts observed in the record.

Directly following Heinrich event 1, the Böling-Allerod hit the study region and the rest of the world. As far north as Greenland, temperatures were rising/summer precipitation was increasing, China Monsoon intensity was increasing, and in the study region temperatures/summer precipitation increased, vegetation shifted and trace element ppm increased in response to these changes. In the study region, however, the B-A appears to have been of lesser intensity in the study region assuming age interpolation to be accurate. Precipitation increased during this time as well.

The Younger Dryas was another climate episode seen world-wide. From about 13 to 11.5 kyrs BP, monsoon intensity decreased in China and temperatures plummeted in Greenland. In the study region, however, the Younger Dryas was, like the B-A, less intense in the study region, assuming age interpolation accuracy. The YD in the United States reflected only a 1‰ shift in $\delta^{18}O$. Vegetation was barely affected, trace elements seemed unresponsive and precipitation was relatively unchanged by the climatic episode. It is difficult to speculate the cause for such an abbreviated YD, as it is otherwise recognized in climate reconstructions world-wide.

In direct contrast to the YD, the Pre-Boreal appeared in the CCC-001 record with intensity. Temperatures spiked/summer precipitation increased, soil cover increased and precipitation was increased as determined by drip rate. In other regions of the world, the Pre-Boreal was reflected by an increase in temperatures and an increase in monsoon intensity.

The early Holocene (10 kyrs to about 6.8 kyrs BP), though relatively stable in comparison to the rest of the CCC-001 record, was marked by two climatic oscillations, the 8.2 and 9.2 kyr events. These events were each approximately 1 century in duration and were characterized by dropping temperatures/increase in winter precipitation and a soil cover which was depleted in trace elements, $\delta^{13}C$ and $\delta^{18}O$.

From about 6.8 kyrs BP to the cessation of speleothem growth at ~5.5 kyr BP, middle Holocene temperatures stabilized overall with an increase in the oscillatory nature of trace elements (see Figure 4.5). This, coupled with an increased growth rate during this interval, may signify the North American Monsoon and the affect it had on the study region.

4.7 Section 4.7- *Can the lead up to the m iddle Holocene warming assist in defining how the modern climate m ight evolve under greenhouse war ming conditions* (Jansen et al., 2007)*?*

The middle Holocene Hypisthermal which began about 6.8 kyrs BP in the study region, was preceded by two climatic shifts, the 8.2 and 9.2 kyr BP events. These events were very abrupt and represented a dramatic shift in temperature/increase in winter precipitation in only about 100 years. The rest of the lead up to the Holocene Hypisthermal was relatively stable in comparison to these events. Can events such as these be expected in the course of the modern climate's evolution and what caused these shifts? What is the vegetative response to shifts such as these and is the global ppm of CO_2 reflected in these records? These are the questions which need to be addressed in order to fully evaluate the modern evolution of the climate system. It is unknown if events such as the 8.2 and 9.2 kyr BP events are a possibility in the modern climatic system. However, in examining the CCC-001 climate record, the period just before these events took place was characterized by a generally increasing trend in temperatures/increase in summer precipitation and an elevation in trace elements, interpreted here as a function of drought. The vegetation and soil cover response to these events was such that as temperatures began to fall the $\delta^{13}C$ record shifted as well. According to Williams et al. (2004) CO_2 is linked to $\delta^{13}C$ by 2‰. For every 100 ppm increase in CO_2, there is a 2‰ depletion in $\delta^{13}C$ (Williams et al., 2004). The CCC-001 record does not reflect this shift during the time interval of the climatic events. A cold event would imply the storage of atmospheric CO_2, and would reflect in the record as an enrichment of $\delta^{13}C$ rather than the depletion that is recorded. In this case then, it is difficult to speculate about relative abundances of atmospheric CO_2. Furthermore, perhaps the more pressing question is, what caused the Hypisthermal warming to originally initiate, especially after such dramatic temperature drops in the preceding centuries? The answer to this question remains elusive at this time.

