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Stable Isotope Analysis of Lake Sediments from Laguna Santa Elena and Laguna Azul, Costa Rica

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To the Graduate Council:

I am submitting herewith a thesis written by Matthew Timothy Kerr entitled "Stable Isotope Analysis of Lake Sediments from Laguna Santa Elena and Laguna Azul, Costa Rica." I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Geography.

Sally P. Horn, Major Professor

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Stable Isotope Analysis of Lake Sediments from Laguna Santa Elena and Laguna Azul, Costa Rica

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DEDICATION

To my wife, Jacqueline, for all the things you do that inspire me.

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The isotope analyses I describe here were carried out in the isotope lab in the Center for Marine Science at the University of North Carolina Wilmington, with the support of lab director Dr. Chad Lane. Supply and analysis costs were covered by Sally Horn using research funds provided by the University of Tennessee. In June 2013 I visited Laguna Santa Elena and the former site of Laguna Azul with Sally Horn and graduate student Erik Johanson on a research trip to Costa Rica supported by funds awarded to Sally Horn by the University of Tennessee. Maureen Sánchez and Gerardo Alarcón of the Laboratory of Archaeology of the University of Costa Rica arranged and accompanied us on the visits to the lake sites.

I especially thank Maureen Sánchez for sharing her extensive knowledge of the archaeology and history of Laguna Santa Elena and the surrounding area, and for her patience, time, and effort when showing me the lake and other field sites. A guided archaeological tour of southern Costa Rica is something that most people would describe as a once in a lifetime experience, but my sincere hope is that we can do it again in the future. University of Costa Rica archaeology student María López, who accompanied us on the trip, was an excellent travel companion and became a good friend. She taught me about Costa Rica beyond the University and research, and endured my painful attempts to negotiate life in Spanish.

The Laguna Santa Elena sediment core was recovered by Sally Horn, Kevin Anchukaitis, Lisa Kennedy, and Martin Arford, and first studied by Kevin Anchukaitis in his M.S. thesis research at the University of Tennessee. I offer special thanks to Kevin Anchukaitis for his past work, which formed the foundation for my research. Core recovery and prior research were funded by grants from The A.W. Mellon Foundation to Sally Horn and Robert Sanford, Jr., and by a STAR Fellowship from the Environmental Protection Agency and a University of Tennessee teaching assistantship awarded to Kevin Anchukaitis.

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ABSTRACT

Lake sediments are increasingly important archives of human-environment interactions and paleoclimate in the neotropics. In Costa Rica, Anchukaitis and Horn (*Palaeogeography, Palaeoclimatology, Palaeoecology* 221: 35–54, 2005) established a land-use history for Laguna Santa Elena (8.9306 N, 82.9275 W, 1055 m elevation), a small lake in the Diquís archaeological region, based on pollen and charcoal analyses of a 7-meter sediment core. I carried out stable carbon and nitrogen isotope and loss-on-ignition analyses at higher resolution to extend the existing 2000-year record. The new geochemical data parallel major trends in botanical proxies but also reveal aspects of human and environmental dynamics not apparent in the prior analysis. Inferred changes in land use in the watershed are consistent with archaeological evidence. Geochemical trends strongly suggest a population collapse at the site around the time of the Terminal Classic Drought of the Mayan region. The generally close correspondence between microfossil assemblages and geochemistry in the Santa Elena core demonstrates the usefulness of stable isotope analysis as a first line of investigation in paleoenvironmental research.

Sediment samples for carbon isotope analysis need to be acidified to remove carbonates that can affect isotope measurements, and debate exists over whether nitrogen isotope analysis can use these acidified samples or require non-acidified samples. My thesis research tested the effects of pre-analysis acidification of sediment and soil samples from Laguna Santa Elena and a second lake in Costa Rica, Laguna Azul (9.9558 N, 83.6519 W, 630 m elevation) in the Central Highlands-Atlantic Watershed archaeological region. Results show that acidification may cause statistically significant differences in nitrogen isotope values. These differences appear to be random and unpredictable, and can manifest as either positive or negative shifts that have the

potential to alter or even reverse relative trends in nitrogen isotope signals in lake sediment profiles. More tests are needed, but the results of this analysis suggest that researchers should avoid dual-mode analysis, in which data for both stable carbon and nitrogen isotopes are obtained from a single acidified sample, and should continue analyzing an additional non-acidified sample to obtain nitrogen isotope values.

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CHAPTER I

INTRODUCTION

The study of lake sediments as archives of paleoenvironmental history typically involves the sampling of a single core from the deepest part of the lake (Davis 1989; Lane et al. 2010; Taylor et al. 2013a). A variety of microfossils preserved in sediments provide evidence of prehistoric human activity around lakes. The presence or absence of *Zea mays* subsp. *mays* L. (maize) pollen in sediment cores is used as a proxy for the presence or absence of humans in a watershed (Goman and Byrne 1998; Clement and Horn 2001; Anchukaitis and Horn 2005; Dull 2007; Wahl et al. 2007). Additionally, the abundance of macroscopic and microscopic charcoal is used as an indicator of local and regional biomass burning (Clark 1990; Whitlock and Larsen 2001; Whitlock and Anderson 2003; Prichard et al. 2009; Denis et al. 2012). While grains of maize pollen in sediments do indicate agriculture, and charcoal fragments can signal agricultural fires, the temporal sensitivity of these proxies to changes in land use can be limited, particularly in single-core analyses (Lane et al. 2010; Taylor 2011; Taylor et al. 2013a).

Limnological conditions and processes of sediment transport, particularly sediment-focusing in the deepest portion of the lake (Lehman 1975; Davis and Ford 1982; Larson and MacDonald 1994), strongly affect concentrations of pollen in lake sediments and create a generalizing effect that homogenizes basin inputs and can induce a time lag in the paleoenvironmental record (Davis and Ford 1982; Burden et al. 1986; Taylor 2011; Taylor et al. 2013a). While lake-sediment analyses can reveal important evidence of maize (Bush et al. 1992; Islebe et al. 1996; Northrop and Horn 1996; Fisher et al. 2003; Oldfield et al. 2003; Horn 2006), grains of maize pollen are much larger than most pollen grains and their deposition is governed by a complexity of factors. These include distance from the lakeshore (Raynor et al. 1972; Islebe et al. 1996; Lane et al. 2010), wind speeds, and roughness of land surfaces (Jarosz et al. 2003, 2005), all of which can limit the presence of maize pollen in sediments.

In southern Costa Rica and western Panama, debate exists over the timing and intensity of maize agriculture, the use of maize as a subsistence or special-use crop, and the importance of climate versus the Spanish Conquest as a driver of population movement and decline (Linares and Sheets 1980; Drolet 1988; Hoopes 1991, 1996; Anchukaitis and Horn 2005; Palumbo 2009; Taylor 2011; Taylor et al. 2013b). Lake-sediment analyses can help resolve this debate, but due to the potential limitations of maize pollen analysis, such investigations can benefit from the study of additional proxies.

In small neotropical watersheds, stable carbon isotope analysis can enhance evidence of land-use history revealed by pollen and charcoal assemblages and allow researchers to reconstruct a sensitive, temporally-explicit record of the scale and intensity of prehistoric agriculture and human land use (Lane et al. 2004, 2008, 2009; Taylor 2011; Taylor et al. 2013b). Analyses of total organic carbon and nitrogen abundance, carbon/nitrogen ratio, and stable nitrogen isotopic composition in bulk lake sediments can provide additional geochemical evidence of agricultural history (Russell et al. 2009; Taylor 2011; Taylor et al. 2013a, b). Stable carbon isotope ratios ($\delta^{13}C$) are an especially efficient and effective proxy for reconstructing timelines of land-cover change and the intensity of maize agriculture from the sediments of small lakes in tropical settings in which conversion of wild vegetation to agriculture involves a shift in dominant photosynthetic pathways. Plants of tropical lowland and montane forests primarily use the C_3 photosynthetic pathway, producing organic matter with $\delta^{13}C$ values ranging from –35 to –20‰ V-PDB (Bender 1971; O'Leary 1981; Brown 1999; Sage et al. 1999). Maize and many agricultural weeds use the C_4 photosynthetic pathway, producing organic matter with $\delta^{13}C$ values between –14 and –10‰ V-PDB (Bender 1971; O'Leary 1981). Anthropogenic forest clearance and replacement of native vegetation by maize and agricultural weeds causes a positive shift in $\delta^{13}C$ in lake sediments due to changing terrestrial (allochthonous) organic inputs. This shift in $\delta^{13}C$ can be detected through stable isotope analysis and paired with pollen and charcoal evidence to reconstruct timelines of prehistoric land use (Lane et al. 2004, 2008, 2009).

Lake sediments comprise both allochthonous and autochthonous carbon (Meyers and Ishiwatari 1993; Meyers 1994; Meyers and Lallier-Vergés 1999). Certain algae can produce a signal enriched in the heavier ^{13}C isotope under conditions of limited dissolved CO_2, which can cause a false C_4 vegetation signal in the $\delta^{13}C$ of sediments (Mook et al. 1974; Smith and Walker 1980; Lucas 1983; Huang et al. 1999). Stable carbon isotope ratios in bulk sediments from lakes with extensive C_4 vegetation may show $\delta^{13}C$ values that fall within the range associated with organic matter from C_3 plants. However, despite the skew to the heavier isotope that can result from autochthonous carbon, relative shifts of $\delta^{13}C$ over time record land-use history. More positive (negative) values for $\delta^{13}C$ indicate increasing (decreasing) C_4 signals from the watershed (Lane et al. 2004, 2008, 2009).

Carbon/nitrogen ratios (C/N) and stable nitrogen isotope ratios ($\delta^{15}N$) provide further insight into processes operating within lakes and watersheds (Talbot 2001). C/N ratios identify the source of organic matter input into lakes (Meyers and Ishiwatari 1993; Tyson 1995; Meyers and Lallier-Vergés 1999; Talbot 2001), which can help to sort out terrestrial versus aquatic contributions to the $\delta^{13}C$ of sediments. C/N ratios of sediments with high terrestrial input are generally > 20. Sediments with high aquatic productivity have C/N ratios in the range of 3–9.

C/N ratios of 10–20 indicate mixed aquatic and terrestrial input (Meybeck 1982; Hedges et al. 1986; Tyson 1995; Meyers 1997; Sharpe 2007).

Changes in $\delta^{15}N$ of lake sediments can be driven by a variety of factors, both internal and external to the lake, such as climatic aridity, phytoplankton and microbial activity, changes in water depth, sudden pulses of sediment input, natural changes in trophic state, human alteration of the watershed, and others (Hassan et al. 1997; Talbot 2001; Russell et al. 2009; Tepper and Hyatt 2011; Torres et al. 2012). Interpreting shifts in $\delta^{15}N$ can be difficult due to the number of biogeochemical processes and sources of N fractionation, but $\delta^{15}N$ nevertheless can provide valuable paleoenvironmental information when combined with other proxies (Talbot 2001), such as diatoms, $\delta^{13}C$, C/N ratios, and other geochemical indicators.

While bulk stable carbon and nitrogen isotopes are common proxies for paleoenvironmental reconstruction, researchers have disagreed over sample preparation methods (Brodie et al. 2011a, b, c). Each sample analyzed on an isotope ratio mass spectrometer (IRMS) yields C and N abundance data, as well as $\delta^{13}C$ and $\delta^{15}N$ values. Processing of carbonate-containing soils and sediments for $\delta^{13}C$ analysis requires acidification of samples prior to analysis to remove carbonates and allow an accurate measurement of organic carbon content and organic $\delta^{13}C$ values. Brodie et al. (2011a, b, c) reported that acidification interferes with accurate determinations of N content and $\delta^{15}N$ values, primarily by causing a negative directional shift in $\delta^{15}N$ values, thus requiring the analysis of a non-acidified fraction for N and $\delta^{15}N$ data and an acidified fraction for C and $\delta^{13}C$ data. For projects with many samples, these additional IRMS runs can require a large amount of human labor and instrument time.

Recent datasets generated by the Stable Isotope Laboratory at the University of North Carolina Wilmington (UNCW), directed by Dr. Chad Lane, suggest that while differences in

$\delta^{15}N$ values due to pre-analysis sample acidification may be statistically significant, they may not be large enough to alter paleoenvironmental interpretation of the results (C. Lane, personal communication, 2012). If this is true, then analyzing a non-acidified fraction for N data is an unnecessary step and eliminating it could reduce instrument time and sample costs by half. Additionally, while Brodie et al. (2011a, b, c) tested several methods of sample acidification, including an in-capsule fumigation method, they did not evaluate the method used by the UNCW Stable Isotope Laboratory. The volume of recent work on paleoenvironmental proxies from lake and swamp sediments in Costa Rica (e.g. Arford and Horn 2004; Lane et al. 2004, 2009, 2011; Anchukaitis and Horn 2005; Haberyan and Horn 2005; Horn 2006, 2007; Horn and Kennedy 2006; Kennedy and Horn 2008; Filippelli et al. 2010; Taylor 2011; Lane and Horn 2013; Taylor et al. 2013a, b; Horn and Haberyan forthcoming) makes the area a valuable location for testing this idea.

