8-2015

Evidence of Late Quaternary Fires from Charcoal and Siliceous Aggregates in Lake Sediments in the Eastern U.S.A.

Joanne P. Ballard
University of Tennessee - Knoxville, joanne.ballard@hbu.cas.cz

To the Graduate Council:

I am submitting herewith a dissertation written by Joanne P. Ballard entitled "Evidence of Late Quaternary Fires from Charcoal and Siliceous Aggregates in Lake Sediments in the Eastern U.S.A.." I have examined the final electronic copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Geography.

Sally P Horn, Major Professor

We have read this dissertation and recommend its acceptance:

Henri Grissino-Mayer, Yingkui Li, Steven G. Driese, Chad S. Lane

Accepted for the Council:

Carolyn R. Hodges

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

Evidence of Late Quaternary Fires from Charcoal and Siliceous Aggregates in Lake Sediments in the Eastern U.S.A.

A Dissertation Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Joanne P. Ballard
August 2015

DEDICATION

This dissertation is dedicated to my dear children, Rachel Jasmine Ballard and Austin Yoder, Nathan Grant Ballard and his wife Marty Ryan Ballard, Pascalle Rose Ballard Scudder and her husband James Scudder, my “co-child” Karoline Elizabeth Mikolajewski; and my late parents Patrick and Pearl Clark Sheridan.

ACKNOWLEDGEMENTS

First and foremost, I want to thank my advisor, Sally P. Horn, who has spent many hours advising me and countless hours editing this dissertation. I feel privileged to have had such a quintessential editor helping me polish this document. During my four years at UT, I have appreciated Dr. Horn's fast response to emails and our many long discussions about this project. She also encouraged me to participate in conferences, and these experiences have enriched my academic career.

I thank my committee, Henri Grissino-Mayer, Philip Li, both at the University of Tennessee; Chad Lane at the University of North Carolina, Wilmington (UNCW), and Steven Driese at Baylor University in Waco, Texas. My committee members have all helped tremendously with editing and with general discussion. I thank Zheng-Hua Li, PI with Sally Horn on the NSF grant that funded this research, for early discussions on this project.

The siliceous aggregate project would not have been possible without Steven Driese and his expertise in analyzing sediment thin sections. Many others helped to make it a success. Bryson Conner constructed special racks for the samples with his grandfather. Edward Schilling and Ken McFarland provided space for the acid rain experiments in the Hesler greenhouse and lab, and were supportive of the research. Ken McFarland advised on the algae and cyanobacteria populations in the greenhouse. Jason Cottrell and the UT groundskeepers helped me obtain beech wood from the UT property on Lyons View. Roger Horn cut up the beech wood. David Pratt and his workers in the Biological Sciences shop provided helpful tips on setting up the ash experiments. Bryson Conner, Matthew and Jacquelyn Kerr, and Benjamin Sheridan assisted with the burning of different batches of wood. Carol Harden provided a combustion washtub, sediment samples for silt extraction, and the use of her muffle furnace. Christopher Lehmann, National Atmospheric Deposition Program, gave advice on rainwater pH.

I also very much appreciate Chad Lane, who kindly made available his lab at UNCW to run isotope samples on the IRMS. Funding from the UNCW Center for Marine Science and UNCW College of Arts and Sciences, as well as the NSF grant, supported these isotope analyses. Charcoal analyses of sediment cores and isotope sample preparation was carried out in the Laboratory of Paleoenvironmental Research at the University of Tennessee, directed by Sally Horn and Philip Li. Roger Horn was very kind in helping out with numerous aspects of this research, such as cutting up beech wood and sediment cores. For permission to collect sediment cores from Pigeon Marsh, Georgia, I thank the Georgia Department of Natural Resources and managers at Crockford-Pigeon Mountain Wildlife Management Area. The coring trip and permit were arranged by Sally Horn and the coring team consisted of Sally, Roger Horn, Mathew Boehm, Paul Lemieux III, and myself.

I want to thank the original researchers who constructed the foundation for this research with their pollen work on cores from Anderson, Cahaba and Jackson Ponds—Hazel and Paul Delcourt and Gary Wilkins. William Watts' pollen work at Pigeon Marsh was very helpful in guiding the field work at that site. I thank Scott Meeks for facilitating access to the original Anderson Pond, Cahaba, and Jackson Pond lake-sediment cores and other materials from the Delcourt's research, including pollen slides from Anderson Pond. I thank Steve Jackson, Jack Williams, and James Kocis for collecting the 2007 Anderson Pond cores and sharing them with our lab at the University of Tennessee. I would like to thank Mathew Boehm for training on microscopic point counting methods and other laboratory assistance. I thank David Anderson, Nicholas Nagle, Chris Fedo, Latisha Brengman, Mathew Boehm, Matthew Valente, Yanan Li, Andre Bijkerk, Al Goodyear, Benoit Lafleur Michel Legrand, Brad Lepper, Jean-Luc Mercier, J. Barry Maynard, and H. Greg McDonald for helpful discussions. Thomas Waldrop of the USDA Forest Service provided helpful discussion regarding fires and forests in the Southeast. I thank Dave Morris and staff with the Ministry of Natural Resources and Forestry in Thunder Bay, Ontario, Canada, for insights into the ecology of various boreal forest trees. I thank cartographer Timothy Price for assistance with maps.

Special thanks to Bas van Geel, Universiteit Amsterdam, for preparation of a pollen slide to help identify myriad dinoflagellate resting cysts in Cahaba Pond at the time of major reorganization of aquatic and terrestrial plant assemblages. Special thanks also to Jamey Fulton, Baylor University for analyzing a Cahaba Pond sample for biomarkers of cyanobacteria.

It was a great experience to work with my wonderful lab assistants, Bryson Conner, Paul Lemieux III, Elizabeth Maclennan, and Karoline Mikolajewski. I also thank Jan Simek for making available an XRF analyzer, and Sierra Bow.

Thanks to Norma Galyon, Pamela Sharpe, and Tracy Branch in the Geography office for their encouragement and support during my time at the University of Tennessee. Thanks to all my fellow graduate students at the University of Tennessee, who have made my experience at the University of Tennessee a memorable one. Thank you to all the faculty in the Geography Department for being supportive of students, and to Derek Alderman for his fearless leadership. I appreciate the support provided by the Graduate Student Senate, the Geography Department, and the College of Arts and Sciences to present findings of this research at meetings of the Association of American Geographers and the Southeastern Archaeological Conference.

One AMS radiocarbon analysis included in this dissertation was made at the National Ocean Sciences Accelerator Mass Spectrometry Facility (NOSAMS) located at the Woods Hole

Oceanographic Institution. NOSAMS is supported by NSF cooperative agreement number OCE-0753487.

The work of the data contributors and the Neotoma community is gratefully acknowledged (Neotoma Paleoecology Database http://www.neotomadb.org). This research was supported by the National Science Foundation under Grant EAR-0822824 awarded to Zheng-Hua Li and Sally Horn.

ABSTRACT

The late-glacial transition to the Holocene, 15,000–11,600 cal yr BP, is an enigmatic period of dynamic global changes and a major extinction event in North America. Fire is an agent of disturbance that transforms the environment physically and chemically, and affects plant community composition. To improve understanding of the linkages between fire, vegetation, and climate over the late glacial and Holocene in the eastern U.S., I analyzed lake-sediment cores for charcoal and indicators of wood ash, and compared results to existing pollen records. A new microscopic charcoal record from Anderson Pond, Tennessee revealed high fire activity from 23,000–15,000 cal yr BP when conifers dominated, and during the Mid-Holocene Warm Period (8000–5200 cal yr BP), when hardwoods dominated. Macroscopic charcoal analysis of sediments from Pigeon Marsh, Georgia showed high fire activity from 16,500–14,500 cal yr BP, below a major hiatus. Jackson Pond, Kentucky and Cahaba Pond, Alabama had low macroscopic charcoal concentrations during the late glacial; largest charcoal peaks occurred around 5000 cal yr BP at Jackson Pond, and from 1370–640 cal yr BP at Cahaba Pond.

Thin sections were prepared for cores from the four southeastern U.S. sites and from Swift and Slack Lakes, Michigan, and analyzed together with nitrogen isotopes and element data from XRF. Thin sections showed the presence of siliceous aggregates, a unique grain type, in sediments from five sites. These grains are rare, occurring in only three periods, around 19,250, 14,000 and 12,400 cal yr BP. In laboratory experiments, I produced siliceous aggregates from wood ash with simulated rain, and found their formation requires silt, but not high acidity. On the landscape, siliceous aggregates form after fires in wood ash by the action of water. The alkaline pH of the wet ash dissolves phytoliths, and amorphous silica nucleates around silt-sized quartz grains. Then aggregates are transported into lake sediments. My research demonstrates

that siliceous aggregates are a new proxy for wildfires in paleoenvironmental records. The wildfire-derived siliceous aggregates in cores examined from the eastern U.S. are contemporaneous with combustion signals in Greenland ice cores, suggesting widespread late-glacial fire events.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Chapter 1

Introduction

Purpose and Overview

In this research, I investigated fire-vegetation-climate interactions in the eastern U.S. over the late glacial and Holocene as revealed by charcoal, other plant remains, and biogeochemical indicators in lake-sediment cores. Clark and Richards (1996) emphasized the need to develop stratigraphic charcoal records to characterize the role of fire in the late glacial. Charcoal records of past fire are also useful in ecosystem management (Heyerdahl and Card 2000). I developed charcoal records from four sites in the southeastern U.S. to increase our understanding of fire and its origins and controls from the Last Glacial Maximum (LGM) to modern times, including the late glacial period of dynamic environmental change. These sites are: Anderson Pond, Tennessee; Cahaba Pond, Alabama; Jackson Pond, Kentucky; and Pigeon Marsh, Georgia. The new microscopic record from Anderson Pond and the macroscopic charcoal records I developed at the other sites provide some of the only data available on paleofires in the interior southeastern United States. I compared the charcoal data to pollen data from prior studies at the same sites, and to charcoal records from Swift and Slack Lakes, Michigan, that I developed for my M.S. research at the University of Cincinnati.

Fire transforms the geochemistry of the environment. Biomass is reduced to charcoal (carbon) and wood ash (calcium and other elements) on the landscape, while particulate matter enters the atmosphere and is deposited in terrestrial and aquatic environments, and on ice sheets. These indicators of fire are preserved in sediment profiles and ice cores. Charcoal fragments are commonly studied in lake-sediment cores to build long-term fire histories, but evidence of wood ash in sediments has not been studied. In this dissertation research I also investigated wood ash and siliceous aggregates, which form diagenetically from wood ash, to add to our understanding of sources of evidence of past fires, and compared results with ice core evidence of combustion.

Thin sections were prepared for micromorphological analysis from cores from the four sites in the southeastern U.S. and the two Michigan lakes. Steven Driese identified a unique type of grain, siliceous aggregates, in some of the samples, and the formation and distribution of siliceous aggregates became one of the foci of my research. Siliceous aggregates are composed of silt-sized quartz grains cemented together with amorphous silica, sometimes with organic detritus and calcite as inclusions. They seem to be a rare phenomenon, limited in the cores I studied to two separate times in the late glacial, and one around the LGM. I designed and carried out controlled laboratory and greenhouse experiments to test whether I could create siliceous aggregates from wood ash, and to explore the factors that may be needed for their formation on the landscape. I also used Xray fluorescence to identify peaks in calcium and other elements that comprise wood ash that might co-occur with the siliceous aggregates.

Forests can be considered storehouses of calcium. Fire liberates the calcium from plants, which remains after complete combustion as wood ash in the form of calcium carbonate ($CaCO_3$), or if fire temperatures are high enough, calcium oxides. If the $CaCO_3$ ash is transported into a lake, its genesis from wood ash may be overlooked by paleolimnological researchers, because limestone is a feature of karst regions and common in many environments. I used Greenland ice core (GISP2 and GRIP) data to compare the timing of siliceous aggregate occurrences with timing of peaks in aerosols that signal large-scale biomass burning, such as nitrate, ammonium, oxalate, formate, and acetate (GRIP: Legrand et al. 1992, De Angelis et al. 1997, Fuhrer and Legrand 1997; GISP2: Yang et al. 1995, Mayewski et al. 1997). In Greenland ice, ammonium, formate, and oxalate are good indicators of forest fires (M. Legrand, pers. communication, June 29, 2015). Levoglucosan is considered an unambiguous marker of biomass burning by Kehrwald et al. (2012) but levoglucosan records of late-glacial age from ice cores are not available. I also compared peaks in lake-sediment calcium and other wood ash elements with peaks in GISP2 ice core data for calcium, potassium, and magnesium to compare local to global signals for wood ash and other dust.

I also investigated nitrogen isotopes of lake sediments which, along with the study of wood ash inputs, led me to consider evidence of changes in pH, cyanobacteria, and nutrient flow during times of major disturbances of ecosystems in the Northern Hemisphere. Cyanobacteria prefer an alkaline environment and fix nitrogen from the atmosphere. Peaks in total nitrogen and perturbations in $\delta^{15}N$ were compared to nitrate and ammonium in the GISP2 (Yang et al. 1995, Mayewski et al. 1997) and GRIP (Legrand et al. 1992, De Angelis et al. 1997, Fuhrer and Legrand 1997) ice core records to compare local to global signals in nitrogen. Peaks in total nitrogen peaks and perturbations in $\delta^{15}N$ were also compared to occurrences of siliceous aggregates in the lake core records. One hypothesis I considered to explain the nitrogen signals during the late glacial in the lake-sediment records was the occurrence of a nitric acid rain event, triggered by an airburst shockwave of an extraterrestrial event. Firestone et al. (2007) hypothesized a bolide strike to North America 12,900 cal yr BP. With this in mind, I tested the hypothesis that nitric acid rain is a requirement for siliceous aggregates occurrences in my laboratory experiments.

1.2 Paleofire Records for the Eastern U.S.A. and Sources of Ignition

Few high-resolution paleofire records exist for eastern North America for the past 15,000 years, a time of dynamic global changes in climate and environments (Peteet 1995, Broecker et al. 2010, Fiedel 2011). Establishing fire-vegetation linkages and timing of major vegetational shifts is crucial for understanding abrupt climate and environmental changes such as the Younger

Dryas abrupt climate reversal some 12,800 years ago (Peteet 1995, Firestone et al. 2007, Broecker et al. 2010, Fiedel 2011). High-resolution charcoal records are available from Binnewater Pond, New York (Robinson et al. 2005); Appleman Lake, Indiana (Gill 2008, Gill et al. 2009); Slack, Swift, and Big Fish Lakes, and Lake Sixteen, Michigan (Ballard 2009); and Silver Lake, Ohio (Gill et al. 2012). Paleofire records for the southeastern U.S. for this time frame are also scarce. This group includes Whiteoak Bottoms, North Carolina (Boehm 2012) and Clear Pond, South Carolina (Hussey 1993). Some coarser-resolution charcoal records also exist for Sandy Run Creek, Georgia (LaMoreaux et al. 2009). Charcoal is mentioned for the purposes of radiocarbon dating in some pollen studies, e.g., by Liu et al. (2013) for Anderson Pond, Tennessee and Jackson Pond, Kentucky and by Taylor et al. (2011) for a pollen study at Fort Jackson, South Carolina.