CO_2 fluctuations in pre-industrial times were significantly smaller than the modern industrial era and were probably caused by natural events and processes. Today's level of CO_2 ppm in the atmosphere is about 380, whereas it did not exceed 300 ppm in the last 650 kyrs, according to ice-core data. While Antarctic temperature increases/decreases show a strong relationship with CO_2 increases/decreases, Antarctic temperatures begin to increase centuries before CO_2 ppm does. Based upon this fact alone, it seems plausible to assume that atmospheric CO_2 and other greenhouse gasses do not trigger climatic warming in themselves. Furthermore, while glacial/interglacial CO_2 variations have heightened climate fluctuations, glacial terminations were not caused by CO_2 variations. Hypothetically, if CO_2 fluctuations did not cause glacial terminations it is also plausible to assume that it did not initiate them. Before the time period in question of the middle Holocene Hypisthermal, a global warming took place just after the LGM of about 4-7^{o}C. This warming occurred 10 times more slowly than the warming of the modern climate system (Jansen et al., 2007).

Based upon the above referenced material a conundrum evolves in the question of climate change: Does CO_2 increases cause climate change or does climate change cause increasing CO_2? Given this problem, a second question, perhaps the most pressing evolves: Does anthropogenic, industrial era CO_2 increases threaten to affect our current and stable temperature? It is important to note that based upon Milankovich cycles, it is not expected that our current climatic state is due to enter an ice age for about another 30 kyrs (Jansen et al., 2007).

It is a well accepted fact that greenhouse gasses such as CO_2 trapped in the atmosphere increase the amount of heat which is contained (IPCC, 2007). This trapped heat in turn causes atmospheric temperatures to rise. A rise in atmospheric temperatures causes a release of more CO_2 from the oceans and from global ice volume. When a cooling event is initiated, be it by climate forcing or a change in oceanic circulation, the CO_2 is again stored. Anthropogenic forced increases in the amount of emitted CO_2 will generate a warming trend due to an enhanced greenhouse effect. Whether this is a trend which is significant enough to jumpstart a climate change is a question yet to be answered. For the purposes of this study, modern climate change is beyond the scope of this work as the CCC-001 record expired at about 5.5 kyrs BP. In answer to the over arching question at hand, it is unlikely that the lead up to the middle Holocene Hypsithermal Episode can assist in defining how the modern climate might evolve under greenhouse warming conditions. The climate system of the mid-Holocene Hypisthermal was not being affected by industrialization or anthropogenic activity which is a serious variable when considering the modern day increases in CO_2 as have not been recorded in over 650 kyrs. Negating anthropogenic practices, the variables which affect climatic signatures and thus, climate oscillations themselves are numerous, as has been exemplified by this study. Considering the multitude of variables, coupled with the addition of anthropogenic practices and industrialization along with the stability of the Holocene climate, not present throughout the previous sections of the CCC-001 record, it is not plausible to use the lead up to the mid-Holocene Hypisthermal as a proxy or predictor for future climate change. Also, based upon current and evolving research which shows that the $\delta^{18}O$ signature of speleothem calcite may be linked more closely to seasonality of moisture rather than to air temperature, the accuracy of past temperature based climate reconstructions may be in question (Rowe et al., in review). The lead up to the mid-Holocene Hypisthermal is however, the only viable point of reference for estimating climatic conditions under greenhouse warming conditions.

