Recent extreme events in a tropical stalagmite: Multi-proxy records and analysis of ecosystem delta carbon-13 value sensitivity to weak climate forcing

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RECENT EXTREME EVENTS IN A TROPICAL STALAGMITE:  
MULTI-PROXY RECORDS AND 
ANALYSIS OF ECOSYSTEM $\delta^{13}C$ VALUE SENSITIVITY TO WEAK CLIMATE FORCING 

BY  

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ABSTRACT

RECENT EXTREME EVENTS IN A TROPICAL STALAGMITE: MULTI-PROXY RECORDS AND ANALYSIS OF ECOSYSTEM $^{13}$C VALUE SENSITIVITY TO WEAK CLIMATE FORCING

by

Amy E. Benoit Frappier

University of New Hampshire, September, 2006

Speleothems are emerging as important and detailed chronological records of environmental change. Integrating exploration of modern speleothem records of environmental variability, related forcing factors, and proxy biogeochemical characteristics reveals gaps in current understanding and suggests new potential proxies. This dissertation demonstrates the potential for developing novel proxy records of past regional environmental extremes, such as tropical cyclones, explosive volcanism, and enhanced seasonal contrasts from speleothems that are sensitive to transient infiltration events through very high-resolution, multi-parameter analysis of a rapidly growing, fracture-fed tropical stalagmite. A series of sample screening steps were developed prior to stalagmite collection in the field in order to increase the likelihood of collecting suitable samples sensitive to tropical cyclone precipitation events. Once the correct annual dating was established for a recent period (2001-1978), a weekly-monthly record of stalagmite stable isotope ratios showed low stable oxygen isotope excursions that corresponded to the historical record of tropical storm strikes in the region. Furthermore, excursion amplitude was related to the maximum intensity of storms prior to landfall. The same stalagmite contains a trace element record of the El Chichón eruption, validated by both Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICPMS) and Scanning X-ray Fluorescence (S-XRF).
dominant, broad spectrum trace element perturbation was recorded by both methods at 1982, coincident with a major explosive eruption of the nearby trachy-andesite El Chichón volcano in Chiapas, Mexico in April of that year. This result demonstrates the ability of stalagmites to record proxy evidence of a major regional tephra fallout event. The LA-ICPMS technique showed greater discriminating power between volcanic and extensive rainfall signals. A lag correlation analysis of weak El Niño forcing in Belize using a large suite of meteorological and satellite datasets required removal of seasonal variance in order to detect any El Niño response. Individual variables responded independently to El Niño, and no coherent lag timescale was evident. Analysis of biological factors including the belowground community will be required to assess the non-linear processes linking small changes in temperature and moisture extremes to large carbon isotope variations. Promising new proxies for tropical cyclone activity and low-latitude explosive volcanism may emerge from this work.
INTRODUCTION

As Earth's climate system comes into better focus, it is increasingly clear that solutions to many outstanding scientific problems are predicated on a more complete understanding of variability and feedback mechanisms within the Earth system. Of particular concern is the fact that climate models that simulate the "correct" recent climate for incorrect reasons may yield an inaccurate view of future behavior of the climate system. Potentially critical feedback effects are not now included in global circulation models, such as the tropical cyclone effect on ocean mixing and heat transport (Emanuel, 2002). Low-latitude volcanic forcing produces different effects than high-latitude eruptions, yet tropical volcanic activity is not well constrained. Proxy records that constrain such feedbacks, forcings, and variability are positioned to advance the state of the science.

However, not all proxy records are equally well-positioned to improve current understanding of climate system dynamics. When seen through the lens of paleoclimatology, our view of past climate system behavior is inverted with respect to the modern climate system viewed through the lens of surface- and satellite-based observational networks. Our view of prehistoric climate is dominated by annual to millennial-scale marine and polar perspectives, but our view of modern climate is dominated by synoptic terrestrial meteorological observations from the tropical regions and northern hemisphere mid-latitudes. Similarly, the understanding of current climate variability has been shaped primarily by daily land-based observations; mobile shipboard observations are relatively less common. In contrast, the current understanding of paleoclimate variability has been shaped primarily by low-resolution marine sediment cores, plus a handful of high-resolution ice core proxy records from the polar and high altitude regions. Only very
recently has global satellite remote sensing technology provided comprehensive coverage of many environmental parameters of interest. Modern and paleo perspectives on the climate system can be brought into better alignment by generating multi-proxy paleoclimate records with annual or better temporal resolution from terrestrial lowlands, particularly in the tropical and subtropical regions (Briffa et al., 1995; Crowley, 2000; Jones et al., 2001; Mann et al., 1999).

Stalagmites are rapidly emerging as sources of high quality proxy records of low-latitude terrestrial environmental change (Bertaux et al., 2002; Burns et al., 2002; Lachniet et al., 2004a; Lachniet et al., 2004b; Lundblad and Holmgren, 2005; Wang et al., 2001; Yadava and Ramesh, 2005). A number of advantages make speleothems particularly sought after, including spatial distribution, relative ease of precise radiometric dating, high temporal resolution, and duration of record. Stalagmites are able to record seasonal and sub-seasonal variations over long periods of time, like small paleo-weather stations (Bertaux et al., 2002; Brook et al., 1999; Fairchild et al., 2001; Fairchild et al., 2000; Frappier et al., 2002a; Frisia et al., 2003; Hellstrom and McCulloch, 2000; Hou et al., 2002; Huang et al., 2001; Ihlenfeld et al., 2003; Kong et al., 2003; McMillan et al., 2005; Pan, 1999; Qin et al., 2000; Roberts et al., 1998; Treble et al., 2003; Treble et al., 2005; Treble et al., 2002). Many different signals can be measured in the same samples, providing a rich view of climatic and biogeochemical events and trends over time. Stalagmites are thus increasingly viewed as the "ice cores" of the tropical lowlands.

However, stalagmite proxy interpretation is still maturing. The complex biogeochemical dynamics of caves are less well understood compared to many other more established, simpler and more direct proxy systems. Despite relatively early recognition of their potential value (Bogli, 1980; Broecker et al., 1960; Dreybrodt, 1980, 1981; Harmon et al., 1979; Hendy, 1971; Pan, 1999), development of speleothem proxies was delayed in part by the complexity of the spelean environment. Cave dripwater delivery rates often vary across a range of timescales, and the chemical and isotopic composition of cave seepage water is spatially and temporally variable. Extension rates are often slow, requiring very high-resolution analytical procedures and dating
techniques to obtain better-than-decadal sampling. As speleothem exploration and modern calibration studies have expanded, understanding of speleothem depositional processes and links to the epikarst and surface environment have also grown (Ayalon et al., 1998; Baker and Brunsdon, 2003; Baskaran and Krishnamurthy, 1993; Dorale et al., 1992; Fairchild et al., 2000; Frisia et al., 2000; Genty et al., 2001; Johnson and Ingram, 2004; Kaufmann, 2003; Kaufmann and Dreybrodt, 2004; McMillan et al., 2005; Railsback et al., 1994; Sancho et al., 2004; Swart et al., 1991; Tooth and Fairchild, 2003; Zhang et al., 2004). Interpretation of carbon isotope ratios and trace element variations in speleothems remains especially problematic (Fairchild et al., 2006; McDermott, 2004; Mickler et al., 2004a). In particular, higher-resolution studies show great promise for uncovering indicators that enable investigators to distinguish between various controls on proxy variations, delimiting cases in which various controls cannot be distinguished, and constraining sensitivity to various forcing factors.

Integrated studies of speleothem stratigraphic records, environmental forcing and extreme events, as well as forest-soil-cave biogeochemical dynamics, are poised to expand the range of questions that speleothem records can address. Each of the following chapters addresses a different aspect of an integrated investigation of the relations between sub-annual to decadal proxy records from a tropical stalagmite and the involvement of forcing factors and cave-forest biogeochemical system. Two studies describe the development of new high-resolution modern calibration-based proxies of environmental extremes, and two studies investigate the importance of environmental forcing and epikarst channel filter characteristics to the resulting stalagmite proxy records. Together, this work points toward a number of new directions for ongoing research on speleothem proxy systematics and paleoenvironmental variability. It is anticipated that high-resolution speleothem records will contribute valuable new insights to paleoclimatology and Earth systems science.
CHAPTER I

A THREE-STAGE SCREENING SYSTEM TO SELECT STORM-SENSITIVE STALAGMITES

Abstract

We describe the field and laboratory speleothem screening process applied by Frappier and co-workers in a successful effort to select a stalagmite suitable for high resolution stable isotope paleotempestology. Field and laboratory criteria were combined in series, to screen out candidates whose characteristics indicated lower sensitivity. Together, this screening system is expected to increase the likelihood that the selected stalagmite would contain large, measurable stable isotope anomalies related to tropical cyclone precipitation. This particular screening process is an important methodological consideration for researchers attempting to replicate the original speleothem stable isotope paleotempestology study, or to apply the technique elsewhere. Furthermore, the overall approach to stalagmite selection presented here can be adapted readily by other investigators in support of different scientific goals.

Introduction

Paleo-environmental research is based upon connecting the impact of environmental factors of interest with measurable properties of a particular proxy archive. Any proxy signal of interest to paleo-environmental investigators is transmitted to the proxy record through a channel
consisting of a series of intervening processes (Brown, 1987). The conduit pathway serves as a filter that can amplify, attenuate, interfere with, add noise to, eliminate, and/or simply the original environmental signals. A scientific instrument (in this case, a proxy) can provide an unobstructed view of the items acting on it despite the characteristics of the proxy archive itself and related channel attributes (Dretske 1981, in Brown, 1987). The common process of instrument calibration is a physical application of this concept. Proxy signals are most reliable where the translating channel is simple and stable with a high signal to noise ratio. The resulting proxy transfer functions are valid so long as the channel remains unchanged through time, facilitating reliable paleo-environmental reconstruction. The assumption of system stationarity is central to paleoclimate reconstruction in general. Replication studies of some proxy systems have established broad applicability of proxy signal-channel transfer functions across a range of locations and ages (Cuffey and Steig, 1998; Grootes et al., 1993; Mann, 2002). On the other hand, rare but valuable quantitative studies of interruptions and distortions found in the proxy record (Cuffey et al., 1994; Lohmann, 1987; Lohmann, 1988; Shackleton and Opdyke, 1973; Spero et al., 1997) have illuminated the understanding of "ancient mechanisms of environmental change, metabolism, or diagenesis encoded in proxy signals" (Weedon, 2003).

Multi-proxy paleo-environmental archives from secondary carbonate mineral deposits in caves, or speleothems, are being developed rapidly (Fairchild et al., 2006; McDermott, 2004). In cave depositional settings, the signal channel is in part, quite literally a conduit that transmits seepage water along pathways from the surface to the cave. As a result of spatial heterogeneities in conduit hydrology, bedrock, surface topography, soil properties, ecosystem structure, cave geometry and microclimate, and seepage water chemical composition, each conduit has a unique combination of vadose/kinetic processes that has the potential to induce considerable variations between speleothem records (Dorale et al., 2002b). A replication test should result in essentially identical proxy records only in the special case where differences in kinetic/vadose zone processes, or "noise", are negligible relative to the proxy signal of interest (Dorale et al., 2002b).
Replication of proxy records thus lends confidence to interpretation as indicative of primary environmental variables of interest (Wang et al., 2001).

Existing replication studies have found both congruence and idiosyncrasy in speleothem records. Similar stalagmites cannot always be identified in every cave, and speleothem replication has often been limited by practical, ethical, and resource considerations (Lundblad and Holmgren, 2005). In the field, speleothem collection is typically subject to severe restrictions from conservation ethics, consideration of cave aesthetics, and/or permits. The quality of internal speleothem stratigraphy cannot generally be determined in the field, with the inevitable result that some collected samples turn out to be useless for paleo-environmental studies. Furthermore, age differences often play a role when the target of the study is ancient, inactive speleothems. It is not unusual for the few promising samples remaining in a collection to differ widely in age, making replication impossible without additional field sampling.

Even when fairly well-replicated records are present, contemporary stalagmite records from the same cave also can reveal different proxy signals. Lack of convergence has been taken by some as a sign that speleothems may be unreliable for paleo-environmental studies (e.g. Betancourt et al., 2002). In this view, individual stalagmites may have rather idiosyncratic sensitivities, and replication of paleo-environmental records is hindered by the very complexity of the spelean depositional environment.

Yet, a growing number of studies have derived valuable insights into paleo-environmental change from attributing differences between speleothem records to surface or vadose zone effects. In some cases, proxy record differences can be attributed to field relationships such different hill slope aspect above the chambers where stalagmites were collected (Denniston et al., 1999). Denniston and colleagues contrasted two stalagmite records, utilizing the water balance differences between stalagmites from cave chambers with different surface aspect in order to distinguish different climatic regimes. Genty and co-workers found that soil richness (or soil respiration rate) controlled δ13C value amplitude in a suite of speleothems from
France (2003). Another group tracked the relations between precipitation and cave dripwater stable isotope composition, finding that two types of vadose pathways feeding different cave drips were sensitive to different aspects of weather variability (Ayalon et al., 1998). Other studies have found dripwater variability related to land-use differences above a cave system, seasonal cave ventilation shifts, soil composition, and distance from cave entrance (Baker, 2002; Baker and Brunsdon, 2003; Musgrove and Banner, 2004; Spötl et al., 2005). In other cases, non-equilibrium factors have been implicated in the origin of idiosyncrasies in individual speleothem records that diverge from signals common to other formations (Mickler et al., 2004a). Thus, detailed observations of field relations and/or modern cave system process studies provide critical aids to proxy interpretation.

As the biogeochemical factors driving stalagmite differences become better understood, this diversity of sensitivity may turn out to be a great strength, when detailed field observations are available. Failure of the replication test can thus indicate less desirable stalagmite types to avoid in future analysis. Reports relating field conditions to speleothem characteristics provide a means for distinguishing between stalagmite types that have conduits sensitive to different aspects of paleoclimate variability (Ayalon et al., 1999; Ayalon et al., 1998; Tooth and Fairchild, 2003). Different kinds of speleothems thus provide different perspectives on the same history, much the same as different species, lake types, and glaciers have been found to exhibit sensitivities to particular environmental factors. In this view, the observed variation between stalagmites presents an opportunity for more precise paleoclimatology – if each type can be identified unambiguously.

Indeed, one expects formations that share specific signal properties to share certain related channel characteristics. If strong links can be established between field characteristics and proxy signal outcomes through cave monitoring and experimental studies, then more efficient speleothem sample collection would advance the scientific value of speleothem proxy records. Such information can be applied in the field in order to 1) avoid collecting unsuitable samples for
investigating the environmental variable of interest, and 2) enhance sensitivity of the target proxy record to the phenomena of interest given the practical limitations of sampling and analytical techniques. Similarly, using non-destructive or minimally destructive methods to target sectioning and analytical foci can be particularly useful in the pre- and post-collection phase (Mickler et al., 2004a; Mickler et al., 2004b). The following section describes a three-stage stalagmite screening system that was used successfully to select a stalagmite sensitive to tropical cyclone precipitation events.

A Three-stage Screening System to Select Storm-sensitive Stalagmites

We wished to develop a screening system to select, from the large number of stalagmites available in the field, a small number of samples suitable for analysis as the basis for a paleo-hurricane research study. Here, a case study is presented that outlines a three-stage screening method used to select stalagmites used to develop a proxy record of individual tropical cyclone rainfall events (Chapter 2). The stepped stalagmite screening approach presented here is a variation on one commonly applied by paleoclimatologists to most expeditiously meet scientific objectives, in which field sites are screened prior to and during fieldwork, and collected materials are further screened in the laboratory. Prior to sample collection, a series of stalagmite screening steps were designed to maximize the likelihood of recovering samples containing tropical cyclone proxy signals that would be measurable using available analytical techniques. In developing the sample screening system, related studies were used to link 1) the tropical cyclone precipitation signal to seepage water, 2) the cave-epikarst system to seepage water chemistry, and 3) the cave-epikarst system to speleothem proxy records. The result of this study (see Chapter 2) supports the importance of the screening system described below for speleothem paleotempestology applications.
On the basis of existing research linking field relations to cave hydrology and spelean geochemistry, a series of factors were developed that should have increased the likelihood of recovering samples containing the target signal, in this case the $\delta^{18}$O anomaly of tropical cyclone precipitation. The screening approach was chosen to filter out candidate stalagmites with lower sensitivity. We screened candidates at three steps: karst regions, cave sites, and finally individual stalagmites, both in the field and after initial analytical assessment. A sequential list of contra-indicators was developed in order to reject less-qualified candidates, and candidates that passed each stage were further subjected to the next step in the screening process. Using the considerations described below as a guide, I selected a region, cave, and stalagmite that resulted in a proxy record that in fact contained the target hurricane proxy records (Chapter 6).

A number of factors were recognized that could affect our ability to resolve the expected tropical cyclone precipitation signal given the limitations of our selected analytical methods. For each problem, we developed criteria to reject less promising candidates, described below. To guide site and sample selection, the potential problems and criteria for each screening step was organized in three practical stages: region, cave, and stalagmite (Table 1-1).

Potential Problems: Region

1. The most basic issue is that a speleothem proxy for tropical cyclone events can only be found where caves and hurricanes co-exist. Thus, the first consideration was to reject karst regions outside the hurricane belt. We favored karst regions in areas where tropical cyclone strikes were high during recent decades, such as Florida, the Yucatan Peninsula, Puerto Rico, Hispaniola, and Cuba.