To understand sources of ignition, we must consider anthropogenic as well as natural origins. Wildland burning by Native Americans is well documented since European contact in eastern North America (Williams 2000). Williams (2000) listed eleven documented uses of fire by Native American Indians that modified ecosystems: hunting, crop management, insect harvesting, pest management, range management, fireproofing settlements, warfare and signaling, economic extortion, clearing travel areas, felling trees, and clearing riparian areas. Dendrochronological studies of fire history provide additional information on fires in recent centuries (Lafon et al. 2014). However, spatial and temporal patterns of fire occurrence prior to the 1600s, whether anthropogenic or non-anthropogenic, must be inferred by using proxies that extend farther back in time, such as lake-sediment charcoal (Whitlock and Larsen 2001), soil charcoal (Horn and Underwood 2014), and carbonized plant material in archaeological settings (Hollenbach 2009).

1.3 Charcoal, Pollen, and Chronologies

Charcoal data from lake sediments provide an important history of fire within the lake basin and beyond (Whitlock and Larsen 2001). When coupled with pollen data, a clearer picture emerges of what may be driving the fire ecology. These two baseline proxies together are an essential starting point for understanding the dynamic environmental changes that took place during the late Quaternary. They provide the backdrop onto which other proxies can be stacked, to gain insights into the cause of abrupt environmental changes during the late glacial and at other times. Carcaillet et al. (2001) compared charcoal data collected from pollen slides (microscopic) with charcoal data obtained by sieving sediments (macroscopic), and suggested that the sieving method serves as a proxy of local fire history, while the pollen-slide method yields data that represent regional trends in fire history. Microscopic charcoal point counting (Clark 1982) is one way of estimating charcoal content on pollen slides, with data reported as charcoal area concentrations, typically in mm^2/cm^3, charcoal to pollen ratios (μm^2 /pollen grain), or charcoal area influx in $mm^2/cm^3/yr$. Macroscopic charcoal analysis is conducted on lake sediments on a volumetric basis, by determining the amount of charcoal in, for example, 2 cm^3 of sediment. The sediment is treated chemically, often with hydrogen peroxide (Schlachter and Horn 2010) or bleach and sodium hexametaphosphate (Whitlock and Larsen 2001) to disaggregate. Hydrogen peroxide and bleach lighten dark organic particles and make it easier to differentiate charcoal particles. After chemical disaggregation, sediment samples are sieved and transferred to a petri dish for counting under the dissecting scope on a gridded coaster.

The six sites on which I focused my analyses (Figure 1.1) include three first studied by Hazel and Paul Delcourt and students, one studied previously by William Watts, and two from my M.S. research. I analyzed the original pollen slides from Anderson Pond, Tennessee prepared and studied by Delcourt (1979) to obtain microscopic charcoal data, and I analyzed lake sediments from Cahaba Pond, Alabama; Jackson Pond, Kentucky; and Pigeon Marsh, Georgia to develop macroscopic charcoal records. The analyses on Cahaba Pond and Jackson Pond were conducted on cores collected for pollen analysis in the 1970s and 1980s by the Delcourts and students (Delcourt et al. 1983; Wilkins et al. 1991). The advantage of revisiting previously collected core material is that the new paleofire data could be unambiguously associated with the existing pollen data for the sites. In-depth vegetation reconstructions have been made for Anderson, Cahaba, and Jackson Ponds by Delcourt (1979), Delcourt et al. (1983), and Wilkins et al. (1991), respectively. New sediment cores were collected from Anderson and Jackson Ponds in 2007 by Steven Jackson and Jack Williams and their research teams at the University of Wyoming and the University of Wisconsin. They conducted pollen analysis and obtained AMS dates on macrofossils (Liu et al. 2013). Jackson and Williams gave Sally Horn a parallel set of the two upper core sections from Anderson Pond (AP 2007). Some of my analyses were based on these core sections.

I studied a core from Pigeon Marsh in northwest Georgia that I helped collect with a team led by Sally Horn in December 2013. Eric Grimm assisted in making the original pollen data of Watts (1975) available for graphing with the charcoal data. We obtained AMS dates for the new core.

Charcoal records already existed for Slack and Swift Lakes, Michigan (Ballard 2009). Age-depth models were constructed for the sites based on calibration of prior radiocarbon dates on bulk sediment and new AMS radiocarbon dates obtained on macrofossils.

1.4 Nitrogen Isotopes

For the six sites in this study, I analyzed bulk lake sediments from the LGM to late Holocene for $\delta^{15}N$ and total nitrogen (TN) to detect major shifts that might have occurred across the late glacial.

Nitrogen (N) accounts for approximately 78% of our atmosphere and, together with phosphorus (P) and iron (Fe), is a major limiting nutrient in Earth ecosystems, yet it is an understudied aspect of past ecosystems due to the number of compounds involved (NOx, N_2, N_2O, NH_4, NH_3) and the complexity of their interactions in ecosystems (Talbot 2001). Important new studies are emerging about the global nitrogen cycle (Houlton et al. 2008, Galbraith et al. 2013, Hastings et al. 2013, McLauchlan et al. 2013a, b) that encouraged me to make a contribution in this area. Nitrogen data from Greenland and Antarctic ice cores can be compared to the sedimentary nitrogen signal.

Nitrogen isotope analysis of lake sediments is usually applied to sediments of historical age to determine influx of agricultural fertilizer, but recently, McLauchlan et al. (2013a) analyzed 86 nitrogen datasets from late Pleistocene and Holocene lake sediments to understand how modern anthropogenic over-use of nitrogen fertilizers is affecting the global nitrogen cycle. Interpretation of the $\delta^{15}N$ and total nitrogen (TN) signals can be complex, though. Talbot (2001) listed five biological processes in lakes that can alter the nitrogen signal: *ammonia and nitrate assimilation* during primary production; *ammonification,* which results from bacterial reduction of organically bound N to NH_3 or NH_4^+ in anoxic sediments; *nitrification,* which is the oxidation of NH_4^+ to nitrate (NO_3^-) or nitrite (NO_2^-) by aerobic bacteria; *denitrification*; which happens when bacteria reduce NO_3^- to N_2 (gas) in anoxic or dysoxic conditions typically within sediments; and *nitrogen fixation* by organisms such as cyanobacteria, which can bring nitrogen into the biological cycle in oligotrophic lakes when another limiting nutrient such as phosphorus or iron, is introduced. Brahney et al. (2014) discussed ways to account for diagenesis in organic lake sediment, and subsequent alteration of the nitrogen isotope signal in oxic lakes.

Talbot (2001) listed two inorganic processes in the lacustrine nitrogen cycle: N_2 dissolution from the atmosphere by aquatic diazotrophes, and ammonia volatilization, which is pH dependent. Significant N loss can occur in alkaline lakes. Lightning can also produce a relatively small amount of ammonia. Ammonia can be produced industrially by the Haber Bosch process, using atmospheric nitrogen and hydrogen derived from methane, an iron-based catalyst, very high pressures, and relatively high temperatures (Clark 2013). The Haber Bosch process has enabled widespread manufacture and application of agricultural fertilizer (Elser 2011). In addition, since the advent of the Industrial Age, nitrates have been introduced to lakes as nitric acid rain from factory pollution (Whitehead et al. 1990). Nitrates can also enter ecosystems via nitric acid rain following an extraterrestrial event. Shock waves from bolide strikes to the earth dissociates the atmospheric N_2 and the stratospheric ozone, and these react to form nitrates, which cycle out of the atmosphere as precipitation for months to years following the events (Prinn and Fegley 1987). Kolesnikov et al. (1998) used nitrogen isotopes and total nitrogen to investigate whether nitric acid rain was associated with the Tunguska extraterrestrial impact of 1908 in Siberia. Whether TN peaks and $\delta^{15}N$ perturbations in lake-sediment records from the late glacial might originate from nitric acid rain could be investigated using diatom analyses to identify past pH shifts. Diatom analyses were beyond the scope of this study, however.

In nitrogen-limited landscapes such as recently deglaciated terrain or oligotrophic lakes, nitrogen-fixing pioneer plant taxa such as *Alnus, Myrica, and Dryas octopetala*, along with cyanobacteria, can introduce nitrogen and carbon (their biomass) into the ecosystem and thereby boost productivity in lacustrine and terrestrial environments. Because cyanobacteria fix N_2 from the atmosphere that has 0 ‰ ^{15}N, their appearance in a lake can be inferred when ^{15}N values in the sediment shift to close to 0 ‰ ^{15}N while total nitrogen increases (Fogel and Cifuentes 1993). Contrary to this, heterotrophic organic matter would increase the ^{15}N of the sediment due to an increase of 3–4‰ with each trophic level (Meyers and Teranes 2001). In lakes, dissolved nitrate has a mean isotope ratio of +7 to +10 ‰ $\delta^{15}N$, plankton has a signature of +8 ‰ ^{15}N, and C_3 land plants have a signature of +1 ‰ ^{15}N (Meyers and Lallier-Vergès 1999). In a study of Florida lakes, sediment and planktonic $\delta^{15}N$ increased from oligotrophic to eutrophic lakes, but declined in hypereutrophic lakes (Gu et al. 1996). An inverse relationship has been shown between surface water nitrate concentration and the $\delta^{15}N$ of the sediment organic matter in lake sediments (Teranes and Bernasconi 2000). Large excursions in $\delta^{15}N$ in a Swiss lake (Teranes and Bernasconi 2000) were attributed to increased productivity depleting the dissolved inorganic nitrogen of surface waters. This resulted in a gradual increase in $\delta^{15}N$ (Teranes and Bernasconi 2000).

Hu et al. (2001) analyzed the nitrogen inputs to lakes from terrestrial *Alnus,* a nitrogen fixer, which transferred N to the aquatic ecosystem nearby. Eutrophication of lakes, via pulses of N or P (or both) into an ecosystem, can alter them in several ways. An increase in N from atmospheric input (Bobbink et al. 1998, 2010) or terrestrially-derived nutrients (Ptacnik et al. 2008) can drive down phytoplankton diversity in aquatic ecosystems. Interlandi and Kilham (2001) analyzed phytoplankton diversity and resources that limit phytoplankton (N,P, Si, and light) in three lakes in the Yellowstone area, over two summers. They found that the highest phytoplankton diversity in aquatic ecosystems occurred when many resources were limiting for phytoplankton communities.

1.4.1 Nitric Acid Rain

Diatom studies of N inputs to ecosystems from nitric acid rain generated by NOx and SO_2 pollution since the Industrial Age (Whitehead et al. 1990) have provided data and methods that can be applied to the study of effects of shock-wave-generated nitric acid rain on paleo-ecosystems. Long-term records have been developed to show the natural pH of lakes in the past using diatoms and chrysophytes in sediments as indicators, informed by studies of relationships between modern lake pH and diatom and chrysophyte assemblages (Smol 1986, Smol et al. 1986, Charles et al. 1990, Whitehead et al. 1990, Stoermer and Smol 1999, Haberyan and Horn 2005, McLauchlan et al. 2013b). Before the amendment in 1990 to the Clean Air Act, acid rain caused by industrial emissions was recorded at Clingmans Dome in the Great Smoky Mountain National Park with a pH of 2.0 (National Geographic 2015). Nitric acid rain from industrial pollution or shock-wave generated nitrates has the same eutrophication effect as runoff from agricultural fertilizers: massive algal blooms.

Firestone et al. (2007) hypothesized that an extraterrestrial event at ca. 12,900 cal yr BP was responsible for the extinction of the mammoths, triggered the Younger Dryas cooling period, ended the Clovis culture, and set off massive wildfires. The Younger Dryas stadial interval spans ca. 12,900–11,600 cal yr BP, ending with the start of the Holocene. The onset of the Younger Dryas is often termed the Younger Dryas Boundary (YDB). Prinn and Fegley (1987) discussed the effects of shockwave-generated nitric acid rain in association with the K/T impact. If a bolide was the trigger for the YDB, nitric acid rain would certainly have been associated with it, but this hypothesis has not been explored until now. The transition from the Bølling-Allerød to theYounger Dryas around 12,900 cal yr BP was very sudden in nature, observed in many proxies in the Greenland ice cores, such as decreases in methane and $\delta^{18}O$, peaks in aerosols such as nitrate, calcium, and potassium (Mayewski etal. 1997), and increased dustiness (De Angelis et al. 1997, Mayewski et al. 1997, Zielinski and Mershon 1997, Alley 2000).

If a nitric acid rain event occurred at the onset of the Younger Dryas (YDB), it might be evident as a sudden increase in productivity in records of lake sediments. Evidence might be found in total nitrogen, $\delta^{15}N$, algae, diatoms, pollen, and macrofossils that may reveal changes in biota. Major shifts in plant communities, particularly aquatic plant assemblages, would be recorded in lake-sediment proxies. Diatom datasets should show a shift from alkaline-preferring to acid-preferring species. Warming is not typically indicated at the YDB for at least Europe and the northeastern U.S. region (Peteet 1995). In the northern Atlantic Ocean, extensive winter sea ice cover is inferred for the Younger Dryas (Brauer et al. 2008) with cooling of adjacent land masses (Broecker et al. 2010). During this time of cold, windy conditions, algae and/or diatoms would not be expected to proliferate, yet they produced massive blooms at many sites in Europe. There, the shift from alkaline to acidic lakes at the onset of the Younger Dryas is apparent in such records as those from Knapowka near Wloszczowa, South Poland (Kaczmarska et al.1973); Loch Sionascaig in northern Scotland (Haworth 1976); Hirschenmoor and Rotmeer in the Black Forest region of Germany (Lotter and Birks 1993); Holzmaar, Germany (Lotter et al. 1995); Meerfelder Maar, Germany (Brauer et al. 1999); Petrašiunai and Juodonys in northeastern Lithuania (Stančikaité et al. 2009); and Lake Brazi in the south Carpathian Mountains, Romania (Buczkó et al. 2013). Sediment cores collected from five lakes in southern Greenland revealed a maximum in the green algae *Pediastrum* from 12,900–12,500 cal yr BP, with two types of *Achnanthes* diatoms becoming dominant at 12,800 cal yr BP (Björck et al. 2002).