Loss-on-ignition analysis (LOI; Dean 1974) is a simple and inexpensive technique for estimating the organic matter (OM), inorganic, and carbonate composition of sediments and soils. Changes in influx of OM and inorganic sediments in a lake can indicate watershed disturbances and changes in land use. Forest clearance and agriculture destabilize soil and increase inorganic contributions to sediments (Oldfield et al. 2003; Enters et al. 2006; Lane et al. 2008; Bookman et al. 2010), which in turn can drive shifts in $\delta^{13}C$ and $\delta^{15}N$ values, providing evidence of anthropogenic impacts in watersheds.

Sediments have important ecological and biogeochemical roles in water quality and carbon cycling (Ballinger and McKee 1971; Sutherland 1998). Organic carbon (OC) is the principle component of sedimentary OM. LOI provides an estimate of OM, but accurate measurement of OC is generally achieved through dry combustion, such as with an induction furnace (Charles and Simmons 1986; Sutherland 1998). LOI is a widely accepted technique for estimating OM in sediments and soils (Gosz et al. 1976; Covington 1981; Craft et al. 1991; Gagnier and Bailey 1994; Van Der Perk and Van Gaans 1997), and many researchers have reported conversion factors between OM and OC developed through regression models comparing values for OM derived from LOI versus OC from dry combustion (Roelofs 1983; Goldin 1987; David 1988; Lowther et al. 1990; Grewal et al. 1991; Soon and Abboud 1991). Sutherland (1998), however, noted widespread concern over the accuracy of LOI for estimating OM and OC by conversion (e.g. Howard 1965; Gibbs 1977; Christensen and Malmros 1982; Mook and Hoskin 1982; Weliky et al. 1983; Gallardo et al. 1987; Howard and Howard 1990; Grewal et al. 1991; Schulte et al. 1991). Sutherland (1998) found that a generally applied conversion factor developed for soils of 1.724 between OM and OC is inaccurate for fluvial bed sediments. The findings of Sutherland (1998) suggest that the soil conversion factor of 1.724 is likely also inaccurate for lake sediments. This thesis research provides an opportunity to compare LOI estimates of OM with IRMS determinations of OC for some Costa Rican lake sediments.

Researchers have documented a long history of anthropogenic landscape disturbance and maize agriculture in southern Costa Rica and western Panama through lake-sediment analyses of pollen and charcoal (Behling 2000; Clement and Horn 2001; Anchukaitis and Horn 2005; Horn 2006), pollen and stable carbon isotopes (Horn et al. 2004; Lane et al. 2004; Taylor et al. 2004), diatoms (Haberyan and Horn 2005), and phosphorous (Filippelli et al. 2010). Recent work at Laguna Zoncho (Taylor 2011; Taylor et al. 2013a), however, questioned the sensitivity of maize pollen deposition to the scale of maize agriculture. Analysis of multiple sediment cores from the Zoncho basin revealed a possible lag effect in maize pollen transport to the center of the lake. Those results suggest that cultural chronologies established through single-core maize pollen studies linking population collapse with Spanish conquest may be inaccurate by hundreds of years, demonstrating the need for more temporally-sensitive proxies of land use in the region.

Anchukaitis and Horn (2005) conducted pollen and charcoal analyses on a sediment core from Laguna Santa Elena, located ca. 15 km north of Laguna Zoncho, to reconstruct prehistoric forest disturbance and maize agriculture in the watershed (Fig. 1). Their results established the presence of maize agriculture and the timing of a possible short interval of catchment abandonment at Laguna Santa Elena. They linked their data with the larger cultural chronology of the area based on archaeological investigations (e.g. Sánchez and Rojas 2002; Soto and Gómez 2002). The Santa Elena core yielded evidence of ca. 2000 years of nearly continuous human occupation at the site (Anchukaitis and Horn 2005).

For this project, I carried out additional studies of the Laguna Santa Elena core to construct a record of the scale of prehistoric land use and maize agriculture in the watershed. I used a suite of geochemical and isotopic paleoenvironmental proxies, focused primarily on stable organic carbon isotope ratios ($\delta^{13}C$), but also including bulk analysis of total organic carbon and nitrogen abundances, ratios, and isotopic compositions (%OC, %N, C/N, and $\delta^{15}N$) (Lane et al. 2004, 2009; Russell et al. 2009; Taylor 2011; Taylor et al. 2013a). I sampled these proxies at the 29 stratigraphic levels included in the original Anchukaitis and Horn (2005) study and at 29 additional levels to increase the sampling resolution from ca. 16–32 cm to ca. 8–16 cm. Additionally, I report data from LOI analysis I performed and previously unpublished data from Anchukaitis and Horn to build an understanding of organic versus inorganic and carbonate sedimentation in the lake, and I compare OM estimated by LOI with OC determined through IRMS analysis. These new results improve the regional paleoenvironmental proxy record with work centered on Laguna Santa Elena, add to the work of Taylor (2011) and Taylor et al.

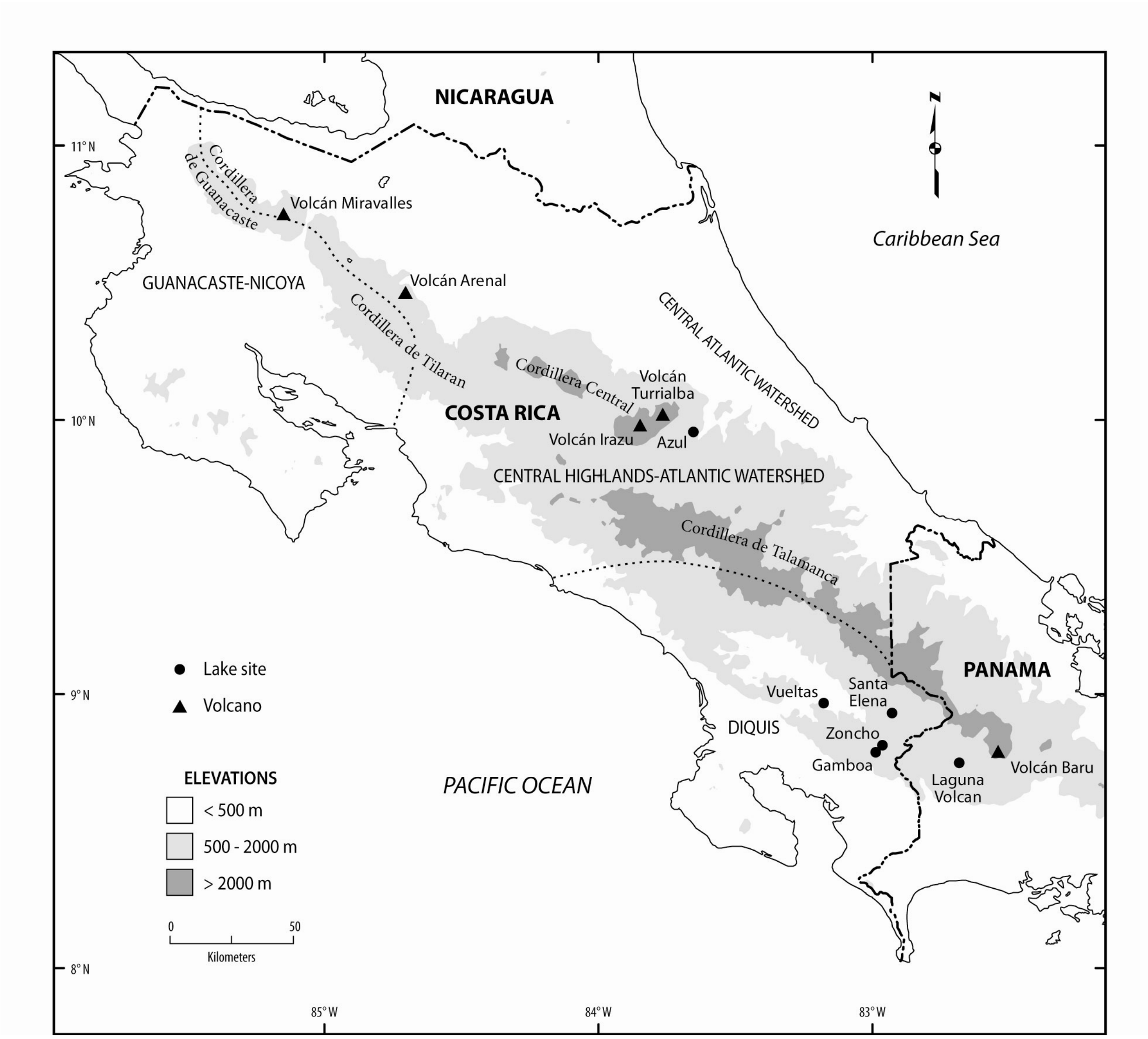

Figure 1: Location of Laguna Santa Elena and Laguna Azul. Map also shows other sites in Costa Rica and Panama mentioned in the text, with additional archaeological regions and selected physical features. After Horn (2006).

(2013a, b) at Laguna Zoncho, and strengthen previous reconstructions of land-use history based on maize pollen and charcoal proxies.

In this thesis I also report the results of an assessment of the effects of pre-analysis sample acidification on $\delta^{15}N$ results for carbonate-containing soils and sediments from Costa Rica. This analysis includes samples from 58 stratigraphic levels of the Laguna Santa Elena lake sediments and underlying soil profile, and 18 samples from a test sediment core from Laguna Azul (Fig. 1), a small lake in the Río Reventazón Valley of Costa Rica near the archaeological site of Guayabo de Turrialba (Horn 2006).

My research was designed to answer the following questions:

1. What do bulk stable isotope and loss-on-ignition analyses reveal about the nature and timing of prehistoric land use at Laguna Santa Elena, and do these analyses confirm or refute the timeline and interpretations established by Anchukaitis and Horn (2005)?
2. How does organic matter content estimated by loss-on-ignition compare to carbon content determined through IRMS analysis for Laguna Santa Elena sediments?
3. How do the results of this research relate to recent work at nearby Laguna Zoncho and ongoing archaeological investigations in southern Pacific Costa Rica and western Panama?
4. Does comparison of $\delta^{15}N$ results from acidified and non-acidified samples from Laguna Santa Elena and Laguna Azul using the UNCW acidification protocol indicate that acidification causes statistically significant differences in $\delta^{15}N$ values that might warrant analysis of an additional non-acidified fraction?
5. If so, are those differences scientifically important or meaningful, in that the differences would affect the paleoenvironmental interpretation of the $\delta^{15}N$ results?

CHAPTER II

ARCHAEOLOGICAL SETTING AND PREVIOUS PROXY ANALYSES AT LAGUNA SANTA ELENA AND LAGUNA AZUL

A. Archaeological Setting of Laguna Santa Elena

Laguna Santa Elena (8°55′50″ N, 82°55′39″ W, 1055 m elevation) (Fig. 1) is a small (0.13 ha), shallow (3.8 m) lake located in southern Pacific Costa Rica (Horn and Haberyan forthcoming). The lake occupies a landslide-truncated stream channel. Anchukaitis and Horn (2005) showed through pollen and charcoal analyses of lake sediments that pre-Columbian human inhabitants in the Laguna Santa Elena watershed practiced landscape management and maize agriculture at varying intensities over a long duration, as found at other sites in southern Costa Rica and Panama (Bush and Colinvaux 1994; Northrop and Horn 1996; Behling 2000; Clement and Horn 2001). The proxies allowed Anchukaitis and Horn to reconstruct a ca. 2000-year history of continuous occupation in the area.

The following summary, adapted from Anchukaitis and Horn (2005), provides an archaeological background for the area that includes Laguna Santa Elena. The lake is situated in the archaeological region designated Greater Chiriquí, which includes southern Pacific Costa Rica and western Panama. Greater Chiriquí is further divided into sub-regions, with the Costa Rican segment designated the Diquís sub-region. Humans have occupied the area continuously for thousands of years (Barrantes et al. 1990; Constenla 1991; Barrantes 1993; Lange 1992, 1993; Corrales 2000; Palumbo 2009).

Developing a cultural chronology for the area continues to be problematic, with most current dates derived from archaeological contexts and pottery comparisons (Corrales et al.