2. We expected proxy signals from individual hurricane precipitation events to persist only briefly. Earlier studies that analyzed speleothems at seasonal to annual resolution were
unable to resolve individual storm signals (Malmquist, 1997; Schwehr, 1998). Tropical cyclones can precipitate a week to a month's equivalent rainfall. In order to meet our target calcite micro-sampling rate of 50 samples per year with the available 20 micron sampling technique, we required a relatively rapid average stalagmite extension rate of \(~1\text{mm yr}^{-1}\). The relatively rapid chemical weathering rates in the tropics increased the likelihood of collecting rapidly growing stalagmites from lower latitude caves as compared to karst regions at higher latitude. Furthermore, snow has a low stable isotope composition similar to tropical cyclone precipitation (Lawrence and Gedzelman, 1998). Avoiding temperate zone karst regions also enabled us to avoid potential confusion between the tropical cyclone and wintertime precipitation. On this basis, we rejected karst regions in the temperate zone for our initial study.

3. We required stalagmites with annual layering in order to accurately date stable isotope variations. A seasonal water deficit seems to contribute to annual calcite banding; thus we rejected stalagmites from regions without a dry season.

4. Stormwater from within the rain shield of a tropical cyclone has a distinct isotopic signature. A study of the isotopic composition of summer precipitation in Texas showed that the precipitation stable isotope anomaly produced by tropical cyclones is large (\(~6\%\)) relative to the analytical precision of modern mass spectrometry (\(<0.1\%\)) (Lawrence, 1998; Lawrence and Gedzelman, 1996; Lawrence et al., 2002; Lawrence et al., 1998). The amount of \(\delta^{18}O\) value variation from tropical cyclones is comparable to typical seasonal variability in tropical precipitation in Central America, where data has been collected (Lachniet and Patterson, 2002). Using stoichiometric reasoning based upon speleothem calcite precipitation equations (Hendy, 1971), the calcite \(\delta^{18}O\) anomaly produced by a \(-6\%\)
precipitation anomaly would be about -2%, still easily resolved by a Kiel carbonate device and Finnigan MAT252 gas source stable isotope mass spectrometer. However, transmission of tropical cyclone water to the cave could be affected by rainfall amount and stormwater infiltration. David Malmquist (personal communication) indicated that tropical cyclones typically produced very little precipitation on the low-lying island of Bermuda. We determined that a record of tropical cyclone precipitation events was more likely in regions where storm rainfall totals are large, i.e. areas of orographic relief (Roe, 2005).

5. Soil thickness is an important factor affecting the chemical and isotopic composition of infiltrating groundwater. Meteoric water passing through thicker soils is more altered than water that has passed through only thin soil cover. The soils of most limestone regions of Florida, Central America, and the Caribbean are relatively thin; thus, these regions are good candidates for high-resolution isotopic investigations (Ford and Williams, 1989).

We selected karst regions for fieldwork by combining the above criteria with the list of areas for which we could obtain access and speleothem collection permits as well as export permits. Using these criteria, we selected the Boundary Fault Karst region in central Belize for our initial project. The region has a distinct dry season, is located in the foothills of the Maya mountains, many large caves, and a historical tropical cyclone recurrence interval of about 3 years.

Potential problems: Cave Configuration and History

6. Tropical cyclone water infiltration and the soil buffer. For our purposes, where sufficient precipitation is generated, stormwater must infiltrate in sufficient quantity to produce a measurable calcite layer on speleothems. The clay-rich soils typical in karst regions often
transmit water slowly and reduce infiltration. However, soils are thinner in upland areas with steep slopes (Brenner, 1978). We determined that a record of tropical cyclone precipitation events was more likely in caves under thin soils, rejecting caves in low-lying areas with low slope angles.

7. **Cave entrance effects.** Although deep cave environments are very stable, light levels, relative humidity, air motion, and temperature may vary considerably near the cave entrance (Mickler et al., 2004a; Spötl et al., 2005). Variations in relative humidity and temperature in the cave can lead to kinetic non-equilibrium effects that interfere with the speleothem record of stable isotopic composition of seepage water (Hendy, 1971). In general, cave environments are stable deeper than 10 m below the surface and greater than 50 m from entrances; however, this can vary with regional climate and cave morphology (Hill and Forti, 1997). Large caves with interior rooms were thus preferred, and small caves were rejected to avoid stalagmites sensitive to unstable cave environmental conditions.

8. **Flooding.** Caves and cave rooms subject to flooding are generally avoided for speleothem paleo-environmental studies (Hill and Forti, 1997). Abrasion and corrosion from floodwaters can erode previously deposited calcite. Even when physical damage is minimal, no dripwater deposition can take place while formations are submerged. After floodwaters drain away, deposition may be further delayed until mud and debris are washed from the speleothem surface. Floodwaters can also deliver residual clays with high Th concentrations to stalagmite surfaces, making U-Th dating more difficult. Flood evidence is often easily recognized in the field, including mud layers, ripple marks, fragments of carbonate and organic debris draped over surfaces, horizontal bathtub-like
rings on the walls, and objects lodged into crevices by flowing water. We avoided any
caves and cave rooms with evidence of recent flooding.

9. **Evaporation and wind.** High humidity inhibits evaporation in cave chambers and promotes
isotopic equilibrium calcite deposition (Hendy, 1972). Internal cave rooms located far
from entrances, and with standing water represent favorable humidity conditions. A
hygrometer was used to quantitatively measure relative humidity in candidate caves. We
planned to reject cave rooms with relative humidity < 85-90%. However, this criterion
was of limited use in this case because such dry conditions were not encountered in any
candidate caves during this project. Similarly, air currents in caves can increase
evaporation and related kinetic effects in speleothem records (Hill and Forti, 1997).
Constricted passageways often inhibit air flow. Air currents may not be apparent to cave
visitors if they appear only seasonally, at a certain time of day, or associated with particular
weather patterns (Spötl et al., 2005). However, the presence of air currents that
substantially affect calcite deposition can be recognized often in the field (Hill and Forti,
1997). Although we felt no air movement in most caves, we avoided sampling in cave
rooms with speleothem evidence of air currents, particularly asymmetric forms (Hill and
Forti, 1997).

10. **Vandalism.** Although we did not have to reject any caves on this basis, we also planned to
avoid caves with substantial vandalism, as this may have reduced the number of available
stalagmites.

11. **Epikarst conduit hydrology.** We also wished to avoid two problems related to hydrologic
pathways through the epikarst. If stormwater travels a short distance through large
conduits and reaches the cave too quickly, it can be undersaturated with respect to calcite,
leaving behind no measurable stable isotope record. On the other hand, while stormwater

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that takes a long and circuitous route through the bedrock’s primary pore network will certainly deposit spelean calcite upon reaching the cave, the stormwater will be extensively homogenized with other vadose groundwaters (Ayalon et al., 1998). In this case, the stormwater will leave behind a highly attenuated stable isotope record that lacks individual storm events, but that nevertheless reflects long-term storm activity. Where feasible, it is desirable to obtain long-term seepage water monitoring data from several candidate drip sites prior to speleothem collection. However, in many instances, dripwater monitoring data is not obtainable prior to collection because of funding limitations and the logistical complications that arise from working in remote cave areas. Because long-term seepage water monitoring data was neither available nor practical in this study, a field observations-based approach (See #10 and 13, below) was designed to select stalagmites with seepage pathways that avoid both extremes.

12. Conduit hydrologic pathway: Calcite undersaturation. Following a significant storm event, the increased height of the groundwater column is expected to cause cave drip rates to increase within hours. A measurable tropical cyclone precipitation signal requires that the storm water percolate slowly enough to reach supersaturation with respect to calcite before reaching the cave. Drips that are undersaturated during periods of high flow (such as storm events) can dissolve calcite in the top of previously-deposited stalagmites, forming a drill-hole morphology (Hill and Forti, 1997). While exploring a number of candidate caves in the field, we noted that shallower caves with thin limestone roofs were more likely to contain stalagmites with drill cups, whereas this morphology was absent in deeper caves. The correlation between epikarst bedrock thickness and conduit infiltration time is not absolute. Nevertheless, in general, as cave overburden thickness increases, seepage water residence time and calcite saturation state both increase, and waters infiltrating from
different precipitation events and seasons becomes increasingly homogenized (Ayalon et al., 1998). Note that the issue of epikarst thickness is separate from that of soil thickness, described above. The presence of stalagmite drill cups indicated undesirable shallow caves where dripwater was likely to be corrosive during periods of high flow, such as hurricane events. However, it is important to distinguish between drill holes caused by undersaturated drips and splash cups related to the height of the drop and rate of the drip (Fig. 1-1).

We used the above criteria to select the cave Actun Tunichil Muknal for sample collection. The air in the upper level cavern where speleothems were collected for this summer had a temperature of 25°C and relative humidity of ~90%. Stalagmites are ideally located far from cave entrances in rooms with restricted air-flow to avoid associated complications in mineral deposition and isotopic fractionation (Hill and Forti, 1997). An advantage is that this cave site has been mapped, and has been visited regularly for the past several years, so there is some local knowledge of environmental variability.

Potential Problems: Stalagmite

Only stalagmites were considered for this study. Speleothems appear in many forms, but stalagmites are preferred for paleo-environmental studies because of their relatively simple stratigraphy (Hill and Forti, 1997). Although a stalagmite’s internal growth form cannot generally be assessed in the field, the pool of available stalagmites can be reduced somewhat through observations of external characteristics.
13. **Irregular growth form.** A stable growth form tends to result from a stable seepage conduit. Highly asymmetrical forms may indicate air motion or an unstable drip location that could affect the proxy record. Stalagmites with irregular form are to be avoided.

14. **Inactive stalagmites.** Ancient stalagmites were not the target of this modern test-of-concept study. Stalagmites without wet surfaces indicating active formation were excluded due to interest in recovering modern material deposited during a period for which the history of storm strikes is known.

15. **Conduit hydrologic pathway: stormwater homogenization.** A measurable tropical cyclone precipitation signal also requires that the storm water reach the cave as a coherent slug of isotopically distinct water. Limestone bedrock usually has "double porosity" hydrology, meaning that some groundwater travels relatively rapidly through fractures, while the rest moves slowly and circuitously through unfractured permeable bedrock (Ford and Williams, 1989). Different residence times and different dripwater conduit pathways produce differences in the isotopic composition of the groundwater. Ayalon et al. (1998) found that fast-drip water that entered a cave through fractures (after brief bedrock residence times) retained isotopic identity related to the source precipitation. In contrast, slow-drip cave water (with longer residence times) had a more homogenous isotopic composition, related to the average accumulated seasonal stable isotope values. In an Israeli cave system, mixing of water derived from these various sources within the top 40-50 m of the vadose zone determines the isotopic composition of the groundwater reservoir (Ayalon et al., 1998). Fracture-fed stalagmites are thus more likely to be sensitive to brief storm events (Fig. 1-2). Fortunately, recognizing fracture-fed stalagmites is a relatively simple matter in the field. Visible lineation traces on the ceiling and linear arrays of stalactites and/or stalagmites indicated the presence of fractures. We rejected stalagmites without evidence...
of a fracture source for seepage water. Of the fracture-fed stalagmites available, those with relatively slow drip rates were less desirable, indicating a less direct hydrologic connection to the surface.

16. **Dirty calcite.** As discussed in the section on flooding, above, clays can contaminate calcite with excess initial Th. So-called “dirty calcite” is more difficult to date precisely using U-Th techniques. The presence of clays can often color speleothem calcite. Although many other impurities can also affect calcite color, white stalagmites are thought to be less likely to contain problematic clays.

17. **Re-crystallization.** Smaller crystals are more desirable than large crystals, which can indicate re-crystallization or weak alteration of the speleothem (Kendall and Broughton, 1978).

For this study, six stalagmites were chosen on the basis of morphology, mineralogy, crystal texture, drip water source, location in cave, soundness of structure, and effect of harvesting on cave aesthetics. Of the six candidates that were collected, these were screened using simple laboratory tests to select one candidate for micromilling and high-resolution stable isotope analysis.

**Lab Selection Procedures**

18. **Mineralogy.** X-ray Diffraction (XRD) was used to detect the presence of aragonite, whose stable isotope systematics differ from that of calcite. The chemical composition and
mineral structure of powdered stalagmite samples was determined by performing X-ray
diffraction using a Siemens D 5000 powder X-ray diffractometer. Powdered samples were
adhered to a quartz mounting plate using petroleum jelly. Each sample was rotated
through an appropriate 2-theta angle. The resulting XRD profiles were compared to
spectra from samples of known composition to test for mineralogical composition. In this
case, mineralogy was not very helpful in selecting formations because all speleothems
collected were composed entirely of calcite.

19. **Stratigraphy.** After stalagmites were halved and polished, the stratigraphy was described.
Speleothems with obvious hiatuses, or irregular growth form were not good candidates for
micro-milling.

20. **Equilibrium test.** Hendy tests were performed to screen for stalagmites deposited outside
of isotopic equilibrium with their source fluid (Hendy, 1971), and although the efficacy of
this test has been called into question (Mickler et al., 2004a), the test is likely valid in the
case of the ultimately selected stalagmite ATM-7 because of its wide bands, a result of
relatively rapid recent growth (see below).

21. **Growth rate.** Radiometric dating was used to measure the vertical extension rate of the
stalagmites. Because our samples were modern, we chose to analyze $^{137}$Cs and $^{210}$Pb.
Stalagmites with higher growth rates were preferred in order to maximize the temporal
sampling rate we could achieve with the available microsampling system.
Stalagmite ATM7 was selected for high-resolution analysis. This stalagmite had the highest drip rate in the field, and was located in a relatively inaccessible section of the upper passage. ATM7 had smooth and relatively even layering, compact calcite with small crystals, and a rapid growth rate in the most recent few centimeters of deposition, making it an excellent candidate for our pilot study. Table 1-1 summarizes the screening system presented in this case study.

Discussion

The first stalagmite selected using this screening system and analyzed at appropriate temporal resolution successfully recorded recent tropical cyclone precipitation stable isotope signals (Chapter 2). This initial success suggests that this screening approach is an important part of the speleothem paleotempestology tool presented in Chapter 2. Not all stalagmites have the appropriate characteristics to record tropical cyclone precipitation amount. Although the stalagmite screening system presented here remains to be validated for different stalagmites and cave sites, we strongly suggest that future efforts to replicate or apply this method for paleotempestology should include the appropriate screening steps described above. In the future, we hope to replicate this work using another stalagmite selected from the same cave site, Actun Tunichil Muknal in central Belize.

More generally, while replication is a strong indicator of excellent proxy records (Dorale et al., 2002b), it requires collecting a set of similar stalagmites. Some speleothem records with different intrinsic sensitivities have the potential to contribute valuable new perspectives to paleoenvironmental studies. Applying explicit field and laboratory sample screening may improve the odds of collecting stalagmites with sensitivity to the desired environmental variable(s), and advance replication efforts. To achieve different scientific goals, other screening procedures could be applied to target an appropriate subset of stalagmites.
Furthermore, field observations can be critical to later interpretation of speleothem proxy records, and it is difficult to over-emphasize the importance of field documentation. In some cases, the overall physical configuration of the cave site, its history and climate may be relatively easy to determine after the fact. However, careful attention should be paid in the field to describing the exact speleothem location and micro-environment in detail and broad-brush, because some observations (such as the rate of water flow on different sides of a stalagmite, any water contributions from adjacent drips) cannot be easily re-constructed after removing the formation. The scientific value of many speleothems in existing collections may be compromised by incomplete descriptions and a lack of field provenance information. Where documentation is lacking, any available information should be developed or compiled as soon as possible, in cooperation with the individuals involved in fieldwork when possible, especially for speleothems collected in past decades.

The reasoning behind field and laboratory stalagmite sample selection should be evaluated in advance with respect to scientific goals. Although different investigators and groups have developed rubrics and helpful observations used during field sample selection, these are rarely published. Sharing selection approaches would advance speleothem paleo-environmental studies in both a forward sense, with regard to sensitivity selection, as well as in an inverse sense, with regard to record interpretation. Such information can also help to bring together parallel efforts by paleo-environmental proxy interpretation experts and groups studying applicable modern processes in cave, vadose hydrology, and soil systems.

Speleothems are a very promising source of high-resolution, multi-proxy continental paleo-environmental records. Ultimately, information linking field relations to proxy records can provide rich sources of new hypotheses for cave systems research. Sharing sample collection approaches should advance ongoing stalagmite collection, replication, and interpretation efforts by the broader scientific community while supporting cave conservation efforts. Attention to the
potential value of speleothems with different intrinsic sensitivities suggests a number of promising avenues for future paleo-environmental research.
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<td>Tropical karst region</td>
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<td></td>
<td>High TC landfall frequency</td>
<td>NOAA National Hurricane Center</td>
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<td>Annual layering</td>
<td>Climatology (Seasonal water deficit)</td>
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<td>High TC rainfall amount</td>
<td>Orographic effect (Topographic maps)</td>
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<td>2</td>
<td>Existing cave information</td>
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<td>Field observations and interviews</td>
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<td>Cave entrance effects</td>
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<td>Flooding</td>
<td>mud, debris, washing of formations</td>
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<td>Air currents</td>
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<td>Dual Porosity bedrock</td>
<td>Field observations of fractures and decorations</td>
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<td>3</td>
<td>Actively growing</td>
<td>Field observations (wet surfaces)</td>
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<td></td>
<td>Fracture-fed</td>
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<td></td>
<td>Shape, color, crystal size</td>
<td>Field observations (broomstick or cone, white, small crystal size)</td>
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<td>δ$^{18}$O and δ$^{13}$C analysis</td>
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<td>$^{210}$Pb and $^{137}$Cs dating</td>
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<td></td>
<td>Hendy Tests</td>
<td>Dental Drill and Stable isotope ratio analysis</td>
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Figure 1-1. Transmission of cyclogenetic stable isotope signal in dual porosity system.