Some evidence also exists for proliferation of freshwater sponges at the YDB in the eastern U.S. and Europe that may be part of a larger regional picture of expansion of certain aquatic species due to a nutrient pulse. Sites showing sponge spicule increases are Cupola Pond, Missouri (Jiang 1990); Jackson Pond, Kentucky (Wilkins et al. 1991); and Swift Lake, Michigan (Ballard 2009). This expansion could be due to fertilization from atmospheric nitric acid rain, possibly dust-delivered iron and silica, or wood ash following wildfire. At Cupola Pond, Jiang (1990) reported a dramatic increase in hooked birotulate gemmoscleres of *Anheteromeyenia ryderi* between 11,200 and 10,500 ^{14}C yr BP (13070–12455 cal yr BP). At Jackson Pond, Wilkins et al. (1991) showed a peak in a hooked type of *A. ryderi/Heteromeyenia latitentata* around the onset of the Younger Dryas. A shift to more acidic water can cause malformations of tissue and spicules of freshwater sponges (Kahlert and Neumann 1997). Tolliver (1998) reported a major shift in diatom taxa from an alkaliphilous assemblage to an acidiphilous assemblage at Anderson Pond, Tennessee, based on analysis of a sediment core collected in 1982. Depth correlation with the 1976 core studied by Delcourt (1979) suggested that this shift occurred during the late glacial (R. Tolliver, pers. communication to S. Horn).

The effects of shockwave-generated nitric acid rain has been studied in association with the Cretaceous/Tertiary extraterrestrial event around 65 Ma by Prinn and Fegley (1987) and Toon et al. (1997); and for the Tunguska event in Siberia in 1908 by Kolesnikov et al. (1998). Shock waves from extraterrestrial events dissociate atmospheric N_2 and stratospheric ozone (O_3), which combine to form nitrates. The nitrates then rain out of the atmosphere as nitric acid rain for estimated months to years (Prinn and Fegley 1987). Prinn and Fegley (1987) estimated that a cometary impact would produce global acid rain with a pH of 0–1.5.

Melott et al. (2010) analyzed the Greenland ice cores to compare peaks in ammonium and nitrate for the Tunguska event with peaks at the onset of the Younger Dryas for a hypothesized comet. While both NH_4 and NO_3 can indicate biomass burning, no fire was associated with the 1908 Tunguska event. Therefore, NH_4 and NO_3 peaks for that time were interpreted to be extraterrestrial (ET) impact signals. Because some evidence of fire exists for the YDB (Ballard 2009, Marlon et al. 2009), these N compounds in the Greenland ice core record are ambiguous for an ET impact. However, it is possible that the combustion signature for nitrate could be differentiated from the shockwave signature by using ^{17}O analysis of the ice cores (Hastings et al. 2013) if sufficient ice is available. The ozone layer is enriched in ^{17}O; if ozone was the source of oxygen for the Greenland ice core nitrate because of a shock wave, the nitrate should be enriched in ^{17}O (Hastings et al. 2013).

Another N-compound dataset that shows a major perturbation for the Younger Dryas is that of nitrous oxide in ice cores from Greenland (NGRIP and GISP2) and from Antarctica (Talos Dome, Taylor Dome, Epica Dome C, Byrd, Vostok, and Dronning Maud Land; Schilt et al. 2010). All these records show a dramatic drop in N_2O at the start of the YD. However, these shifts in N_2O are difficult to interpret because of the presence of dust (Schilt et al. 2010, McLauchlan et al. 2013a) and the suspected *in situ* production of N_2O by microbes (Miteva et al. 2007; Rohde et al. 2008).

A recent high-resolution study of $\delta^{15}N$ of ice core nitrate for historical time revealed a decrease in the $^{15}N/^{14}N$ isotope ratio beginning around 1850, coincident with the advent of the Industrial Age, that may be linked to nitric acid rain pollution (Geng et al 2014). This trend leveled off around 1970 after the U.S. Clean Air Act was implemented (Geng et al. 2014). This study could provide a useful modern comparison for studies of possible past nitric acid rain events.

1.5 Wildfires and Relationship Between Charcoal and Wood Ash

Fire requires heat, oxygen, and fuel (Cottrell 2004). After ignition, the progress of any wildfire depemds on many variables. These include fuel type and quantity, vegetation structure, air temperature, humidity, soil moisture, wind, and oxygen supply. These factors help to determine the intensity of the fire and temperatures at different locations within the burn. Combustion products of fire include charcoal, ash, and volatilized components.

Fire size, intensity, and severity all affect charcoal production and transport into a lake (Whitlock and Anderson 2003). Fire intensity and fire severity are often confused. Fire intensity refers to energy output. Fire severity and the related term, burn severity, is defined as the as the loss of, or change in organic matter both aboveground and belowground, but the precise metric varies with management needs. Both are positively correlated with fire intensity (Keeley 2009). Confusion has arisen because fire or burn severity is sometimes defined in a way that also includes ecosystem responses. Ecosystem responses include soil erosion, regeneration of vegetation, restoration of community structure, faunal repopulation, and a large number of related response variables. Some ecosystem responses are correlated with measures of fire or burn severity, but many important ecosystem processes have either not been demonstrated to be predictable by severity indices or, for some vegetation types, have been shown to be unrelated to severity. This is an important issue for resource managers because fire or burn severity are measurable parameters, with both remote sensing and on the ground, but ecosystem responses are of the most interest to managers (Keeley 2009).

For complete combustion of wood and other biomass to ash, an important factor is the requirement of a constant supply of oxygen to support the fire. White ash on a firescape indicates complete combustion of aerial and surface fuels by an intense fire (Cottrell 2004). Even during intense wildfires, some charcoal evidence will likely remain, although particles may be smaller and fewer. Whether the charcoal on the land surface following fire is deposited in a lake where a future researcher can study it, depends on slopewash (Whitlock and Anderson 2003) or wind entrainment following the fire. Charcoal is also deposited on lake surfaces by wind during fires (Whitlock and Larsen 2001).

Erosion is generally thought to follow severe wildfires, but wood ash can temporarily stabilize the landscape and reduce runoff (Woods and Balfour 2008). In an experiment following a severe forest fire in western Montana, the 2005 Tarkio Fire, Woods and Balfour (2008) applied simulated rainfall to plots of ash and to plots from which they had removed ash. They found that the ash layer provided an additional 1.5 cm of water storage capacity and protected the underlying mineral soil. Sediment runoff and erosion was reduced 74% compared to the plots without ash. Ebel et al. (2011) studied the hydrologic effects of ash overlying burned soils and concluded that ash serves as an important hydrologic buffer by readily storing water at the storm time scale of minutes. Over a period of several days, the ash slowly released water into the burned soils and by evaporation into the atmosphere. In a follow-up study, Woods and Balfour (2010) determined that with thicker ash layers (2–5 cm), the effects of water storage increasingly delayed and reduced the runoff response to the point where no overland flow was produced, regardless of any pore-clogging effect in the underlying soil.

1.5.1 Complete Combustion, Fire-Generated Winds, and Major Ash-producing Fires

Less charcoal and more ash should be produced during an intense forest fire than during a low-intensity one. For an intense fire, how much charcoal might remain with the ash? As an example, Santín et al. (2012) studied pyrogenic carbon following the catastrophic "Black Saturday" Fire in Victoria, Australia in 2009, which burned 450,000 ha of forest. In the three mixed species *Eucalyptus* forests, the canopy, understory, and litter were almost completely consumed, resulting in substantial ash deposition. The carbon sequestration study of Santin et al. (2012) dealt with ash deposition, the amount of carbon contained in the ash layer, and the different forms of carbon in the ash. These were total organic carbon, total inorganic carbon (e.g. calcium carbonate), and water soluble and particulate organic carbon fractions. Depths of ash ranged from 1.0 (±0.3) to 3.8 (±1.9) cm. Total organic carbon data collected from 17 square-meter plots from four sites (3 in *Eucalyptus* forest, 1 in temperate rainforest) ranged from 359 to 968 grams carbon/m^2 with a mean of 582 grams carbon/m^2 for the three *Eucalyptus* sites and a mean of 802 grams carbon/m^2 for the temperate rainforest site. Most carbon contained in the ash was organic, pyrogenic carbon, i.e., charcoal, which is resistant to degradation. Even with the most intense fires, some charcoal will remain in the ash.

More complete combustion of wood to ash requires a constant supply of oxygen. Oxygenation would be facilitated by high winds perhaps generated by the wildfire itself. Fires can produce fire whirlwinds and tornado-like winds. The latter appear to originate high above the ground and then extend down to the ground (Countryman 1964). Martin et al. (1976) noted that fire whirlwinds cause greater damage to natural and manmade resources, and that they were at least partly responsible for the burning of Chicago and Peshtigo, Wisconsin October 8, 1871. The Peshtigo Fire devastated nearly 1.5 million ha of land and killed some 1200 people (National

Park Service 2015). Father Peter Pernin was an eyewitness to the Peshtigo Fire. He wrote that after the firestorm at Peshtigo, no structures remained, ash lay everywhere, and the roots of trees had been burned underground. Trees had been ripped up and reduced to ash (Pernin 1971).

1.5.2 Wood Ash

According to Bodí et al. (2014), the inorganic elements in wood ash include Ca, Mg, K, and Si, with lesser proportions of P, Na, S, Al, Fe, Mn, and Zn. Fresh wood ash is composed mostly of calcite (Humphreys et al. 1987) which is thought to be formed mainly by the decomposition of calcium oxalate crystals present in many trees (Kennedy et al. 1968, Scurfield et al.1973). Calcium oxalate slakes (disintegrates through the action of water) to calcium carbonate. Demeyer et al. (2001) reported that P in ash is the least soluble cation in soils and that ash is basically an N-free fertilizer. Some plant phytoliths may be preserved in ash, as well as silica aggregates and calcium oxalate pseudomorphs.

Plant ash is a proxy for fire that has been used extensively in archaeological studies (e.g., Schiegl et al. 1994, 1996; Canti 2003; Morley 2007). The pH of ash ranges from 9 to over 13 (Demeyer et al. 2001). Shahack-Gross and Ayalon (2013) used carbon and oxygen isotope analyses to try to differentiate between wood ash calcite and geogenic calcite. They found that isotopes varied depending on the temperature of combustion, and that diagenesis after burning also changed isotope values. They noted that differentiating between high temperature wood ash and lime plaster at archaeological sites is currently impossible by any known methods of studying the calcite component (Shahack-Gross and Ayalon 2013). Mentzer and Quade (2013) also attempted to discriminate between calcite from wood ash and lime plaster at archaeological sites. They used thin section analysis of sediments from their sites and used micro-XRF analysis on the epoxied thin section blocks to obtain information on elemental compositions of minerals in the thin sections. These methods hold promise for differentiating wood ash calcite in lake sediments from geogenic calcite. I was unable to include micro-XRF in this study, but I instead used XRF analysis of lake sediments to identify a suite of peaks of elements that make up wood ash (Ca, K, Mg, Fe, Al, Mn, Zn, and Si).

Gabet and Bookter (2011) studied ponderosa pine ash as a geological material and analyzed both natural and lab-created ash. They found that the elemental composition of ashes, determined using inductively coupled plasma emission spectrometry, was predominantly Ca, K, Mg, P, Mn, Fe, and Al. X-ray diffraction analysis of ashes created from various fuels revealed calcite, quartz, and feldspars. Gabet and Bookter (2011) concluded that fuel type and combustion temperature controlled ash mineralogy. Calcium oxalates naturally occur in stems, roots, and leaves of plants.

Siliceous aggregates have been studied at two archaeological sites in Israel, Kebara and Hayonim Caves (Schiegl et al. 1994, 1996, Weiner 2010). Siliceous aggregates are composed of silt-sized quartz cemented with amorphous silica, the latter of which derives from the phytoliths in the wood ash. Siliceous aggregates are a by-product of fire, formed diagenetically by the action of the water in the caves percolating through the ash.

Research in the concrete industry provides some insight into the process by which amorphous silica forms in siliceous aggregates. Bleszynski and Thomas (1998) studied the replacement of Portland cement with fly ash, a technique used to control deleterious expansion in concrete due to the alkali-silica reaction. They immersed concrete samples in alkaline salt solutions for more than three years, and found that the reactive silica (flint) in the concrete transformed to a gel, and leached away.

For siliceous aggregates to be deposited as particles in lake sediments, the mobile amorphous silica gel must solidify, i.e., precipitate around the quartz silt grains. This precipitation must take place on land, and later the siliceous aggregates would be transported into the lake. The process by which the amorphous silica precipitates around the silt-sized quartz grains is likely a lowering the the pH (Maynard 2015) through the action of water—perhaps rainfall, which is slightly acidic (pH 5.7). Organic matter and calcite in the immediate environment may also be cemented with the silt by the amorphous silica.

Studies of Middle Paleolithic Levantine cave sites using experimental fires outside the cave have demonstrated that the silica and phytolith components of wood ash are acid-insoluble (Karkanas et al. 2007). Amorphous silica (from phytoliths) is 12 times more soluble than non-biogenic quartz at 25 ºC, below a pH of 8 (Krauskopf 1967, Fraysse et al. 2006). The dissolution rates of phytoliths in soil in one study (Fraysse et al. 2009) exhibited a minimum at pH ~ 3. Laschet (1984) reported that the main factors that control the solution and precipitation of silica phases are pH, temperature, water turbulence, and the presence of CO_2, although much of his research focused on marine silica. He also stated that iron increases the dissolution of silica.

Canti (2003) studied the weathering of wood ash, and noted that silica and glasses are much more soluble in alkaline environments than in acidic ones. During the weathering process, while silica components in ash are still engulfed in the calcium carbonate, the largest component of ash, they will dissolve fairly quickly. However, once the calcium carbonate has leached away, and if the soil solution is naturally acidic, the remaining siliceous components will likely be preserved. Canti (2003) considered timescales for this process to be a few years to many thousands of years. For comparison, the estimated residence time of biogenic silicon, such as phytoliths, in a tropical forest litter was between 1 month and 6 months (Alexandre et al. 1994).

The presence of silica crystals in wood is relevant to my interpretation of the siliceous aggregates in sediment cores. The sources of biogenic quartz for the amorphous silica cement in siliceous aggregates, silica and calcium oxalate crystals, often occur as intracellular inclusions in the wood of deciduous trees (Scurfield et al 1974). Amos (1952) listed 440 species from 144 genera and 32 families in which silica is formed in the wood. Chattaway (1955) listed 230 woody species distributed across 144 genera and 62 families in which crystals of silica formed in the wood. Scurfield et al. (1973) used scanning electron microscopy, infrared spectroscopy, and X-ray diffraction to characterize the location, form, and chemical composition of these silica crystals. Grass leaves also contain silica crystals (Sangster 1968). Kennedy et al. (1968) stated that angiosperms typically contain crystals but gymnosperms, other than members of the Pinaceae family (Panshin et al. 1964), do not. Kennedy et al. (1968) assessed calcium oxalate crystals in nine species of *Abies* and also noted that silica aggregates are common inorganic inclusions in wood.

Because a pH shift from the alkaline ash to more acidic conditions is needed to precipitate the amorphous silica gel onto the silt-sized quartz grains to form the siliceous aggregates, I hypothesized that the acidifying agent during the late glacial may have been nitric acid rain, or possibly organic acids from a biological source such as algae. While the siliceous aggregates in the Israeli caves provide insights into the formation of this unique grain type, a cave is not quite the same environment as a lake basin. The ash experiments in this study were designed to provide insights into the formation of siliceous aggregates on the open landscape.