1988; Drolet 1992; Hoopes 1996; Corrales 2000; Palumbo 2009). Corrales (2000) dated the earliest sedentary habitation of the Diquís sub-region from 3450 B.P. in the Sinancrá Phase, but the chronology remains poorly established. The Aguas Buenas period, dated by ceramic typology, may have begun sometime between 2450 and 1750 B.P. (Drolet 1984; Haberland 1984a, b; Hoopes 1996; Corrales 2000; Palumbo 2009). The Chiriquí period followed the Aguas Buenas, spanning ca. 1150 to 450 B.P. (Quilter and Vargas 1995; Baudez et al. 1996; Corrales 2000; Anchukaitis and Horn 2005). Hoopes (1996) postulated that populations in the Aguas Buenas period were small and dispersed, while Linares et al. (1975) reported chiefdom-level societies that they termed "Barriles" in western Panama. Bugaba Phase ceramics have been dated to 1750–1350 B.P. in western Panama, which overlaps and corresponds stylistically to typologies of the Aguas Buenas period. Archaeological investigations at Laguna Zoncho (Fig. 1) yielded radiocarbon dates later than 1750 B.P. for Aguas Buenas materials (Soto and Gómez 2002). Considerable debate continues over the timing, chronology, and connections between the Aguas Buenas, Barriles, Bugaba, and other cultural phases and periods in the Greater Chiriquí region (Palumbo 2009).

Several lake-sediment studies have revealed chronologies of maize agriculture in the Greater Chiriquí region. Behling (2000) found maize pollen in a core from Laguna Volcán (Fig. 1) in western Panama beginning ca. 1800 B.P. Clement and Horn (2001) demonstrated a 3000-year history of maize agriculture at Laguna Zoncho, although more recent work on bulk stable carbon isotopes (Taylor et al. 2013b) showed that the decline in maize agriculture that Clement and Horn associated with Spanish Conquest may have occurred a few centuries earlier. These studies showed that maize was cultivated in southern Costa Rica and western Panama prior to the

Aguas Buenas period, confirming its presence in both the Diquís and Chiriquí sub-regions during the Aguas Buenas and the Chiriquí cultural phases (Anchukaitis and Horn 2005).

Several archaeological sites have been identified in the area around Laguna Santa Elena. Sánchez and Rojas (2002; M. Sánchez, personal communication, 2013) identified several house sites on the hilltops surrounding the lake from which they recovered lithic artifacts and Aguas Buenas period ceramics, but no Chiriquí artifacts. They found a larger site named Fila Tigre ca. 2 km east of Laguna Santa Elena that contained predominantly Aguas Buenas period ceramics, but also had a minor presence of Chiriquí period artifacts. Sánchez and Rojas argued that Fila Tigre was likely a significant regional center and that the area conforms to expected settlement patterns of large centers associated with dispersed hamlet sites for the Diquís sub-region (Linares and Sheets 1980; Drolet 1992; Anchukaitis and Horn 2005).

The earliest identified maize macrofossils in the region are from highland Panama and date to 1750 B.P. (Galinat 1980). Though no earlier macrofossils have been found, Galinat (1980) and Smith (1980) argued that maize was introduced prior to 1750 B.P. in the region, which is consistent with the pollen record (Horn 2006). Macrobotanical remains and stone grinding implements from the Chiriquí region of western Panama show a shift to maize and bean subsistence following Archaic occupations (Haberland 1984b); however, Drolet (1992) claimed that similar evidence does not exist for the Diquís sub-region. While carbonized maize and bean remains have been reported for the area (Blanco and Mora 1994), Hoopes (1991, 1996) argued that maize may not have been a staple, but may have instead been a special-use crop, possibly for ritual feasting.

In addition to debate over the archaeological chronology for the Diquís and the cultural and dietary role of maize in the region, disagreement also exists over subsistence strategies and the intensiveness of agriculture (Anchukaitis and Horn 2005; Palumbo 2009). Linares and Sheets (1980) argued that the inhabitants were intensive farmers, while Drolet (1988) emphasized the role of gathered wild resources. Focusing on the wider region, Iltis (2000) and Iltis and Benz (2000) proposed that maize was not initially cultivated in tropical America for its grain, but for its sugary stems. Smalley and Blake (2003) argued that alcohol produced from corn may have played a role in developing complexity.

Despite these many uncertainties, researchers have argued that the development of social complexity in Central and Mesoamerica, including South Pacific Costa Rica, may have been linked to a transition to subsistence-based maize agriculture. For example, Corrales et al. (1988) suggested that the increased importance of maize agriculture may be directly tied to major cultural shifts toward political, economic, and social complexity in the Chiriquí period. However, Hoopes (1996) noted that disentangling the effects of maize intensification and increasing complexity is very difficult. Studies of lake sediments as archives of paleoenvironmental and land use signals have the potential to contribute to knowledge on the subject.

B. Previous Proxy Work at Laguna Santa Elena

Anchukaitis and Horn (2005) recovered a 7.13-m long sediment core in successive one-meter drives from Laguna Santa Elena using a Colinvaux-Vohnout (C-V) locking piston corer (Colinvaux et al. 1999) operated from an anchored floating platform. A plastic tube fitted with a rubber piston was used to recover a core of the uppermost, watery sediments. This mud-water interface (MWI) core was extruded in the field, sliced at 1 cm intervals, and placed in labeled plastic bags. The C-V core sections were returned to the Laboratory of Paleoenvironmental Research at the University of Tennessee in their original aluminum coring tubes, where the tubes were opened on a router. The sediment core sections were sliced longitudinally, photographed, and described. The Laguna Santa Elena sediment core comprises ca. 6 m of lacustrine sediments underlain by ca. 1 m of soil. Anchukaitis and Horn obtained six dates on wood and plant macrofossils using AMS radiocarbon analysis, five from the lacustrine section of the core and one from underlying soil (Table 1). They calibrated dates using CALIB v.4.4 (Stuiver and Reimer 1993) and the INTCAL98 dataset (Stuiver et al. 1998), and used the weighted means of the probability distributions of the calibrated ages and linear interpolation to establish a chronology.

Anchukaitis and Horn (2005) sampled 29 stratigraphic levels of the core at intervals of ca. 16–32 cm for pollen and microscopic charcoal analyses. They obtained and reported microfossil data for 25 samples from the lacustrine portion of the core, in which pollen was well preserved, but did not count the lowest four samples as they contained few pollen grains. They processed additional samples for macroscopic charcoal centered on the intervals sampled for pollen and microscopic charcoal. Loss-on-ignition analysis was carried out at each level sampled for pollen to estimate the organic, inorganic, and carbonate content of the sediments; these data were included on diagrams in Anchukaitis (2002), but not published.

The Laguna Santa Elena record supports archaeological evidence of a long human presence on the landscape (Anchukaitis and Horn 2005). Maize pollen at Santa Elena is consistent with sediment records from Laguna Zoncho (Clement and Horn 2001; Taylor 2011; Taylor et al. 2013a, b) and Laguna Volcán (Behling 2000). At Santa Elena, maize pollen is absent in the level dated to ca. 540 cal yr B.P., which may represent a temporary abandonment of the site near the time of Spanish arrival (Anchukaitis and Horn 2005). Taylor (2011) and Taylor et al. (2013a, b), however, showed that the chronology of maize decline and site abandonment at

Table 1: Radiocarbon dates for the Laguna Santa Elena sediment core.

Sample	Depth	Material Dated	Radiocarbon Age	Calibrated Age yr. B.P. (2-sigma)	Relative Area Under the Calibration Curve	Weighted Mean Calibration Age yr. B.P.
B-158436	156	wood	150 ± 40 yr. B.P.	40–0	0.174	150
				160–60	0.346	
				290–170	0.480	
B-150706	312	mixed plant material	640 ± 60 yr. B.P.	670–540	1.000	610
B-145347	434	wood	1240 ± 40 yr. B.P.	1260–1060	1.000	1170
B-145348	530	charcoal	1510 ± 40 yr. B.P.	1320–1310	0.030	1400
				1420–1330	0.694	
				1510–1430	0.277	
B-141242	580	wood	1880 ± 30 yr. B.P.	1880–1720	1.000	1810
B-121243	683	wood	1950 ± 30 yr. B.P.	1850–1820	0.145	1890
				1950–1860	0.831	
				1970–1960	0.018	
				1990–1980	0.006	

After Anchukaitis and Horn (2005). All analyses were performed by Beta Analytic Laboratory. Radiocarbon ages were calibrated by Anchukaitis and Horn (2005) using CALIB v4.4 (Stuiver and Reimer 1993) and the INTCAL98 dataset (Stuiver et al. 1998). Recalibration using CALIB v7.0.1 (Stuiver and Reimer 1993) and the INTCAL13 dataset (Reimer et al. 2013) yielded age ranges the same or very close to those obtained by Anchukaitis and Horn (2005), with differences of 10 years or less in the weighted means. Weighted means are based on Telford et al. (2004). Calibrated dates are rounded to the nearest decade.

Laguna Zoncho established by Clement and Horn (2001) from pollen analysis of a single central core may be inaccurate by ca. 200 years, indicating a need for additional research on the timing of population movement in the area.

C. Background, Setting, and Previous Proxy Work at Laguna Azul

Laguna Azul (9°57′21″ N, 83°39′07″ W, 630 m elevation) (Fig. 1) was a small lake in the Río Reventazón Valley near the major, complex Period V (1450–950 B.P.) to VI (950–400 B.P.) archaeological site of Guayabo de Turrialba, which is part of the Central Highlands–Atlantic Watershed Archaeological Region (Snarskis 1981; Horn 2006). Horn and colleagues first visited Laguna Azul in 1991 when it was still an intact lake surrounded by agricultural fields (Horn and Haberyan 1993); however, when Horn and students returned to the lake in 1992, destruction of the site was underway for the development of a hydroelectric project (Horn 2006). They recovered a mud-water interface core using a plastic tube fitted with a rubber piston and a 70-cm section beginning about 3 m below the sediment-water interface using a square-rod piston corer (Wright et al. 1984). These were intended as test samples to be followed up by full-scale coring later, but the lake was converted to a cement reservoir before additional coring could take place. Three radiocarbon dates on leaf fragments and bulk sediment from the 70-cm section show that this core segment captured Pre-Columbian sediments (Horn 2006, unpublished data). Pollen analysis showed evidence of maize cultivation in the Laguna Azul watershed during the La Cabaña phase (Period VI) (Horn 2006).

CHAPTER III

STABLE ISOTOPE ANALYSIS OF LAND-USE HISTORY AT LAGUNA SANTA ELENA, COSTA RICA

A. Methods

i. Sampling

I sampled the Santa Elena core for bulk stable carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) isotope analysis at the same 29 levels that Anchukaitis and Horn (2005) examined for pollen and charcoal. I also took samples from 29 additional stratigraphic levels for stable isotope and LOI analyses centered between the intervals investigated by Anchukaitis and Horn, increasing the sampling resolution to ca. 8–16 cm for this study. Samples for isotope and LOI analyses were 1 cm^3 volume. My paleoenvironmental interpretations make use of isotope results for 50 samples from the lacustrine portion of the core, while eight additional samples from the soil profile are added to my investigation of whether $\delta^{15}N$ analysis requires non-acidified samples.

ii. Loss-on-Ignition

Following Dean (1974), samples for LOI analysis were weighed in porcelain crucibles, oven-dried at 100 °C for 24 h to remove water, and reweighed. They were then combusted at 550 °C in a furnace for 1 h, cooled, and weighed to estimate organic matter content. Following the 550 °C burn, the samples were again combusted in a furnace, this time at 1000 °C for 1 h, cooled, and weighed to estimate carbonate and inorganic content.

iii. Sample Acidification and Stable Isotope Analysis

Bulk organic carbon and nitrogen content and isotope analysis followed the methods of Lane et al. (2013a) and the laboratory protocol of the University of North Carolina Wilmington (UNCW) Stable Isotope Laboratory. Samples were oven-dried at 50 °C and then ground to a fine powder and homogenized with an ethanol-rinsed mortar and pestle. The ground samples were split roughly into two aliquots, with one aliquot ready for $\delta^{15}N$ analysis as the non-acidified fraction (Brodie et al. 2011c). Samples analyzed for $\delta^{13}C$ composition were moistened with distilled water and fumigated with 12 N hydrochloric acid (HCl) for 2 h in a desiccator, then vented for 24 h. Following acidification, the samples were dried on a hotplate (surface temperature ca. 60 °C) until free of water and residual acid (ca. 48 h), and then reground. Acidification and drying took place in ceramic crucibles. Sample preparation took place in the Laboratory of Paleoenvironmental Research at the University of Tennessee.