Chapter 4 Graphics

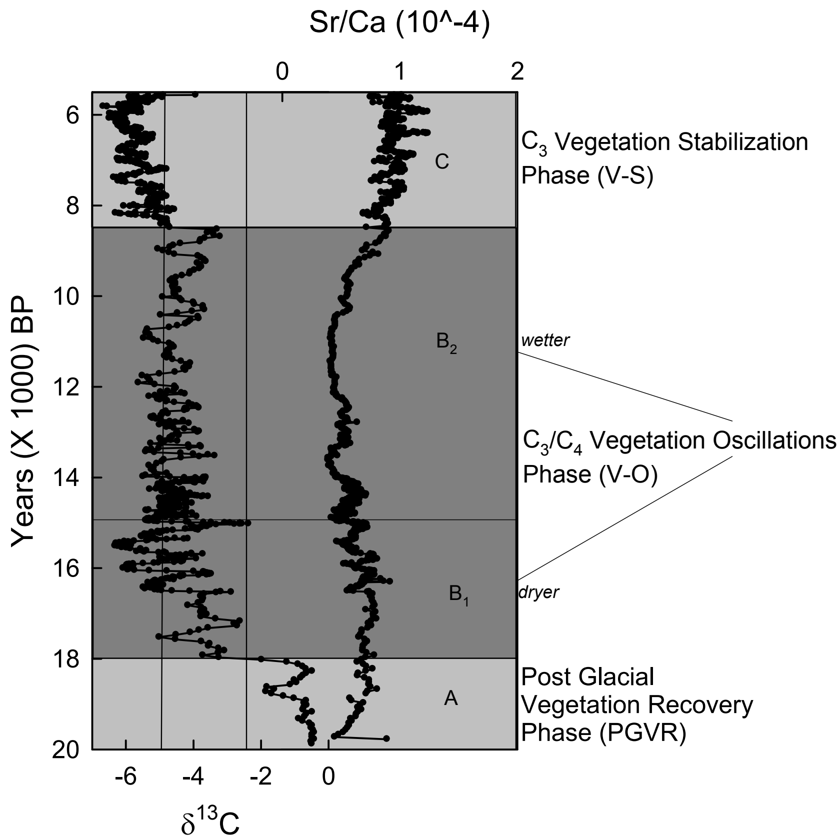

Figure 4.1 A- Post Glacial Vegetation Renewal Phase characterized by elevated $\delta^{13}C$ and lower trace element signatures. Record indicates coldness and aridity during this interval.

B1- Vegetation Oscillations Phase characterized by quasi-periodic vegetation shifts (increase/decrease in veg) and warm, dry conditions.

B2- Vegetation Oscillations Phase characterized by quasi-periodic vegetation shifts (increase/decrease in veg) and increasing warmth with moisture.

C- Vegetation Stabilization Phase characterized by continuous vegetation abundance, warming temperatures and varying trace elements

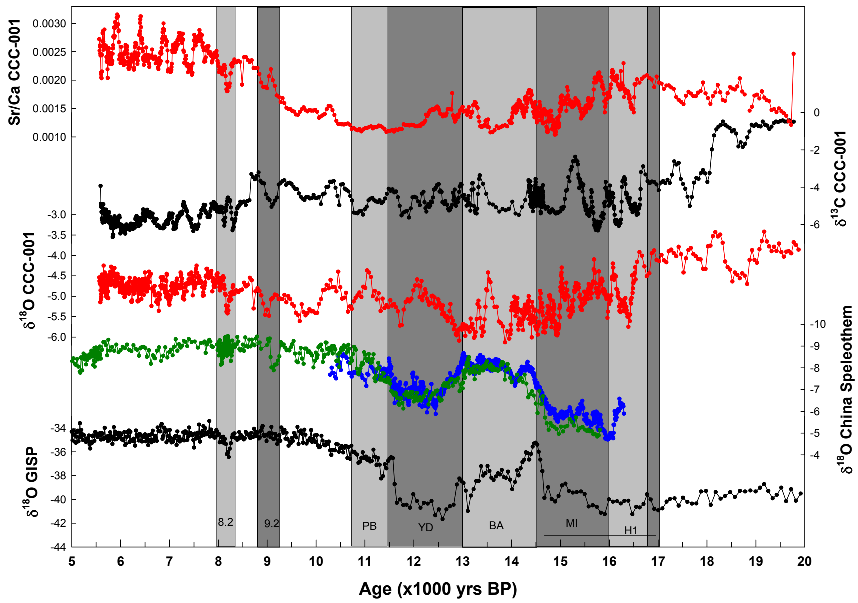

Figure 4.2- Climatic episodes correlated in the CCC-001 δ^{18}O, δ^{13}C and trace element records with episodes documented on a global scale by proxy records.