The silt-sized grains in siliceous aggregates are non-biogenic quartz grains. The source could be loess, which can be transported long distances (Prospero 1999, Muhs 2013); grains from soil; or locally eroded clastic material. The silt has to be available during the fire or soon after for the dissolving phytoliths to contact the grains and form siliceous aggregates, sometimes with terrestrial and aquatic organic detritus. Therefore, I considered that wind-blown silt is the most likely source, possibly from fire-generated winds.

Ecologists have studied the nutrient and pH effects of ash on lakes. Wood ash has been studied as a way to help neutralize acidic lakes in Scandinavia (Salonen et al. 1990, Tulonen et al. 2002), where there is an abundance of ash. Large blooms of algae occurred the spring after the application of ash to ice-covered lakes. XRF analysis can provide data on elements in lake sediments. In this study, I hypothesized that wood ash evidence might be found in the lake-sediment profile by identifying calcium peaks with peaks of lesser elements found in wood ash in varying amounts: potassium, magnesium, manganese, silicon, iron, aluminum, and zinc. If these elemental peaks occurred at the time of siliceous aggregate occurrence, it could provide additional evidence of wood ash input to the lake.

1.6 XRF Analyses

X-ray fluorescence (XRF) is a powerful qualitative and quantitative analytical tool for elemental analysis of materials. It is ideally suited for the identification of specific and trace elements in complex sample matrices, determination of elemental concentration by weight of solids and solutions, and measurement of film thickness and composition. The method is relatively fast and usually requires only minimal sample preparation (XOS 2015). The basic setup for XRF spectrometers is a source, a sample, and a detection system. The source, an Xray tube, irradiates the sample and a detector measures the fluorescence radiation emitted from the sample. When elements in a sample are exposed to the source of high intensity X-rays, fluorescent X-rays will be emitted from the sample at energy levels unique to those elements

(XOS 2015). The benchtop Olympus BTX Profiler I used in the Department of Geography at the University of Tennessee can detect elements from magnesium to uranium in the periodic table. All elements below magnesium are reported together as “LE” or light elements. XRF analyses can also be conducted with portable hand-held Xray “guns.”

To find evidence of wood ash in lake sediments using Xray fluorescence analysis, two instruments were used, a TRACeR III-V+ portable Xray “gun” (pXRF, Bruker AXS company) in the Department of Anthropology at the University of Tennessee, and the benchtop Olympus BTX profiler. The XRF gun can take readings at close intervals along core sections and is non-destructive. The Olympus BTX profiler requires dried, ground samples for each depth. The XRF gun gives output in area under the curve vs. output in ppm on the benchtop BTX Profiler. The TRACeR III-V+ instrument is a handheld energy-dispersive device with silicon-based detectors allowing for identification of multiple elements at the same time. By selecting the appropriate combination of parameters, the various elements in lake-sediment cores can be measured across approximately 1 cm spans at a time. The X-ray intensity represented by the spectrum peaks is directly proportional to the concentration of the various elements in each sample; thus, net areas of the respective analyzed peaks are reported to assess variability among elemental compositions along the depth of the core sections. The net areas under the elemental lines are obtained by means of Gaussian curve fitting, which allows for a semi-quantitative evaluation of the spectral data (Bow 2012). After sample analysis by pXRF instrumentation, spectra are deconvoluted and converted to raw data using Spectra ARTAX software 7.2.0.0 (Bow 2012).

1.7 Natural Ecosystem Acidification

Natural ecosystem acidification became a topic of scientific study following the discovery that pollen of plants typical of acidic mor soils (associated with conifers) increased in relative abundance from oldest to youngest sections of interglacial deposits, while pollen of plants typical of rich mull humus soils (associated with hardwoods or grasses) peaked during the mid-interglacial period and then declined (Iversen 1964a, 1964b; Andersen 1964; Andersen1966; Andersen1969; Iversen 1969; Stockmarr 1976; Ford 1990).

Nutrients, base cations, dissolved organic carbon, and pH are all affected by changes in climate and basin geochemistry. The temporal trend, in general, is for terrestrial and aquatic ecosystems to become acidic (Battarbee et al. 1984). Vegetation can lower pH, if conifers move into a basin (McLauchlan et al. 2013b). If acid rain falls in a carbonate lake basin, alkalization of the lake will result (Lajewski et al. 2003). Industrial Age acid rain has caused “whitings” in Seneca Lake, one of the Finger Lakes in New York (Lajewski et al. 2003). McLauchlan et al. (2013b) reported that whatever mechanism is involved in nutrient input, many long-term sediment records that include proxies for nutrient status reveal Holocene-scale trends in dystrophication of ecosystems (dystrophication: high in humic acids and low in productivity). Increased lacustrine productivity seems to be a widespread phenomenon at the onset of the Younger Dryas (see below), which might be explained by a nutrient input of one or more of the following: nitrogen, phosphorus, silica, and iron. N and P can be determined by using diatoms as indicators (Davis et al. 1985, Smol 1987, Fritz 1989, McLauchlan 2013b).

A diatom study for Anderson Pond, Tennessee (Tolliver 1998) using a core collected in 1982 revealed a marked shift from alkaline to acidic conditions in sediments that were regarded as late glacial in age based on depth correlation with the core from 1976 studied by Delcourt

(1979). The acid conditions persisted upcore into the Holocene. Lakes in the southeastern U.S. typically form by the mechanism of a collapse of a sinkhole (Delcourt 1979, Delcourt et al. 1983). Lakes in Michigan are typically kettle lakes, formed by the slow melting of large chunks of ice from the Laurentide Ice Sheet; these lakes were typically alkaline to begin with. Marl is common in Michigan and Indiana lakes, where it is precipitated by charophytes and cyanobacteria (Murphy and Wilkinson 1980). Collapsed sinkhold ponds, at least in the beginning, are expected to be alkaline, since they form in limestone Evidence of widespread diatom blooms around the time of the onset of the Younger Dryas (and in most cases a shift from alkaline to acidic conditions) in the eastern U.S. have been reported at Kirchner Marsh, Minnesota (Florin 1970), and at the Shelton Mastodon site, Michigan (Stoermer et al. 1988). At Cahaba Pond, cyanin evidence from cyanobacteria has been found for the time of major vegetational shifts during the late glacial (pers. communication by Jamey Fulton to Steven Driese, 30 May 2014). Algal mats, also known as "black mats" have been reported in the American southwest for the beginning of the Younger Dryas (Haynes and Huckell 2007). Haynes (2008) studied "black mat" sites across the U.S. and reported that two-thirds of the 97 geoarchaeological sites contained a black organic-rich layer in the form of mollic paleosols, aquolls, dark gray to black diatomites, or algal mats with radiocarbon ages between 10,900–9,800 ^{14}C yr BP (12,764–11,219 cal yr BP). This distinctive layer or mat, largely across the western U.S. with a few sites in the eastern U.S., overlies the Clovis-age landscape or surface on which the last remnants of the terminal Pleistocene megafauna are recorded (Haynes 2008).

Whitehead et al. (1989) studied three lakes along a gradient in the Adirondack Mountains in New York State and reported that all three lakes were slightly alkaline (pH 7–8) and more productive in late glacial time, but then became acidic and less productive at the end of the late glacial and early Holocene. Part of the problem of definitively placing the alkaline-to-acid shift during the late glacial is the reliance on coarse radiocarbon dates on bulk sediments for many early studies. The alkalinity reported by Whitehead et al. (1989) was attributed to leaching of base cations from glacial till, and thought to be facilitated by the development of histosols under the emerging spruce woodlands. A pulse of lake productivity at the late glacial/Holocene boundary was linked to the expansion of alder (*Alnus*) trees, which are nitrogen fixers. Alders had a significant effect on the watershed, and in turn, the lake biogeochemistry. Whitehead et al. (1989) concluded that the natural acidification of the three lakes was a slow process, taking a thousand or more years to change one pH level. Therefore, a nitric acid rain input lasting a couple of years at most (Prinn and Fegley 1987) might be differentiated from acidification resulting from plant succession using paired nitrogen and diatom analyses at high-resolution.

1.8 Paleonutrient Studies to Place Total Nitrogen Data in Context

McLauchlan et al. (2013b) investigated how past nutrient fluxes might be studied to obtain a natural baseline to evaluate the anthropogenic effects of nutrient loading of N and P. Higher production and higher transport of biologically available forms of P from terrestrial to aquatic ecosystems occur in wetter climates, resulting in P loading (McLauchlan et al. 2013b).

Increased nutrient input to lakes and wetlands in modern times can occur from delivery of nitrates and phosphates from agricultural fertilizers, human sewage, or soil erosion. Another inadvertent source of nutrient input to aquatic ecosystems in recent times is acid rain, which supplies nitrates and sulfates. These inputs result in detrimental algal blooms in regions affected by acid rain such as the Appalachians; acid rain (as well as agricultural runoff) also contributes to dead zones in the Gulf of Mexico. In contrast, the absence of certain elements can limit or prevent growth of phytoplankton and cyanobacteria. These limiting nutrients include iron, molybdenum, and sometimes silicon, N and P. P is an element in wood ash and following a fire, may wash into streams or lakes; N is typically volatilized during a fire (Demeyer et al. 2001). Vivianite (iron phosphate) found in lake sediments might derive from wood ash, or fecal pellets, or some other P source. Miller (1978) examined vivianite in sediments from five lakes in Minnesota, and noted marked increases in many sites in the amount of non-apatite inorganic phosphate (NAIP) when deposition began of post-glacial organic sediments, suggesting a change in the quantity and mechanism of phosphorus delivery to the lake and lake sediments. NAIP is thought to precipitate out of the lake water, while organic phosphate is thought be almost exclusively detrital (Miller 1978). Certainly, for vivianite to form, sources of iron and phosphorus must be available.

Silica and iron inputs to lakes in the eastern U.S. may include the long-range-transport of African dust (loess) (Prospero 1999). Muhs (2013) studied Quaternary dust in the geologic record and noted that a fertilization effect of marine organisms should have occurred from the Fe-enriched dust, which in turn could draw down CO_2 levels in the atmosphere. He showed that marine diatoms increased around the start of the Younger Dryas (Muhs 2013). He inferred that this increase in diatom productivity was caused by both increased upwelling brought about by stronger winds, and higher levels of iron and silica delivered as dust (Muhs 2013). Dust triggered widespread algal blooms in 2002 off the coast of California under Santa Ana wind conditions (Muhs 2013).

Enters et al. (2010) conducted a biogeochemical and pollen study of Sacrower See in northeastern Germany, and Kirilova et al. (2009) investigated diatoms at that site. The nitrogen isotope record developed by Enters et al. (2010) encompassed the Younger Dryas (YD, 12,700 –

11,600 cal yr BP) and also included C, P, and Fe. At the onset of the YD, this record showed increase in P, dry deposition, eutrophication, acidification, and increase in productivity inferred from increased TOC and biogenic silica (Enters et al. 2010). A drop in $\delta^{15}N$ occurred at the onset of the YD. Enters et al. (2010) attributed the C/N and the $d^{15}N$ signals to an allochthonous input. Fe increased at the onset of the YD for Sacrower See.

1.9 Organization of Dissertation

This dissertation consists of five chapters, with chapters 2–4 written as manuscripts to be submitted to journals. In Chapter 2, I report on fire history at Anderson Pond as revealed by microscopic charcoal. In Chapter 3, I present new macroscopic charcoal records for Cahaba Pond, Jackson Pond, and Pigeon Marsh, and relate these records to existing pollen data and other proxies, and to charcoal data from Anderson Pond and Slack and Swift Lakes. In Chapter 4, I present research on siliceous aggregates found during thin section analyses of lake-sediment cores, and compare the timing of occurrences of siliceous aggregates to charcoal, nitrogen, pollen, and elements in the sediments and to global signals of biomass burning in Greenland ice cores. I also report on my laboratory experiments using simulated rain on wood ash, designed to explore the genesis and paleoenvironmental significance of the siliceous aggregates. In Chapter 5, I summarize this dissertation research and conclude with some suggestions for future directions for this work.

My research questions for the microscopic charcoal study of Anderson Pond sediments (Chapter 2) were:

1. How does the paleofire record at Anderson Pond from the LGM through the Holocene compare with the vegetation record as shown by pollen percentages in the same samples?

2. Do patterns of fire occurrence at Anderson Pond match the prediction from a recent global synthesis of fire records that greater fire activity should be associated with warmer temperatures?

3. How do microscopic charcoal concentrations and charcoal:pollen ratios for Anderson Pond compare with charcoal indices at other sites in the eastern U.S.?

For the macroscopic charcoal studies of sediments from Cahaba and Jackson Ponds and Pigeon Marsh (Chapter 3), I asked:

1. How do the new macroscopic charcoal records from the southeastern U.S. compare with prior pollen reconstructions from the LGM into the Holocene at these sites?

2. To what extent do patterns show similarities with the comparison records from Anderson Pond, Tennessee, and Swift and Slack Lakes, Michigan?

3. What are the implications of the new records and comparisons for understanding patterns in human and natural fire ignition and linkages between fire, climate, and vegetation across the late glacial and Holocene?

For the siliceous aggregate paper, Chapter 4, I asked these research questions:

1. Does the timing of the occurrences of siliceous aggregates in sediment records from lakes in the eastern U.S. show a relationship to peaks in total nitrogen and $\delta^{15}N$ in these records?

2. Can siliceous aggregates be produced in the laboratory in samples of wood ash?

3. Do siliceous aggregates require rainwater, nitric acid rain, or organic acids from e.g. algae, to form?

4. How much time is required for siliceous aggregates to form?

5. Is silt important for the formation of siliceous aggregates?

6. Are the occurrences of siliceous aggregates in the lake-sediment records examined contemporaneous, suggesting the possibility of large-scale events?

7. Is there evidence in ice cores of large-scale biomass burning at the time of siliceous aggregate occurrences?

1.10 References

Alexandre, A.; Colin, F.; Meunier J.-D. 1994. *Les phytolithes, indicateurs du cycle biogéochimique du silicium en forêt équatoriale.* Phytoliths as indicators of the biogeochemical turnover of silicon in equatorial rainforest. *Comptes rendus de l'Académie des sciences. Série 2. Sciences de la Terre et des Planètes* 319(4): 453–458.

Alley, R.B. 2000. The Younger Dryas cold interval as viewed from central Greenland. *Quaternary Science Reviews* 19(1–5): 213–226.

Amos, G.L. 1952. *Silica in Timbers*. Bulletin 267. CSIRO Australia.

Andersen, S.T. 1964. Interglacial plant successions in the light of environmental changes. *In: Report of the Sixth International Congress on the Quaternary*. Volume 2. Paleobotanical section. Lodz, Poland, pp. 421–428.

Andersen, S.T. 1966. Interglacial vegetational succession and lake development in Denmark. *Palaeobotanist (Lucknow)* 15: 117–127.