Subsamples for $\delta^{13}C$ and $\delta^{15}N$ analysis were loaded into tin capsules and shipped to the UNCW Stable Isotope Laboratory. Isotope samples were randomized for analysis in the loading process so that they did not enter the IRMS in stratigraphic sequence relative to the sediment core. All samples were analyzed in 100% duplicate. The 30 samples with the highest standard deviation between duplicate analyses were run a third time, yielding ca. 26% triplicate analyses to better approximate true data values. Results from replicate runs were averaged to produce a single value for each datum. The samples were analyzed on a Costech Elemental Analyzer coupled to a Thermo Delta V Plus Mass Spectrometer. Carbon and nitrogen isotopic compositions are reported in standard δ-per mil notation, with carbon values relative to the Vienna-Pee Dee belemnite (V-PDB) marine carbonate standard and nitrogen values relative to AIR, where $R = {}^{13}C/{}^{12}C$ or ${}^{15}N/{}^{14}N$ and:

$$\delta^{13}C \text{ or } \delta^{15}N(\text{permil}) = 1000[(R_{sample}/R_{standard})\text{-}1] \quad (1)$$

Repeated analyses of USGS 40 glutamic acid standard indicated that instrument precision for these samples was better than ±0.16‰ for C and N.

Results for stable isotope analysis and loss-on-ignition for the Laguna Santa Elena samples were plotted along with original pollen and charcoal data using C2 (Juggins 2007). Whereas Anchukaitis and Horn (2005) plotted proxies by depth, I plotted previous and new proxy data by calibrated age. I used the weighted means of the probability distributions (Telford et al. 2004) of the calibrated ages of the five dates on the lacustrine section (Table 1), together with a surface age of –51 cal yr B.P. (AD 2001, year of core collection), to estimate the ages for each sampled horizon using linear interpolation. Recalibration of the AMS dates using CALIB v7.0.1 (Stuiver and Reimer 1993) and the INTCAL13 dataset (Reimer at al. 2013) yielded age ranges the same or very close to those obtained by Anchukaitis and Horn (2005) using the INTCAL98 dataset (Stuiver et al 1998), with differences of 10 years or less in the weighted means. Due to the small difference, and to facilitate comparison with the original study, I constructed my chronology using the weighted means reported by Anchukaitis and Horn (2005).

iv. Statistical Methods for OM/OC Comparison

Organic carbon percentages determined by IRMS analysis were compared to organic matter percentages estimated by LOI for 48 sediment samples using simple linear regression. The regression equation is:

$$\%OC = \pm \text{Intercept} + \text{Slope} * \%OM \quad (2)$$

The conversion factor between OM and OC is then derived from:

$$CF = 1 / \text{Slope} \quad (3)$$

if the intercept approximates zero (Sutherland 1998). Carbon content data from the non-acidified fractions were used to replicate the analyses of Sutherland (1998). The lowest sediment sample (584 cm depth, ca. 1840 cal yr B.P.) was excluded from the analysis due to unusually low C and N contents. A second sample (427 cm, ca. 1140 cal yr B.P.) was identified as an outlier and removed.

Two regression models were compared. The first included all 48 sediment samples. Examination of model residuals revealed that the regression was heavily influenced by samples with low (< 20%) and high (> 42%) OM. In the second model, three stratigraphic samples with OM < 20% (32, 40, and 53 cm) and two samples (427 and 440 cm) with OM > 42% were removed. Two-tailed paired t-tests were used to compare %OC determined through IRMS analysis to %OC obtained through conversion from %OM. Regression modeling was performed in the R Version 3.0.1 environment for statistical computing (R Core Team 2013). Graphical outputs were produced in R using the "ggplot2" package (Wickham 2009).

B. Results

i. Paleoenvironmental Reconstruction

Anchukaitis and Horn (2005) provided a detailed core description, which is summarized here. The upper ca. 6 m of the Laguna Santa Elena core consists of lacustrine silts and clays with organic matter contents of ca. 15–43%, as estimated by loss-on-ignition. The lake sediments are underlain by ca. 1 m of soil. The lacustrine portion contains three volcanic tephra layers at 538, 415–417, and 312–314 cm. Radiocarbon analyses of six samples revealed a normal stratigraphic sequence dating to 1950±30 ^{14}C yr B.P., based on a wood fragment in the underlying soil (Table 1). The base of the lacustrine core (596 cm) is 16 cm below a radiocarbon date of 1880±30 ^{14}C yr B.P. (1880–1720 cal yr B.P.; weighted mean 1810 cal yr B.P.).

Anchukaitis and Horn (2005) found variations over time in pollen percentages of trees and herbaceous taxa in the Santa Elena core, although maize pollen was present in all but three samples (Fig. 2), based on additional low-power scans of up to five microscope slides from each level (Horn 2006). All 50 isotope samples yielded isotopic signals in abundances adequate for interpretation (Fig. 3). Anchukaitis and Horn (2005) delineated informal zones based on microfossil assemblages and the regional archaeological chronology. I maintain their zonation here for ease of discussion. Below I present the LOI and isotope analyses in the context of the major trends in botanical proxies documented by Anchukaitis and Horn.

Zone 3 (ca. 1840 to 1510 cal yr B.P.)

Geochemically, this zone corresponding to the earliest interval of lacustrine sedimentation is characterized by the lowest $\delta^{13}C$ values in the record and $\delta^{15}N$ values that are also low, with both increasing at the upper boundary. Pollen shows intact mature tropical premontane forest with a high diversity of pollen taxa, tree pollen typical of moist lowland and premontane forests in Costa Rica (Rodgers and Horn, 1996), and rare occurrences of disturbance taxa. The minor presence of maize pollen, coupled with the lowest levels of charcoal in the core, shows a slight human presence on the landscape at this time. High total organic matter, along with high organic C content and low $\delta^{13}C$ values, support the interpretation of low disturbance

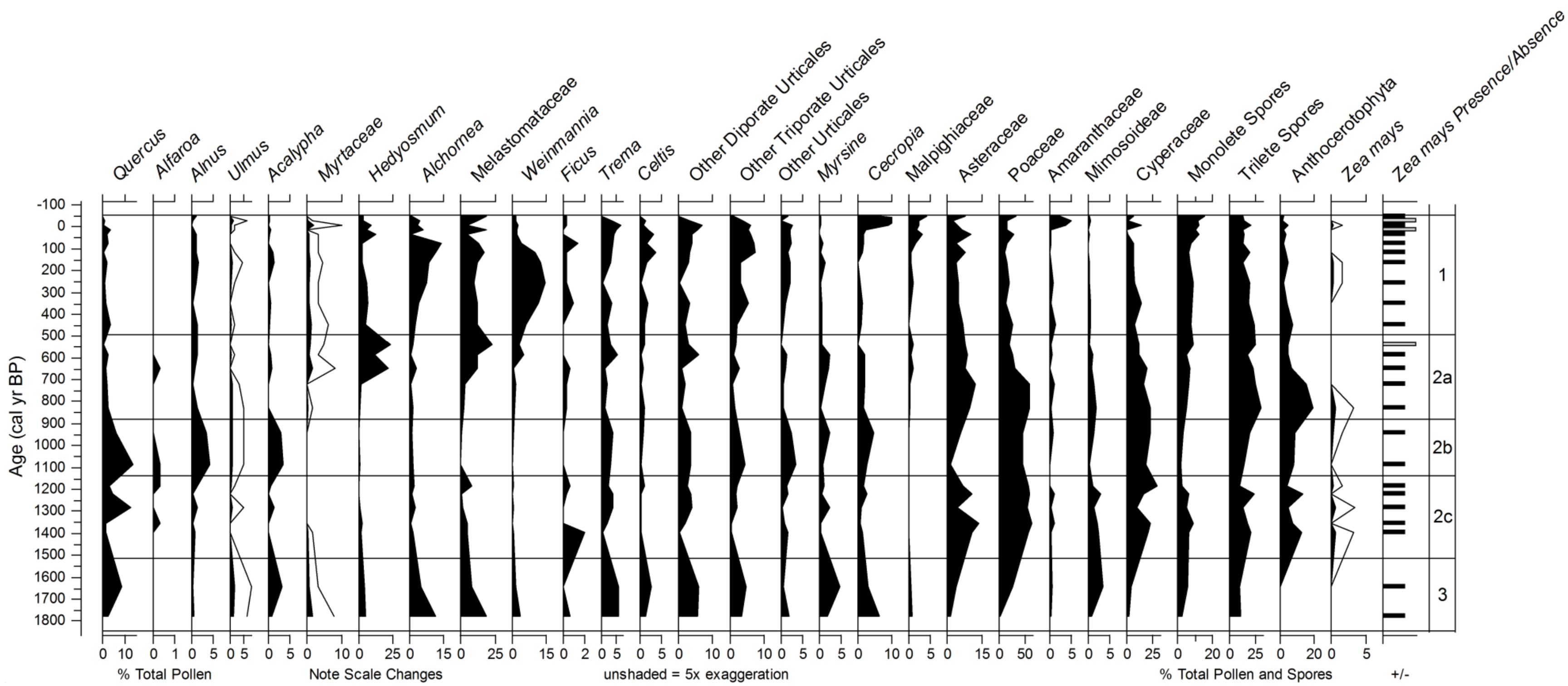

Figure 2: Laguna Santa Elena pollen diagram. All data are from Anchukaitis and Horn (2005) but plotted here by estimated age. Ages were estimated using linear interpolation between levels dated by AMS ^{14}C analyses of macrofossils, with the weighted mean of the probability distributions of the calibrated ages used as the single age estimate for each dated level. Taxa are arranged by life form, with trees and shrubs on the left, followed by herbs and ferns. Undifferentiated pollen in the Urticales order and Mimosoideae pollen could include both woody and herbaceous taxa. Pollen percentages for all taxa except Cyperaceae are calculated based on a pollen sum that excludes Cyperaceae. Monolete and trilete fern spores and Anthocerotophyta spores are expressed as percentages of total pollen plus spores. Spores of Anthocerotophyta in the Santa Elena sediments may be an indicator of agricultural activity (Anchukaitis and Horn 2005). *Zea mays* refers to *Zea mays* subsp. *mays*, or maize pollen. Bars indicate the presence/absence of maize pollen as revealed by additional low-power scans (black +, longer gray –). Zones were informally delineated by Anchukaitis and Horn (2005) based on microfossil assemblages and are retained here.