Blue indicates vadose water with background isotopic composition, red indicates tropical cyclone water. Purple indicates intermediate compositions.
Figure 1-2. Conceptual model of the effect of epikarst thickness (i.e. transmission rate or flow pathway) on speleothem sensitivity to brief storm events.
CHAPTER II

A STALAGMITE STABLE ISOTOPE RECORD OF RECENT TROPICAL CYCLONE EVENTS

Abstract

A 23-year tropical stalagmite record of recent stable isotope variations (1978 - 2001) at monthly-weekly temporal resolution contains abrupt low excursions in the stable oxygen isotope ratio ($\delta^{18}O$ value) of calcite that correspond temporally with recent historical tropical cyclones in the vicinity of the cave. A newly developed logistic discriminant model can reliably identify tropical cyclone proxy signals using the measurable parameters $\delta^{18}O$ value, $\delta^{13}C$ value, and single point changes in $\delta^{18}O$ value. The logistic model correctly identified 80% of low $\delta^{18}O$ value excursions as storm events and incorrectly classified only one of nearly 1200 non-storm sampling points. In addition to enabling high-resolution tropical cyclone frequency reconstruction, this geologic proxy also reveals information about the intensity of individual storm events. A multiple regression predicted storm intensity ($R^2 = 0.48 \ p=0.030$) using sampling frequency and excursion amplitude. Consistent with previous low-resolution studies, we found that the decadal average $\delta^{18}O$ value was lower during the 1990s when several tropical cyclones produced rainfall in the area and conversely, was higher during the 1980s when only one storm struck. Longer, accurately-dated, high-resolution speleothem stable isotope records thus may contribute a useful new tool for paleotempestology to clarify associations between highly variable tropical cyclone activity and the dynamic range of Quaternary climate.
Introduction

Tropical cyclones, including hurricanes, cyclones, and typhoons, are among the most deadly and costly natural hazards. Tropical cyclone intensity, frequency, spatial distribution, and economic damages are highly variable and respond to an array of global and regional climatic factors including the El Nino-Southern Oscillation System, or ENSO (Klotzbach and Gray, 2004) and references therein, Landsea, 2000; Pielke et al., 1999; Tartaglione, et al. 2003). Conversely, these storms may be an important yet poorly understood feedback in the climate system, possibly controlling rates of marine poleward heat transport and thermohaline circulation (Emanuel, 2001). Despite the ongoing research effort to understand Earth’s climate system, associations remain controversial between highly variable tropical cyclone activity and the dynamic range of Quaternary climates (Emanuel, 2005; Giorgi et al., 2001; Henderson-Sellers et al., 1998; Pielke et al., 2005; Walsh, 2004; Walsh et al., 2004). Historical records from most tropical cyclone regions contain few examples of the most catastrophic storms. Paleo-tempestological evidence of past storms preserved in sedimentary and biogeochemical archives (Donnelly et al., 2001a; Donnelly et al., 2001b; Liu and Fearn, 1993, 2000, 2002; Nott and Hayne, 2001; Nott, 2003) has already illuminated centennial-millennial variations in tropical cyclone activity (Elsner and Liu, 2003; Elsner et al., 2000; Nott, 2004; Nott, 2003). Paleotempest proxies with annual-decadal resolution could clarify the controversial problem of tropical cyclone hazard climatology and offer an independent test of posited feedbacks among the climate system, thermohaline circulation, and tropical cyclone activity (Emanuel, 2005). Toward that end, we present a new, high-resolution tool for paleotempestology that uses the proxy record of past tropical cyclone rainfall preserved in a calcite stalagmite, a type of speleothem or cave formation.
Hurricane Stable Isotope Values and Cave Depositional Settings

The $\delta^{18}O$ value of average tropical cyclone precipitation is $\sim 6\%$ lower than other summer season rainwater (Gedzelman et al., 2003; Gedzelman and Lawrence, 1982; Lawrence, 1998; Lawrence and Gedzelman, 1996; Lawrence et al., 2002), and perturbs the stable isotopic composition of groundwater and streams in the storm's wake (Lawrence, 1998). Recognition of this natural isotopic tracer 'spike' by Lawrence (1998) led to exploration of potential paleohurricane archives in corals (Cohen, 2001), fish otoliths (Patterson, 1998), tree rings (Miller et al., 2003), and speleothems (Malmquist, 1997; Schwehr, 1998). Early attempts to develop a speleothem isotope proxy for individual tropical cyclones were frustrated by low sampling resolution (~annual). Nevertheless, these studies established significant decadal/multidecadal anti-correlations between storm frequency and average speleothem calcite $\delta^{18}O$ values, indicating that intervals of enhanced tropical cyclone precipitation can depress speleothem isotopic composition in affected regions on decadal timescales. A high-resolution speleothem isotope-based paleotempest proxy would lend a number of complementary advantages to established coastal paleotempest proxies, including relative ease of radiometric dating, high temporal resolution, continuous deposition, storm intensity indicators, a detailed background climatic record, and a stable depositional environment independent of Quaternary sea level variability. Only tropical cyclones that produced significant rainfall could be recorded, and the proxy would be limited to karst regions. Advances in micro-sampling technology for isotopic analysis of carbonates (Carpenter, 1996; Frappier et al., 2002b) now enable us to examine the speleothem record at sufficiently high resolution to detect proxy evidence of individual tropical cyclones.

A hurricane rainfall event over a cave results in a slug of low $\delta^{18}O$ value water infiltrating through soil and karst bedrock overburden; ultimately, an isotopic "spike" is recorded by growing speleothems as a low $\delta^{18}O$ value excursion. Inter-storm meteoric water with more typical, higher $\delta^{18}O$ values provides the requisite isotopic contrast. To precipitate a measurable isotopic
excursion in speleothem calcite, the hydrologic pathway through the epikarst must 1) allow infiltrating tropical cyclone water to reach supersaturation with respect to calcite, and 2) avoid excessive homogenization of tropical cyclone water with other soil- and groundwaters. Even absent excessive mixing, diffusion and dispersion during infiltration cause some tropical cyclone water to be released slowly, affecting the isotopic composition of dripwater and calcite for some time after the primary isotopic ‘spike’ passes through the conduit system. For individual storms, the size of precipitation δ18O value anomalies increases with tropical cyclone intensity, and decays with distance from the eye of the storm (Lawrence and Gedzelman, 1996; Lawrence et al., 1998). The size of δ18O value anomalies at any site may reflect the “apparent local intensity” of the storm, raising the possibility that the amplitude of individual stalagmite δ18O excursions may contain paleotempest intensity information. In contrast, tropical cyclones are unlikely to substantially perturb dripwater δ13C values. To investigate the suitability of speleothems as a proxy archive for paleotempestology, we analyzed a stalagmite stable isotope record from Belize over a recent 23-year period for which the history of nearby storm tracks and intensity is known (Fig. 2-2-1, Table 2-1).

Methods

In January, 2001 we collected several actively growing stalagmites from the cave Actun Tunichil Muknal in central Belize (additional site information is included in Appendix 1). Stalagmite ATM7 was sectioned longitudinally, polished, and dated. Micro-sampling and stable isotope analyses were performed at the Paul H. Nelson Stable Isotope Laboratory at University of Iowa (Frappier et al., 2002, Appendix 2). Microsamples (approximately 0.02 to 0.05 mg of CaCO3 for each sample) were milled along the growth axis continuously at 20 μm resolution (Fig. 2-2) using a computer-controlled microsampling device (Appendix 2). Analytical precision
Identifying and Dating Isotopic Excursions

We visually inspected the stable isotope record for the largest brief, low excursions in \( \delta^{18}O \) value not also associated with substantial declines in \( \delta^{13}C \) value. It was necessary to account for covariation between \( \delta^{18}O \) values and \( \delta^{13}C \) values in order to distinguish the isotopic signature of tropical cyclone precipitation from ENSO-related inter-annual climatic and ecological variability (Frappier et al. 2002). We also updated and verified a previously developed age model (Frappier et al., 2002b) to reflect new recognition of sub-annual layers (Appendix 3). We used the resulting age model to identify the year in which each low \( \delta^{18}O \) value excursion was deposited.

Results and Discussion

The ATM7 oxygen isotope record contains 11 large (> ~ 0.5 %), short-lived, low excursions in \( \delta^{18}O \) values that are not coupled with similar decreases in \( \delta^{13}C \) values (< 0.2 %) and are correlated with historical tropical cyclones near the cave (Fig. 2-3A, B). No similar \( \delta^{18}O \) value excursions are evident during years lacking nearby tropical cyclones. These \( \delta^{18}O \) value excursions are associated with historical storms ranging in intensity from Tropical Storm to Catastrophic Hurricane, and with storm tracks whose eyes passed the cave at distances of 40 to 370 km. The record also reflects inter-storm deposition, enabling accurate estimates of between-storm intervals (Fig. 2-3A, B). Multiple \( \delta^{18}O \) value excursions occurred in years with multiple storm strikes, as well as 1998 when Hurricane Mitch re-intensified as it passed the site a second...
time (Fig. 2-2-1). In 1996, when Dolly and Kyle struck two months apart, the two excursions are separated by several samples (Fig. 2-4). In 1995, when Opal and Roxanne struck two weeks apart, the two excursions are separated by a single intervening point (Fig. 2-4). Hurricane Keith’s stormwater signal was not recorded in 2000 as ATM7 was collected only three months after Keith made landfall while the tropical cyclone-derived, or “cyclogenic” water was most likely still moving down through the epikarst toward the cave. In agreement with previous studies (Malmquist, 1997; Schwehr, 1998), decadal average $\delta^{18}O$ values in ATM7 were lower (higher) by $1.87\% \pm 0.19\%$ during the 1990’s (1980’s), a decade when many (few) tropical cyclones affected the region (Fig. 2-3B).

To test the suitability of high-resolution stalagmite stable isotope records for detecting unknown pre-historic tropical cyclones, we applied a simple numerical technique to distinguish the proxy record of cyclogenic excursions from background variability in this dataset. Within the 11 historical excursions we identified as cyclogenic, we coded the sampling point with the lowest $\delta^{18}O$ value as a storm event (1); all other sampling points were coded as non-storm (0). During Hurricane Mitch’s long traverse across this region, the storm made landfall in both Honduras and Yucatán; thus, we coded the two largest low $\delta^{18}O$ excursions in 1998 as storm events. A binary logistic regression of sampling points identified as storm/non-storm with the predictor variables $\delta^{18}O_d$ (the difference in $\delta^{18}O$ value between adjacent samples), $\delta^{18}O$ value, and $\delta^{13}C$ value, resulted in a probability function to quantify the likelihood that any sample represents a storm event:

$$\text{(1) } \text{Probability} = -11.01 * \delta^{18}O_d - 1.85 * \delta^{18}O + 0.51 * \delta^{13}C - 12.86$$

Because of adjacent missing data due to a machine error on one side of the dual inlet system, a cyclogenic excursion in 1993 was not included in this model as the $\delta^{18}O_d$ could not be...
calculated. Using equation (1), logistic probability values greater than 0.5 captured excursions related to 8 of the 10 remaining isotopic excursions included in the model (Fig. 2-3D). Of over 1200 non-storm data points, the logistic probability model identified as a cyclogenic signal only one sample that we coded as non-storm, with a logistic probability cut-off value greater than 0.5. A third low δ¹⁸O excursion in 1998 identified by the model was also associated with Hurricane Mitch. We can thus infer that multiple excursions can be produced by a single storm system that produces multiple local precipitation events. Overall, this model reliably identified tropical cyclone signals in an isotopic record with substantial background variability, and will serve as a testable model for future speleothem paleotempestology records.

Investigating Potential Indicators of Storm Intensity

We examined relations between the proxy (low δ¹⁸O value excursion amplitude) and the characteristics of recorded storm events. We postulated that annual sampling frequency (S, # stable isotope samples per year) could be an important secondary control on the amplitude of measured excursions as a result of inter-annual growth rate fluctuations (Appendix 4). A standard multiple regression using maximum storm intensity (I), proximal storm track distance (D), and S as the independent variables explained 56.6% of variation in δ¹⁸O value excursion amplitude (p<0.031) (Appendix, Table A1). The most important predictors of excursion amplitude were I (semi-partial R² = 0.354) and S (semi-partial R² = 0.382), indicating that this application is limited by microsampling technology. Surprisingly, excursion amplitude was not substantially related to D (semi-partial R² = 0.025). We interpret these results to indicate that in this dataset, excursion amplitude was primarily related to tropical cyclone intensity and was not substantially confounded by storm track distance. This finding is surprising given observed radial stable isotope gradients in tropical cyclones, but consistent with the observation that tropical cyclone
rainfall $\delta^{18}O$ value is an integrated signal of the storm’s history (Lawrence et al., 1998). Storm intensity was a better predictor of excursion amplitude than local precipitation amount (Appendix 4). Toward reconstructing tropical cyclone intensity from measurable predictor variables ($S$ and excursion amplitude), we performed a linear regression that explained 48.0% of variance in maximum storm intensity ($p<0.030$). High-resolution pre-historic speleothem proxy datasets can thus provide the basis for accurately reconstructing paleo-hurricane intensities. However, a robust test of the models presented here for reconstructing paleotempest incidence and intensity was precluded by the absence of an independent dataset of similar quality. A larger number of recorded historical-era tropical cyclone events will be required to fully test the sensitivity of this stable isotope proxy to various storm characteristics identified by Lawrence and co-workers (1998) (e.g. various storm track distance and intensity measures, storm duration or short-term intensity changes, storm radius, storm quadrant affecting the site).

Conclusions

The low $\delta^{18}O$ value excursions identified in this stalagmite record represent an accurate, measurable high-resolution proxy for past tropical cyclone precipitation events, opening the door to more detailed records of past hurricane frequency and intensity. The overall success of simple statistical tools to distinguish cyclogenic $\delta^{18}O$ value excursions from a relatively noisy background gives us confidence that individual tropical cyclone events can be reliably identified in pre-historic speleothems. Additional independent stable isotope records and longer calibration-period records are needed to test the proxies for tropical cyclone activity presented here. Close agreement between this speleothem proxy archive and the historical record suggests that this tool can bridge the gap between historical/meteorological hurricane observations (synoptic to multi-decadal scale) and low-resolution (centennial to millennial scale) paleotempest proxy records.
The speleothem proxy complements existing coastal paleotempestology proxies, lending advantages related to ease of dating, independence from Holocene sea-level changes, and potential applicability throughout the Quaternary. The proxy is limited by the availability of storm-sensitive speleothems, stable isotope sampling frequency, and potential interference in temperate regions from snow-melt infiltration (Dansgaard, 1964a). Only tropical cyclones that produce significant rainfall in karst regions could be recorded. Between 1851 and 2004, this cave site alone was affected by 6% of major hurricanes and 8% of all named landfalling tropical cyclones in the Atlantic Basin. Thus, several cave sites from karst regions across the Atlantic Basin may yield a representative record that reflects seasonal to centennial variation in overall Atlantic paleotempest activity during Quaternary intervals of paleoclimatic interest. A spatially and temporally distributed network of high-resolution paleotempest proxy records in multiple tropical cyclone basins may ultimately contribute to coastal risk assessment and detection/attribution programs aimed at investigating potential impacts of climate change on tropical cyclone activity (Nott, 2004).
Table 2-1. Historical intensity, precipitation, and best track data for Atlantic tropical cyclones (NOAA Tropical Prediction Center). Intensity categories represent the maximum intensity at or prior to landfall in Central America, such that 0 indicates tropical storms, and values 1-5 indicate Saffir-Simpson hurricane intensity categories 1-5. Total rainfall during storm days is reported from the Central Farm meteorological station, less than 15 km from the cave site. * Combined rainfall from both Hurricane Mitch landfall events.

<table>
<thead>
<tr>
<th>Storm</th>
<th>Landfall Date</th>
<th>Intensity</th>
<th>Distance between storm track and cave (km)</th>
<th>Storm Precipitation, Central Farm (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Keith</td>
<td>Oct. 2000</td>
<td>4</td>
<td>120</td>
<td>264</td>
</tr>
<tr>
<td>Katrina</td>
<td>Oct. 1999</td>
<td>0</td>
<td>158</td>
<td>15</td>
</tr>
<tr>
<td>Mitch 2</td>
<td>Nov. 1998</td>
<td>0</td>
<td>369</td>
<td>*</td>
</tr>
<tr>
<td>Mitch</td>
<td>Oct. 1998</td>
<td>5</td>
<td>282</td>
<td>246*</td>
</tr>
<tr>
<td>Kyle</td>
<td>Oct. 1996</td>
<td>0</td>
<td>147</td>
<td>59</td>
</tr>
<tr>
<td>Dolly</td>
<td>Aug. 1996</td>
<td>1</td>
<td>233</td>
<td>51</td>
</tr>
<tr>
<td>Roxanne</td>
<td>Oct. 1995</td>
<td>3</td>
<td>311</td>
<td>43</td>
</tr>
<tr>
<td>Opal</td>
<td>Sep. 1995</td>
<td>0</td>
<td>248</td>
<td>68</td>
</tr>
<tr>
<td>Gert</td>
<td>Sep. 1993</td>
<td>0</td>
<td>86</td>
<td>24</td>
</tr>
<tr>
<td>Diana</td>
<td>Aug. 1990</td>
<td>0</td>
<td>259</td>
<td>24</td>
</tr>
<tr>
<td>Hermine</td>
<td>Sep. 1980</td>
<td>0</td>
<td>138</td>
<td>131</td>
</tr>
<tr>
<td>Greta</td>
<td>Sep. 1978</td>
<td>4</td>
<td>42</td>
<td>179</td>
</tr>
</tbody>
</table>
Figure 2-1. Location map indicating the stalagmite collection site, cave Actun Tunichil Muknal (star) and nearby tropical cyclone storm tracks (1978 - 2001). Black storm tracks indicate hurricanes; gray storm tracks indicate tropical storms (NOAA National Hurricane Center).
Figure 2-2. Photographs of stalagmite ATM7 showing depth of radiometric dating samples, and micro-milling track. White circles show the depth of $\gamma$-activity samples with positive $^{137}\text{Cs}$ activity; gray circles indicate zero (undetectable) $^{137}\text{Cs}$ activity. We interpret the onset of $^{137}\text{Cs}$ $\gamma$-activity to indicate local deposition of global fallout from atmospheric thermonuclear bomb testing after 1953. The polished cross section of the top portion of ATM7 shows the stable isotope micromilling track (blue outline), which was positioned to maintain alignment with the growth center and perpendicularity to growth banding throughout sampling (1978-2001).
Figure 2-3. Recent tropical cyclones near Belize with stalagmite $\delta^{18}$O timeseries, $\delta^{13}$C timeseries with SOI, and storm proxy model results. Horizontal axes for A, B, and D are identical (1978-2001); C is offset by a 1.5 year lead.Dating uncertainty for ATM7 is a few weeks to months; thus, events named in A and highlighted in B should not be expected to match exactly. A. Historical records of storm distance (black bars) from cave to nearby tropical cyclone storm tracks and local maximum intensity [red bars indicate Saffir-Simpson intensity categories TS (tropical storm) to H5 (Category 5 Hurricane)]. Blue circles denote storm rainfall totals from three meteorological stations near the cave site. B. ATM7 $\delta^{18}$O and $\delta^{13}$C values are shown in black and blue, respectively. Cyclogenic low $\delta^{18}$O value excursions (A-K) are highlighted. Note the different vertical scales for $\delta^{18}$O values and $\delta^{13}$C values. C. The Southern Oscillation Index (SOI) is shown inverted. Major El Niño events (vertical bars) during the period of record are associated with high $\delta^{13}$C and $\delta^{18}$O values in ATM7. D. Logistic regression model results to discriminate cyclogenic excursions from background isotopic variation and the amplitude of isotopic excursions. Solid circles denote excursions the model classified correctly as cyclogenic. Open circles (1980, 1995) denote excursions classified incorrectly as non-cyclogenic. One data point the model classified as cyclogenic (black) was associated with Mitch, but not a unique historical storm.
Figure 2-4. For locally active hurricane seasons, $\delta^{18}O$ value detail across corresponding annual couplets are shown to highlight cyclogenic excursions (A-K) and background isotopic variability.
CHAPTER III