Andersen, S.T. 1969. Interglacial vegetation and soil development. *Meddelanden fra Dansk Geologiske Forendlingen Kobenhavn* 19: 90–102.

Ballard, J.P. 2009. *A Lateglacial Paleofire Record for East-Central Michigan.* M.S. Thesis, University of Cincinnati.

Battarbee, R.W.; Thrush, B.A.; Clymo, R.S.; Le Cren, E.D.; Goldsmith, P.; Mellanby, K.; Bradshaw, A.D.; Chester, P. F.; Howells, G.D.; Kerr, A. 1984. Diatom analysis and the acidification of lakes [and discussion]. *Philosophical Transactions of the Royal Society of London* 305: 451–477.

Björck, S.; Bennike, O.; Rosén, P.; Andresen, C.S.; Bohncke, S.; Kaas E.; Conley D. 2002. Anomalously mild Younger Dryas summer conditions in Southern Greenland. *Geology* 30(5): 427–430.

Bleszynski, R.F.; Thomas, M.D.A. 1998. Microstructural studies of alkali-silica reaction in fly ash concrete immersed in alkaline solutions. *Advances in Cement-Based Materials* 7: 66–78.

Bobbink, R.; Horning, M.; Roelofs, J.G.M. 1998. The effects of air-borne nitrogen pollutants on species diversity in natural and semi-natural European vegetation. *Journal of Ecology* 86: 717–738.

Bobbink, R.; Hicks, K.; Spranger, T.; Alkemade, R.; Ashmore, M.; Bustamante, M.; Cinderby, S.; Davidson, E.; Dentener, F.; Emmett, B.; Erisman, J.-W.; Fenn, M.; Gilliam, F.; Nordin, A.; Pardo, L.; De Vries, W. 2010. Global assessment of nitrogen deposition effects on terrestrial plant diversity: a synthesis. *Ecological Applications* 20(1): 30–59.

Bodí, M.B.; Martin, D.A.; Balfour, V.N.; Santín, C.; Doerr, S.H.; Pereira, P., Cerdà, A.; Mataix-Solera, J. 2014. Wildland fire ash: production, composition and eco-hydro-geomorphic effects. *Earth-Science Reviews* 130: 103–127.

Boehm, M.S. 2012. *Late Pleistocene Climate, Vegetation, and Fire History from a Southern Appalachian Bog, Whiteoak Bottoms, Nantahala National Forest, North Carolina, U.S.A.* M.S. Thesis, University of Tennessee.

Bow, S.M. 2012. *A Tale of Two Shelters: Using XRF Analysis to Assess Compositional Variability of Pottery from Two Sites in Franklin County, Tennessee.* M.S. Thesis, University of Tennessee.

Brahney, J.; Ballantyne, A.P.; Turner, B.L.; Spaulding, S.A.; Otu, M.; Neff, J.C. 2014. Separating the influences of diagenesis, productivity and anthropogenic nitrogen deposition on sedimentary $\delta^{15}N$ variations. *Organic Geochemistry* 75: 140–150.

Brauer, A.; Endres, C.; Negendank, J.F.W. 1999. Lateglacial calendar year chronology based on annually laminated sediments from Lake Meerfelder Maar, Germany. *Quaternary International* 61: 17–25.

Brauer, A.; Haug, G.H.; Dulski, P.; Sigman, D.M.; Negendank, J.F.W. 2008. An abrupt wind shift in western Europe at the onset of the Younger Dryas cold period. *Nature Geoscience* 1: 520–523.

Broecker, W.S.; Denton, G.H.; Edwards, R.L.; Cheng, H.; Alley, R.B.; Putnam, A.E. 2010. Putting the Younger Dryas cold event into context. *Quaternary Science Reviews* 29: 1078–1081.

Buczkó, K.; Magyari, K.; Braun, M.; Bálint, M. 2013. Diatom-inferred Late Glacial and Holocene climatic variability in the south Carpathian Mountains (Romania). *Quaternary International* 293: 123–135.

Canti, M.G. 2003. Aspects of the chemical and microscopic characteristics of plant ashes found in archaeological soils. *Catena* 54(3): 339–361.

Carcaillet, C.; Bouvier, M.; Fréchette, B.; Larouche, A.C.; Richard, P.J.H. 2001. Comparison of pollen-slide and sieving methods in lacustrine charcoal analyses for local and regional fire history. *The Holocene* 11(4): 467–476.

Charles, D.F.; Battarbee, R.W.; Renberg, I.; van Dam, H.; Smol, J.P. 1990. Paleoecological analysis of lake acidification trends in North America and Europe using diatoms and chrysophytes. *In: Acidic Precipitation, Advances in Environmental Science Series,* Volume 4 (Eds.: Norton, S.A.; Lindberg, S.E.; Page, A.L.), Springer, The Netherlands, pp 207–276.

Chattaway, M. M. 1955. Crystals in woody tissues. Part I. *Tropical Woods* 102: 55–74.

Clark, R.L., 1982. Point count estimation of charcoal in pollen preparations and thins of sediments. *Pollen et Spores* 24 (3–4): 523–535.

Clark, J.S.; Richards, P.J.H 1996. The role of paleofire in boreal and other cool-coniferous forests. *In*: *Fire in Ecosystems of Boreal Eurasia* (Eds.: Goldammer, J.G.; Furyaev, V.V.), Springer, The Netherlands, pp. 65–89.

Clark, J. 2013. *The Haber Process*. http://www.chemguide.co.uk/physical/equilibria/haber.html [Accessed June 20, 2015]

Cottrell, Jr., W.H. 2004. *The Book of Fire.* Mountain Press Publishing Company, Missoula, in cooperation with the National Park Foundation.

Countryman, C.M. 1964. Mass fires and fire behavior. *U.S. Forest Service Research Paper PSW-19*, Pacific Southwest Forest and Range Experiment Station.

Davis, M.B.; Moeller, R.E.; Likens, G.E.; Ford, M.S.; Sherman, J.; Goulden, C. 1985. Paleoecology of Mirror Lake and its watershed. *In: An Ecosystem Approach of Aquatic Ecology, Mirror Lake and its Environment* (Ed.: Likens G.E.), Springer, The Netherlands, pp. 410–429.

De Angelis, M.; Steffensen, J.P.; Legrand, M.; Clausen, H.; Hammer, C. 1997. Primary aerosol (sea salt and soil dust) deposited in Greenland during the last climatic cycle: comparison with east Antarctic records. *Journal of Geophysical Research* 102: 26,681–26,698

Delcourt, H.R. 1979. Late Quaternary vegetation history of the eastern Highland Rim and adjacent Cumberland Plateau of Tennessee. *Ecological Monographs* 49(3): 255–280.

Delcourt, H.R.; Delcourt, P.A.; Spiker, E.C. 1983. A 12,000-year record of forest history from Cahaba Pond, St. Clair County, Alabama. *Ecology* 64(4): 874–887.

Demeyer, A.; Nkana, J.V.C.; Verloo, M.G. 2001. Characteristics of wood ash and influence on soil properties and nutrient uptake: an overview. *Bioresource Technology* 77: 287–295.

Dyke, A.S. 2004. An outline of North American deglaciation with emphasis on central and northern Canada. *In: Quaternary Glaciations: Extent and Chronology.* Volume 2 (Eds.: Ehlers, J.; Gibbard, P.L.; Hughes, P.D.), Elsevier, Amsterdam, pp. 373–424.

Ebel, B.A.; Moody, J.A.; Martin, D.A. 2011. Hydrologic conditions controlling runoff generation immediately after wildfire. *Water Resources Research* 48: 1–13.

Elser, J.J. 2011. A world awash with nitrogen. *Science* 334: 1504–1505.

Enters, D.; Kirilova, E.; Lotter, A.F.; Lucke, A.; Parplies, J.; Jahns, S.; Kuhn, G.; Zolitschka, B. 2010. Climate change and human impact at Sacrower See (NE Germany) during the past 13,000 years: a geochemical record. *Journal of Paleolimnology* 43: 719–737.

Fiedel, S.J. 2011. The mysterious onset of the Younger Dryas. *Quaternary International* 242: 262–266.

Firestone, R.B.; West, A.; Kennett, J.P.; Becker, L.; Bunch, T.E.; Revay, Z.S.; Schultz, P.H.; Belgya, T.; Kennett, D.J.; Erlandson, J.M.; Dickenson, O.J.; Goodyear, A.C.; Harris, R.S.; Howard, G.A.; Kloosterman, J.B.; Lechler, P.; Mayewski, P.A.; Montgomery, J.; Poreda, R.; Darrah, T.; Hee, S.S.; Smith, A.R.; Stich, A.; Topping, W.; Wittke, J.H.; Wolbach, W.S. 2007. Evidence for an extraterrestrial impact 12,900 years ago that contributed to the megafaunal extinctions and the Younger Dryas cooling. *Proceedings of the National Academy of Sciences of the United States of America* 104(41): 16016–16021.

Florin, M.-B. 1970. Late-glacial diatoms of Kirchner Marsh, southeastern Minnesota. *Nova Hedwigia* 31: 667–756.

Fogel, M.L.; Cifuentes, L.A. 1993. Isotope fractionation during primary production. *In: Organic Geochemistry: Principles and Applications* (Eds.: Engel, M.H.; Macko, S.A.), Plenum Press, New York, pp.73–98.

Ford, M.S. 1990. A 10,000-year history of natural ecosystem acidification. *Ecological Monographs* 60(1): 57–89.

Fraysse, F.; Pokrovsky, O.S.; Schotta, J.; Meunier, J.-D. 2006. Surface properties, solubility and dissolution kinetics of bamboo phytoliths. *Geochimica et Cosmochimica Acta* 70(8): 1939–1951.

Fraysse, F.; Pokrovsky, O.S.; Schott, J.; Meunier, J.-D. 2009. Surface chemistry and reactivity of plant phytoliths in aqueous solutions. *Chemical Geology* 258(3–4): 197–206.

Fritz, S.C. 1989. Lake development and limnological response in prehistoric and historic land-use in Diss, Norfolk, U.K. *Journal of Ecology* 77: 182–202.

Fuhrer, K.; Legrand, M.R. 1997. Continental biogenic species in the Greenland Ice Core Project ice core: tracing back the biomass history of the North American continent. *Journal of Geophysical Research* 102: 26735–26745.

Gabet, E.J.; Bookter, A. 2011. Physical, chemical and hydrological properties of ponderosa pine ash. *International Journal of Wildland Fire* 20: 443–452.

Galbraith, E.D.; Kienast, M.; the NICOPP Working Group Members 2013. The acceleration of oceanic dentrification during deglacial warming. *Nature Geoscience* 6: 579–584.

Geng, L.; Alexander, B.; Cole-Dai, J.; Steig, E.J.; Savarino, J.; Sofen, E.D.; Schauer, A.J. 2014. Nitrogen isotopes in ice core nitrate linked to anthropogenic atmospheric acidity change. *Proceedings of the National Academy of the Sciences of the United States of America* 111(16): 5808–5812.

Gill, J.L. 2008. *Investigating Biotic Drivers of Quaternary Landscape Change: Late Glacial No Analog Communities and the North American Megafaunal Extinction*. M.S. Thesis, University of Wisconsin-Madison.

Gill, J.L.; Williams, J.W.; Jackson, S.T.; Lininger, K.B.; Robinson, G.S. 2009. Pleistocene megafaunal collapse, novel plant communities, and enhanced fire regimes in North America. *Science* 326: 1100–1103.

Gill, J.L.; Williams, J.W.; Jackson, S.T.; Donnelly, J.P.; Schellinger, G.C. 2012. Climatic and megaherbivory controls on late-glacial vegetation dynamics: a new, high-resolution, multi-proxy record from Silver Lake, Ohio. *Quaternary Science Reviews* 34: 66–80.

Gu, B.; Schelske C.L.; Brenner, M. 1996. Relationship between sediment and plankton isotope ratios and primary productivity in Florida lakes. *Canadian Journal of Fisheries and Aquatic Sciences* 53: 875–883.

Haberyan, K.A.; Horn, S.P. 2005. Diatom paleoecology of Laguna Zoncho, Costa Rica. *Journal of Paleolimnology* 33: 361–369.

Hastings, M.G.; Casciotti, K.L.; Elliott, E.M. 2013. Stable isotopes as tracers of anthropogenic nitrogen sources, deposition, and impacts. *Elements* 9(5): 339–344.

Haworth, E.Y. 1976. Two late-glacial (late Devensian) diatom assemblage profiles from Northern Scotland. *New Phytologist* 77(1): 227–256.

Haynes Jr., C.V. 2008. Younger Dryas "black mats" and the Rancholabrean termination in North America. *Proceedings of the National Academy of the Sciences of the United States of America* 105(18): 6520–6525.

Haynes Jr., C.V.; Huckell, B.B. 2007. *Murray Springs: a Clovis Site with Multiple Activity Areas in the San Pedro Valley, Arizona*. Anthropological Papers of The University of Arizona No. 71. The University of Arizona Press, Tucson.

Heyerdahl, E.K.; Card, V. 2000. Implications of paleorecords for ecosystem management. *Trends in Ecology and Evolution* 15(2): 49–50.

Hollenbach, K.D. 2009. *Foraging the Tennessee River Valley, 12,500 to 8,000 Years Ago.* The University of Alabama Press, Tuscaloosa.

Horn, S.P.; Underwood, C.A. 2014. Methods for the study of soil charcoal as an indicatora of fire and forest history in the Appalachian region, U.S.A. *In: Proceedings, Wildland Fire in the Appalachians: Discussions among Managers and Scientists* (Ed.: Waldrop, T.A.), General Technical Report SRS-199. Asheville, North Carolina, U.S.D.A. Forest Service, Southern Research Station, pp. 104–110.

Houlton, B.Z.; Wang, Y.P.; Vitousek, P.M.; Field, C.B. 2008. A unifying framework for dinitrogen fixation in the terrestrial biosphere. *Nature* 454: 327–331.

Hu, F.S.; Finney, B.P.; Brubaker, L.B. 2001. Effects of Holocene *Alnu*s expansion on aquatic productivity, nitrogen cycling, and soil development in southwestern Alaska. *Ecosystems* 4: 358–368.

Humphreys, G.S.; Hunt P.A.; Buchanan, R. 1987. Wood ash stone near Sydney, NSW—a carbonate pedologial feature in an acidic soil. *Australian Journal of Soil Research* 25(2): 115–124.

Hussey, T.C. 1993. *A 20,000 Year History of Vegetation and Climate at Clear Pond, Northeastern South Carolina.* M.S. Thesis, University of Maine.

Interlandi, S.J.; Kilham, S.S. 2001. Limiting resources and the regulations of diversity in phytoplankton communities. *Ecology* 82(5): 1270–1282.

Iversen, J. 1964a. Plant indicators of climate, soil, and other factors during the Quaternary. *In: Report of the Sixth International Congress on the Quaternary.* Volume 2, Paleobotanical section. Lodz, Poland, pp. 421–428.