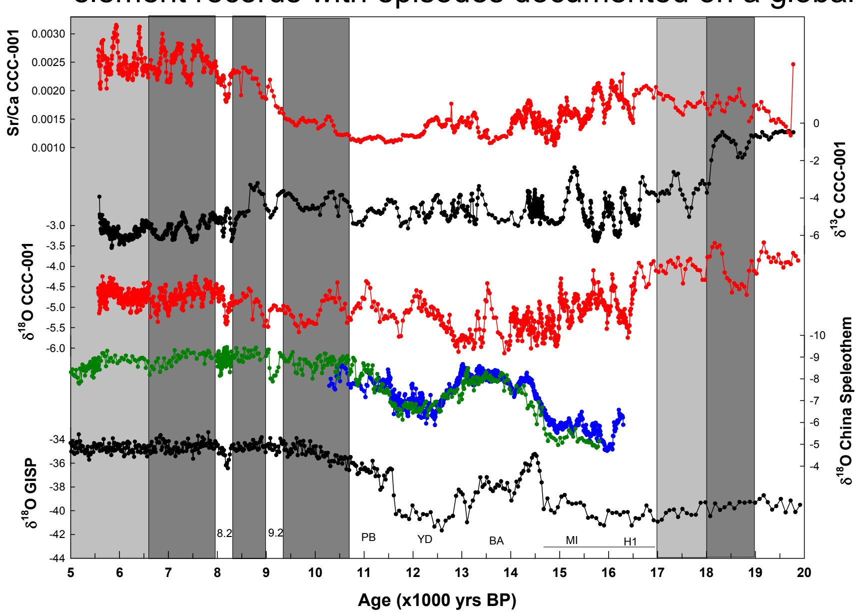

Figure 4.3- Climatic episodes correlated in the CCC-001 δ^{18}O, δ^{13}C and trace element records with episodes documented on a global scale by proxy records.