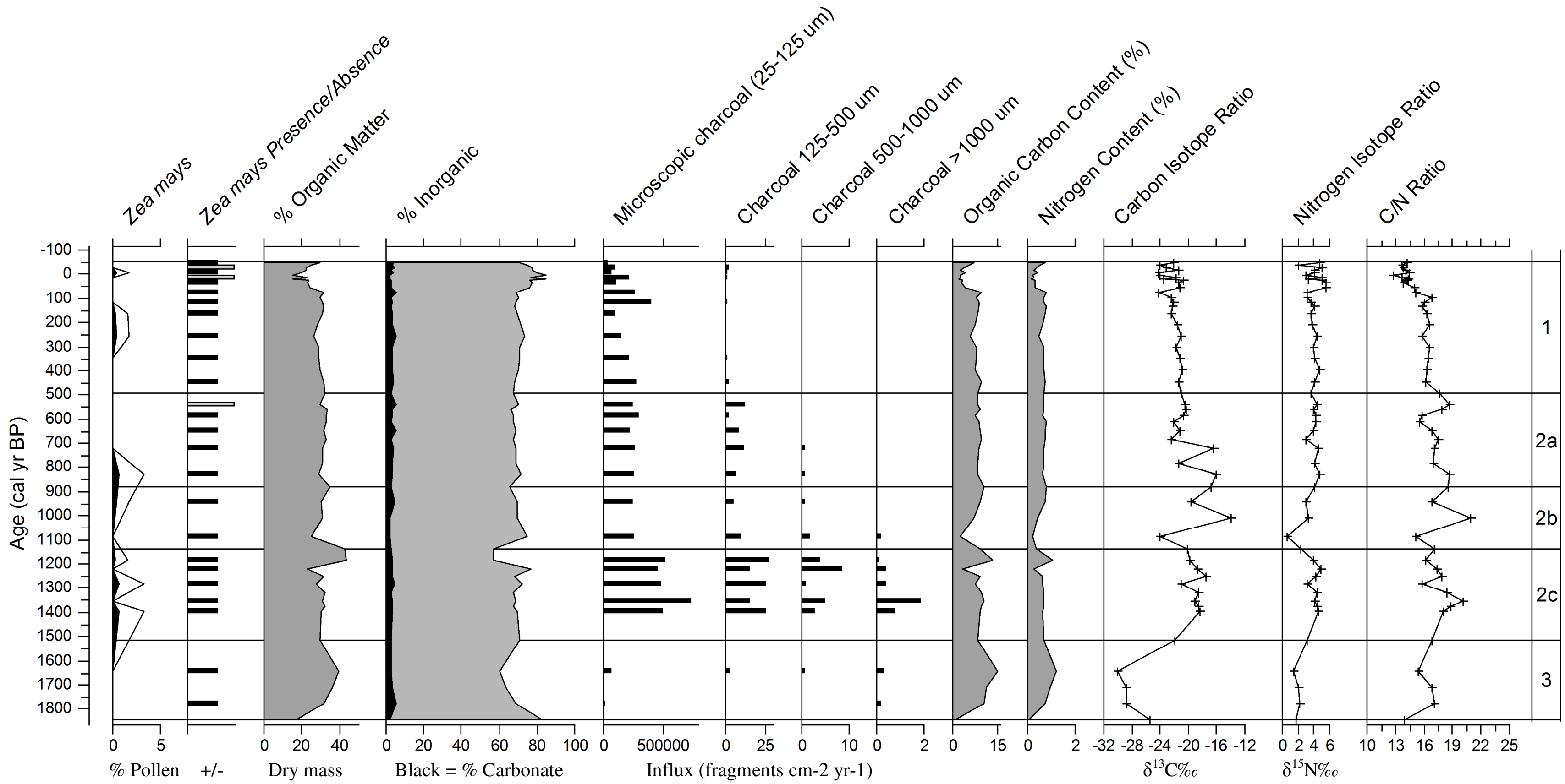

Figure 3: Laguna Santa Elena proxy diagram. Figure includes maize pollen and results from LOI, charcoal, and geochemical analyses. Ages used for plotting proxies were estimated using linear interpolation between levels dated by AMS ^{14}C analyses of macrofossils, with the weighted mean of the probability distributions of the calibrated ages used as the single age estimate for each dated level. Isotopic geochemistry and some LOI results are from the present study; other proxy data are from Anchukaitis and Horn (2005 and unpublished). *Zea mays* refers to *Zea mays* subsp. *mays* (maize). Bars indicate the presence/absence of maize pollen as revealed by additional low-power scans (black +, longer gray –). For % inorganic, gray shading shows total inorganic content and black shows carbonate. Nitrogen content and nitrogen isotope ratio are based on non-acidified samples, while carbon content and carbon isotope ratio are based on acidified samples. C/N ratio is reported for acidified samples to avoid bias from inorganic carbonates.

and predominantly C_3 tropical vegetation in the watershed during the initial interval of lacustrine sedimentation following formation of the lake. The low $\delta^{15}N$ values suggest low aquatic productivity with low terrestrial nutrient delivery. C/N ratios indicate mixed terrestrial and aquatic inputs.

Zone 2c (ca. 1510 to 1140 cal yr B.P.)

This zone shows a marked intensification of agriculture and land clearance in the Santa Elena watershed beginning no later than ca. 1510 cal yr B.P. Organic C and N contents drop between zone 3 and zone 2c, while $\delta^{13}C$ and $\delta^{15}N$ ratios increase substantially in response to forest clearance and increased maize agriculture. C/N ratios increase to the middle of zone 2c (ca. 1360 cal yr B.P., 512 cm), suggesting an increase in the terrestrial component of the sediment. LOI data indicate increased inorganic composition of the lake sediments, perhaps from erosion from agricultural fields. Pollen counts indicate clearance of tropical forest and replacement by grasses and other disturbance taxa. This zone also shows increased maize pollen percentages and the highest charcoal influx in the profile. Zone 2c has abundant charcoal fragments in the 500–1000 µm and > 1000 µm size classes, which are found only sporadically in other parts of the core. However, the top of zone 2c begins a transition in human activity, including reduced maize agriculture and a period of forest regrowth, indicated by a shift in proxy data.

The timing of this shift just below the zone 2c/2b boundary at ca. 1140 cal yr B.P. (427 cm) is around the time of the transition between the Aguas Buenas and Chiriquí cultural phases and also roughly corresponds to the onset of the Mayan Terminal Classic Drought. The samples at depths of 440 cm (estimated age 1180 cal yr B.P.) and 427 cm (ca. 1140 cal yr B.P.) show the highest organic content in the core and continued high charcoal influx. The low inorganic content at this time suggests a decline in soil disturbance due to decreased agriculture in the basin. A negative excursion of $\delta^{13}C$ and $\delta^{15}N$ values continues through the top of zone 2c, indicating decreasing maize agriculture and an increasing C_3 vegetation signal as the Aguas Buenas period ends.

Zone 2b (ca. 1140 to 880 cal yr B.P.)

This zone shows changes in proxy signals that indicate changes in the pattern of human activity in the watershed beginning ca. 1140 cal yr B.P. The negative excursion of isotopic values that started in zone 2c continues into the beginning of 2b, paralleled by decreases in organic C and N content. The trend in $\delta^{13}C$ values indicates a shift toward more C_3 vegetation, and $\delta^{15}N$ reaches its lowest values in the core at ca. 1090 cal yr B.P., early in zone 2b. The influx of microscopic and macroscopic charcoal decreases sharply across the zone 2c/2b boundary. These changes point to reduced agricultural activity, an interpretation supported by increased percentages of pollen of forest and successional taxa (*Quercus*, *Alnus*, *Acalypha*, and Urticales) and a slight decrease in disturbance taxa. However, toward the middle of zone 2b, $\delta^{13}C$ and $\delta^{15}N$ values increase, with the former reaching its highest values in the profile, suggesting increased maize agriculture beginning ca. 1010 cal yr B.P. (399 cm). C/N ratios peak for the core in this same sample, indicating increased terrestrial input to the lake, likely caused by increased agricultural activity in the watershed.

Zone 2a (ca. 880 to 490 cal yr B.P.)

This zone begins with a peak in maize pollen, and $\delta^{13}C$ values show a high C_4 vegetation signal. But within zone 2a, at ca. 720 cal yr B.P. (336 cm), tree pollen percentages increase, grass and other disturbance taxa decrease, and carbon isotopic ratios shift strongly toward C_3 vegetation, indicating forest regrowth. The absence of maize pollen led Anchukaitis and Horn (2005) to propose a possible brief hiatus in maize agriculture at ca. 540 cal yr B.P. (288 cm), but this interpretation is not supported by $\delta^{13}C$ data. Charcoal influx, organic matter, and C and N contents remain relatively stable through zone 2a. C/N ratios across the zone suggest mixed terrestrial and aquatic inputs. Values for $\delta^{13}C$ and $\delta^{15}N$ also stabilize toward the top of zone 2a, with $\delta^{13}C$ particularly establishing a constant background transitioning from the Chiriquí period into Post-Contact.

Zone 1 (ca. 490 cal yr B.P. to present)

This zone begins the Post-Contact period and shows the return of maize agriculture and land use, albeit with an increased level of forest and successional taxa (*Alchornea*, Melastomataceae-Combretaceae, *Weinmannia*, *Hedyosmum*, *Celtis*, and Urticales) relative to previous levels. Signals remain stable across all proxies until modern time. Beginning at 80 cm (ca. 50 cal yr B.P.), inorganic input increases, and $\delta^{13}C$ and $\delta^{15}N$ values show positive excursions. Maize pollen increases and low C/N ratios suggest increased productivity in the lake, likely signaling increased settlement around the lake. Proxy signals remain highly variable, with maize agriculture and landscape disturbance continuing to the top of the core.

ii. Comparison of Organic Matter to Organic Carbon

The first regression model using 48 stratigraphic sediment samples yielded an r^2 value of 0.883, with intercept = –9.861 ± 1.066 ($p < 0.001$) and slope = 0.673 ± 0.036 ($p < 0.001$) (Table 2). This gives a conversion factor of ca. 1.486 between OM and OC. The second regression model, with three low OM (< 20%) and two high OM (> 42%) samples removed, yielded an r^2 value of 0.899, with intercept = –14.671 ± 1.284 ($p < 0.001$) and slope = 0.832 ± 0.043 ($p < 0.001$). This gives a conversion factor of ca. 1.111 between OM and OC.

C. Discussion

i. Land-Use History

What do bulk stable isotope and loss-on-ignition analyses reveal about the nature and timing of prehistoric land use at Laguna Santa Elena, and do these analyses confirm or refute the timeline and interpretations established by Anchukaitis and Horn (2005)?

My thesis research yielded a fine-grained reconstruction of prehistoric land use and maize agriculture in the watershed of Laguna Santa Elena that extends prior proxy interpretations based on pollen and charcoal. Isotopic analysis at twice the resolution of the original pollen and charcoal study revealed new details of land use history. Stable isotope evidence indicates rapid forest clearance and increased maize agriculture shortly after ca. 1650 cal yr B.P. Stable carbon isotope signals of intensive maize agriculture and high charcoal influx indicative of extensive biomass burning are present between ca. 1500 and 1140 cal yr B.P. These signals, together with higher maize pollen percentages, suggest a strong human presence in the Santa Elena watershed during the Aguas Buenas period. Data for $\delta^{13}C$, $\delta^{15}N$, and C/N show a

Table 2: Regression model statistics for comparison of OC and OM.

Model	r^2	Intercept ± SE	$P_{Intercept}$	Slope ± SE	P_{Slope}	CF[1]
48 Samples	0.883	–9.861 ± 1.066	< 0.001	0.673 ± 0.036	< 0.001	1.486
43 Samples	0.899	–14.671 ± 1.284	< 0.001	0.832 ± 0.043	< 0.001	1.111

[1]CF = Conversion factor obtained by dividing one by the regression slope.

negative excursion and a discontinuity in land use beginning ca. 1140 cal yr B.P., corresponding to the transition from the Aguas Buenas to the Chiriquí period. As noted by Anchukaitis and Horn (2005), the timing of this isotopic discontinuity roughly coincides with a regional drought event in Costa Rica (Horn and Sanford 1992) and with the Mayan Terminal Classic Drought (Hodell et al. 2005), which affected the wider circum-Caribbean region (Lane et al. in press). While the continued presence of maize pollen across the 2c/2b transition indicates a low-intensity human presence in the watershed, the abrupt decline in proxy signals of land use ca. 1140 B.P. likely indicate population collapse at Santa Elena (see below).

The discontinuity in land use following the transition from the Aguas Buenas to the Chiriquí period is followed by an increase in isotopic values to the strongest $\delta^{13}C$ signal of C_4 agriculture in the profile at ca. 1010 cal yr B.P. Values for $\delta^{13}C$ and signals of maize agriculture fluctuate through the early Chiriquí period from ca. 1010 to 720 cal yr B.P. These fluctuations may indicate that the extent of maize agriculture in the watershed varied across time, an interpretation not supported by the maize pollen data alone. Values for $\delta^{13}C$ decline following the final signal of expansive C_4 vegetation at 720 cal yr B.P. Both maize pollen and $\delta^{13}C$ values from that time forward indicate limited maize agriculture in the watershed, a pattern that continues into modern times. Beginning ca. 70–50 cal yr B.P., proxy signals of intensive landscape disturbance and maize agriculture return to the Santa Elena watershed. Charcoal influx increases, followed by maize pollen percentages and inorganic content. Values for $\delta^{13}C$ and $\delta^{15}N$ become highly variable, with $\delta^{15}N$ particularly increasing, likely in response to increased inorganic input. C/N ratios decrease, indicating possible increased lake productivity in response to increased terrestrial nutrient delivery.

Values for $\delta^{13}C$ in the Santa Elena sediments range between ca. –30‰ and –14‰. This range is much wider than many other lakes in Costa Rica and the circum-Caribbean, including nearby Laguna Zoncho. This suggests that periods of both maize agriculture and forest recovery were very intense in the watershed and that the Santa Elena core recorded very strong signals of land use over the history of the lake. A portion of the isotopic shifts toward increased C_4 signals is probably attributable to increased aquatic productivity; however, the range of $\delta^{13}C$ values is nevertheless noteworthy. Further research aimed at reconstructing lake productivity at Laguna Santa Elena could help sort out the contributions of C_4 terrestrial vegetation to the $\delta^{13}C$ pool in the sediments.

Values for $\delta^{15}N$ remain relatively steady across the history of the lake after the establishment of intensive maize agriculture in zone 2c, averaging 3.93‰ (SD 0.60‰). Two periods of major shifts mark the $\delta^{15}N$ record, including the establishment of modern maize farming at the top of the core and in the early part of zone 2c, at ca. 1090 cal yr B.P. C/N ratios across the history of Santa Elena generally indicate mixed terrestrial and aquatic contributions to sediments. Two points in the C/N record suggest periods of increased terrestrial input: at ca. 1360 cal yr B.P. during the height of Aguas Buenas period agricultural intensification, and at ca. 1010 cal yr B.P. during the Chiriquí period intensification. Decreasing C/N ratios across the zone 2c/2b transition, along with decreased inorganic input, suggest a higher contribution of aquatic organic matter to the sediment pool at that time. Decreasing C/N ratios in the period of modern maize agriculture suggest increased lake productivity in response to increased nutrient delivery.