Iversen, J. 1964b. Retrogressive vegetation succession in the post-glacial. *Journal of Ecology* 52: 59–70.

Iversen, J. 1969. Retrogressive development of a forest ecosystem demonstrated by pollen diagrams from fossil mor. *Oikos* 12: 35–49.

Jiang, L. 1990. *Paleoecological Reconstructions Utilizing Freshwater Sponge Spicule Distributions in Sediments of Cupola Pond and Powers Fort Swale in Missouri and Hood Lake in Arkansas.* M.S. Thesis, Western Carolina University.

Kaczmarska, I. 1973. Late-glacial diatom flora at Knapówka near Wloszczowa (South Poland). *Acta Palaeobotanica* 14(3): 179–193.

Kahlert M.; Neumann D. 1997. Early development of freshwater sponges under the influence of nitrite and pH. *Archiv für Hydrobiologie* 139(1): 69–81.

Karkanas, P.; Shahack-Gross, R.; Ayalon, A.; Bar-Matthews, M.; Barkai, R.; Frumkin, A.; Gopher, A.; Stiner, M.C. 2007. Evidence for habitual use of fire at the end of the lower paleolithic: site-formation processes at Qesem Cave, Israel. *Journal of Human Evolution* 53: 197–212.

Keeley, J.E. 2009. Fire intensity, fire severity and burn severity: a brief review and suggested usage. *International Journal of Wildland Fire* 18: 116–126.

Kehrwald, N.; Zangrando, R.; Gabrielli, P.; Jaffrezo, J-L.; Boutron,C.; Barbante, C. 2012. Levoglucosan as a specific marker of fire events in Greenland snow. *Tellus B* 64:1–9.

Kennedy, R.W.; Sastry, C.B.R.; Barton, G.M. 1968. Crystals in the wood of the genus *Abies* indigenous to Canada and the United States. *Canadian Journal of Botany* 46: 1221–1228.

Kirilova, E.M.; Heiri, O., Enters, D.; Cremer, H.; Lotter, A.F.; Zolitschka, B.; Hubener, T. 2009. Climate-induced changes in the trophic status of a central European lake. *Journal of Limnology* 68(1): 71–82.

Kolesnikov, E.M.; Kolesnikova, N.V.; Boettger, T. 1998. Isotopic anomaly in peat nitrogen is probably trace of acid rains cause by the 1908 Tunguska bolide. *Planetary and Space Science* 46(2–3): 163–167.

Krauskopf, K.B. 1967. *Introduction to Geochemistry.* McGraw-Hill, Columbus, Ohio.

Lafon, C.W.; Grissino-Mayer, H.D.; Aldrich, S.R.; DeWeese, G.G.; Flatley, W.T.; LaForest, L.B.; Hoss, J.A 2014. Three centuries of Appalachian fire history from tree rings. *In: Proceedings, Wildland Fire in the Appalachians: Discussions among Managers and Scientists* (Ed.: Waldrop, T.A.), General Technical Report SRS-199. Asheville, North Carolina, U.S.D.A. Forest Service, Southern Research Station, pp. 99–103.

Lajewski, C.K.; Mullins, H.T.; Patterson, W.P.; Callinan, C.W. 2003. Historic calcite record from the Finger Lakes, New York: impact of acid rain on a buffered terrane. *Geological Society of America Bulletin* 115(3): 373–384.

LaMoreaux, H.K.; Brook, G.A.; Knox, J.A. 2009. Late Pleistocene and Holocene environments of the southeastern United States from the stratigraphy and pollen content of a peat deposit on the Georgia coastal plain. *Palaeogeography, Palaeoclimatology, Palaeoecology* 280(3): 300–312.

Laschet, C. 1984. On the origin of cherts. *Facies* 10: 257–290.

Legrand, M.R.; De Angelis, M.; Staffelbach, T.; Neftel, A.; Stauffer, B. 1992. Large perturbations of ammonium and organic acids content in the Summit-Greenland ice core. Fingerprint from forest fires? *Geophysical Research Letters* 19: 473–475.

Liu, Y.; Andersen, J.J.; Williams, J.W.; Jackson, S.T. 2013. Vegetation history in central Kentucky and Tennessee (U.S.A.) during the last glacial and deglacial periods. *Quaternary Research* 79(2): 189–198.

Lotter, A.E.; Birks, H.J.B. 1993. The impact of the Laacher See Tephra on terrestrial and aquatic ecosystems in the Black Forest, southern Germany. *Journal of Quaternary Science* 8(3): 263–276.

Lotter, A.E.; Birks, H.J.B.; Zolitschka, B. 1995. Late-glacial pollen and diatom changes in response to two different environmental perturbations: volcanic eruption and Younger Dryas cooling. *Journal of Paleolimnology* 14: 23–47.

Marlon, J.R.; Bartlein, P.J.; Walsh, M.K.; Harrison, S.P.; Brown, K.J.; Edwards, M.E.; Higuera, P.E.; Power, M.J.; Anderson, R.S.; Briles, C.; Brunelle, A.; Carcaillet, C.; Daniels, M.; Hu, F.S.; Lavoie, M.; Long, C.; Minckley, T.; Richard, P.J.H.; Scott, A.C.; Shafer, D.S.; Tinner, W.; Umbanhowar Jr., C.E.; Whitlock, C. 2009. Wildfire responses to abrupt climate change in North America. *Proceedings of the National Academy of the Sciences of the United States of America* 106(8): 2519–2524.

Martin, R.E.; Pendleton, D.W.; Burgess, W. 1976. Effect of fire whirlwind formation on solid fuel burning rates. *Fire Technology* 12(1): 33–40.

Mayewski, P.A.; Meeker, L.D.; Twickler, M.S.; Whitlow, S.I.; Yang, Q.; Lyons, W.B.; Prentice, M. 1997. Major features and forcing of high-latitude Northern Hemisphere atmospheric circulation using a 110,000-year-long glaciochemical series. *Journal of Geophysical Research* 102(C12): 26,345–26,366.

Maynard, J. Barry 2015. Chapter 5. Mineral-water interactions: silicates and alumino-silicates. http://homepages.uc.edu/~maynarjb/Frontpage520sites/603/GeochemWater/chapter_5.htm [Accessed June 16, 2015]

McLauchlan, K.K.; Williams, J.J.; Craine, J.M.; Jeffers, E.S. 2013a. Changes in global nitrogen cycling during the Holocene epoch. *Nature* 495: 352–357.

McLauchlan, K.K.; Williams, J.J.; Engstrom, D.R. 2013b. Nutrient cycling in the palaeorecord: fluxes from terrestrial to aquatic ecosystems. *The Holocene* 23(11): 1635–1643.

Melott, A.L.; Thomas, B.C.; Dreschhoff, G.; Johnson, C.K. 2010. Cometary airbursts and atmospheric chemistry: Tunguska and a candidate Younger Dryas event. *Geology* 38: 355–358.

Mentzer, S.M.; Quade, J. 2013. Compositional and isotopic analytical methods in archaeological micromorphology. *Geoarchaeology: An International Journal* 28: 87–97.

Meyers, P.A.; Teranes, J.L. 2001. Sediment organic matter. *In: Tracking Environmental Change Using Lake Sediments,* Volume 2 (Eds.: Last, W.M.; Smol, J.P.), Kluwer Academic Publishers, Dordrecht, The Netherlands, pp. 239–169.

Meyers, P.A.; Lallier-Vergès, E. 1999. Lacustrine sedimentary organic matter records of Late Quaternary paleoclimates. *Journal of Paleolimnology* 21(3): 345–372

Miller III, J.A. 1978. *Occurrences of Vivianite in Minnesota Lake Sediments.* M.S. Thesis, University of Minnesota.

Miteva, V.; Sowers, T.; Brenchley, J. 2007. Production of N_2O by ammonia oxidizing bacteria at subfreezing temperatures as a model for assessing the N_2O anomalies in the Vostok ice core. *Geomicrobiology Journal* 24: 451–459.

Morley, M.W. 2007. *Mediterranean Quaternary Rockshelter Sediment Records: A Multi-Proxy Approach to Environmental Reconstruction.* Ph.D. Dissertation, University of Manchester.

Muhs, D.R. 2013. The geologic records of dust in the Quaternary. *Aeolian Research* 9: 3–48.

Murphy, D.H.; Wilkinson, B.H. 1980. Carbonate deposition and facies distribution in a central Michigan marl lake. *Sedimentology* 27: 123–135.

National Geographic 2015. *Acid Rain: Invisible Menace*, America's Wild Spaces: Appalachian Trail. Video. http://channel.nationalgeographic.com/videos/acid-rain-invisible-menace/ [Accessed July 28, 2015]

National Park Service 2015. *Fire and Aviation Management, Large Fires and Fatalities*. http://www.nps.gov/fire/wildland-fire/learning-center/fireside-chats/history-timeline.cfm [Accessed June 13, 2015]

Panshin, A.J.; DeZeeuw, C.; Brown, H.P. 1964. *Textbook of Wood Technology.* McGraw-Hill, Columbus, Ohio.

Pernin, P. 1971. The Great Peshtigo Fire: an eyewitness account. *The Wisconsin Magazine of History* 54(4): 246–272.

Peteet, D. 1995. Global Younger Dryas? *Quaternary International* 28: 93–104.

Prinn, R.G.; Fegley Jr., B. 1987. Bolide impacts, acid rain, and biospheric traumas at the Cretaceous-Tertiary boundary. *Earth and Planetary Science Letters* 83: 1–15.

Prospero, J.M. 1999. Long-range transport of mineral dust in the global atmosphere: impact of African dust on the environment of the southeastern United States. *Proceedings of the National Academy of the Sciences of the United States of America* 96(7): 3396–3403.

Ptacnik, R.; Solimini, A.G.; Andersen, T.; Tamminen, T.; Brettum, P.; Lepistö, L.; Willén, E.; Rekolainen, S. 2008. Diversity predicts stability and resource use efficiency in natural phytoplankton communities. *Proceedings of the National Academy of the Sciences of the United States of America* 105(13): 5134–5138.

Robinson, G.S.; Burney, L.P.; Burney, D.A. 2005. Landscape paleoecology and megafaunal extinction in southeastern New York State. *Ecological Monographs* 75(3): 295–315.

Rohde, R.A.; Price, P.B.; Bay, R.C.; Bramall, N.E. 2008. In situ microbial metabolism as a cause of gas anomalies in ice. *Proceedings of the National Academy of the Sciences of the United States of America* 105: 8667–8672.

Salonen, K.; Järvinen, M.; Kuoppamäki, K.; Arvola, L. 1990. Effects of liming on the chemistry and biology of a small acid humic lake *In: Acidification in Finland* (Eds: Kauppi, P.; Anttila, P.; Kenttämies K.), Springer, The Netherlands, pp. 1145–1167.

Sangster, A.G. 1968. Studies of opaline silica deposits in the leaf of *Sieglingia decumbens* L.'Bernh.', using the scanning electron microscope. *Annals of Botany* 32(2): 237–240.

Santín, C.; Doerr, S.H.; Shakesby, R.A.; Bryant, R.; Sheridan, G.J.; Lane, P.N.J.; Smith, H.G.; Bell, T.L. 2012. Carbon loads, forms and sequestration potential within ash deposits produced by wildfire: new insights from the 2009 'Black Saturday' fires, Australia. *European Journal of Forest Research* 131(4): 1245–1253.

Schiegl, S.; Lev-Yadun, S.; Bar-Yosef, O.; El Goresy, A.; Weiner, S. 1994. Siliceous aggregates from prehistoric wood ash: a major component of sediments in Kebara and Hayonim Caves (Israel). *Israel Journal of Earth Science* 43(3–4): 267–278.

Schiegl, S.; Goldberg, P.; Bar-Yosef, O.; Weiner, S. 1996. Ash deposits in Hayonim and Kebara Caves, Israel: macroscopic, microscopic and mineralogical observations, and their archaeological implications. *Journal of Archaeological Science* 23: 763–781.

Schilt, A.; Baumgartner, M.; Schwander, J.; Buiron, D.; Capron, E.; Chappellaz, J.; Loulergue, L.; Schupbach, S.; Spahni, R.; Fischer, H.; Stocker, T. 2010. Atmospheric nitrous oxide during the last 140,000 years. *Earth and Planetary Science Letters* 300(1): 33–43.

Schlachter, K.J.; Horn, S.P. 2010. Sample preparation methods and replicability in macroscopic charcoal analysis. *Journal of Paleolimnology* 44: 701–708.

Scurfield, G.; Michell, A.J.; Silva, S.R. 1973. Crystals in woody stems. *Botanical Journal of the Linnean Society* 66(4): 277–89.

Scurfield, G.; Anderson, C.A.; Segnit, E.R. 1974. Silica in woody stems. *Australian Journal of Botany* 22(2): 211–229.

Shahack-Gross, R.; Ayalon, A. 2013. Stable carbon and oxygen isotopic compositions of wood ash: an experimental study with archaeological implications. *Journal of Archaeological Science* 40(1): 570–578.

Smol, J.P. 1986. *Diatoms and Lake Acidity: Reconstructing pH from Siliceous Algal Remains in Lake Sediments*, Springer, The Netherlands.

Smol, J.P.; Battarbee, R.W.; Davis, R.B.; Merilainen, J. 1986. *Diatoms and Lake Acidity: Reconstructing pH from Siliceous Algal Remains in Lake Sediments.* W. Junk Publishers, The Netherlands.

Smol, J.P. 1987. Methods in Quaternary ecology #1. Freshwater algae. *Geoscience Canada* 14(4): 208–217.

Stančikaitė, M.; Kisieliene, D.; Moe, D.; Vaikutienė, G. 2009. Late glacial and early Holocene environmental changes in northeastern Lithuania. *Quaternary International* 207: 80–92.

Stockmarr, J. 1976. Retrogressive forest development, as reflected in a mor pollen diagram from Mantingerbos, Drentre, the Netherlands. *Paleohistoria* 17: 37–51.

Stoermer, E.F.; Kociolek, J.P. ; Shoshani, J.; Frisch, C. 1988. Diatoms from the Shelton Mastodon site. *Journal of Paleolimnology* 1(3): 193–199.

Stoermer, E.F.; Smol, J.P. 1999. *Diatoms: Applications for the Environmental and Earth Sciences. Encyclopedia of Quaternary Science*, Cambridge University Press, the United Kingdom.

Talbot, M.R. 2001. Nitrogen isotopes in palaeolimnology. *In: Tracking Environmental Change Using Lake Sediments,* Volume 2 (Eds.: Last, W.M.; Smol, J.P.), Kluwer Academic Publishers, Dordrecht, The Netherlands, pp. 401–439.

Taylor, B.E.; Rich, F.J.; Brooks, M.J.; Ivester, A.H.; Clement, C.O. 2011. Late Pleistocene and Holocene vegetation changes in the Sandhills, Fort Jackson, South Carolina. *Southeastern Geology* 48(3): 147–163.