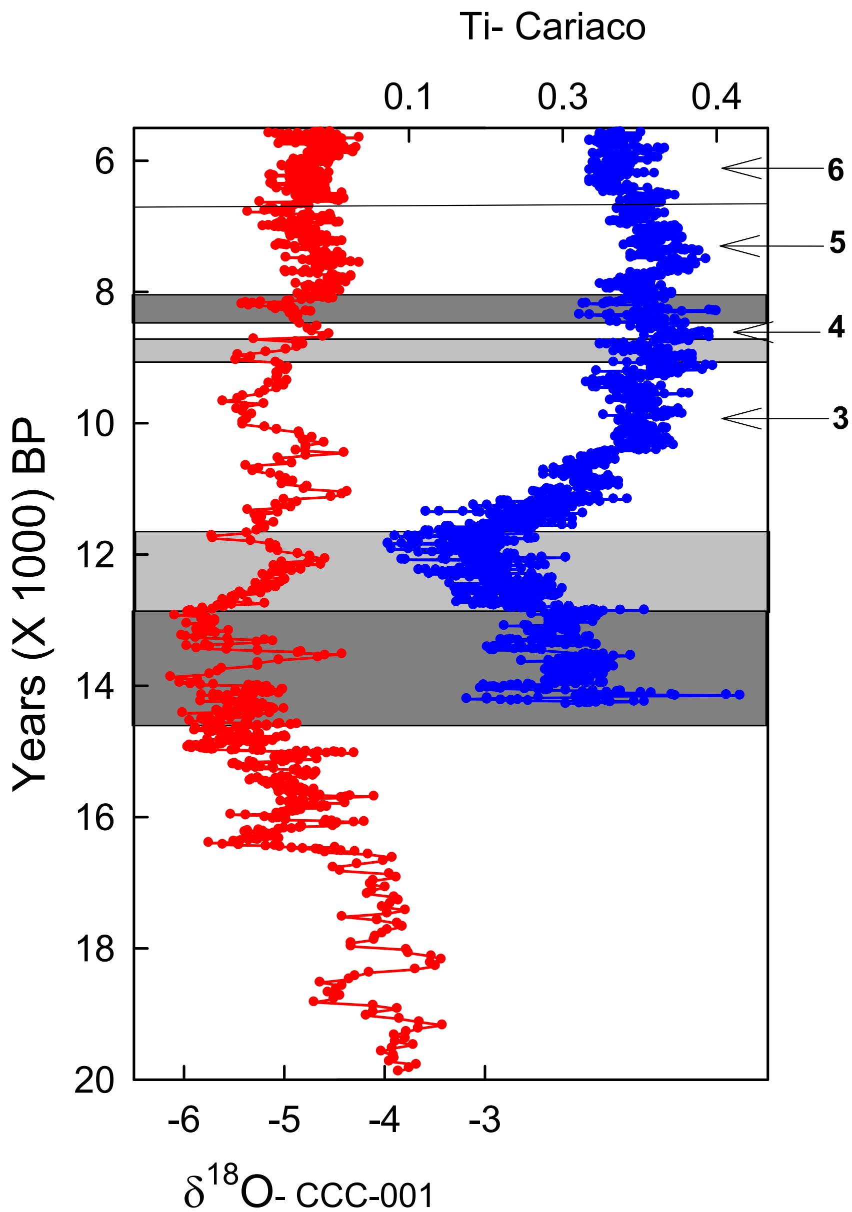

Figure 4.4- Global and regional events evidenced in CCC-001, correlated to Cariaco Basin Ti sediment records. Third through sixth regional events are numerically marked.

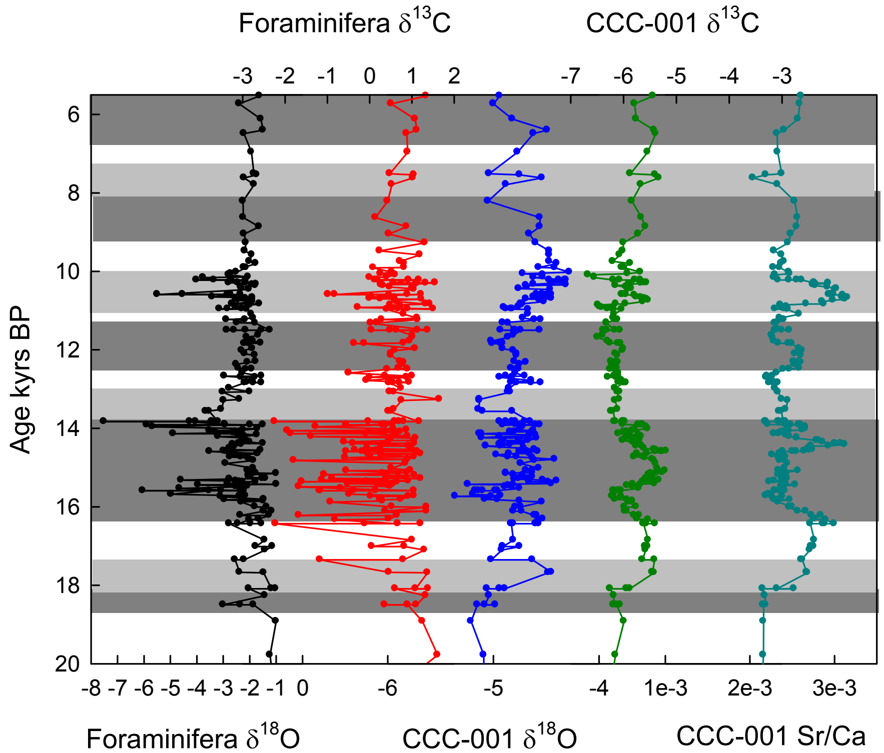

Figure 4.5- GOM meltwater pulses as evidenced by foraminifera calcite correlated with CCC-001.