The stable isotope signal at Laguna Santa Elena reveals an uncommon pattern in which values for $\delta^{15}N$ closely track those of $\delta^{13}C$ (Fig. 3). Shifts in $\delta^{15}N$ in lake sediments can be driven by a variety of factors, both allochthonous and autochthonous, such as climatic aridity, phytoplankton and microbial activity, changes in water depth, sudden pulses of sediment input, natural changes in trophic state, human alteration of the landscape in the watershed, and others. Shifts in $\delta^{13}C$ are easier to interpret and are primarily caused by changes in C_3 vs. C_4 terrestrial vegetation and changes in lake productivity, and often a combination of both. The relationship between $\delta^{15}N$ and $\delta^{13}C$ at Santa Elena, in which increasing (decreasing) $\delta^{15}N$ values track closely with increasing (decreasing) signals of C_4 agriculture, suggests that both proxy signals are responding to changes in human activity and land use in the watershed. While parts of the relative shifts in $\delta^{13}C$ and $\delta^{15}N$ in the Santa Elena sediments are almost certainly due to changes in primary productivity in response to concurrent changes in terrestrial nutrient delivery, the close correspondence between $\delta^{13}C$ and $\delta^{15}N$ suggests the intriguing possibility of cultural eutrophication at the lake.

Torres et al. (2012) reported results of isotopic analysis on modern sediments from hypereutrophic Lake Apopka in Florida. Apopka had been receiving cultural nutrient inputs for several decades prior to analysis. Patterns in variation of $\delta^{13}C$ and $\delta^{15}N$ in the sediments displayed a close correspondence, similar to that at Laguna Santa Elena. While Torres et al. concluded that the enriched $\delta^{15}N$ signal from Lake Apopka was likely caused by a synergy of factors, including autochthonous N sources and processes, the primary producer community, and water depth, Apopka is also the only lake in their study that received heavy cultural nutrient inputs. I suggest that the patterns of $\delta^{13}C$ and $\delta^{15}N$ variation in sediments from Laguna Santa Elena are a consequence of human agricultural and waste disposal activities, and that the $\delta^{15}N$ signal represents a lake on the border of eutrophication as a result. Fecal biomarkers can provide further insight into fluctuations in $\delta^{15}N$ in response to agricultural and waste disposal activities of prehistoric populations (Evershed et al. 1997; Bull et al. 1999; D'Anjou et al. 2012), but elucidating such causes will require considerable further research. Analysis of diatom assemblages in the Santa Elena core would also help to sort out the causes and consequences of shifts in $\delta^{15}N$. Stable carbon and nitrogen isotope ratios in the sediments of nearby Laguna Zoncho (Taylor 2011) show a generally similar relationship between C and N as sediments from Laguna Santa Elena, suggesting that the pattern between C and N signals at Santa Elena may be representative of a broader local or regional phenomenon. Isotopic analyses at additional lakes in the region could help to further elucidate this pattern.

ii. Estimating Organic Carbon from Organic Matter Content

How does organic matter content estimated by loss-on-ignition compare to carbon content determined through IRMS analysis for Laguna Santa Elena sediments?

Conversion factors for obtaining %OC from %OM estimated using LOI can be derived from the regression equation by dividing one by the regression slope, but only if the intercept approximates zero. This is because when %OM is truly zero, %OC must also be zero. An intercept that does not pass through the origin represents measurement error in the OM/OC relationship and biases the results obtained through a conversion factor. If the intercept of the regression model is not equal to zero, but is not significantly different from zero, then the regression line could be forced through the origin. Sutherland (1998), however, cautioned against forcing the regression line, as doing so assumes *a priori* that no bias exists in measurement—a scientific and statistical impossibility.

For Laguna Santa Elena, the model including 48 stratigraphic sediment samples yielded a conversion factor (CF) of 1.486 (Table 2). This model has an intercept of –9.861 ± 1.066, which is significantly different from zero ($p < 0.001$), indicating considerable bias. Converting %OM to %OC for the Santa Elena samples using CF = 1.486 yielded values for %OC that are significantly different from the observed values of %OC determined by IRMS analysis ($p < 0.001$). An approximate conversion factor between %OM and %OC for these samples, obtained by dividing %OM by %OC for all strata and calculating the mean of those results, would be 3.471 (SD = 1.388), instead of 1.486. If the full regression equation is used, which accounts for the bias in the intercept, rather than CF = 1.486, then the conversion becomes:

$$\%OC = (\%OM * 0.673) - 9.861 \qquad (4)$$

which yields values for %OC that are not significantly different from those determined by IRMS analysis ($p = 0.945$). Use of a general conversion factor of 1.724, which Sutherland (1998) found highly inaccurate, also produced poor results for %OC that were significantly different from IRMS values ($p < 0.001$).

Using the full regression equation that accounts for bias in the intercept accurately converts %OM to %OC ($r^2 = 0.883$; Fig. 4). The conversion factor derived from the regression by dividing one by the slope, however, does not produce accurate results. This suggests that for high-resolution sediment core studies including many stratigraphic samples, a regression model comparing %OM estimated by LOI to %OC determined through IRMS analysis for a subset of samples (here, $n = 48$), well-distributed across the core, could yield a conversion factor that is sufficiently accurate to extrapolate onto the rest of the core. Doing so requires accurate determination of a local conversion factor for the specific samples under investigation and precludes using general published conversion factors.

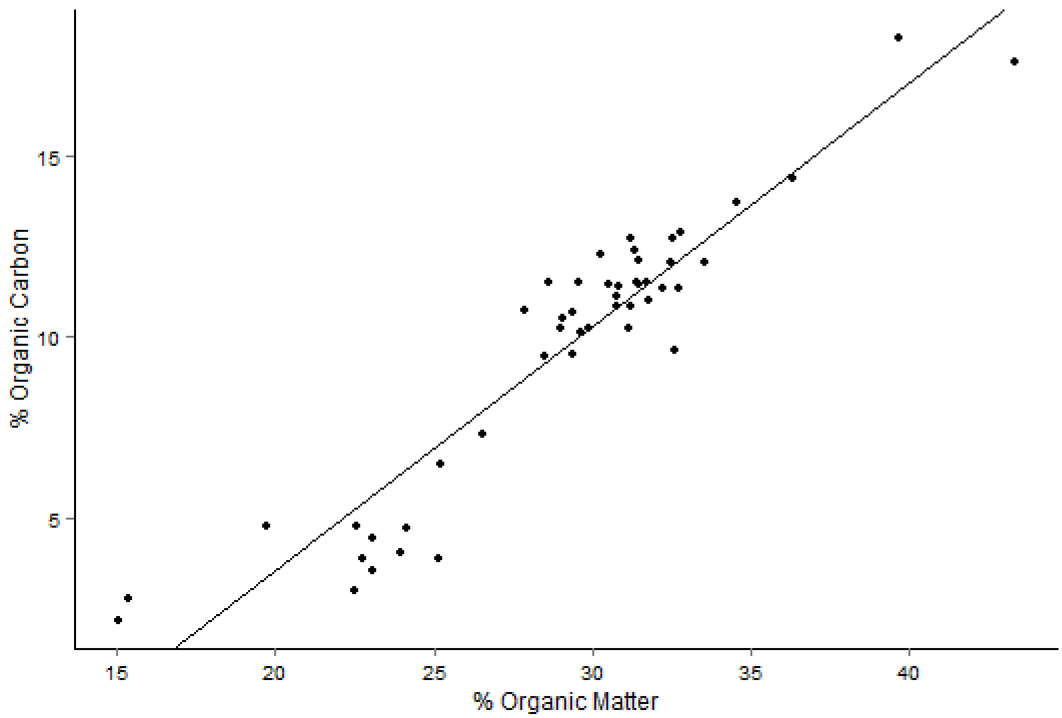

Figure 4: %OC versus %OM in Laguna Santa Elena sediments. Percent organic carbon determined through IRMS analysis plotted against percent organic matter estimated through LOI for Laguna Santa Elena sediments (r^2 = 0.889, intercept = –9.861, slope = 0.673).

Examination of regression residuals indicated that the first model was heavily influenced by high (> 42%) and low (< 20%) values for %OM, but the second regression model with five stratigraphic samples removed introduced additional bias (intercept = –14.671 ± 1.284). The conversion factor obtained from this model of 1.111 yielded converted values for %OC that are significantly different from %OC observed through IRMS analysis ($p < 0.001$). Using a full regression equation that accounts for the intercept also yielded %OC results that are significantly different from the IRMS values ($p < 0.001$). Comparison of the two regression models through ANOVA was not possible due to the removal of five samples in the second model. ANOVA can only be performed on models using the same datasets. While the first regression model was heavily influenced by values at the extreme ends of the %OM distribution, removal of the samples produced unsatisfactory results and is not recommended.

iii. Population Collapse at Laguna Santa Elena

The cultural transition between the Aguas Buenas and Chiriquí periods across zone 2c/2b at ca. 1140 cal yr B.P. is marked by major shifts in proxy signals, indicating large changes in the pattern, scale, and intensity of land use and maize agriculture at Laguna Santa Elena (Figs. 2 and 3). Pollen percentages show a decrease in maize and disturbance taxa and concomitant forest regeneration. Charcoal influx declines across all size classes, indicating decreased biomass burning. Inorganic input decreases due to lower human soil disturbance, causing a decrease in primary productivity and values for $\delta^{15}N$ responding to lower terrestrial nutrient delivery. Values for $\delta^{13}C$ display a large negative shift toward a C_3 signal at the beginning of zone 2b due to changing terrestrial vegetation and decreased aquatic productivity. C/N ratios have relatively lower values as well, further indicating decreased terrestrial contribution to sediments. The geochemistry of a sediment sample analyzed at the zone 2c/2b boundary showed an odd ratio of 42.83% OM to 6.23% OC. This sample does not fit the overall pattern of the OM/OC relationship in the Santa Elena core, suggesting a significant change in geochemical processes at the site. Elucidating a possible cause for this disruption will require further research. Archaeological excavation revealed the presence of Aguas Buenas period ceramics, but no Chiriquí materials at Santa Elena (Sánchez and Rojas 2002), indicating that permanent settlement sites in the watershed were abandoned. Additionally, the timing of this major shift in land use coincides with the widespread Terminal Classic Drought. All the evidence taken together strongly suggests collapse and depopulation of the Laguna Santa Elena watershed ca. 1140 cal yr B.P., likely in response to severe drought in the region.

iv. Santa Elena in a Broader Perspective

How do the results of this research relate to recent work at nearby Laguna Zoncho and ongoing archaeological investigations in southern Pacific Costa Rica and western Panama?

Proxy signals from Laguna Santa Elena yielded a reconstruction of land-use history that coincides well with evidence from nearby Laguna Zoncho. Taylor (2011) and Taylor et al. (2013b) reported two periods of agricultural decline at Zoncho, between ca. 1150–970 and 860–640 cal yr B.P., that correspond to severe droughts in the region and throughout the circum-Caribbean. Taylor et al. (2013b) suggested that population patterns and agricultural intensity at Zoncho and in the wider area, including at Santa Elena, were controlled by climate and precipitation variability. The scale and intensity of land use and maize agriculture declined at Santa Elena after ca. 1140 and 720 cal yr B.P. These times fall within the intervals of agricultural decline recognized at Laguna Zoncho. Anchukaitis and Horn (2005) reported a brief hiatus in maize agriculture at Santa Elena at ca. 540 cal yr B.P., but this finding is not well-supported by $\delta^{13}C$ values and may simply represent the chance failure of maize pollen to be captured in that particular sample.

Taylor et al. (2013b) reported that maize agriculture, and presumably also people, were nearly absent at Zoncho ca. 220 years before the arrival of the Spanish. In contrast, stable carbon isotope ratios and maize pollen signals suggest that the Laguna Santa Elena watershed was continuously occupied, despite possible population collapse after ca. 1140 cal yr B.P. and a smaller decline in the scale of agriculture beginning after ca. 720 cal yr B.P. The Santa Elena core shows negative shifts in carbon isotope values at ca. 1250 and 720 cal yr B.P., following peaks in C_4 signals. The shift beginning at 720 B.P. is accompanied by decreased Poaceae pollen and increased forest regrowth. Continued charcoal influx and the presence of maize pollen, however, suggest that low-intensity maize agriculture continued despite the declines.