EMPIRICAL ORTHOGONAL FUNCTION ANALYSIS OF MULTIVARIATE STALAGMITE TRACE ELEMENT DATA: DETECTING THE 1982 EL CHICHÓN VOLCANIC ERUPTION AND OTHER ENVIRONMENTAL EXTREMES

Abstract

We used Empirical Orthogonal Function (EOF) analysis to evaluate a recent Belize stalagmite record of trace element concentrations obtained using Laser Ablation-Inductively Coupled Plasma Mass Spectrometry (LA-ICPMS) and Scanning X-Ray Fluorescence (XRF). A major perturbation in dripwater geochemistry occurred in 1982, coincident with local ash fallout from Mexico’s El Chichón volcano. Tephra deposition had a marked effect on the trace element geochemistry of this stalagmite that was not otherwise evident in visible stratigraphy or stable isotope ratios. A different LA-ICPMS trace element fingerprint in 1979 is associated with a distinct color change and an extended period of low stable oxygen isotope values, coincident with extremely high rainfall during that year. The XRF series included some species not included in the LA-ICPMS analysis, such as S, K, and Cl; likewise, LA-ICPMS series include species not analyzed by XRF, such as Na. As a result, XRF was more sensitive to major volcanic events, and LA-ICPMS showed greater discriminating power between volcanic events and years of high precipitation. Applying Empirical Orthogonal Function (EOF) analysis to a smaller, more recent window of LA-ICPMS data without extreme events (1984 – 2001) revealed an additional mode of Sr:Mg anticorrelation that may reflect seasonal to interannual changes in drip-rate. The dominant EOF modes extracted depend on the environmental controls that dominated during different
intervals; major environmental events can dominate brief trace element records, overshadowing the weaker seasonal to interannual signals. EOF is a promising data analysis technique for distinguishing between different modes of geochemical variability in long multivariate speleothem records, and also providing a means to distinguish between environmental triggers. High-resolution, multivariate trace element analysis revealed stalagmite sensitivity to various environmental events, including major regional volcanic eruptions and extensive precipitation anomalies. These observations suggest new potential speleothem proxies for extreme events, including low-latitude tephrochronology.

**Introduction**

It has been long established that major volcanic eruptions can introduce large quantities of sulfate into the stratosphere, with widespread climatic effects (Briffa et al., 1998; Lamb, 1970; Robock, 2000; Stott et al., 2000). Stratospheric sulfuric acid aerosols derived from volcanic SO₂ backscatter incoming solar radiation and trap longwave radiation, cooling the troposphere and warming the stratosphere for years after an eruption (Toon and Pollack, 1980). Global coverage of the direct effects of aerosol loading began with satellite observations in 1979 (Bluth et al., 1993; McCormick et al., 1993). Since then, the global effects of two major eruptions, Pinatubo (1991) and El Chichón (1982) have been studied extensively. However, understanding the climate system response to past variations in volcanic forcing is restricted by incomplete knowledge of the history of past eruptions, as well as the sulfate loading produced by individual volcanic episodes (Bradley and Jones, 1992).

Historical records of volcanic eruptions and related climatic anomalies have been extended by development of volcanic eruptive records based on geologic evidence (e.g. (Sigurdsson et al., 1984) and/or ice core records (Clausen et al., 1997; Delmas et al., 1992; Lyons...
et al., 1990; Palmer, 2001; Thompson et al., 1986; Yalcin et al., 2003; Zielinski et al., 1996; Zielinski et al., 1994). The vagaries of atmospheric transport ensure that multiple ice cores from different regions are needed to provide a more complete record of major volcanic eruptions in the past (Clausen and Hammer, 1988; Delmas et al., 1985; Zielinski et al., 1997). The atmospheric transport and climatic effects differ considerably between tropical and high-latitude volcanoes (Stendel et al., 2006), and comparison between Greenland and Antarctic records has been used to differentiate between N. Hemisphere, S. Hemisphere, and equatorial volcanic eruptions. Relatively few annually-resolved tropical records of past volcanism have been produced, and dating tropical eruptions using eruption products has comparatively low precision (10^3 yrs) (Bluth et al., 1997; Thompson et al., 1986), leaving the essential quantities of the timing and latitudinal resolution of volcanic aerosol pulses poorly known (Stendel et al., 2006).

The first major volcanic plumes observed by satellites were the 1982 trachy-andesite eruptions of El Chichón (17°21'N, 93°13' W, 1150 m elevation), classified as V.E.I. 5 on the Volcano Explosivity Index (Newhall and Self, 1982). Tephra deposits were produced in three phases: a major Plinian eruption on March 28th (V.E.I. 4+) was followed by two larger eruptions on April 4th (V.E.I. 5) (Tilling et al., 1984; Varekamp et al., 1984). The eruption column reached stratospheric altitudes of at least 26 km, and within weeks the aerosols were transported completely around the equatorial belt (Robock and Matson, 1983). El Chichón (VEI 5) is about 400 km west of the cave site. AVHRR and TOMS satellite imagery of the tephra and SO₂ clouds shows that ash was transported over central Belize on April 3rd-6th (Figure 3-1) (Bluth et al., 1997). Rampino and Self (1984) showed that El Chichón is a source of unusually large quantities of sulfate aerosol. El Chichón is the source of with one of the largest and most climatically active volcanic eruptions in the entire Holocene (Palais et al., 1992). The volcano’s history is also of interest to anthropologists because earlier eruptions are associated with the decline of Maya civilization, including an eruption ~1250 A.D. that has been linked to a major volcanic horizon in Greenland ice cores in 1259 A.D. (Gill, 2000; Oppenheimer, 2003). Although the hypothesized
impact of volcanoes on the El Niño-Southern Oscillation System (ENSO) has long been a source of controversy (Robock and Free, 1995; Self et al., 1997), Adams and co-workers (Adams et al., 2003) showed that large ash plumes from equatorial volcanoes such as El Chichón can double the chances of an El Niño event the following winter.

Recent developments in speleothem research have led to a number of precisely dated, high-resolution, multi-proxy speleothem records of environmental change (Genty et al., 2003; Wang et al., 2001). Although ice core and tree-ring records are the primary annually-resolved volcanic proxy records, there is some suggestion that speleothems (cave mineral deposits such as stalagmites) may record volcanic signals. The spatial distribution of speleothem records is different from ice cores and centered in the tropics. Establishing reliable speleothem proxy records of regional volcanic episodes could lead to more complete records of their timing and location, particularly in the low-latitude belt and in regions with few glaciers. A Scottish stalagmite recorded a dramatic four-year cooling episode that has been tentatively linked to the Icelandic Hekkla eruption in 1104 (Baker, 1999; Baker et al., 1995). Atmospheric sulfate signals related to volcanism have recently been identified in stalagmites from northern Italy, yielding sulfate deposition records comparable to ice cores (Frisia et al., 2005). However, direct tephra fallout has not yet been identified in speleothems, and ice core work has shown that multiple chemical species in ash must be analyzed in order to fingerprint the source volcano. We had available a well-dated modern stalagmite of opportunity, ATM7, (Frappier et al., 2002a) from a region that experienced fallout from the 1982 El Chichón eruption in Chiapas, Mexico. During the 1982 El Chichón eruption, Terry McCloskey (Louisiana State University) was farming in the village of Santa Marta in eastern Belize, not far from the Actun Tunichil Muknal cave site. Dust fallout on crops was noticeable for some time after the eruption (McCloskey, 2006, personal communication). McCloskey's local experience provides ground truth for the expectation of tephra fallout derived from remote sensing of the tephra cloud was actually deposited in central Belize (Schneider et al., 1999). The goal of our investigation was thus to test the potential to
measure stalagmite tephrochronology signals by analyzing the multivariate trace element “fingerprint” of the 1982 El Chichón eruption.

Unlike glaciers, where post-depositional chemical transformations of aerosols are relatively small, atmospheric deposition in karst regions is filtered by the overlying ecosystem and soil biogeochemical systems before any signal is transmitted by infiltrating water to growing speleothem surfaces (Fairchild et al., 2006). Speleothem geochemistry may be perturbed in a number of ways by volcanic eruptions, primarily controlled by soil zone processes. Wet deposition of volcanic sulfate may alter soil water geochemistry, leading to rapid leaching toward the underlying cave (Frisia et al., 2005). However, strong wind shear during the 1982 El Chichón eruptions separated the SO2 gas cloud from the silicate tephra cloud (Schneider et al., 1995). The tephra cloud was carried eastward over Central Belize (Fig. 3-1), but the stratospheric sulfate precursors traveled further to the west. Thus, we expect most of the geochemical effects of this volcanic event to be driven primarily by tephra; most sulfate delivered to Central Belize in the initial plume phase was probably adsorbed by tephra particles and deposited in dry form (Rose, 1977). The effects of direct sulfate deposition were probably secondary and related to slow fallout of stratospheric sulfate months to years after the eruption (Bluth et al., 1997). Fresh tephra is rapidly weathered on contact with water (Varekamp et al., 1984), and can be expected to have multiple effects on soil geochemistry, with complex interactions with organic matter and clay mineral phases present. Leaching products of tephra include metallic ions common in silicates (Varekamp et al., 1984).

In general, investigations of inter-annual to sub-annual relationships between trace element proxies and their controlling variables have been reported by a number of groups, (Fairchild et al., 2001; McMillan et al., 2005; Treble et al., 2003). It is frequently the case that multiple factors affect individual measurable trace element species and modern calibration is required to establish any causal relationships between a speleothem record and volcanic eruptions. The soil and epikarst filter makes it unlikely that tephra particles will be found in
stalagmites. Instead, we explored the stalagmite for evidence of geochemical perturbations triggered by chemical weathering of tephra and associated secondary biogeochemical effects. To distinguish the signature of event types which have affected the area (e.g. hurricanes, heavy rainfall, tephra fallout), we analyzed a large suite of trace elements and applied principle component analysis to derive common modes of variability. Here we report the results of our exploration of a very high-resolution modern trace element record measured in stalagmite ATM7.

**Methods**

Actively growing stalagmites were collected from Actun Tunichil Muknal in January, 2001 (Frappier et al., 2002a). After sectioning stalagmite ATM7 vertically, a thick section was cut from the upper portion and polished. The stalagmite was dated using layer counting after testing for annual growth patterns using the onset of $^{137}$Cs activity (Chapter 2).

A smaller piece was cut to approximately 25 mm x 20 mm in order to fit the LA-ICPMS sample cell mount. Laser ablation was carried out at the LA-ICPMS facility at the Department of Geological Sciences at Boston University. We followed the methodology of Treble et al. (2003), analyzing multiple trace element concentrations collected in rapid sequence during slow scans; however, we made a few modifications. The instrument consists of a VG Plasma ExCell Quadrupole ICPMS fitted with a VG Merchantek LUV MP II frequency-quintupled 213 nm Nd-YAG laser ablation microprobe. The laser energy profile was flat at 101 J/cm$^2$. The laser was operated with a spot size of 40 μm and 50% output at 10Hz. Analyses were conducted while scanning the sample mounted on a motorized stage moving at 3 mm/min to create a continuous transect. The surface was pre-cleaned by scanned ablation using a larger laser spot size (300 μm spot size and 30% power at 10 Hz) prior to data collection on each transect section in order to remove surface impurities. We analyzed 11 parallel transects at 50 micron spacing (Fig. 3-2). Microscopic observation showed that the width of each resulting ablation line was approximately
A stream of Argon gas carried the laser-ablated sample material into the plasma source for ionization. Nineteen species were measured, each with an integration time of 0.05 s (\(^{11}\)B, \(^{23}\)Na, \(^{26}\)Mg, \(^{27}\)Al, \(^{28}\)Si, \(^{31}\)P, \(^{43}\)Ca, \(^{44}\)Ti, \(^{45}\)Ti, \(^{55}\)Mn, \(^{57}\)Fe, \(^{85}\)Rb, \(^{88}\)Sr, \(^{89}\)Y, \(^{90}\)Zr, \(^{138}\)Ba, \(^{140}\)Ce, \(^{232}\)Th, and \(^{238}\)U). This method produces approximately 100 data points per mm of transect, although smoothing of the series is produced by partial overlapping of successive measurements.

Each transect was collected in three overlapping sections, which were spliced to create each continuous transect. Background counts (carrier gas background with the laser off) were collected before and after each section. Before and after each transect, a NIST612 glass standard was also analyzed (Pearce et al., 1996). Although this silicate glass standard is not ideal for this work, a widely accepted calcite standard with the range of species found in NIST 612 is not available as an alternative. The raw data was processed by subtracting background counts, taking the ratio of each species relative to the Calcium signal, and standardizing with respect to the NIST612 analyses. Following Treble et al. (2003), all 11 parallel transects were stacked prior to data analysis in order to assimilate between-track variability. We correlated the LA-ICPMS transect to the adjacent, well-dated stable isotope transect from ATM7 (Chapter 2) in order to determine the vertical extension rate along the LA-ICPMS transect (Fig. 3-2). Age model error is on the order of a few months.

Scanning XRF analysis was carried out at Woods Hole Oceanographic Institute. Scanning XRF is a rapid, non-destructive analytical technique that captures a series of broadband emissions spectra from a sample surface after excitation with a focused x-ray beam as the sample is translated under the beam. Spectral peaks can be analyzed to quantify the chemical composition of the sample surface at relatively high resolution. We scanned 23 elements (Al, Si, P, S, Cl, Ar, Ca, K, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Br, Rb, Sr, Ba, W, Pb) along a single sampling track (Fig. 3-2). The scanning XRF system is designed to analyze sediment cores, and the x-ray beam is a slit with a fixed width of 5mm and adjustable length (20 microns to 500 microns). A polished slab of ATM7 was mounted on the scanning track, and translated through
the scanner at 30 s timesteps with the beam length set at 200 μm. This yields an average of 6 sampling points per year.

Data Analysis: LA-ICPMS

In order to determine the principle modes of variability present in the entire 18-species trace element series, we performed Empirical Orthogonal Function (EOF) analysis, a method of principle component analysis (Meeker et al., 1995; Peixoto and Oort, 1992). The EOF technique partitions the total variance present in the data set into uncorrelated, orthogonal patterns, termed empirical orthogonal functions, eigenvectors, or modes. The resulting modes describe the uncorrelated linear combinations of observations that are most efficient in explaining the variance in the data. The first mode explains the largest percentage of variance in the dataset. Each successive mode explains decreasing amounts of variance, and any two modes are independent and uncorrelated. Each eigenvector is “loaded” with a combination of variables, where the factor loading for each species is the correlation coefficient between the mode and that variable. The different modes thus presumably represent different kinds of variability, each driven by a different process. The ice core community has applied this technique widely in order to differentiate between sources and transport mechanisms through interpreting the relationships between individual species described by each mode (Mayewski et al., 1994). Each mode thus may reveal information about how the biogeochemical system of a stalagmite is controlled by a different environmental parameter. EOF analysis was performed using L. D. Meeker’s Matlab script toolbox (Meeker et al., 1995). Eigenvector factor loading and variance were recorded, and EOF modes were plotted over time for comparison to the local historical record.

We also re-analyzed the EOF modes from 1983 – 2001 to explore smaller-amplitude events during a more stable period of deposition. The late-period EOF modes showed that trace elements were fairly stable throughout this interval, except for a few events deposited in 1996-
The character of the 1996 and 1997 events were chemically similar to the 1982 and 1981 events, although considerably smaller in amplitude.

**Data Analysis: XRF**

23 species were analyzed in order to determine whether this method was also able to capture volcanic signals. In particular, we were interested in a few species that could not be analyzed using LA-ICPMS, including S, K, and Cl. A few species of interest were only rarely detectable using this method (P, Cu, Cl). The data were normalized to Ca. Reported XRF concentrations are relative, because no calcite standard materials were available for analysis. We hope to obtain reference materials in the future to report more quantitative values using this new method. Nevertheless, this rapid, non-destructive trace element analytical method produced well-behaved data with considerable structure as described below. As before, we performed EOF analysis on the XRF series. Eigenvector factor loadings and variance were recorded, and EOF modes were plotted for comparison to the local historical record and LA-ICPMS data.