Teranes, J.L.; Bernasconi, S.M. 2000. The record of nitrate utilization and productivity limitation provided by values in lake organic matter—a study of sediment trap and core sediments from Baldeggersee, Switzerland. *Limnology and Oceanography* 45(4): 801–813.

Tolliver, R. 1998. *Late-Quaternary Diatoms from Anderson Pond, Tennessee.* Ph.D. Dissertation, University of Tennessee.

Toon, O.B.; Turco, R.P.; Covey, C.; Zahnle, K.; Morrison, D. 1997. Environmental perturbations caused by the impacts of asteroids and comets. *Reviews of Geophysics* 35(1): 41–78.

Tulonen, T.; Arvola, L.; Ollila, S. 2002. Limnological effects of wood ash application to the subcatchments of boreal, humic lakes. *Journal of Environmental Quality* 31(3): 946–953.

Watts, W.A. 1975. Vegetation record for the last 20,000 years from a small marsh on Lookout Mountain, northwestern Georgia. *Geological Society of America Bulletin* 86: 287–291.

Weiner, S. 2010. *Microarchaeology: Beyond the Visible Archaeological Record.* Cambridge University Press, the United Kingdom.

Whitehead, D.R.; Charles, D.F.; Goldstein, R.A. 1990. The PIRLA Project (Paleoecological Investigation of Recent Lake Acidification): an introduction to the synthesis of the project. *Journal of Paleolimnology* 3(3): 187–194.

Whitehead, D.R.; Charles, D.F.; Jackson, S.T.; Smol, J.P.; Engstrom, D.R. 1989. The developmental history of Adirondack (N.Y.) Lakes. *Journal of Paleolimnology* 2(3): 185–206.

Whitlock, C.; Larsen, C. 2001. Charcoal as a fire proxy. *In: Tracking Environmental Change Using Lake Sediments,* Volume 3 (Eds.: Smol, J.P.; Birks, H.J.B.; Last, W.M.; Bradley, R.S.; Alverson, K.), Kluwer Academic Publishers, Dordrecht, The Netherlands, pp. 75–97.

Whitlock, C.; Anderson, R.S. 2003. Fire history reconstructions based on sediment records from lakes and wetlands. *In: Fire and Climatic Change in Temperate Ecosystems of the Western Americas*. (Eds.: Veblen, T.T.; Baker, W.L.; Montenegro, G.; Swetnam, T.W.), Springer-Verlag, New York, pp. 3–31.

Wilkins, G.R.; Delcourt, P.A.; Delcourt, H.R.; Harrison, F.W.; Turner, M.R. 1991. Paleoecology of central Kentucky since the Last Glacial Maximum. *Quaternary Research* 36(2): 224–229.

Williams, G.W. 2000. Introduction to aboriginal fire use in North America. *In*: *Fire Management Today* 60(3): 8–12.

Woods, S.W.; Balfour, V.N. 2008. The effect of ash on runoff and erosion after a severe forest wildfire, Montana, USA. *International Journal of Wildland Fire* 17(5): 535–548.

Woods, S.W.; Balfour, V.N. 2010. The effects of soil texture and ash thickness on the post-fire hydrological response from ash-covered soils. *Journal of Hydrology* 393(3–4): 274–286.

XOS 2015. XOS Analyzers. Xray fluorescence definition. XOS Corporation, 15 Tech Valley Drive, East Greenbush, NY 12061 U.S.A. http://www.xos.com/technologies/xrf/ [Accessed May 13, 2015].

Yang, Q.; Mayewski, P.A.; Whitlow, S.I.; Twickler, M.S.; Morrison, M.C.; Talbot, R.W.; Dibb, J.E.; Linder, E. 1995. Global perspective of nitrate flux in ice cores. *Journal of Geophysical Research* 100(D3): 5113–5121.

Zielinski, G.A.; Mershon, G.R. 1997. Paleoenvironmental implications of the insoluble microparticle record in the GISP2 (Greenland) ice core during the rapidly changing climate of the Pleistocene-Holocene transition. *Geological Society of America Bulletin* 109(5): 547–559.

Chapter 1 Appendix

Figure 1.1. Map of eastern North America with the six study sites indicated with yellow stars. Core sites studied by others are shown in smaller, blue font. The red line represents the maximum extent of the Laurentide Ice Sheet (LIS) roughly 20,000 years ago. Ice sheet reconstruction after Dyke (2004).

Chapter 2

A 23,000-Year Microscopic Charcoal Record from Anderson Pond, Tennessee, U.S.A.

This chapter is in preparation for submission to the journal *Palynology*. My use of "we" in this chapter refers to my co-authors, Sally P. Horn and Zheng-Hua Li, and myself.

2.1 Abstract

Charcoal records of past fires are important for reconstruction of paleoenvironments and paleoclimate, particularly when compared with pollen records of past vegetation, but such records are scarce in the southeastern U.S. To address the question of how fire activity at Anderson Pond, Tennessee, changed from the Last Glacial Maximum (LGM) into the Holocene as vegetation changed, we developed a new microscopic charcoal record based on point counting of microscopic charcoal fragments on pollen slides from Anderson Pond studied by Delcourt (1979). The record we produced spans the interval from the LGM to recent and is directly tied to the original pollen record. Charcoal:pollen ratios and area concentrations are high during the late glacial and track the coniferous pollen record from the LGM to the late glacial, at which point spruce and jack pine pollen markedly diminished along with fire activity. From around 15,000 cal yr BP to the Mid-Holocene Warm Period (MHWP: 8200–5000 cal yr BP), charcoal indices are low. High fire activity began around the onset of the MHWP, and remained high across that interval, coincident with an increase in indeterminate pollen grains interpreted to signal drier conditions. Charcoal area concentrations declined following the MHWP. Viewed against the original pollen record, the patterns in microscopic charcoal abundance from the LGM to recent at Anderson Pond argue for the strong influence of vegetation as well as climate in driving fire occurrence in eastern temperate North America.

2.2 Introduction

The analysis of charcoal particles in sediment profiles from lakes and wetlands can extend records of fire history obtained from historical documents and fire-scarred trees (Whitlock and Larsen 2001). Studying charcoal along with pollen in sediment cores can provide important insights into fire-vegetation-climate linkages, and the relationships between humans and fire (Horn 1993, Clement and Horn 2001, Whitlock and Larsen 2001). In eastern North America, wildland burning by Native Americans is well documented since European contact (Williams 2000), but patterns of anthropogenic and lightning fires prior to the 1600s must be inferred from charcoal and other sedimentary proxies of fire. Charcoal records of fire history are of interest in fire management (Heyerdahl and Card 2000, Matlack 2013) and are crucial for understanding past climate and environmental changes, such as the Younger Dryas abrupt climate reversal some 12,800 years ago (Peteet 1995, Firestone et al. 2007, Broecker et al. 2010, Fiedel 2011).

Studies of fire history from sedimentary charcoal typically involve the quantification of macroscopic or microscopic charcoal fragments (Whitlock and Larsen 2001). In macroscopic charcoal analysis, sediment samples are removed from cores at contiguous or close intervals, chemically disaggregated, and wet-sieved with fine-mesh screens (usually 125 or 250 µm), with the retained charcoal counted on the sieves or following transfer to Petri dishes. Microscopic charcoal analysis is usually performed on samples prepared for pollen analysis, with wider sample spacing following the pollen sample spacing. Microscopic charcoal fragment numbers are tallied along pollen transects, and sometimes measured to determine charcoal area (Whitlock and Larsen 2001), or are quantified using point counting (Clark 1982), which provides estimates of the areal coverage of charcoal on pollen slides. Microscopic charcoal data obtained from pollen slides may represent a regional fire signal, while macroscopic charcoal data obtained by sieving lake sediments serves as a proxy of local fire history (Carcaillet et al. 2001).

Here we provide a microscopic charcoal record for Anderson Pond, Tennessee that spans the period from 23,000 cal yr BP to recent, including the Mid-Holocene Warm Period (MWHP). Charcoal data were obtained from pollen slides prepared by Delcourt (1979) from a core obtained in 1976. We address the following research questions: 1) How does the paleofire record at Anderson Pond from the LGM through the Holocene compare with the vegetation record as shown by pollen percentages in the same samples? 2) Do patterns of fire occurrence at Anderson Pond match the prediction from a recent global synthesis of fire records that greater fire activity should be associated with warmer temperatures? 3) How do microscopic charcoal concentrations and charcoal:pollen ratios for Anderson Pond compare with charcoal indices at other sites in the eastern U.S.?

2.3 Sedimentary Charcoal Records in Eastern Temperate North America

Macroscopic charcoal records that extend back to the late glacial period exist for sites in New York (Robinson et al. 2005), Indiana (Gill 2009), Michigan (Ballard 2009), and Ohio (Gill et al. 2012), but in the southeastern U.S. only for one site in Georgia (LaMoreaux et al. 2009). Taylor et al. (2011) analyzed sediments from a pocosin wetland at Fort Jackson, South Carolina for pollen and noted the presence of macroscopic charcoal throughout the core. In addition to these macroscopic records, pollen and microscopic charcoal across the late glacial were studied by Boehm (2012) at Whiteoak Bottoms, North Carolina and Hussey (1993) at Clear Pond, South Carolina. The Clear Pond record extended through the Holocene.

The replacement of conifers by hardwoods at the end of the Pleistocene was widespread across the eastern U.S., with oaks typically rising to dominance among early Holocene tree taxa and remaining dominant throughout the Holocene (Delcourt 1979, Delcourt et al. 1983, Hussey 1993, Maenza-Gmelch 1997, Goman and Leigh 2004, Hupy and Yansa 2009, LaMoreaux et al. 2009). Spruce and jack pine co-occur today in the southern boreal forests of Canada and the lake states of Minnesota, Wisconsin and Michigan. Presently, red spruce (and Fraser fir) only occur in Tennessee on the highest peaks along the North Carolina border in the Great Smoky Mountains. On the coastal plain, pines returned to dominance in the middle Holocene (Hussey 1993, Taylor et al. 2011), although *Pinus banksiana* was replaced by other *Pinus* species such as *Pinus palustris* (longleaf pine) and *Pinus elliottii* (slash pine) (Carey 1992a, 1992b).

Recent efforts to assemble a global database of sedimentary charcoal records (Power et al. 2010) have resulted in a series of papers on regional to global scale trends in fire activity. Marlon et al. (2013) synthesized charcoal records across the Holocene at regional, continental, and global scales. They focused on linkages between fire, climate, and anthropogenic activities. They reported that globally, fire activity was low in the early Holocene—although there were some locations with episodes of high fire activity—but that fires increased through the Holocene. The regions that experienced high fire activity in the early Holocene were periglacial regions in Alaska, Canada, and northeastern Europe in the Northern Hemisphere; Patagonia in the Southern Hemisphere; and the Mediterranean and monsoonal Africa and Asia. Marlon et al. (2013) suggested that fire activity was influenced by physical features such as mountain ranges, and a sensitivity to atmospheric circulation patterns during the early Holocene such as a shifting jet stream and storm track positions (Carcaillet and Richard 2000, Whitlock et al. 2007), and monsoon-influenced shifts in precipitation patterns that affect plant communities and fire regimes. They concluded that neither changes in human populations nor land use change can explain the Holocene biomass burning record at regional or continental scales.

Daniau et al. (2012) analyzed charcoal records from the Last Glacial Maximum (LGM) to the present to explore the sensitivity of fire to climate. They found that changes in fire regimes were predictable from changes in regional climates. Their analyses showed that fire increased uniformly with changes in temperature, peaking at intermediate moisture levels. They concluded that temperature is the most important driver of shifts in biomass burning during this time interval.

Marlon et al. (2009) synthesized charcoal studies from the U.S. and Canada to determine whether a widespread signal for fire existed at the boundary between the Bølling Allerød interstadial and the Younger Dryas stadial at 12,900 cal yr BP, known as the Younger Dryas Boundary (YDB). Their study aimed to test the Firestone et al. (2007) hypothesis that an extraterrestrial impact at 12,900 cal yr BP triggered massive wildfires. On the basis of datasets available at the time, Marlon et al. (2009) concluded that only a moderate charcoal peak occurred at the YDB. For eastern North America, data from only five sites were available for the analysis. Since publication of the Marlon et al. (2009) study, additional sites have been analyzed that provide late-glacial fire data for eastern North America. Four coarsely-dated records from lakes in east-central Michigan (Slack, Swift, Sixteen, and Big Fish) showed large charcoal peaks around 14,000 cal yr BP and around the interpolated YDB (Ballard 2009). At Swift Lake, fire activity was continuous from the onset of the Holocene to about 5400 cal yr BP, the top of the sediment record. Charcoal analysis of sediments from Appleman Lake, northern Indiana, showed a charcoal record similar to that of Swift with peaks during the late glacial and then more continuous, high peaks through the Holocene, when oak dominated (Gill et al. 2009). The charcoal record for Silver Lake, Ohio (Gill et al. 2012) revealed fires beginning around 17,000 cal yr BP. Intermittent charcoal peaks occurred from 16,000 to14,500 cal yr BP when spruce forest was the dominant vegetation. Spruce pollen showed a sharp decline at 14,000 cal yr BP. The largest peaks in charcoal in the record occur between 14,000 and 13,400 cal yr BP. After 14,000 cal yr BP, pollen percentages for *Fraxinus*, *Ostrya*-type, *Acer, Quercus* and *Ulmus* began to increase. Fire frequency increased from ca. 12,300 to 8,300 cal yr BP with peaks clustered between ca. 12,000 and 11,000 cal yr BP, when pine and spruce pollen both rose to about 30%. At 11,000 cal yr BP, oak became the dominant taxa, accounting for up to 60% of the upland pollen sum. A group of charcoal peaks also occurred ca. 9600 and 8500 cal yr BP, when oak (*Quercus*), hickory (*Carya*), and elm (*Ulmus*) dominated the pollen record.

Robinson et al. (2005) found microscopic charcoal throughout a sediment profile from Binnewater Pond, New York, with highest values of 75 mm^2/cm^3 around 14,000 cal yr BP when spruce and pine were dominant. After 14,000, charcoal area concentrations dropped to around 10 mm^2/cm^3 until 10,000 cal yr BP. During this interval spruce and pine were still present, but *Betula* and *Alnus* were increasing. At ca 10,000 cal yr BP, oak pollen sharply increased to >60% and charcoal indices went from 10 to a range of 20–40 mm^2/cm^3. The Whiteoak Bottoms, North Carolina charcoal and pollen record developed by Boehm (2012) revealed fire activity from 14,500–12,600 cal yr BP when alder, oak, and birch along with sedge dominated the pollen record. Pollen of *Ostrya/Carpinus,* spruce, fir, and Asteraceae were also present in this interval, but pine pollen percentages were relatively low (<6 %).