Archaeological evidence from southern Pacific Costa Rica and western Panama shows population movement, increasing social complexity, and culture change across the transition from the Aguas Buenas to the Chiriquí period ca. 1150 cal yr B.P. Excavations at Laguna Santa Elena revealed the presence of house sites on hilltops surrounding the basin (Sánchez and Rojas 2002; M. Sánchez, personal communication, 2013). These sites contained Aguas Buenas period artifacts, but no Chiriquí materials. Archaeological evidence suggests that the Santa Elena watershed was abandoned and proxy evidence from lake sediments suggest a population collapse ca. 1140 B.P., but with signals of low-intensity maize agriculture continuing across the cultural transition. Five human generations later, pollen and $\delta^{13}C$ signals of maize agriculture increased to the strongest C_4 signature in the history of Laguna Santa Elena ca. 1010 cal yr B.P., but the archaeological record does not show evidence that residences returned to the watershed (M. Sánchez, personal communication, 2013).

A major question remains for Laguna Santa Elena. If archaeological and sedimentary evidence suggests that people moved out of the Santa Elena watershed following the end of the Aguas Buenas period, but proxy data from lake sediments show that maize agriculture continued and later intensified, where did people go and why? Sánchez and Rojas (2002) reported the presence of a larger site named Fila Tigre ca. 2 km east of Laguna Santa Elena that contained predominantly Aguas Buenas period ceramics, but also had a minor presence of Chiriquí artifacts. They argued that Fila Tigre was likely a significant regional center and that the area conforms to expected settlement patterns of large centers associated with dispersed hamlet sites for the Diquís sub-region (Linares and Sheets 1980; Drolet 1992; Anchukaitis and Horn 2005). Fila Tigre would have been a likely location for initial population agglomeration during environmental stress and collapse in the hinterlands.

The minor presence of Chiriquí period artifacts at Fila Tigre suggests that the site was not occupied for a long duration following the Aguas Buenas to Chiriquí transition. Considering severe drought, population movement and decline, and increasing hierarchy and social complexity in the region across the cultural transition, one logical conclusion is that people were relocating from the hinterlands to primary population centers larger than Fila Tigre, and were maintaining small sites like Laguna Santa Elena and Laguna Zoncho for farming. Conversations with archaeologist Maureen Sánchez of the University of Costa Rica (personal communication, 2013) revealed that other sites exist in the area that are known to locals, but are yet uninvestigated by professional archaeologists. Future archaeological and paleoenvironmental research in the area may help to resolve activities and movements of the people who occupied the Laguna Santa Elena watershed and the wider area during the Aguas Buenas–Chiriquí period transition.

CHAPTER IV

EFFECTS OF ACID FUMIGATION ON STABLE NITROGEN ISOTOPE RATIOS IN SEDIMENTS AND SOILS FROM LAGUNA SANTA ELENA AND LAGUNA AZUL, COSTA RICA

A. Methods

i. Sampling

The Laguna Santa Elena sediment core comprises ca. 6 m of lacustrine sediments underlain by ca. 1 m of soil. Anchukaitis and Horn (2005) sampled 29 stratigraphic levels of the core at intervals of ca. 16–32 cm for pollen and charcoal analyses, including 25 levels from the lacustrine portion and 4 levels from the soil. For my thesis research I sampled the core for bulk stable isotope analysis at the same 29 intervals examined by Anchukaitis and Horn (2005), and at 29 additional, intervening stratigraphic levels, increasing the sampling resolution to ca. 8–16 cm for this study. My analysis of the effects of acid fumigation on $\delta^{15}N$ results used 50 samples from the lacustrine portion of the core and 8 additional samples from the underlying soil profile in total. Samples were 1 cm^3 volume.

The Laguna Azul profile is composed of 60 cm of near-surface sediments and a 70-cm section that begins 3 m below the mud-water interface. Eighteen samples of 1 cm^3 volume were collected for stable isotope analysis at irregular intervals of 2–24 cm through the two sections. Sampling intervals were guided by previous proxy work (Horn 2006, unpublished data).

ii. Sample Acidification and Stable Isotope Analysis

Bulk organic carbon and nitrogen content and isotope analysis followed the methods of Lane et al. (2013a) and the laboratory protocol of the University of North Carolina Wilmington

(UNCW) Stable Isotope Laboratory. Samples were oven-dried at 50 °C and then ground to a fine powder with an ethanol-rinsed mortar and pestle. The ground samples were split roughly into two aliquots, with one aliquot ready for $\delta^{15}N$ analysis as the non-acidified fraction (Brodie et al. 2011c). Samples analyzed for $\delta^{13}C$ composition were moistened with distilled water and fumigated with 12 N HCl for 2 h in a desiccator, then vented for 24 h. Following acidification, the samples were dried on a hotplate (surface temperature ca. 60 °C) until free of water and residual acid (ca. 48 h), and then reground. Acidification and drying took place in ceramic crucibles. Sample preparation took place in the Laboratory of Paleoenvironmental Research at the University of Tennessee. Subsamples for $\delta^{13}C$ and $\delta^{15}N$ analysis were loaded into tin capsules and shipped to the UNCW Stable Isotope Laboratory. All samples from Laguna Santa Elena and Laguna Azul were analyzed in 100% duplicate. Additional analyses run to provide triplicates for selected levels for other parts of my thesis work were not considered here.

The samples were analyzed on a Costech Elemental Analyzer coupled to a Thermo Delta V Plus Mass Spectrometer at the UNCW Stable Isotope Laboratory. Carbon and nitrogen isotopic compositions are reported in standard δ-per mil notation with carbon values relative to the Vienna-Pee Dee belemnite (V-PDB) marine carbonate standard and nitrogen values relative to AIR, where R = $^{13}C/^{12}C$ or $^{15}N/^{14}N$ and:

$$\delta^{13}C \text{ or } \delta^{15}N(\text{permil}) = 1000[(R_{sample}/R_{standard})-1] \quad (5)$$

Repeated analyses of USGS 40 glutamic acid standard indicated that instrument precision for these samples was better than ±0.16‰.

iii. Statistical Methods

Calculations were performed in the R Version 3.0.1 environment for statistical computing (R Core Team 2013). Graphical outputs were produced in R using the "ggplot2" package (Wickham 2009). Two-tailed paired t-tests were used to compare the $\delta^{15}N$ results for the non-acidified versus the acidified fractions at the $\alpha = 0.05$ significance level. The t-tests were performed on several combinations of the data, including on Laguna Santa Elena and Laguna Azul separately and together, and on the duplicate analyses both separately and averaged together. While a paired t-test was not the ideal test for this situation with duplicate samples, it was the most appropriate one to compare the before-and-after acidification results. ANOVA was inappropriate as isotopic signatures of each stratum of the Santa Elena and Azul profiles reflect paleoenvironmental conditions at a certain point in time, thus data are paired. The difference between $\delta^{15}N$ values for the non-acidified and acidified fractions, defined here as $\Delta^{15}N = \delta^{15}N_{non-acidified} - \delta^{15}N_{acidified}$, was plotted against depth in the sediment cores to facilitate a qualitative assessment of whether the magnitude of the difference would be likely to affect paleoenvironmental interpretation of trends.

B. Results

Initially, the duplicate results for $\delta^{15}N$ were averaged together to obtain a single value for $\delta^{15}N$ non-acidified and $\delta^{15}N$ acidified for each sampled depth in the sediment cores to replicate how the results would be presented for paleoenvironmental interpretation. For Laguna Santa Elena and Laguna Azul together, $\delta^{15}N$ in the non-acidified fraction was significantly different from $\delta^{15}N$ in the acidified fraction ($p = 0.01$) (Table 3). The non-acidified $\delta^{15}N$ values were also significantly different from the acidified $\delta^{15}N$ values for Santa Elena alone ($p < 0.002$) and for

Table 3: T-test results for $\delta^{15}N$ values for Laguna Santa Elena and Laguna Azul.

Samples	df[1]	t-value	p-value	Samples	df[1]	t-value	p-value
Averaged				**Individual**			
Both Lakes	75	3.339	0.010	Both Lakes	151	2.869	0.005
Santa Elena	57	3.975	0.002	Santa Elena	115	3.471	0.001
Azul	17	-3.564	0.002	Azul	35	-3.761	0.001
Acid 1 vs. Acid 2				**Non 1 vs. Non 2**			
Both Lakes	75	2.900	0.005	Both Lakes	75	1.470	0.146
Santa Elena	57	2.694	0.009	Santa Elena	57	1.263	0.212
Azul	17	1.473	0.159	Azul	17	1.351	0.194
Acid 1 vs. Non 1				**Acid 1 vs. Non 2**			
Both Lakes	75	3.339	0.001	Both Lakes	75	3.716	0.001
Santa Elena	57	3.975	0.001	Santa Elena	57	4.007	0.001
Azul	17	-3.564	0.002	Azul	17	-0.765	0.455
Acid 2 vs. Non 1				**Acid 2 vs. Non 2**			
Both Lakes	75	-0.017	0.987	Both Lakes	75	1.166	0.247
Santa Elena	57	0.608	0.545	Santa Elena	57	1.511	0.136
Azul	17	-3.499	0.003	Azul	17	-2.246	0.038

[1]df = degrees of freedom

Azul alone ($p < 0.002$). When non-acidified $\delta^{15}N$ was compared to acidified $\delta^{15}N$ with all duplicate samples included, but not averaged together, the t-test indicated significant differences in both lakes together ($p < 0.005$), and at Santa Elena ($p < 0.001$) and Azul ($p < 0.001$) separately. Duplicate samples in the acidified fraction were significantly different from each other for both lakes together ($p < 0.005$) and for Santa Elena alone ($p = 0.009$), but not for Azul ($p = 0.159$). Values for $\delta^{15}N$ in the duplicate runs for the non-acidified fraction were not significantly different in any situation ($p = 0.146$ for both lakes together).

Values for $\delta^{15}N$ in the first set of acidified samples were significantly different from values for $\delta^{15}N$ in the first set of non-acidified samples for both lakes together ($p = 0.001$), and for Santa Elena ($p < 0.001$) and Azul ($p = 0.002$) separately. Comparing $\delta^{15}N$ in the first set of acidified samples with the second set on non-acidified samples yielded a significant difference for both lakes together ($p < 0.001$) and for Santa Elena alone ($p < 0.001$), but not for Azul ($p = 0.455$). Results for the second set of acidified samples were not significantly different from results for the first set of non-acidified samples for both lakes together ($p = 0.987$) or for Santa Elena alone ($p = 0.545$), but were different for Azul alone ($p < 0.003$). Results for the second set of acidified samples also did not differ significantly from results for the second set of non-acidified samples for both lakes together ($p = 0.247$) or for Santa Elena alone ($p = 0.136$), but did show a difference for Azul alone ($p = 0.038$).

Using the non-averaged $\delta^{15}N$ values, for Laguna Santa Elena and Laguna Azul together $\Delta^{15}N$ ranged from –1.925 to 2.598, with a mean value of –0.131 (SD = 0.562) (Table 4). For Santa Elena alone, $\Delta^{15}N$ ranged between –1.925 and 2.598, with a mean value of –0.200 (SD = 0.622). For Azul alone, $\Delta^{15}N$ ranged from –0.241 to 0.423, with a mean value of 0.094 (SD = 0.150).

Table 4: $\Delta^{15}N$ between non-acidified and acidified samples.

Samples	Mean $\Delta^{15}N$	Std. Dev.	Range
Both Lakes	–0.131	0.562	–1.925 – 2.598
Santa Elena	–0.200	0.622	–1.925 – 2.598
Azul	0.094	0.150	–0.241 – 0.423

C. Discussion

Does comparison of $\delta^{15}N$ results for acidified and non-acidified samples from Laguna Santa Elena and Laguna Azul indicate that acidification causes statistically significant differences in $\delta^{15}N$ values that might warrant analysis of an additional non-acidified fraction?

The results for this portion of the investigation are inconclusive. When $\delta^{15}N$ results are averaged together to produce a single value for acidified and non-acidified samples from each stratigraphic level sampled from the sediment cores, the $\delta^{15}N$ values are significantly different between the two fractions (Table 3). If the samples had been analyzed only once, rather than in duplicate, $\delta^{15}N$ values between the acidified and non-acidified fractions may have shown a significant difference (i.e. for the first acidified versus non-acidified set of analyses), or they may not have shown a difference (i.e. second acidified versus non-acidified analyses). These results suggest that the effects of the acidification reaction on $\delta^{15}N$ results using the UNCW protocol may be unpredictable. The observed differences may be due to a number of factors, including residual acid content in the samples, hygroscopic water drawn in by residual acid, the acidification reaction and process itself, contamination or measurement error, or simple random chance. Additionally, the mixed results for this analysis, including the finding that $\delta^{15}N$ values in duplicate analyses of acidified samples are significantly different, while $\delta^{15}N$ values in duplicate non-acidified samples are not different, suggest that analysis of a non-acidified sample fraction for $\delta^{15}N$ is warranted, pending further investigation and analysis of more samples. Furthermore, given that $\delta^{15}N$ values in duplicate acidified samples are significantly different, researchers opting to use dual-mode analysis despite the findings presented here should exercise considerable caution when interpreting data from analyses of single samples at each stratigraphic level.