**Results**

**LA-ICPMS**

All measured species show significant high-frequency variability (Fig. A-4). A few species show long-term trends and inter-annual variability (Mg, Sr). Although additional information about biogeochemical variability can be revealed through time-series analysis of individual EOF modes, this application is limited by the short length of the ATM7 dataset.
Without measured chlorine concentrations we were unable to correct for variations in cyclic salt concentrations.

The first three EOF modes accounted for nearly 60% of the total variance in the trace element dataset (Fig. 3-3, Fig. A-4). The remaining modes had low explanatory power (<~5% variance), and are not reported here. Timeseries plots (Fig. 3-4) show how each mode, or multivariate fingerprint, varied over the last few decades. The factor loadings and temporal variability provide the basis for interpreting the most likely environmental factors that underlie each mode. Variance was partitioned evenly across the first two EOF modes for Sr and Si; thus EOF is not a particularly diagnostic tool for investigating either Si or Sr in this dataset.

EOF1 explains 37.1% of the total variance in the dataset, and is positively loaded with all measured species. Several species are loaded at greater than 50% variance (Ti, Mn, Rb, Y, Ba, Ce, Th, and U), while Ba, Na, and Fe were loaded at less than 25%. EOF1 variability is concentrated in a single major event positive around 1982, with two lesser events centered at 1979 and 1981. EOF2 contains 14.5% of total variance, with a more complex chemical pattern. The factor loadings of anticorrelated species have opposite sign, such that the concentrations of species are high when those species loadings are negative, as in EOF2. The species B, Mg, Sr, and Al are anticorrelated with Fe. EOF 2 is not loaded on Na, P, Ti, Mn, Rb, Y, Zr, Ba, Ce, Th, U. Figure 3-4 shows that EOF2 has a slight downward trend throughout the series, driven primarily by Mg (Fig. 3-5). Positive events in EOF2 occurred ~1976 and in 1979. In 1982, a major negative event in EOF2 is concurrent with a positive event in EOF1. In 1981, EOF2 shows an increase in variability without a clear signal or trend. EOF3 incorporates 7.9% of total variance, primarily related to high-frequency P and Fe variations. EOF3 shows a single positive spike in 1981 (Fig. 3-4; See also Fig. A-5).
All measured species show significant high-frequency variability. A few species are detectable in a minority of samples (K, Cu, Ar). The first EOF pattern explains 28.7% of the total variance in the dataset, and is positively loaded with most measured species (Fig. 3-5). As for the LA-ICPMS results, EOF1 variability is concentrated in a single major event around 1982.

Another large event occurred prior to the mid-1970s. The XRF EOF2 is somewhat different from the second mode identified in LA-ICPMS. Here, EOF2 contains 15.7% of total variance, where the transition metals (K, Ti, Fe, Cu, Zn) vary opposite to Al. The XRF EOF2 also shows major events around 1982 and the early 1970s. The first two XRF modes are both dominated by two events: 1982 and the early 1970s; although the modes are positively correlated for the early event and anticorrelated during the latter event. These differences in loadings between modes indicate that the two events are chemically different.

**Discussion**

The chemical and temporal fingerprint of each EOF pattern can be interpreted with respect to the most likely controlling processes that could generate the observed mode. Tropical cyclones striking the vicinity in 1978, 1980, 1990, 1993, 1995 (twice), 1996 (twice), 1998, 1999, and 2001 resulted in brief $\delta^{18}$O value excursions (Chapter 2). No major chemical perturbations related to tropical cyclones have been observed in this record using either LA-ICPMS or Scanning XRF analytical techniques. This suggests that the high-resolution stable isotope proxy
demonstrated by Frappier and colleagues is thus far the only demonstrated speleothem proxy that can distinguish tropical cyclones from background environmental variability.

For both LA-ICPMS data and XRF data, EOF1 represents a general flux of trace elements into the groundwater system, likely related to extended periods of extreme wetness, external input of silicate material, and/or changes in soil pH/redox conditions. The brief dataset and lack of sea-salt correction in the LA-ICPMS data prevents us from distinguishing entirely between these potential drivers. High La-ICPMS EOF2 values represent input of silicate aluminosilicate minerals (clays) varying opposite to Fe, pointing to a physical flushing control washing clays into the system. P and Fe are primarily loaded on LA-ICPMS EOF3. For the XRF data, the additional loading from S in the XRF EOF1 mode suggests a stronger volcanic signature, particularly during the 1982 event. The loadings of the second XRF mode strongly suggest that it is also related to silicate minerals varying opposite to transition metals. If both XRF EOFs are related to volcanic tephra, the second mode may represent differences in composition between events. We now can interpret each trace element event (early 1970s - 2001).

Around 1978-1979, the stalagmite shows a striking increase in LA-ICPMS EOF2 and EOF1 that is coincident with color changes in stalagmite stratigraphy, stalagmite stable isotope perturbations, and major historical rainfall events (Fig. 3-4C). Local meteorological records for 1979 show that rainfall exceeded three standard deviations above the climatological mean (Figure 3-6). At this time, the stalagmite shows a distinct rusty-colored layer in stalagmite stratigraphy and an extended period of very low stable oxygen isotope ratio (low δ18O values) (Chapter 2). The positive EOF2 anomaly in 1979 reflects increased flushing of clays from the soil and into the cave conduit system; this is consistent with that year’s extreme rainfall season. However, this event does not seem to have affected EOF 3 significantly, indicating that P and Fe leaching were not affected especially by this period of wetness. Because P is generally insoluble, the lack of a response in EOF3 in 1979 is also consistent with control by an extended period of extreme
wetness. The XRF data shows no major event at this time, suggesting that species analyzed only by LA-ICPMS may be the primary driver behind this geochemical event (e.g. Ba, Mg).

An explanation for the 1981 excursion in all LA-ICPMS EOFs is not immediately apparent; however, the unique spike in EOF3 at the onset of this event may hold the key to understanding the driver of this event (Fig. 3-4B). No environmental extreme or event was reported that year in the region, although local meteorological observations indicate that rainfall was somewhat lower than normal (Fig. 3-6). A rather speculative explanation is that the 1981 event represents the influence of fire. Although this cave site is located in the Tapir Mountain Nature Preserve, at that time the preserve had only recently been established. Local subsistence farmers living in the area practiced slash-and-burn agriculture in the riparian floodplain nearby, traditionally setting fires just prior to the onset of the summer monsoon. The presence of large trees at the cave site shows that no major forest clearing or major canopy fires took place in recent decades. Understory biomass burning is one plausible explanation for the sudden leaching of all species in 1981, particularly the release of biologically important species such as P and Fe. The mineral form of P is particularly insoluble in the soil, while soluble P is tightly cycled within the ecosystem (???). Fires combust organic matter, leaving soluble P behind in the ash, contributing to short-lived post-burn P leaching (Hernandez et al., 1997; McColl and Grigal, 1975). Available P is quickly absorbed by primary producers, leached by infiltrating groundwater, and converted to insoluble carbonates and phosphates (Ewel et al., 1981). Fe is also limiting in many forest environments, and available Fe is quickly absorbed by organisms; thus the Fe response is similar to P. Thus, the brief duration of the 1981 EOF2 event is consistent with a fire source. If the 1981 stalagmite signal was pyrogenic, the XRF analysis should reveal increased K and reduced S deposition at this time, because K is highly soluble and fire volatilizes S (Ewel et al., 1981). An alternative interpretation is that the 1981 event in EOF1 and EOF2 is a volcanic tephra signal, but a smaller event from a different volcanic center with a different geochemical fingerprint from El Chichón’s signal, described below. If this represents a volcanic signal, we
would expect XRF to reveal an increase in S from tephra deposition (Frisia et al., 2005). However, the XRF data shows no 1981 event, and no conclusive interpretation can be made for this event given the available data.

The largest element perturbation in both the LA-ICPMS and XRF data also occurred around 1982 (Fig. 3-4A). Although the ash cloud from El Chichón covered the cave site in 1982, no visible changes in the stalagmite stratigraphy were observed. On the other hand, stable isotope perturbations were evident in 1982: both δ¹⁸O and δ¹³C values dropped sharply by about 0.2 per mil (Chapter 2). This discontinuity in an otherwise remarkably continuous dataset points to a period of non-deposition. The small stable isotope record offset and lack of stratigraphic manifestation indicates that the hiatus was brief (on the order of weeks to months). For LA-ICPMS, EOF1 and EOF2 show an inverse relation during the 1982 event, indicating greatly increased leaching of all species from the soil (EOF1), but with enhanced Fe and P and without flushing of clays (EOF2). We interpret broad leaching spectrum as a tephra weathering product signal from El Chichón (Varekamp et al., 1984). The first two XRF modes suggest tephra deposition with proportionally reduced (but still very high) concentrations of K and Fe and enhanced proportion of Ar and Cl. This event is the most striking geochemical signal in the entire period of record. The EOF fingerprint of this event points to the influence of tephra from El Chichón.

The second largest XRF event occurred in the early 1970s, prior to the start of the LA-ICPMS laser track. EOF1 shows that the early 1970s event was generally similar to, but considerably smaller than, the 1982 event. This similarity suggests a possible volcanic origin for the early 1970s event. In addition, this event is more heavily loaded on EOF2, an indicator of alumino-silicate minerals with more Fe and transition metals. Thus, the early 1970s event can be interpreted as a volcanic event with higher levels of Fe and other transition metals compared to El Chichón. This pattern is consistent with ash deposition from the largest volcanic eruption in the Neotropics during the 1970s, the late 1974 VEI 4 eruption of Fuego near Antigua, Guatemala.
Fuego is a large stratovolcano volcano about 350 km from the cave site. Calc-alkaline basaltic ash from the 1974 eruption produced volcanic sunsets across the northern hemisphere (Rose et al., 1978). Thus, the greater Fe and transition metal content in the 1974 event compared to 1982 is consistent with the more mafic eruptive content of Fuego compared to El Chichón. No similarly large geochemical perturbations are visible in ATM7 either around 1992-93, related to the Pinatubo eruption in the Philippines, or around 1996-97, related to the Caribbean eruption of Montserrat. No other major tropical eruptions occurred in Central America during the period of record. The XRF series appears to be dominated by major volcanic eruptions in Central America. Thus, the ATM7 stalagmite is highly sensitive to recording regional tephra fallout from VEI 4 or greater eruptions.

Since 1983, the ATM7 trace element record has been relatively quiet. Results of a second LA-ICPMS EOF analysis on the more recent period (1983 – 2001) show smaller events in 1996-1997 with some similarities to both El Chichón ash fall and to the high rainfall period of 1979 (Fig. 3-7, EOF1 and EOF2). Local rainfall was in the normal range in 1997 and although the previous two years had somewhat strong dry seasons, this is not particularly unusual (Fig. 3-5). We can thus have little confidence in attributing the 1997 trace element event to unusual seasonality. Another explanation for the geochemical character of the late 1990s trace element events, biomass burning immediately over the cave, can be ruled out by reports from locals and anthropologists working at the site during this period. Regional drought and fires in 1998 related to El Niño may be a source of aerosol particles, however, the EOF analysis does not show a clear biogenic signal. Alternatively, moderate Central American volcanic eruptions of at least VEI 3 in the late 1990s could be related to the observed signal. Regional eruptions during this period of at least VEI 3 include Popocatepetl, Mexico in June 1997 (~1000 km west of the cave site), and Papaya, Guatemala in May 1998 (~300 km south of the cave site). Tephra aerosol trajectories for these eruptions could rule out this explanation, although these are not readily available for the listed eruptions. A definitive interpretation for the late 1990s trace element events remains
elusive, although these events are orders of magnitude smaller than the 1982 event. In order to distinguish biomass burning events from tephra deposition, it may be helpful to analyze more distinguishing species, such as K and S, in addition to considering a much larger number of events of both types. Analyzing speleothem material from a site with a known history of burns could contribute to resolving this problem. EOF 3 represents changes in the ratio of Sr + Ba:Mg, which vary on inter-annual and annual time-scales. Anticorrelation between Mg and Sr indicates control by crystal growth on the stalagmite surface, related to dripwater chemistry and/or drip rate (Fairchild et al., 2006; Huang et al., 2001). To assess intervals not dominated by volcanic influence, it is evident that controlling for sea-salt input will be important for assessing non-marine influences.

This analysis illustrates one way in which stalagmite geochemical records of regional volcanic eruptions may be distinguished from other sources of geochemical change. Speleothem-based records of explosive volcanism in the surrounding region would open the door to improved understanding of tropical volcanic forcing and related climatic impacts. Furthermore, TIMS dating error bars are large for speleothems with low Uranium content, such that identifiable tephra events could provide absolutely dated horizons for additional age control. Although this stalagmite was selected for its tendency to record brief infiltration events such as tropical cyclones, ATM7 also recorded the geochemical signature of the 1982 El Chichón tephra cloud; however, the brief hiatus associated with the eruption suggests that a longer infiltration time might be more appropriate for the purpose of detecting volcanic events.

**Conclusions**

A rapidly growing, modern tropical stalagmite recorded the multivariate influence of a number of environmental factors from 1978-2001. Applying EOF analysis to an exploratory LA-
ICPMS multivariate stalagmite trace element dataset effectively separated the geochemical signatures of several different geochemical factors, including the 1982 El Chichón eruption, extremely wet conditions during 1979, and some smaller events that will require additional analyses to interpret with confidence. No geochemical signal was linked specifically to historical tropical cyclone events, indicating that stable isotope analysis remains the sole speleothem tropical cyclone proxy identified to date. However, this interpretation was hampered by lack of Cl analysis, which would enable a sea-salt signature to be identified. The geochemical fingerprint of the 1982 El Chichón eruption was positively identified by both LA-ICPMS and XRF data analysis, and we further suggest that a similar signature in the early 1970s reflects the 1974 Fuego eruption. Furthermore, during periods when extreme events do not dominate the geochemical signature of the stalagmite, seasonal to inter-annual fluctuations of Sr+Ba:Mg ratios appear to be driven by growth rate as well as other dripwater chemistry changes. Additional species, such as S and K, may prove diagnostic for distinguishing between potential drivers such as local biomass burning and tephra fallout.

Tephra deposition over a cave site can result in distinctive and overwhelming geochemical perturbations that persist for months after the fallout event, even when S is not included in the analysis. The rapid, non-destructive Scanning XRF technique readily identified volcanic signatures in ATM7, verifying the LA-ICPMS analysis. We find that Scanning XRF seems to be a rapid and straightforward technique for identifying volcanic events in stalagmite stratigraphy; however, several analyses per year are required to resolve the ~annual-scale volcanic signals. Scanning XRF has a number of critical advantages over LA-ICPMS, including the ability to place entire stalagmites into the instrument and rapid, high-resolution multiple species analytical capability. However, for speleothems with slow extension rates or growth laminae that are asymmetrical, Scanning XRF is limited by the x-ray beam size and single-axis scanning. Longer records with a larger number of volcanic signals will be required to further test the sensitivity of a potential stalagmite proxy for tephra deposition, and to determine what species
are most useful for discerning volcanic signals from other geochemical event types. A larger number of spatially distributed speleothem records around a volcanic region such as Central America will enable the spatial sensitivity of speleothem tephrochronology records. Pursuing potential speleothem records of volcanism could ultimately enhance the understanding of volcanic forcing in the climate system, and contribute to global climate model validation studies. In regions where speleothem uranium concentrations are low, tephra layer recognition may provide additional marker horizons useful for dating. Elsewhere, it may be possible to use more precisely-dated speleothem records of ashfall events to investigate the history of low-latitude explosive volcanism.

EOF analysis of multiparameter stalagmite records through decomposition of dataset variability is a powerful method for investigating the underlying mechanisms of biogeochemical change in these sensitive geologic recorders. The EOF modes reveal the common responses of the cave-epikarst biogeochemical system to various forcing factors, geochemical fingerprints whose dynamics can be traced through time. Although annual-scale trace element variations have been identified in several stalagmite studies (Fairchild et al., 2001; Fairchild et al., 2000; Huang et al., 2001; Treble et al., 2003; Treble et al., 2002), we find that it may be inappropriate to use the EOF technique to identify annual variations in very short records containing large volcanic events that overwhelm background variability, such as the ATM7 record presented here. Longer records may enable better separation of small annual geochemical variations from intermittent extreme events. The EOF analysis approach to multivariate speleothem proxy data may prove fruitful in the ongoing effort to understand interactions between the atmosphere, hydrosphere, biosphere, and rock record preserved in caves.
Figure 3-1. AVHRR satellite imagery showing atmospheric transport of El Chichón tephra imaged on April 5, 1982. Colors of ash plume denote ash concentrations. Note eastward transport of large quantities of tephra from the volcano (⊙) toward Belize and the cave site (⊙). The location of Fuego is also shown (⊙). Bar graph shows dates of ash and sulfate satellite observations (gray and yellow triangles) after the two eruptions on 4/4. Modified from Schneider et al., 1999.
Figure 3-2. Photographs of stalagmite ATM7. Polished upper cross-section shows the location of the laser ablation tracks (green) and XRF track (black) relative to the stable isotope micro-milling track (blue).
Figure 3-3. Chart of LA-ICPMS EOF factor loadings for the first three modes. The total variance explained by each mode of variance (EOF) is indicated. Positive loadings indicate positive correlation of a chemical species with mode; negative loadings indicate an inverse correlation of species with mode. Species with loadings of opposite sign on the same mode are anti-correlated. Species with small loadings, explaining less than 10% of variance, are not particularly important or well described by the mode in question.

EOF 1: 37.9 % variance

EOF 2: 11.1 % variance

EOF 3: 7.7 % variance

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Figure 3-4. Timeseries plot of LA-ICPMS variance in the first three EOFs. Y-axes are standardized variance values for each mode. Events in 1979 (A), 1981 (B), and 1982 (C) are highlighted. Event A (EOFs 1 and 2) is coincident with the 1982 El Chichón eruption. Event B (EOF 1, 2, 3) marks a suspected local fire or smaller volcanic event in the region. Event C (EOF 1 and 2) is coincident with a rusty-colored layer, low δ¹⁸O values, and extreme precipitation throughout most of 1979 when local rainfall was greater than three standard deviations above the norm. The first three EOF modes show relatively little variability from 1983 – 2001.
Figure 3-5. ATM7 Scanning XRF EOF results. Note major events A (1982), B (1979), and C (1974?).