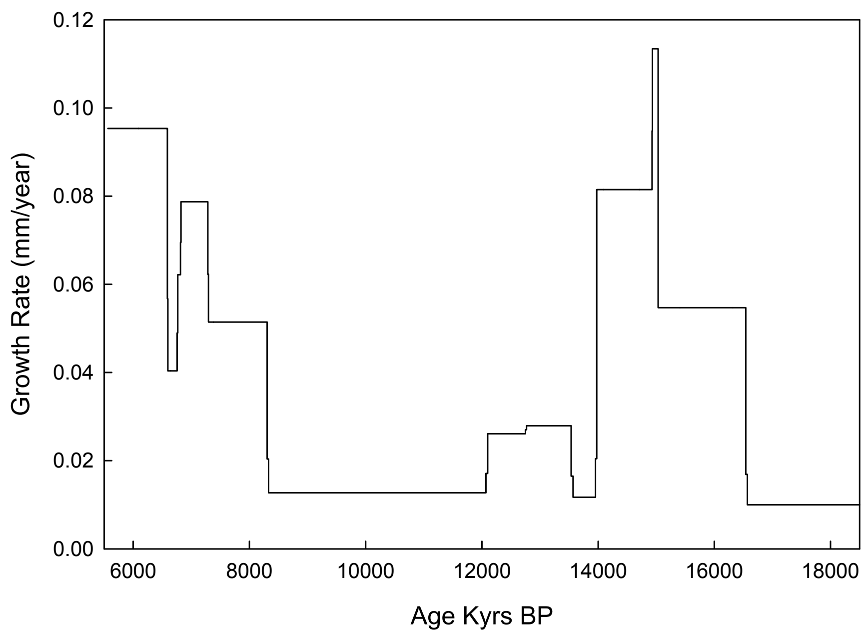

Figure 4.6- Growth rate/drip conditions of CCC-001. Note that growth rate is not clearly defined by known times of known climatic episodes.

5.0 Chapter 5.0- Conclusions/Summary

Stable isotope and geochemical signatures obtained from stalagmites may be useful for interpreting climate change. Stable carbon isotopes are used to reconstruct records of vegetation and stable oxygen isotopes are used to infer past atmospheric temperature and precipitation along with seasonality of moisture. Used jointly with trace elements, which help to understand regional hydrology, it is possible to reconstruct a record of regional to global climate change based upon these signatures.

Records of past climate change have been collected from around the world at both high and low latitudes including Greenland, the Cariaco Basin in Venezuela and various caves in China. A mid-latitude record of similar resolution, such as that of stalagmite CCC-001, obtained from Culverson Creek Cave in southern West Virginia, has proven to be synchronous with these records, indicative that processes which govern the climate may have affected all of these regions. The CCC-001 record is especially useful because it depicts climatic events on human timescales at sub-centennial resolution.

CCC-001 reflects seven major climatic oscillations which are able to be correlated to other global episodes. Regionally, an additional six climatic oscillations are evidenced. The global episodes are Heinrich event 1, The Mystery Interval, The Böling-Allerod, The Younger Dryas, the Pre-Boreal, and the 8.2 and 9.2 kyr events. The regional episodes are primarily influenced by moisture from the Gulf of Mexico, the position of the ITCZ and the North

American Monsoon at 6.5 kyrs BP. Regional drought and cold post glacial aridity have also been factors in determining regional climate shifts.

While stalagmite CCC-001 grew continuously throughout the climate record, growth rate/drip rate did fluctuate, assuming consistent age interpolation between determined dates. The drip rate and growth rate fluctuated throughout the record and did not seem to be consistently governed by climatic episodes in themselves.

Considering the age of the death of speleothem CCC-001 at approximately 5.5 kyrs BP and the lack of anthropogenic practices throughout its growth, the lead up to the mid-Holocene Hypisthermal should not be used to determine how the modern climate system might evolve under greenhouse warming conditions.

APPENDICES

δ– per mil *or* per one-thousand

$$\delta^{13}\mathbf{C} = [((^{13}C/^{12}C)_{SAMPLE} - (^{13}C/^{12}C)_{STANDARD}) \,/\, (^{13}C/^{12}C)_{STANDARD}] \times 1000$$

$$\delta^{18}\mathbf{O} = [((^{18}O/^{16}O)_{SAMPLE} - (^{18}O/^{16}O)_{STANDARD}) \,/\, (^{18}O/^{16}O)_{STANDARD}] \times 1000$$

Mean annual $\delta^{18}O$ of precipitation to mean annual air temperature is ~0.6 ‰/°C

Equilibrium fractionation factor between calcite and water is -0.26 ‰/°C

C_3 (more depleted in ^{13}C) -14 to -6 ‰

C_4 (less depleted in ^{13}C) -6 to +2‰

Kyrs- thousand years

BP- before present

PDB (VPDB) - PeeDee Belemnite (Vienna PeeDee Belemnite)

Bedrock carbon- $\delta^{13}C$- 0 ‰

Regular Calcite- $\delta^{13}C$ -2‰ to 2‰

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