Are the differences due to acidification scientifically important or meaningful, in that the differences would affect the paleoenvironmental interpretation of the $\delta^{15}N$ results?

To address this question, $\delta^{15}N$ values for replicate analyses were averaged together to produce a single value for $\delta^{15}N$ acidified and $\delta^{15}N$ non-acidified for each stratigraphic level. $\Delta^{15}N$ was then calculated for each stratum. The differences in $\delta^{15}N$ values in the Laguna Santa Elena sediments and soils have an overall negative trend (mean $\Delta^{15}N$ = –0.200; SD = 0.467), which matches the directional trend reported by Brodie et al. (2011a, b, c). Results for the Laguna Azul samples, however, have a generally positive trend (mean $\Delta^{15}N$ = 0.094; SD = 0.109), contrary to the findings of Brodie and collaborators.

For the Santa Elena samples, $\Delta^{15}N$ values range between –1.482 and 1.097, which is likely not a large enough change to alter overall paleoenvironmental interpretations (Figs. 5 and 6). Note that for Santa Elena, many of the error bars (1 SD) overlap (Fig. 5). While the overall temporal trends for the Santa Elena $\delta^{15}N$ data are maintained and would likely be interpreted similarly, the change in $\delta^{15}N$ due to acidification appears to be unpredictable and can manifest as either positive or negative. This finding has important implications, as paleoenvironmental interpretations are based on relative changes in $\delta^{15}N$ values over time. The variable and unpredictable nature of $\Delta^{15}N$ due to acidification can alter the intensity of relative $\delta^{15}N$ changes and could potentially cause reversals in directional trends through a profile, thus imparting a false signal in the $\delta^{15}N$ record.

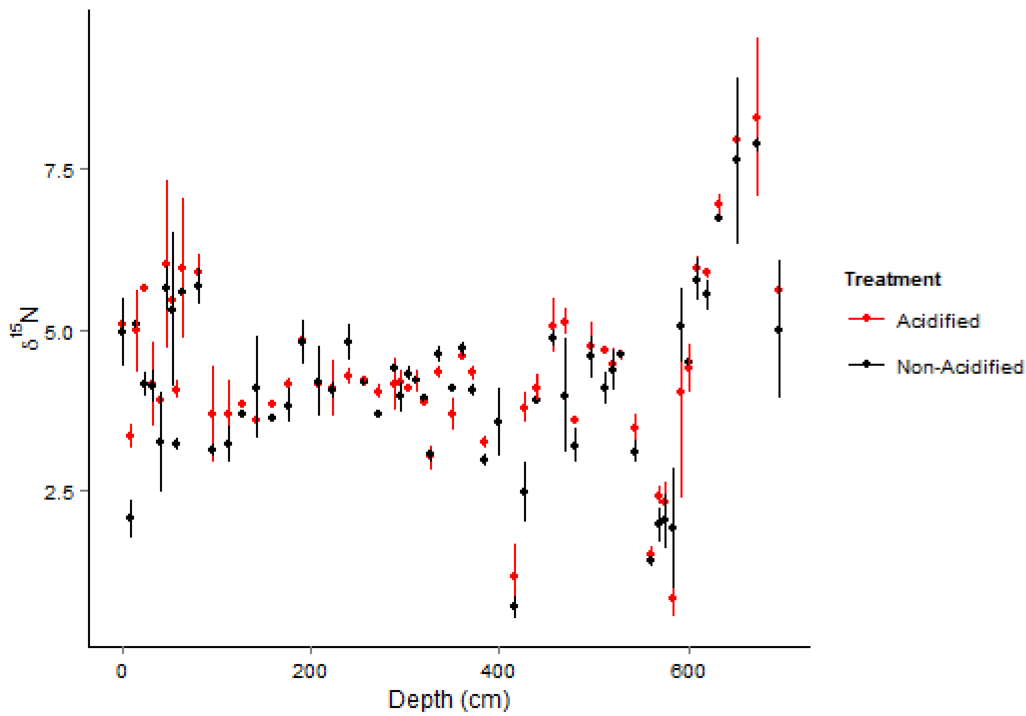

Figure 5: $\delta^{15}N$ plotted against depth for Laguna Santa Elena samples. Error bars = 1 SD.

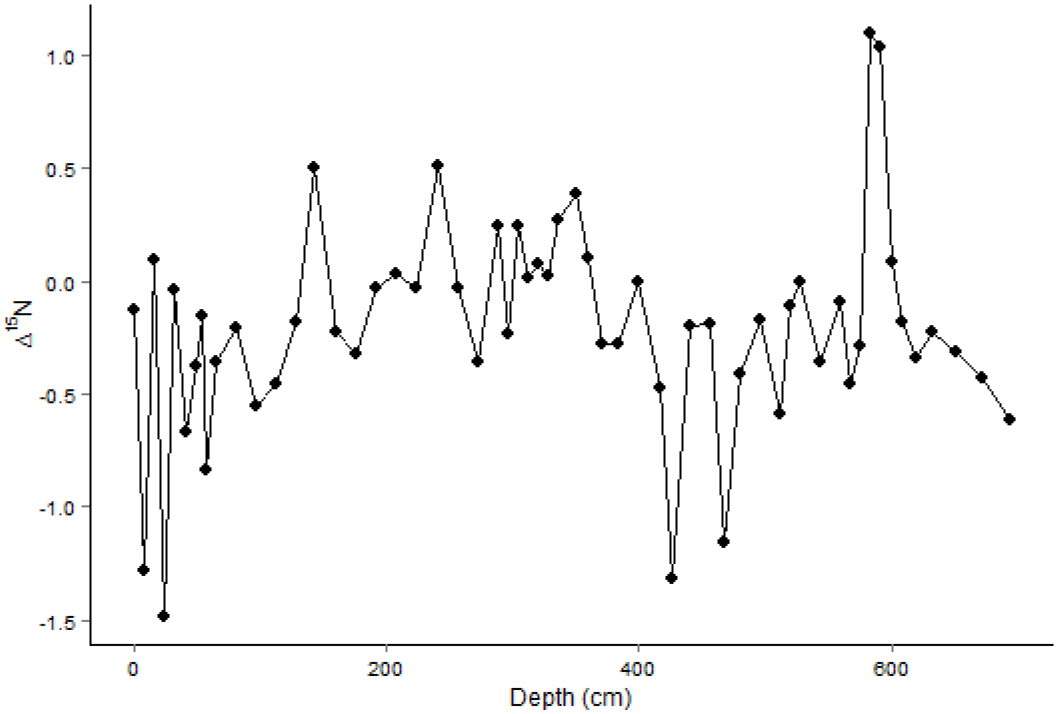

Figure 6: Δ^{15}N plotted against depth for Laguna Santa Elena samples.

For the Laguna Azul samples, $\Delta^{15}N$ values range from –0.108 to 0.245 (not shown). The magnitude of the changes for Azul is very small and would not alter paleoenvironmental interpretations. An important point to note, though, is that the changes due to acidification manifested differently for the two lakes. Although this study included only two lakes, the different results for Laguna Santa Elena and Laguna Azul suggest that whether or not acidification affects $\delta^{15}N$ values in carbonate-containing soils and sediments is unresolved at this point. A final consideration is the comparability of $\delta^{15}N$ values between sites. The wide range and unpredictability of changes in $\delta^{15}N$ values due to acidification in the Santa Elena samples suggests that researchers must use caution when comparing paleoenvironmental reconstructions between sites, particularly when considering actual $\delta^{15}N$ values, rather than just relative trends over time. Further research, including analysis of sediment and soil samples from additional locations, is necessary to better understand the scientific implications and potential influences of acidification on $\delta^{15}N$.

CHAPTER V

SUMMARY AND CONCLUSIONS

The results of this study extend the pollen- and charcoal-based record from Laguna Santa Elena established by Anchukaitis and Horn (2005), showing geochemical trends that in some cases parallel trends in botanical proxies and in others reveal new aspects of human and environmental dynamics at the site. The present study also builds on the work of Taylor (2011) and Taylor et al. (2013a, b) at Laguna Zoncho, adds a robust suite of data to ongoing efforts to disentangle climate change and human-environment interactions in Central America, and contributes temporally-explicit data to archaeological investigations in the region. These results reinforce the conclusions of Lane et al. (2004; 2009) that $\delta^{13}C$ is a reliable proxy for forest clearance and maize agriculture in the neotropics. This work at Laguna Santa Elena builds a foundation for further proxy studies aimed at disentangling the effects of humans versus climate on the local environment.

These data demonstrate the usefulness of bulk stable isotope analysis for reconstructing a record of the scale of maize agriculture and land use at mid-elevation lakes in Costa Rica. The low cost, time investment, sediment volume, and chemical processing requirements of stable isotope analysis as compared to pollen and charcoal analyses argues for the routine inclusion of bulk stable isotope analyses in palynological studies. This technique is a strong line of initial inquiry for generating pilot data prior to more extensive work. Patterns revealed by isotopic signals can then direct further targeted proxy research on sediment cores.

Pre-analysis acidification of sediment and soil samples from Laguna Santa Elena and Laguna Azul following the UNCW Stable Isotope Laboratory protocol may cause statistically significant differences in $\delta^{15}N$ values between the acidified and the non-acidified fractions. While the magnitude of the changes might not be sufficient to alter paleoenvironmental interpretations, the changes do have the potential to alter and even reverse relative trends in $\delta^{15}N$ signals in lake sediment studies. Additionally, the change in $\delta^{15}N$ values due to acidification appears to be random and unpredictable, and can manifest as either positive or negative shifts. Given the evidence revealed by this study, researchers should avoid dual-mode analyses and continue analyzing an additional non-acidified sample to obtain $\delta^{15}N$ values, pending further investigation. These findings are particularly relevant for studies using strictly quantitative approaches where absolute isotopic values are more important than temporal trends.

This study forms the basis for future work involving targeted experimental biomarker and compound-specific isotope analyses. Such work could be aimed at the direct detection of maize agriculture (Reber and Evershed 2004; Reber et al. 2004; E. Reber, personal communication, 2012), compound-specific analyses to sort out the effects of human activity versus climate in the watershed (Russell et al. 2009), further work on C_3/C_4 vegetation changes, and hydrogen isotope analysis of precipitation changes in the region (Russell et al. 2009; Lane and Horn 2013; Lane et al. 2013b, in press). Biogeochemical proxies drawn from lake sediments have a high potential to reveal finely detailed signals of paleoenvironmental change and human land use. This proxy work at Laguna Santa Elena contributes a strong initial dataset to be enhanced by further work in the region.

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VITA

Matthew Timothy Kerr was born in Seneca, Pennsylvania on February 19, 1979. He graduated from Cranberry Area High School in Seneca in 1997. He enlisted in the United States Army in May of 2001 and served two combat tours of duty in Operation Iraqi Freedom. He was honorably discharged from active duty in May of 2006. He then attended the University of North Carolina Wilmington, where he graduated in 2012 *summa cum laude* with a Bachelor of Arts in Anthropology, a minor in history, and honors in Anthropology. He became interested in archaeogeochemistry, stable isotope biogeochemistry, mass spectrometry, and prehistoric human-environment interactions while working with Dr. Eleanora Reber and Dr. Chad Lane. Matthew's undergraduate research, published in the *Journal of Archaeological Science,* focused on the persistence of caffeine in experimentally-produced pottery residues.

Matthew entered the graduate program in geography at the University of Tennessee in 2012 to study paleoenvironments and prehistoric human-environment interactions in Costa Rica. While at the University of Tennessee, Matthew was a research assistant with the Initiative for Quaternary Paleoclimate Research, which includes faculty from the departments of Geography, Anthropology, Earth and Planetary Sciences, and Ecology and Evolutionary Biology. Matthew was also supported during his master's degree work by a graduate teaching assistantship in the Department of Geography. He instructed physical geography laboratory classes for Geography of the Natural Environment I and II. After completing his M.S. degree, Matthew will continue his research in prehistoric human-environment interactions and geochemistry in the PhD program in geography at the University of Tennessee.