EOF1: 28.7% variance

EOF2: 15.7% variance

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Figure 3-6. Monthly weather observations at Central Farm, Belize, showing water balance (difference between precipitation and pan evaporation) in gray, and mean maximum temperature in black. Two hydrological years are highlighted: a very wet year 1979 (A), and a slightly dry year 1981 (B).
Figure 3-7. LA-ICPMS EOF results for quiet latter period (1984 – 2001). Factor Loadings and timeseries plots of the first three EOF modes. Note that in the absence of volcanic dominance, lower-amplitude trends are apparent (see EOF3). Here, EOF 3 represents changes in the ratio of Sr + Ba:Mg, which vary on inter-annual and annual time-scales. The event in 1996-1997 (EOF1 and 2) is similar in character to the volcanic signals in the overall record, but much smaller in amplitude.
CHAPTER IV

ROOTING OUT THE AMPLIFICATION MECHANISM
LINKING A WEAK ENSO TELECONNECTION SIGNAL
AND A STRONG STALAGMITE CARBON ISOTOPE RECORD

Introduction

The El Niño-Southern Oscillation (ENSO) system is a primary driver of variations in global weather conditions on interannual time scales (Philander, 1990). The ENSO system oscillates chaotically between warm phases (El Niño events) and cold phases (La Niña events). Regions with strong ENSO teleconnections typically experience major changes in average rainfall and/or temperature regimes during strong El Niño events (Diaz and Kiladis, 1992). Some regions, such as central Belize, show weak or instrumentally undetectable ENSO teleconnection patterns (Belize National Meteorological Service). We were thus surprised to find a strong record of El Niño events in the carbon isotopic record of a Belize stalagmite (Frappier et al., 2002).

Stalagmites (mineral deposits typically composed of calcium carbonate) are formed in caves by slowly dripping groundwater. The ultimate source of this water is precipitation; however, the carbon isotopic ratios and dissolved ionic composition of rainwater is altered by interactions with the overlying biogeochemical system before reaching the cave. Stalagmite carbon (C) comes from three primary sources: local bedrock, atmospheric carbon dioxide (CO₂), and CO₂ produced by soil respiration. Carbon dissolved in percolating drip water is the approximate carbon source to the growing stalagmite. Thus, if the local bedrock carbon source is...
invariant, variations in stalagmite carbon isotopic ratios ($\delta^{13}C$ values) reflect changes in the overlying ecosystem’s carbon usage. However, large variations in groundwater carbon isotopic ratios on inter-annual and shorter time scales had not been measured previously (Figure 4-1).

The ATM7 stalagmite $\delta^{13}C$ record shows a marked rise in $\delta^{13}C$ values corresponding to recent El Niño events which occur with negative values on the Southern Oscillation Index (SOI), a key indicator of ENSO phase (Troup, 1965). The amplitude of the recorded $\delta^{13}C$ excursions varies between individual El Niño events, from about 5 to 10 per mil. Stalagmite stable carbon isotopic ratio variations have been used as a proxy for ancient biome variations over caves (e.g. C-3 forests vs. C-4 prairies) at century to millennial time scales (e.g. Denniston et al., 1999). In this record, the variation occurs across a 6-month period, yet the amplitude range is similar to that reported between forest and prairie biomes (Tieszen et al., 1989). Previous biome-based interpretations of speleothem records are not called into question by the work of Frappier et al., (2002), because the isotopic changes occur over sufficiently long periods of time to allow soil carbon turnover, and because they are consistent with lower-resolution regional pollen records. However, on short, interannual timescales, there is no theoretical prediction of a relationship between ENSO and carbon isotopes in terrestrial ecosystems, groundwater, or stalagmites – even though biospheric carbon fluxes are closely tied to ENSO (e.g. Jones et al., 2001). The ATM7 record revealed the operation of some poorly constrained carbon cycle process(es) (Frappier et al., 2002).

The discovery of a relationship between ENSO and carbon isotopic fractionation within terrestrial ecosystems is particularly puzzling in light of the lack of significant local temperature or precipitation anomalies during El Niño and La Niña intervals (Frappier et al., 2002). During the past few decades, local meteorological variables had no significant variation in the interannual (ENSO) band. A multivariate analysis showed that weather anomalies in Belize are also not significantly related to ENSO. The ATM7 record indicates that the magnitude of El Niño
teleconnections at this site has apparently been amplified by the ecosystem carbon cycle with respect to local weather variations. This result raises a series of important questions:

- How does ENSO affect ecosystem carbon fluxes in regions without significant weather teleconnections?
- What is the relative importance of physical processes (e.g. barometric pressure) compared to biological processes (e.g. soil respiration rates)?
- How does the carbon biogeochemical system amplify the apparent local magnitude of ENSO forcing?
- What are the most appropriate variables to capture ENSO’s impact on terrestrial ecosystems?
- What are the implications of these processes for our current understanding of terrestrial carbon cycle dynamics?

In the absence of significant ENSO-related variations in daily meteorological observations, the teleconnection between ENSO and Belize must be controlled by variables that are not reported by the Belize Meteorological Service and/or distributed among multiple environmental factors (Taylor et al., 2002). One way to explore the nature of the ENSO-Belize teleconnection is through modeling. Another approach that is the subject of this paper is remote sensing. NASA’s archive of remote sensing products enabled us to explore various environmental factors for significant relationships to ENSO and Belize during recent decades.

Interannual variability in carbon fluxes from terrestrial ecosystems is more than twice that of marine sources (Bousquet et al., 2000). ENSO-driven variability in terrestrial ecosystem carbon cycle dynamics from regions without obvious teleconnections may constitute an important contribution to global CO₂ fluxes (Frappier et al., 2002). Identifying the specific carbon cycle
processes and their climatic controls is important for projecting future atmospheric greenhouse
gas concentrations. It is thus essential to determine how this stable carbon isotope record was
produced to understand the implications (if any) of this discovery for climate-carbon cycle
interactions.

Given the problem of identifying the local ENSO teleconnection driver(s), a key
observation to consider is the relative amplitude of the annual cycle compared to the inter-annual
signal. The annual cycle dominates local weather records; yet although the stalagmite contains
approximately annual layers, the ENSO signal clearly dominates the stable isotope record. We
expected to identify strong interannual variability in some local factors. Any proposed
mechanisms must be capable of producing the rapid and continuous response of groundwater
carbon isotopes to ENSO that are implied by the dynamical details of the SOI captured by the
ATM7 record. We expected the local teleconnection factor or factors involved to show a
relatively strong correlation or lag correlation with the SOI. Furthermore, the unknown
teleconnection factor or factors that drive this system may be dominated by physical (climatic)
processes or could be dominated by non-linear vegetation responses to physical forcing. For
example, forest canopy openness and soil respiration rates can affect the carbon isotopic
composition of soil gas (Amundson et al., 1998; Cerling et al., 1991; Sternberg et al., 1997).
Candidate drivers for the ENSO teleconnection must be characterized by temporal variations in
Belize with maximum power in the interannual band, correlate with ENSO phase, and be
consistent with local meteorological data. The behavior of these variables during ENSO phase
transitions may also be particularly critical (Behrenfeld et al., 2001).

In order to understand the links connecting El Niño events and ATM7 δ¹³C values, two
major issues must be addressed: 1) the teleconnection factor(s) by which ENSO affects this
cosystem, and 2) the biogeochemical dynamics that transfer the ENSO signal to groundwater
δ¹³C values. This study focuses on former, which can be addressed by analyzing a variety of
remotely sensed environmental parameters for Belize during past ENSO cycles. The objective of this study was thus to explore the nature of the ENSO teleconnection in central Belize using a wide array of available observations, including local ground-based and remotely sensed measurements of physical and biological factors. A set of hypotheses have been generated to address the relative importance of the most likely teleconnection factors linking ENSO and the local carbon cycle that can be explored by analyzing patterns in local weather and remote sensing datasets:

H1: ENSO affects weather variables not measured by local meteorological stations.
H2: ENSO has a coherent effect that is distributed across a set of atmospheric parameters.
H3: ENSO has a weak effect on local weather, amplified by ecosystem changes in the forest canopy.
H4: ENSO has a weak effect on local weather, amplified by ecosystem changes below the forest canopy.

This paper explores variations in atmospheric and forest canopy parameters in relation to the SOI in order to examine what support there is for any of the aforementioned hypotheses. We explore variables readily available in the scientific literature that might provide indications regarding the links between ENSO and the carbon cycle at the cave site in central Belize. Parameters of interest include barometric pressure, surface temperature, atmospheric CO₂ concentration, dust, cloud amount and optical thickness, potential evaporation, relative humidity, precipitation, soil moisture, canopy openness, and leaf color indices (Graham et al., 2003; Schaefer et al., 2002). The first and second hypotheses can be tested by incorporating a larger number of remotely sensed parameters into a time-series lag correlation matrix using the SOI as the predictor variable. The third hypothesis can be tested by comparing the SOI and local weather teleconnections to remotely sensed forest canopy measures. The fourth hypothesis falls
outside the scope of this paper, but could be addressed by monitoring the micrometeorology and carbon cycle dynamics at the forest-cave site across an ENSO cycle.

Methods

To investigate the relationships between the Southern Oscillation and the local weather and forest ecosystem response, we collected several long-term remote sensing and meteorological datasets describing weather, atmosphere, and vegetation near the cave site (Table 4-1). The Trenberth Southern Oscillation Index (SOI) served as our primary ENSO descriptor (Trenberth, 1984). As SOI is a monthly index, we also sought descriptors of Belizean weather, atmosphere, and vegetation at monthly temporal resolution. The Belize Meteorological Service supplied daily weather observations of temperature, precipitation, and evaporation from the nearby Central Farm station (17°11' N lat., 89° W long., elevation 64 m). We compiled these daily observations into monthly indices describing the maximum, minimum, mean, and in some cases totals within a month, for each daily temperature, precipitation, sunshine, and pan evaporation (Table 4-1).

In all cases, the datasets containing the satellite-derived descriptors covered relatively large areas measured in fractions of degrees. Thus, for all remote-sensing datasets, we used the highest resolution grid datasets available (see Table 4-1) and queried the parameter value of the pixel best centered on the cave site at 17.1167° N lat., 88.8833° W long., 100 m elevation. We queried all MODIS, TOMS, and TRMM datasets using the GES-DISC Interactive Online Visualization ANd aNalysis Infrastructure (Giovanni) web-based data archive query tool at NASA's Goddard Earth Sciences (GES) Data and Information Services Center (DISC); these datasets can be found at NASA’s permanent data archive center Distributed Active Archive Center (DAAC, 2006). Our measure of vegetation amount over the cave was the Fourier-Adjusted, Solar-zenith-angle corrected, Interpolated, Reconstructed (FASIR) Normalized
Difference Vegetation Index (NDVI) available as monthly observations from 1983-1998 (Hall et al., 2005). Again, we selected for each month the quarter degree pixel best centered over the cave site.

Most of the variables showed strong seasonal trends that were much stronger than any interannual variations. We removed seasonal signals from each parameter by calculating monthly means for each parameter and subtracting the monthly means from each observation in their respective months. We then calculated time-series cross-correlations between the SOI and the monthly variables describing local surface weather, atmospheric conditions, and vegetation (Table 4-1). Many satellite-derived parameters were only available for short time periods, covering only one or two ENSO events (Fig. 4-1). We calculated correlation lags of between 0 and 24 months, with the SOI as the leading indicator, for the weather variables from the Belize Meteorological service and the FASIR-NDVI. For all other remote-sensing derived variables (primarily the satellite-derived atmospheric descriptors), we calculated only 12 month lags as the data were available for only 5-6 years (Fig. 4-2); longer lags would have resulted in too small a sample size to adequately calculate correlation coefficients. Confidence intervals were calculated for all of the cross-correlations to determine the likelihood the correlation coefficients were noise. Correlations beyond the 95% confidence intervals we considered likely to be real. All statistical analyses were performed using R 2.0.1 (R et al., 2004).

Results

Most weather variables showed cross-correlations with the SOI beyond the 95% confidence intervals at some lag between 0 and 24 months (Table 4-2). However, the maximum correlation coefficient (R value) was 0.368 (Latent heat at 4-5 km, Table 4-2) indicating that the univariate cross-correlations between SOI and weather and atmospheric properties in Belize were
weak. This finding is consistent with results from a more simple lag correlation analysis using only local weather data (Frappier et al., 2002a). In addition, there were no clear patterns in the lag periods; variables seem to respond independently to ENSO forcing (Table 4-2).

Examining the variables separately, the strongest links to SOI were related to atmospheric moisture. SOI seemed to be positively correlated (correlation coefficients between 0.270 and 0.368) with latent heat at between the surface and 6 km above the Earth’s surface 5 months later (Table 4-2). The SOI was negatively related to atmospheric column water vapor content between lags of 0 and 6 months (correlation coefficients between 0.261 and 0.292; Table 4-2). SOI was positively related to the maximum monthly evaporation with lags of 0 to 7 months (R between 0.191 and 0.289; Table 4-2). However, we cannot infer that significant, longer lags do not exist in the short-term variables. Because of the brief length of these series, lack of evidence for long lags is not evidence of their absence.

A few variables showed weaker correlations that appeared much later; not surprisingly, these longer lags were apparent in the longer observational series. El Niño did not affect average temperature or precipitation amount, but increased the monthly extreme maximum daily temperature by about +1.6 °C, about 13-14 months after SOI changes in the Pacific. The ENSO effect is weak but significant in a multivariate 13-month regression, including maximum daily temperature (both extreme daily max and min), maximum daily precipitation, hours of sunshine (reflective of cloudiness), and evaporation.

To investigate the potential response of the forest canopy to ENSO, we also conducted a lag correlation analysis on NDVI data. Like most other variables included in this analysis, the seasonal NDVI variations are large compared to the interannual mode. Similar to the weather observations and remotely sensed data described above, ENSO correlations were not significant at the 95% confidence level unless seasonal variations were removed. NDVI analysis of a 0.25 degree grid cell containing the field site in Belize showed that while the ENSO effect is significant, it is rather weak compared to seasonal effects. This NDVI effect size comparison is
consistent with the difference in the amplitude of climate forcing in Belize at the seasonal vs. interannual scales. The NDVI lag was significant at 14-15 months. Interestingly, the longest NDVI lag follows changes in local temperature extremes by only about 1-2 months, but follows the most widespread weather changes by about 6 months.

**Discussion**

We cast a wide net with the goal of capturing the teleconnection mechanism linking ENSO variability in the Pacific with central Belize environmental conditions. Toward that end, we combined data series of different length. This approach had the advantages of including more variables and El Niño events, but also made it inherently more difficult to assess longer-period lags. Thus, finding short-period ENSO lags in the brief satellite data series does not rule out the possibility that atmospheric variables may also play a role over a longer term. This result is consistent with previous work showing that the lag response of terrestrial ecosystem productivity to relatively small ENSO-driven temperature change is biome-specific, and varies in strength and even sign at different lag periods from zero to three years (Braswell et al., 1997). As the satellite series grow over time, the links may become more clear between regional atmospheric conditions over Central America and the Caribbean and local weather extremes in Belize. Some weather variables not measured by local meteorological stations show an ENSO response (e.g. latent heat, aerosols, cloudiness, and vegetation NDVI), lending some support to H1.

Each potential local forcing factor seems to respond independently. While no ENSO lag correlations were found when seasonal variations were not removed (Frappier et al., 2002), the present analysis of seasonally de-trended weather data found weak lags at 0-8 months and 13-14 months, distributed across several variables with respect to the SOI. The lack of a coherent lag pattern distributed across several weather patterns refutes H2.
Both Belize surface weather observations and remotely sensed parameters show the same overall pattern: weak interannual variations superimposed upon very strong annual cycles. This contrasts with the stalagmite stable isotope record which is dominated by ENSO, with a weaker seasonal cycle. The present analysis confirms the presence of some integration or amplification of the interannual signal and/or damping of the seasonal signal, operating in the gap between the local teleconnection and the stalagmite surface. Some non-linear process(es) of carbon isotope dynamics involved in amplifying the interannual effect of ENSO remain unexplained.

Nevertheless, the present analysis does point toward some interesting aspects of the local manifestation of ENSO. Stronger lag correlations are associated with weak anomalies in daily weather extremes (e.g. precipitation intensity, extreme daily temperatures), suggesting that daily weather anomalies are involved in driving the stalagmite ENSO signal. Atmospheric moisture also seems to be involved, though only short lags have been identified (5 months for latent heat in the lower troposphere; 0-7 months for ground-based maximum daily evaporation). The mechanism(s) through which these anomalies in moisture and daily extremes are translated into carbon isotope dynamics is a critical part of this puzzle that requires further investigation using different methods.

However, the lower-amplitude ENSO signal in the ATM7 stable oxygen isotope ratio ($\delta^{18}O$ value) record provides some direction (Chapter 2, Fig. 3). This related proxy indicates that local weather is affected by ENSO through one or more of the following mechanisms: precipitation or evaporation amount, storm tracks, or the isotopic composition of the water vapor source (organization of the tropical atmosphere) (Dansgaard, 1964b; Lawrence et al., 2004). In particular, the extended period of increased evaporative extremes at lag periods of 0-7 months could have important impacts on soil microbial activity. Simple changes in storm tracks or the isotopic composition in local precipitation are unlikely to perturb $\delta^{13}C$ values. There is no evidence for substantial changes in local precipitation amount related to ENSO, although El Niño increases precipitation variability by contributing a slight increase to the intensity of daily rainfall.
at 0-3 months. Thus, we infer that the local effect of ENSO is probably a temperature and moisture signal delivered primarily through changes in evaporation and precipitation intensity.

Similar to the weather and remote sensing analysis, ENSO signals are not apparent in NDVI data when seasonal patterns are not removed. ENSO has a small effect on the forest canopy superimposed on a stronger seasonal cycle. The canopy responds weakly to a similarly weak ENSO teleconnection distributed across an array of lags and a number of weather and atmospheric variables. The seasonally de-trended NDVI lag analysis shows a long lag of 13-15 months, following the 11-13 month SOI lag in temperature extremes by 1-2 months. Research supports variable canopy response timescales (Braswell et al., 1997). This suggests that the local vegetation may be responding to either the ~1-year local temperature lag, or the shorter atmospheric moisture/precipitation lag of 0-6 months found in the remote sensing series.

It is important to note that NDVI is a fairly coarse measure of vegetation cover, and may not be the most appropriate measure for exploring ENSO-ecosystem links. Vegetation may participate in the ENSO signal transmission through three primary factors: canopy openness (CO₂ recycling), δ¹³C values of respired CO₂, and δ¹³C values of photosynthetic products (Farquhar et al., 1989). We suggest that a more conclusive study of canopy involvement could be conducted using LANDSAT data. LANDSAT coverages are more spatially-resolved and contain a range of spectral bands that can be queried in many combinations in order to focus on particular signals, such as water stress, leaf area, and nutrient limitation (ERDAS, 1999; Lauer et al., 1997). A more detailed analysis of LANDSAT data could provide a more quantitative assessment of the role played by the forest canopy.

Ecological systems are notoriously non-linear, and can be extraordinarily sensitive to small environmental changes at critical control points (Burkett et al., 2005). Belowground communities in particular can respond very rapidly to changes in environmental extremes as well as mean conditions (Wardle, 2002). Furthermore, related studies have not shown ENSO variability in speleothem growth rate or trace element concentrations (Chapters 2 and 3).
have not ruled out a physical controlling process. If the latent heat changes (5 month lag) and barometric pressure variability (no lag) are related to changes in atmospheric turbulence, any soil CO₂ efflux response would change the δ¹³C value of soil CO₂ (Malhi et al., 1998). However, two lines of evidence in particular make it difficult to envision a purely physical driver for the carbon isotopic manifestation of ENSO and point toward some biological amplification mechanism: 1) the apparent weakness of the interannual local manifestation of ENSO compared to the seasonal pattern, and 2) the confinement of the ENSO signal to the stable isotope ratios.

Conclusions

The ENSO teleconnection to Belize is only apparent after correcting for seasonal variations. The effect of ENSO on Belize weather is weak, distributed amongst several weather variables. The most important teleconnection factors linking ENSO to central Belize's ENSO appear to be anomalous moisture and temperature/precipitation extremes. While some remotely sensed variables respond with a lag timescale of zero to six months, a more coherent set of weather variables respond with a lag of about 13-14 months. The ENSO teleconnection in Belize lags behind the equatorial Pacific by several months to a year, consistent with recent studies showing a lag for the Caribbean region (Chiang and Sobel, 2002; Giannini et al., 2001; Giannini et al., 2000).

A weak El Niño signal in the NDVI data was found to most closely follow the local temperature lag. This pattern points toward a sub-canopy amplification mechanism; however, canopy involvement cannot be ruled out on the basis of relatively coarse NDVI data alone. We have also argued that the biogeochemical amplifying factors of the local ENSO teleconnection are most likely non-linear biological processes sensitive to small changes in moisture and temperature extremes.
Future analyses could narrow the list of potential teleconnection drivers by exploring forest canopy involvement using more sensitive LANDSAT coverages, and by assessing possible longer ENSO lag signals distributed among remotely sensed atmospheric parameters. Remote sensing techniques cannot detect sub-canopy or belowground linkages between ENSO forcing and local carbon cycle. Rather, the transformation of a weak ENSO teleconnection signal into a strong groundwater signal can be investigated most effectively through real-time monitoring of local micrometeorology, ecosystem carbon processing, cave dripwater chemistry, and direct measurements of local carbon reservoirs, carbon fluxes, and microbial activity. Monitoring across an ENSO cycle will be vital to identifying the mysterious processes involved in the ATM7 record. The data obtained in such an effort may also contribute to the thorny disciplinary problem of $\delta^{13}$C value interpretation in speleothem records.

While this analysis has advanced our understanding of the nature of the ENSO teleconnection in central Belize, many outstanding questions remain and the local manifestation of ENSO remains incompletely understood. Any assessment of the potential implications of the $\delta^{13}$C signal for the current understanding of the interactions between climate variability and terrestrial carbon cycling, must be postponed until the proxy systematics that underpin the ATM7 record can be unraveled through higher resolution analyses and sub-canopy investigations. From the perspective of paleoenvironmental research, it remains troubling that a sedimentary proxy record should reflect local environmental factors in such a biased manner. The apparent Gordian knot posed by the ATM7 record remains to be solved by future research.
Table 4-1. Data Sources.

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Table 4-2. SOI Lag Cross-Correlation Coefficients. Items in bold were significant at the 95% confidence interval.

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<td>Min (mm)</td>
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Figure 4-1. ATM7 carbon isotope record and Southern Oscillation Index (SOI). Stalagmite $\delta^{13}C$ values (black) with the SOI (gray, inverted axis). N.B. The time scales and associated curves are offset, reflecting the time lag between SOI and ATM7 calcite deposition (teleconnection time plus time for rain water percolation from surface to cave). The El Niño events of 1987-88, 1997-98 and 1982-83 are readily apparent. Lower amplitude events in the early 1990's, 1979-81, and late 1970's are also evident. ATM7 was collected in January 2001. After Frappier et al., 2002.
Figure 4-2. Timeline of Data Sources. Abbreviations as in Table 4-1.

1 - SOI

2 - BMS Observations

3 - FASIR-NDVI

4 - MODIS/Terra Atmosphere (MOD08_M3)

5 - TRMM V6 Monthly TMI (3A12 V6); ISLSCP II
CONCLUSIONS

In the preceding chapters, I have demonstrated the sensitivity of a rapidly-growing, fracture-fed tropical stalagmite record to regional tropical cyclone activity, major regional volcanic tephra deposition events, and weak El Nino teleconnections. The implications of this research are exciting, as this work has generated far more questions than it has answered. In particular, this work forms the basis for new approaches to paleotempestology, and contributes to an emerging effort to generate speleothem-based records of explosive volcanic activity in the past. The field of speleothem paleoclimatology is in its infancy, and there is great potential for scientific discoveries in this area of inquiry. The results discussed herein form a foundation upon which to develop new tools for paleo-environmental research that will enable the broader research community to address outstanding fundamental questions in new ways, for example:

Do field sample selection methods actually result in more sensitive stalagmite proxy records?

What conditions must be satisfied for speleothem proxy records to be reproducible?

How common are stalagmites that are sensitive recorders of tropical cyclone rainfall?

What is the return period for catastrophic tropical cyclone strikes in regions without extensive historical records?

What was hurricane activity like during intervals of paleoclimatic interest, such as the Last Glacial Maximum and the Eemian interglacial?

What are the relations between tropical cyclone landfalls and large-scale climate boundary conditions?
How does weak hurricane activity during pre-historic "hyperactive" tropical cyclone periods compare to the 20th century (e.g., Liu, 2000)?

Can stalagmite trace element spectra distinguish between tephra from different volcanoes?

How sensitive are stalagmites to regional and pan-tropical volcanic fallout?

Do major volcanic eruptions generate marker horizons recognizable in stalagmites across a region?

Can stalagmites provide annually resolved records of tropical volcanic forcing akin to polar ice core records of high-latitude volcanism?

By what mechanism(s) are weak local teleconnections amplified into strong carbon isotope proxy signals?

The fidelity and sensitivity with which different speleothems record proxy evidence of various environmental factors depends fundamentally on the epikarst channel that acts as a signal filter between the aboveground environment and an active stalagmite surface. The amplitude of a proxy may not reflect the amplitude of the local forcing mechanism (Chapter 2, Chapter 4). Stalagmites that are ideally sensitive to one factor (such as hurricane infiltration events) may be less faithful recorders of other factors of interest. Trade-offs abound; for example, stalagmites selected for their responsiveness to brief, flashy infiltration may also be more likely to contain visible layering related to sub-annual events that must be carefully distinguished from annual layers (Chapter 2).

The internal cave environment is often very stable; yet, stochastic events can cause singularities that must be distinguished from environmental controls. Coherence between multiple records is strong evidence of reliable proxy signals (Dorale et al., 2002a). Although analyzing multiple stalagmites was beyond the scope of the present work, replication of stalagmite records is a necessary next step in the development of paleo-tempest and paleo-
volcanism proxies. For the potential of speleothem approaches to Earth System Science research to be realized, existing singular records must be replicated.

Developing new, multi-proxy records at the highest possible resolution is one avenue that leads effectively toward greater insight into the mechanisms and history implied by the stalagmite records. Comparing the behavior of different parameters can provide greater insight into system dynamics. Consider the findings that no ENSO events are evident in the trace element record, and that no volcanic signals are found in the stable isotope record. Even when the mechanisms are incompletely known, speleothem record exploration can reveal processes of interest occurring in the cave, ecosystem, or regional environment (Chapters 1-4).

It is critical to conduct modern calibration of stalagmite proxy signals at all study sites as soon as it is feasible to deploy the monitoring equipment, particularly in cases where the exact mechanism of signal emplacement is unknown. Thus, a second line of inquiry that is likely to revolutionize our understanding of the possibilities and pitfalls of speleothem records involves modern process studies. This approach can integrate basic observational, experimental, and modeling approaches, and has been used successfully by the ice core community (Dibb, 1989; Wake et al., 1993; Wake et al., 2002). Few tropical cave sites are subject to systematic monitoring (Mickler et al., 2004a; Sondag et al., 2003). At this time, advancing in the state of the science particularly requires systematic, real-time studies of the links between modern cave systems, the overlying above- and below-ground ecosystem that acts as a biogeochemical signal processor, and external forcing factors from precipitation, climatic variability, aerosol deposition. Field relations indicating epikarst pathway characteristics and likely sensitivities as well as sensitivity trade-offs should be included in field sample collection and laboratory selection procedures in order to focus analytical resources on samples (e.g. Chapter 1).
Future Directions

My current research track has two rails: terrestrial carbon cycling and paleo-tempestology, the emerging science of past hurricanes. Through the former, I hope to shed light on the relation between climate variability and the natural/perturbed carbon cycle. Through the latter, I hope to quantify the relations between climate regimes and hurricane activity, a matter only beginning to come to the attention of the general public. Going forward, I am dedicated to contributing key datasets that could be used to address fundamental scientific questions with societal relevance, such as:

- Beyond the instrumental record, how is hurricane activity related to climate factors such as ocean temperature and ENSO?
- What links exist between hurricane activity and thermohaline circulation?
- How important are the tropics in controlling climate change?
- What triggers rapid changes in tropical moisture (e.g. Mega-droughts)?
- How extensively do weak climatic variations perturb the terrestrial carbon cycle?
- How have seasonal climate variability/weather extremes affected ecosystems/human culture? For example, in Central America, the relative importance of socioeconomic vs. environmental factors in precipitating cultural change will remain unresolved until the history of climatic and ecological changes are better constrained.

The initial stalagmite tropical cyclone proxy record was validated against the historical record (Frappier et al., 2002; Chapter 2, Chapter 3). Based on our initial stalagmite record, we developed and calibrated a quantitative proxy model to reconstruct tropical cyclone frequency and intensity. However, to further validate the approach, it will be necessary to obtain additional
speleothem records on which to apply the model to determine its universal applicability so that it can be subsequently applied to times prior to observational records. Once the proposed paleohurricane proxy technique has been fully tested, it should be possible for paleotempestologists to quantify variations in tropical cyclone landfall frequency and intensity in any tropical cyclone basin during intervals of paleoclimatic interest throughout the Holocene and in the more distant past. Toward that end, I am pursuing a follow-up project to replicate and further validate the new speleothem paleo-Hurricane proxy. I have proposed to develop and test the proxy by producing three century-long high-resolution stalagmite stable isotope records and then apply it to an ancient century-long time interval for which we have no instrumental record.

In collaboration with my colleagues from a variety of institutions, I will continue to pursue paleotempestology and the modern and ancient expressions of terrestrial biogeochemical change. Despite their devastating impact on societies throughout history, we know very little about the interactions between tropical cyclones and the climate system. I plan to apply my newly-developed tool to investigate hurricane frequency and intensity in the past during different climate regimes, which will provide new and valuable perspectives to inform modeling efforts and advance understanding of the consequences of global climate change for hurricane activity.

Developing a spatially distributed network of cave sites is central to addressing the questions posed above. I recently helped establish a new international Collaborative Research Network for Paleotempestology. The Inter-American Institute for Global Change Research (IAI) has just awarded our group a major five-year grant to develop a pan-Caribbean network of paleohurricane records and to translate our findings into a regional risk GIS database for policy-makers and other stakeholders. My role in the network will be to lead the effort to sharpen the new speleothem hurricane proxy into a broadly applicable scientific tool.

I am also developing relationships with ecologists in order to investigate the impact of the area’s weak El Niño teleconnections on carbon fluxes and ecosystem function in more detail, from a systems perspective. I hope to advance this research in cooperation with local Belizean
scientists by establishing a regular sampling program for water and soil carbon, and outfitting the
site with an array of datalogging sensors. This will lay the groundwork for future terrestrial
paleoecological and carbon cycling studies.

This dissertation research has demonstrated that speleothems are a very promising source
of high-resolution, multi-proxy paleo-environmental data. Speleothems are indeed emerging as
the ‘ice cores of the lowland tropics’. In particular, I am optimistic about the potential for
tropical speleothem records to revolutionize the current understanding of key climate system
interactions, principally volcanic climate forcing, tropical cyclone-climate interactions, and the
links between land-use history and terrestrial carbon cycling. Our understanding of past, present,
and future interactions within the Earth System will grow as speleothem-based paleoclimatology
matures. I anticipate contributing to this effort by building on the lines of inquiry initiated during
this dissertation research.
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Climate in Belize is tropical to subtropical. The average annual temperature in Central Belize is \(-25^\circ C\) with about 1600 mm of annual rainfall (Frutos, 2006). Central Belize has a seasonal water deficit during the dry season (early March through late May), followed by summer monsoon rainfall (Fig. A1). The wet season extends from June through January, transitioning to cold front precipitation by November. Precipitation is moderate in August during the so-called “little dry” period. Tropical cyclones have made landfall in Belize from June through November, although September is the most active month (Fig. A2) (Frutos, 2006). Tropical cyclone events are bracketed by other frontal and convective precipitation. Tropical cyclones bring heavy rainfall and flooding to Belize with a recurrence interval of \(-2.5\) years, contributing approximately 2.5% of annual precipitation (calculated for 1978 - 2001). Climate data is courtesy of the Belize Meteorological Service’s Central Farm meteorological station, located less than 15 km from the field site.

Located between true rainforest of Southern Belize and the Yucatan tropical scrub to the north, the dominant forest type at the site is mature subtropical moist semi-evergreen broadleaf forest (Vreugdenhil et al., 2002). The cave is located in the Tapir Mountain Nature Reserve, which was donated to the Belizean government in 1975 and formally designated as a preserve in 1986. Common tree species include *Swietenia macrophilla* (mahogany), *Manilkara zapota* (chicle), *Brosimum alicastrum* (Ramon breadnut), *Orbigyna cohune* (cohune palm), *Cryosophila stauracantha* (“Give-and-Take Palm”), *Agonandra sp.* (guinweo vine), *Ficus crassiuscula* (strangling fig), *Cedrela odorata* (Spanish “cedar”).
Monthly Precipitation and Evaporation (mm)

Figure A1. Belize Climatology (Central Farm Meteorological Station, 1973-2005), including monthly precipitation (thin blue line), evaporation (dashed line), and mean temperature (bold red line). Water balance (precipitation - evaporation) is negative from February through May.

Figure A2. Seasonality of Belize Hurricanes (1883 - 2005). After Frutos, 2006. Tropical cyclones occur in the middle of the wet season.
Limestones and dolomites of Late Cretaceous age and Paleozoic limestones make up the bulk of local bedrock (Miller, 1996). The cave site used in this study, Actun Tunichil Muknal (ATM), is developed in a massive pink limestone breccia. This bedrock unit correlates with a locally described rock unit in Central Belize known as the Albion formation or “Teakettle Diamictite,” which has been identified as the K-T boundary in central Belize (King and Jr., 1996; Pope and Ocampo, 2000). This breccia unit, common in the Boundary Fault Karst region of Belize, has low primary porosity with major speleogenesis occurring in conjunction with fractures (Miller, 1996).

ATM is an active, multi-level phreatic cave with an underground river flowing through low passages (Miller, 1990). The river enters ATM through a sink in a different drainage basin, flowing underground for 5 km and ultimately emptying into Roaring Creek about 100 m from the resurgence. The keyhole-shaped lower cave entrance shows clear geomorphic evidence of the downcutting origin of multiple upper-level passages. Elevated cave passages in ATM are heavily decorated with speleothems, and were used for ceremonial purposes by the Maya civilization c. 400-900 CE (Miller, 1990). Some speleothems are actively forming, while others appear desiccated. An upper level passage, about 500 m from the cave entrance, where speleothems were collected for this study has a stable temperature of 25°C and relative humidity of >90%. Bedrock overburden above this portion of the cave is at least 10 m in thickness, but may extend a few tens of meters. Soil cores taken on the hill above the cave yielded thin, clay-rich soils (5-30 cm depth) with a minimal organic horizon and a thin covering of leaf litter. Carbonate bedrock outcrops also attest to the thin upland soils over ATM.
APPENDIX B

MICRO-MILLING AND STABLE ISOTOPE ANALYSIS

Micro-samples were milled continuously from the surface of ATM7 the polished stalagmite slab at 20 μm intervals (Fig. A2) with a CM-1 micro-milling system custom-built by Scott J. Carpenter. The system combines a fixed drill (Brasseler UP 200 controller and a UG 12 handpiece fitted with a 0.3 mm tungsten carbide dental bur), computer-controlled stage, and observation under a Nikon SMZU microscope. A rotational stage allowed us to rotate the sample relative to the drilling axis as milling progressed in order to maintain alignment with the growth axis (Fig. A2).

The width of the continuously-milled micromilling track is shown as a blue outline in Fig. A2. The depth of all micro-samples from the surface of the slab was approximately 0.5 mm. The first 37 samples (two annual layers in the uppermost 1.48 mm) were milled at 40 micron intervals, and 5-6 mm in width. It was clear at this point that a smaller drilling track would generate sufficient material for stable isotope analysis. The remaining micro-samples were milled at 20 micron intervals, where the track was approximately 2.5 mm across. Individual calcite powder samples were transferred using a stainless steel scalpel from the milled surface to individual stainless steel-sample containers. Static electricity enables the calcite powder to cling to the scalpel so that samples can be recovered reliably. Between samples, the drill bit and milling surface were cleaned with a stream of compressed air. Each 20 micron micro-sample represents one to several weeks of deposition. Some commercially available micro-milling equipment can be used to the same effect.
Stable Isotope Analysis was performed at the Paul H. Nelson Stable Isotope Laboratory at University of Iowa. Calcite powders were roasted in vacuo at 380°C for one hour to remove volatile contaminants and then desiccated. We analyzed ~1300 samples using a Finnigan-MAT 252 IRMS with a Kiel III automated carbonate device. Powdered calcite samples (approximately 0.02 to 0.05 mg of CaCO₃ for each sample) were reacted with 2 drops of anhydrous phosphoric acid at 75°C. Daily analysis of NIST powdered carbonate standards (NBS-18, 19, 20) and several in-house standards were conducted. Analytical precision on these standards was better than ±0.1 ‰ for both δ¹⁸O and δ¹³C values. All results are reported in per mil (‰) relative to V-PDB.
APPENDIX C

AGE MODEL

We have updated the age model initially published for this stalagmite record to correct counting errors in a previously published dataset (Frappier et al., 2002). We show that these counting errors are related to the direct hydrological effects of heavy tropical cyclone precipitation. It is important to note that while the low δ¹⁸O excursions were important in identifying counting errors, the stable isotope excursions themselves are not used as a dating tool. We avoid a circular argument for dating the low δ¹⁸O excursions by using independent lines of evidence to test the updated age model, outlined below. Thus verified, the updated age model can be used to determine the year in which low δ¹⁸O excursions were deposited and compare those dates with the historical record of tropical cyclone activity in the area. In this section, we describe the initial age model development and justify the changes in the present work.

Major groundwater flushing events can result in double bands or couplets of speleothem calcite, representing a single annual period (e.g. Asmerom and Polyak, 2004) and references therein; (Baker et al., 1993; Kaufmann and Dreybrodt, 2004; Proctor et al., 2000). The oscillation between seasons with positive and negative water balance triggers seasonal shifts in dripwater volume and isotopic composition, color, luminescence, trace element concentrations, and/or crystal fabric. Central Belize experiences an annual water deficit from March through May followed by onset of the summer monsoon (Fig. A1), conditions amenable to generating annual variations in dripwater chemistry and calcite morphology. The initial and updated age models are based on our interpretation of visible band pairs as annual deposits. After describing age model development and changes below, we show that both age models are supported by ¹³⁷Cs dating,
and that the updated age model is further supported by independent stratigraphic, isotopic, and trace element evidence.

**Radiometric Dating**

The $^{137}$Cs activity depth profile was used to test whether layer counting was consistent with an annual pattern of calcite deposition (Fig. A3). Although no classic radiometric decay curve is evident in the data, the onset of $^{137}$Cs activity is clearly demarcated. It is important to note that a classical decay curve is not necessarily predicted in this depositional setting. Cesium substitutes strongly for the macronutrient Potassium; as a result, in tropical ecosystems $^{137}$Cs is not simply transmitted to the cave but is tightly cycled within the overlying ecosystem and soil (Dörr and Münnich, 1989; Ritchie and McHenry, 1990; Robison et al., 1997; Walker et al., 1997). However, the depth of $^{137}$Cs activity onset provides sufficient age control to test the presence or absence of annual banding in this stalagmite. Using this approach, the error in $^{137}$Cs dating is primarily related to the spatial resolution of $^{137}$Cs samples and the assumptions used to derive ages from the depth of $^{137}$Cs activity onset.

The onset of $^{137}$Cs activity at a depth between 48 mm and 39 mm marks the start of global atmospheric fallout from thermonuclear weapons testing (Robinson et al., 2002) (Fig. A3). We bracketed growth rates for the upper portion of ATM7 with three different assumptions:

1. The highest stratigraphic level at which zero $^{137}$Cs activity was measured (-48 mm) reflects pre-atmospheric weapons testing conditions that prevailed in 1953 or earlier. This assumption yields a maximum growth rate of 1.02 mm·yr$^{-1}$.

2. The depth of $^{137}$Cs activity onset (-39 mm) may represent the onset of atmospheric fallout as early as 1954. This assumption yields a minimum growth rate of 0.85 mm·yr$^{-1}$.
Figure A3. ATM7 $^{137}$Cs activity profile. Error bars are 1 standard deviation. Note that the activity of $^{137}$Cs exceeds zero above 4.8 mm.

3. An early maximum of $^{137}$Cs activity (~39 mm) may also represent the peak of thermonuclear fallout in 1963. This assumption yields a growth rate of 1.05 mm·yr$^{-1}$. The average of these three radiometrically-constrained growth rates was 1.03 mm·yr$^{-1}$ ± 0.08.

**Layer Counting and Initial Age Model**

Paired visible couplets of clear and opaque calcite laminae in ATM7 are thought to correspond to the dry and wet seasons during the March – February hydrological year (Frappier et al., 2002a). The average radiometrically constrained growth rate estimate for the upper 60 mm (1.03 mm·yr$^{-1}$ ± 0.08) was indistinguishable from the layer-counting growth rate calculated for the
same section (1.04 mm·yr⁻¹). However, we observed that layer thickness was greater in the upper
two dozen couplets, the portion of ATM7 subjected to high-resolution stable isotope analysis
(Fig. 2). We surmised that the growth rate was higher than average in the uppermost portion of
ATM7. The layer-counting-based growth rate in the micro-sampled portion was slightly higher,
1.15 mm·yr⁻¹. The radiometric age model and the more detailed annual layer-counting-based age
model are consistent with one another.

Having established consistency between ATM7 stratigraphic patterns and ¹³⁷Cs dating,
we concluded that opaque-clear couplets represent annual depositional cycles. We assigned a
linear growth function to each annual couplet to generate a refined age model with a March date
for the base of each hydrological year (Frappier et al. 2002). In the absence of counting errors, the
simplifying assumption of linear growth within each hydrological year results in variable dating
error for individual stable isotope samples on the order of a few weeks to a few months.

**Age Model Changes**

We identified counting errors in the original age model through recognition of stratigraphic
associations between a few visible layers and large tropical cyclone-related δ¹⁸O value
excursions. In addition to annual banding generated by strong seasonal water balance variations,
smaller rainfall events could likewise perturb drip rates and calcite morphology. In fact, we
observed many minor fluctuations in opacity within the clear portions of annual band couplets.
Annual layer counting was not affected by most lesser rainfall events, which apparently do not
perturb speleothem growth extensively enough to cause confusion with annual layers. However,
infiltration from particularly intense rain events (e.g. Hurricane Keith produced over 26 cm of
rain) would rapidly raise the hydraulic head of the drip water source conduit. The resulting
sudden change in drip rate could temporarily perturb speleothem deposition to a greater degree.
than more frequent but smaller storms. It is important to note that in the case of a major precipitation event, drip rate in the cave would be affected immediately upon stormwater infiltration, but water isotopic composition at the speleothem surface would not reflect the storm event until after enough time had passed to allow the isotopically-distinct stormwater to infiltrate from the surface to the cave site. Thus, we expected any physical changes in crystal opacity resulting from tropical cyclone events to occur stratigraphically below any measured stable isotopic excursions.

In ATM7, one visible couplet that we originally classified as annual was deposited a few months before stalagmite collection, about the time that major Hurricane Keith struck Belize. We originally classified three additional visible couplets as annual deposits that we later found to be located stratigraphically below associated low δ¹⁸O value excursions. On further examination, compared to other band pairs that we classified as annual, these four low δ¹⁸O value excursion-related layers, or “storm couplets” were more akin to the minor sub-annual opacity variations than to other annual band pairs: storm couplets were typically much thinner, less distinct, and morphologically rougher and more angular. As a result of our present analysis, we now recognize these storm couplets as sub-annual events generated by tropical cyclone rainfall rather than complete annual periods. Although weak fluctuations in opacity were also associated with other low δ¹⁸O value excursions, apparently, most tropical cyclone precipitation events and other major storms did not affect speleothem stratigraphy enough to affect the initial layer-counting process.

Importantly, the high-resolution stable isotope record enabled us to distinguish clearly between the few cyclogenetic storm couplets and annual couplets within the visible banding pattern. This discovery enabled us to refine the annual layer counting in the age model used in our previous analysis of this stalagmite (Frappier et al., 2002).

After accounting for the storm couplets, we re-assigned a linear growth function to each annual couplet as before to generate an updated age model with a March date for the base of each hydrological year (Fig 2-2). The storm couplet at the top of the stalagmite (presumably generated
by stormwater from Hurricane Keith) shifted the entire record forward by several months, and
three older layers associated with low δ¹⁸O value excursions (1990, 1980, and 1978) further
shifted the lower part of the record.

Tests of the Updated Age Model

When plotted using the updated age model, ATM7 stable isotope, stratigraphic, and trace
element variations are very consistent with regional climatology and local meteorological
observations. Three lines of evidence validate the updated age model:

1. The ENSO teleconnection correlation previously identified in ATM7 (Frappier et al. 2002)
remains robust and stable in the updated age model (Fig. 3). Previously, we showed a total
correlation offset (or proxy record lag) between the ATM7 stable isotope record and the SOI of
approximately 1.5 years (Frappier et al. 2002). This lag has two components, comprised of the
teleconnection time (time between changes in the core ENSO region of the equatorial Pacific and
subsequent changes in Belize), plus an infiltration or recharge component (time for meteoric
water to percolate through the epikarst to the stalagmite surface). A total lag of about 1.5 years is
also inferred from the updated age model. We now infer that the teleconnection lag component is
approximately 1 year, based on studies showing that Caribbean weather responds to ENSO
forcing after a lag of approximately one year (Tourre and White, 1995, 2005).

The remainder of the correlation offset between the SOI and ATM7 stable isotope record
(~0.5 years) also enables us to estimate the percolation portion of the total time lag at
approximately 6 months. While we have not yet been able to conduct a long-term tracer test to
quantify the exact timescale of recharge, additional information enables us to bracket the
infiltration time to 3-6 months. The updated age model gives dates for each low δ¹⁸O value
excursion in the ATM7 record that match years of local tropical cyclone activity (Figure 2-3). Another constraint comes from the lack of observation of any excursion from Hurricane Keith, which struck Belize just three months before the stalagmite was collected in January 2001. Given the excellent fidelity of the proxy record to earlier tropical cyclone events, we surmise that cyclogenic water from Hurricane Keith was still percolating down through the epikarst at the time of collection, and the infiltration time must be at least 3 months. An infiltration time of 3–6 months is reasonable for this site, and is consistent with the duration of the stratigraphic offset between storm couplets and associated low \( \delta^{18}O \) value excursions. The consistency between the ATM7 record, 1-year regional teleconnection lag, and infiltration time estimate, combined with the stability and clarity of the ENSO correlation together provide strong evidence that the updated age model is correct.

2. The extended low \( \delta^{18}O \) value interval near the base of the ATM7 record (located between K and J in Fig. 3) now dates to 1979, a year when local precipitation exceeded 2856 mm, more than three standard deviations (\( \sigma = 323 \text{ mm yr}^{-1} \)) above the climatological average (1618 mm yr\(^{-1} \)). This extended period of low \( \delta^{18}O \) values is thus an expression of the “amount effect” and is unrelated to tropical cyclone precipitation events (Rozanski et al., 1997). Visible stratigraphy also reflects the extreme wetness of 1979. A distinct, rusty-colored layer apparent in the polished cross-section (Fig. 2) and trace element event (described below) is embedded within this extended period of low \( \delta^{18}O \) values. This isotopic, trace element, and stratigraphic horizon constitutes an event horizon that is best explained by the combined effects of the extremely wet weather conditions that prevailed in central Belize during 1979.

3. Two different, major trace element perturbations in this stalagmite are dated to 1979 and 1982 using the updated age model (Chapter 2, see also Figure A-4 and A-5). The 1979 trace element event corresponds to the wet year and associated stratigraphic and isotopic changes in the ATM7
record described above. The 1982 trace element event represents an even greater disruption of the
site's biogeochemistry, and is unique in the record (2001 – 1978). The 1982 trace element event
is significant because it occurred in a year when clouds of tephra from the eruption of the El
Chichón volcano in nearby Chiapas, Mexico were observed to cover the study area (Chapter 2).
This 1982 trace element event thus constitutes a marker horizon of known age that confirms the
validity of the ATM7 age model update presented here.

Together, these three independent and consistent lines of evidence provide a rigorous test
of the updated age model. Isotopic, stratigraphic, and trace element evidence consistently support
the updated age model, enabling us to avoid the circular use of the low $\delta^{18}$O value excursions to
date the stalagmite itself. The excellent temporal match observed between the history of storm
events in this area and low $\delta^{18}$O value excursions in ATM7 is thus an application of the updated
age model, and not a support for that age model. However, this is discussed in further detail
above. The remaining age model error is related to the assumption of linear deposition within
each annual couplet, indicating dating uncertainty for individual stable isotope samples of a few
weeks to a few months.
APPENDIX D

PALEO-HURRICANE INTENSITY PROXY ANALYSIS

To investigate the relations between signal amplitude and storm characteristics, we performed a standard multiple linear regression for the eleven storm signals we identified as cyclogenic. The four independent variables were storm maximum intensity at or prior to landfall (integer Saffir-Simpson intensity categories, Table 1) \( I \), minimum distance between storm track and cave site (km) \( D \), mean storm precipitation recorded at three nearby meteorological stations (mm) \( P \), and sampling frequency (number of micro-samples per year) \( S \).

Sampling frequency could exert a strong control on the ability of this technique to resolve the isotopic signature from very brief individual storm infiltration events. Given a constant sampling interval of 20 \( \mu \)m, inter-annual and sub-annual variations in stalagmite growth rate would control extent of contamination in storm micro-samples by adjacent, isotopically “normal” background calcite. Variations in the relative thickness of micro-samples compared to annual layers may modulate the resolving power of the stable isotope record for detecting storm events and/or intensity (Chapter 2). Although seasonal growth rate variations may be large, the tropical cyclone events in this dataset all occur within the rainy season (Fig. A2). Sampling rate is thus likely to be relatively stable for different storm events occurring within the same season. For multiple tropical cyclones in the same year, the measured amplitude of excursions is more likely to be controlled by differences in precipitation \( ^{18} \text{O} \) values. In contrast, growth rate differences between years has a relatively large effect on the amount of time represented by each sample, and thus could substantially affect the measured amplitude of different cyclogenic excursions. The
parameter sampling frequency varies with annual growth rate, but remains constant for multiple
storm strikes during a single year, in keeping with our understanding of the relations among
sampling, growth rate, and measured excursion amplitude. For example, within the multiple strike
years 1995 and 1996, sampling frequency was stable and more intense storms were associated
with larger excursions.

The overall regression model results (Adj. $R^2 = 0.653$, $p=0.031$) are explained in Results,
and tabulated below (Table A1). Distance to storm track was not a significant contributor to the
overall model, and was not correlated with any other independent variables. Not surprisingly,
local rainfall was highly correlated with storm maximum intensity. The correlation between storm
maximum intensity and local precipitation means that reconstructions of past storm intensity also
closely reflect the amount of local precipitation generated by those storm events. Interestingly,
local storm precipitation is not significantly correlated with $\delta^{18}O$ signal size, suggesting that given
sufficient sampling resolution $\delta^{18}O$ signal size is controlled substantially by the maximum
intensity reached by the storm while producing rainfall at the cave site, and is not a direct
expression of the local “amount effect”.

Table A1. Results of a multiple linear regression to investigate storm and speleothem
factors related to the signal size of measured $\delta^{18}O$ value excursions.

<table>
<thead>
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<th>Factor</th>
<th>Coefficients</th>
<th>correlations</th>
<th>toleranc e</th>
<th>sig.</th>
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</thead>
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<td>Standard-</td>
<td>zero-</td>
<td>semi-</td>
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<tr>
<td></td>
<td>ized</td>
<td>ized</td>
<td>order</td>
<td>partial</td>
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<tr>
<td>Constant</td>
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<td>-</td>
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<td>0.595</td>
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<tr>
<td>Resolution (samples/ yr)</td>
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<td>0.381</td>
<td>0.618</td>
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<tr>
<td>Distance to Storm Track (km)</td>
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<td>0.247</td>
<td>0.158</td>
</tr>
<tr>
<td>Local Precipitation (mm)</td>
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<td>-0.639</td>
<td>0.383</td>
<td>-0.303</td>
</tr>
</tbody>
</table>

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Figure A-4. ATM7 LA-ICPMS species concentrations (counts per second normalized to Ca and NIST 612).
Th 232

U 238

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Figure A-5. ATM7 LA-ICPMS data comparison with first three EOF modes (y-axis). EOF modes are plotted as loading factors; P$^{31}$, Na$^{23}$, and Sr$^{88}$ are plotted as counts per second normalized to Ca.