2.4 Study Site and Previous Studies

Anderson Pond (36.0298 ºN, 85.5019 ºW) is a ca. 35 ha sinkhole pond located in White County, Tennessee at about 300 meters elevation on the eastern Highland Rim. It formed in dolomitic limestone of the St. Louis Formation of Mississippian age (Garman and Taylor 1971).

The adjacent Cumberland Plateau rises to 600 m elevation. Anderson Pond is situated in what was once the species-rich Mixed Mesophytic Forest region as defined by Braun (1950). Today, much of the land has been cleared. Annual rainfall in nearby Sparta, Tennessee, is 1385 mm (54.5 inches). Sparta has a July average maximum temperature of 31.4 ºC (88.5 ºF) and July average minimum temperature of 18.8 ºC (65.9 ºF) (Western Regional Climate Center 2014).

Delcourt (1979) analyzed pollen and macrofossils in a 10 m long core recovered from Anderson Pond in 1976. Recently, Liu et al. (2013) described vegetation history at Anderson Pond from a new core recovered in 2007. Pollen percentage changes were similar to those of Delcourt (1979). Liu et al. (2013) commented that transitions in pollen assemblages appeared to occur about 1000 years later in the Delcourt pollen diagram, but that diagram was plotted by radiocarbon age not calibrated age. When the original Delcourt pollen data are plotted by calibrated age, as we have done here, the transitions in the two records appear to occur either at similar times, or earlier in the Delcourt record. However, as Liu et al. (2013) noted, differences in sampling density and in methods of age modeling complicate close comparison of the pollen records from the 1976 and 2007 sediment cores from Anderson Pond. We focus here on the pollen shifts in the 1976 profile, to which our charcoal data are directly linked.

Liu et al. (2013) did not study microscopic or macroscopic charcoal in their 2007 core from Anderson Pond, but did report two radiocarbon dates on charcoal. Both charcoal samples dated to the Last Glacial Maximum, with calibrated ages (95% confidence ranges) of 19,396–18,834 and 21, 131–20,308 cal yr BP. To explore long-term fire history at Anderson Pond and its relationship to late-glacial and Holocene vegetation change, we quantified microscopic charcoal on the original pollen slides from core AP-76B studied by Delcourt (1979).

2.5 Methods

We performed microscopic charcoal point counting (Clark 1982) on 57 of the original Delcourt pollen slides, from the mud-water interface at 25 cm to a depth of 700 cm. We used an Olympus BH2 microscope at 400x magnification and a modified version of the Clark method, in which we counted marker pollen grains in each field of view (Appendix I). During charcoal point counting, 3850–5500 points were applied to each slide. The area estimates were converted to charcoal area concentration (mm^2/cm^3) using counts of *Eucalyptus* pollen grains added by Delcourt during pollen processing as controls. Charcoal values were also expressed as charcoal:pollen ratios (μm^2/pollen grain). Pollen and spore data were downloaded from the Neotoma database (http://www.neotomadb.org) and taken from Delcourt (1978). We used information on *Eucalyptus* marker grains added to each sample and original counts for *Eucalyptus* grains and total upland pollen and spores to calculate charcoal:pollen ratios. Pollen percentages for major plant taxa were plotted together with microscopic charcoal using C2 software (Juggins 2010).

We chose not to report charcoal area influx values because these calculations require the assumption that sedimentation rates were consistent between dated horizons of the core. That the dates on the AP-76B core were bulk dates spanning 5–15 cm intervals and include only three dates for the Holocene make this assumption problematic. Instead, we present microscopic charcoal area concentrations on a volumetric basis (mm^2/cm^3), which do not take into account the amount of time represented by the samples, and charcoal:pollen ratios (μm^2/pollen grain), which reveal periods of higher and lower influx of charcoal as compared to pollen, without requiring influx calculations.

The integrity of the material on the ca. 35-year old slides was checked by comparing the density of *Eucalyptus* marker grains observed during charcoal point counting to their estimated density when the original pollen counts were made (Delcourt 1979). If pollen grains had degraded in the intervening years or if the residue had seeped out from under the cover slip, a reduced density of *Eucalyptus* pollen grains would have been evident. Determining *Eucalyptus* grain densities at the time of point counting involved a straightforward calculation in which the number of grains tallied was divided by the product of the number of fields of view examined and the area of each field of view, yielding a density value in grains/mm^2 of slide area. We estimated the density of *Eucalyptus* grains on the slides at the time of the original pollen counts using unpublished notes by H. Delcourt on the number of transects examined on each slide and two estimates for the diameter of the field of view of the microscope she originally used at the University of Minnesota, which was unavailable for examination. Delcourt (1979) reported that she counted the slides using a Leitz Ortholux microscope at a magnification of 450x, using 1140x when fine detail was needed. Based on that information and on standard microscope configurations available in the 1960s and 1970s, we surmised that she used 45x and 114x objectives with 8x Periplanatic eyepieces and a tube magnification factor of 1.25. The eyepieces could have been 8x/16 or 8x/18, with the two different values (field numbers or FN) corresponding to the size of the diaphragm of the eyepiece. We calculated the diameter of the field of view (FOV) for both possible eyepieces using the equation: FOV = Eyepiece FN/(Magnification of the Objective x Magnification of the Tube), resulting in FOV estimates of 0.284 mm and 0.320 mm. We then multiplied these FOV diameters by 22 cm (the width of the cover slip on the Anderson Pond pollen slides) and by the number of transects counted to determine the area of the slide examined in the original pollen counts. For each pollen level from the original study for which we counted charcoal in our study, we produced two estimates of the original density of *Eucalyptus* grains on the slides by dividing the *Eucalyptus* count by Delcourt by the estimates of slide area examined made using our two FOV estimates. These two estimates produced two series of values that we separately compared to the values for *Eucalyptus* density determined during our point counts to test the null hypothesis that no change in *Eucalyptus* grain density had occurred on the Anderson Pond slides over the ca. 35 years between the pollen count by Delcourt and our charcoal analysis. We used a paired samples two-tailed t-test to separately compare the *Eucalyptus* grain density we observed to the estimates of the original *Eucalyptus* density using the FOV estimates of 0.284 and 0.320 mm for the Leitz Ortholux microscope. We found no significant difference in the original density values using the 0.284 FOV estimate (M=2.56, SD=3.53) and our density determinations (M=2.47, SD=2.80) (t(76)=0.125, p=0.901), or between the original density values using the 0.320 mm FOV estimate (M=2.27, SD=3.14) and our density determinations (t(76)=–0.295, p=0.769). This analysis gives us confidence that little or no degradation of the pollen or loss of residue on the slides had occurred, and that the slides can be used to quantify charcoal abundance and link changes in charcoal to changes in pollen assemblages at the site.

We calibrated the original radiocarbon dates on bulk sediment obtained by Delcourt (1979) using the radiocarbon calibration software CALIB 7.0.2 (Stuiver and Reimer 1993) and the dataset of Reimer et al. (2013), and CALIBomb (Reimer et al. 2004) for one recent date. Ages for each pollen and charcoal sample were interpolated linearly using the weighted means of the probability distributions of the calibrated ages (Telford et al. 2004).

We compared Anderson Pond charcoal indices with those in other microscopic charcoal records to put our results in context. We chose studies of microscopic charcoal that also expressed charcoal abundances as area concentrations and charcoal to pollen ratios. These sites are: Key Deer Pond in the pine rocklands in south Florida (Albritton 2009); Whiteoak Bottoms, a wetland in the Nantahala National Forest, North Carolina (Boehm 2012); Binnewater Pond, near Otisville, southeastern New York State (Robinson et al. 2005); Lake of the Clouds, Minnesota (Swain 1973); Calf Island in Boston's Outer Harbor (Patterson et al. 2005); and Lost and Grizzly Lakes in the boreal forest of Alaska (Tinner et al. 2006). Charcoal records or portions of records were categorized as conifer-dominated or hardwood-dominated, and compared to conifer-dominated and hardwood-dominated sections of the Anderson Pond charcoal record.

2.6 Results

Our point counting revealed variable charcoal abundance over the past ca. 23,000 years (Figure 2.1, Table 2.1). We found two broad intervals of high fire activity at Anderson Pond: 23,000 to 15,000 cal yr BP, and from about 8200 to 5000 cal yr BP. These times of high fire activity were separated by an interval of very low fire activity.

Charcoal area concentrations (mm^2/cm^3) are high from the LGM until shortly before 15,000 cal yr BP (25 pollen slides). Only nine pollen slides were available for the period 15,000–8200 cal yr BP. Point counting revealed low charcoal concentrations, except for one sample at ca. 9600 cal yr BP. Charcoal concentrations were highest across the MHWP (8200–5000 cal yr BP). Charcoal values diminished from 4900 cal yr BP to present. The values for charcoal area concentrations across the MHWP were double to five times or more greater than values in the pre-15,000 cal yr BP section.

Charcoal to pollen ratios (μm^2/pollen grain) are also lowest between 15,000 and 8200 cal yr BP, but this charcoal index shows a different pattern than charcoal area concentration before and after this time because the ratios are affected by variations in the amount of pollen in the samples. Pollen concentrations are highest in mid-Holocene sediments at Anderson Pond (Delcourt 1979), and the high concentrations of pollen result in lower charcoal:pollen ratios.

Comparing the charcoal indices to pollen percentages reveals that the charcoal pattern from the LGM to around 15,000 cal yr BP corresponds closely to the spruce and pine pollen curves (Figure 2.1). During the time of low fire activity between about 15,000 and 8200 cal yr BP, hophornbeam/ hornbeam (*Ostrya/Carpinus*) and oak (*Quercus*) pollen increased. The increased fire activity in the middle Holocene matches sharp increases in alder (*Alnus*) and buttonbush (*Cephalanthus*), and an increase in indeterminate (damaged) pollen grains.

Our comparisons between charcoal indices at Anderson Pond and those at other sites for which investigators had presented comparable data revealed that Anderson Pond had the highest values for charcoal indices in three of four categories (Tables 2.2 a-d, Table 2.3). For the hardwood intervals, Anderson Pond had a maximum charcoal area concentration of 5448 mm^2/cm^3 compared to 189 mm^2/cm^3 for Whiteoak Bottoms, and only 40 mm^2/cm^3 for Binnewater Pond (Table 2.2a). Comparing conifer intervals by charcoal area concentration, the maximum was 2730 mm^2/cm^3 for Anderson Pond, 863 mm^2/cm^3 for Key Deer Pond, 157.1 mm^2/cm^3 for Grizzly Lake, 87.5 mm^2/cm^3 for Lost Lake, and only 75 mm^2/cm^3 for Binnewater Pond (Table 2.2b). Comparing hardwood intervals by charcoal:pollen ratios, Anderson Pond had a maximum of 3199 μm^2 charcoal per pollen grain, while Whiteoak Bottoms had 744 μm^2/grain (Table 2.2c). We found that Anderson Pond had the second highest charcoal:pollen maximum in the conifer interval comparison, with 16,382 μm^2 charcoal per pollen grain; Key Deer Pond had a maximum ratio of 20,297 μm^2/grain, Calf Island Marsh had 6935 μm^2/grain, and Lake of the Clouds had only 10 μm^2/grain (2.2d).

2.7 Discussion

Daniau et al. (2012) focused on climate as the driver of wildfire occurrence over the past 21,000 cal yr BP. Their global data compilation and analysis indicated a strong relationship between temperature and fire, with warm temperatures associated with greater biomass burning. However, fires were common at Anderson Pond from 21,000–15,000 cal yr BP, a period interpreted by Delcourt (1979) to be relatively cool. Comparison of the charcoal and pollen data indicates that fire is strongly associated with the presence of pines and other conifers from prior to the LGM until the beginning of the late-glacial period. That times of pine dominance would be times of greater burning is not surprising given the strong ecological relationships between pines and fire in ecosystems around the world and through time (Agee 1998). However, the charcoal trends at Anderson Pond stand in contrast to the relationships found to exist on the global scale by Daniau et al. (2012), which would predict lower fire activity during cooler periods at Anderson Pond. Fires at Anderson Pond during the Late Pleistocene and early Holocene may have been driven more by vegetation type than temperature, with fire activity decreasing with warming during the late glacial and early Holocene, as hardwoods largely replaced pines and other conifers. Hu et al. (2006) reported similar fire-vegetation-climate interactions for seven sites in Alaska during the Holocene. Whenever *Picea mariana* (black spruce) became established at a site, during cooler, wetter times, its presence led to increased fires, despite the expectation that fewer fires would occur when the climate was cooler and wetter. Hu et al. (2006) attributed the increased fires to the highly flammable black spruce vegetation. In addition, Hu et al. (2006) reported higher charcoal indices at Grizzly Lake during the Little Ice Age than for preceding and subsequent warmer periods (Tinner and Hu 2001) and attributed the increase in fires to drier conditions possibly with more dieback.

Fauria and Johnson (2008) studied fire-vegetation-climate linkages in the Canadian boreal forest, and noted that the relationship between climate, fire frequency, and vegetation composition is complex. Climate change modifies the fire frequency, which along with climate change itself, facilitates shifts in vegetation composition. Shifts in vegetation composition can then further influence fire frequency if the density of forest stands change, for example from open to closed canopy or the reverse (Fauria and Johnson 2008). Large fires in closed-canopy stands of boreal forest occur when lightning strikes following 10 to 15 days of persistent drought, required to dry the fuel (Nash and Johnson 1996, Fauria and Johnson 2008).

In the Alaskan boreal forest, high intensity crown fires are common, and during active fire years, millions of hectares may burn (Olson et al. 2011). On June 16, 2015, wildfires were actively burning near Anchorage, and 2630 ha had already burned (Alaska Fire Service 2015, Anderson 2015). Erratic winds had contributed to the spread of the fires. Both fire and dominant vegetation respond to changing climate, and vegetation can provide positive or negative feedbacks to fire severity and frequency (Higuera et al. 2009). Brubaker et al. (2009) found that the mid-Holocene expansion of black spruce in the boreal forests of Alaska fundamentally changed the landscape flammability and caused fire regimes to shift in a direction counter to that predicted by the direct effects of climate (Brubaker et al. 2009, Higuera et al. 2009). Our findings are consistent with the conclusions of Brubaker et al. (2009) that vegetation flammability is a primary driver of fire regimes, with flammability during the Pleistocene strongly linked with the presence of conifers.

However, the relationship between temperature and fire found by Daniau et al. (2012) in their global synthesis of charcoal records does appear to be reflected in the Holocene record of fire at Anderson Pond, which is characterized by high charcoal area concentrations during the MWHP.

2.7.1 Comparing and Interpreting Microscopic Charcoal Indices

One issue with comparing charcoal records between sites to compare fire histories is the diversity of ways in which charcoal is quantified and charcoal abundances are expressed. For our study, we chose to express charcoal abundance on a concentration basis and as charcoal:pollen ratios, rather than as charcoal influx expressed in $mm^2/cm^2/yr$. The charcoal to pollen ratio (μm^2 charcoal/pollen grain) has several advantages over charcoal influx values (Swain 1973). The calculation of influx values requires estimating the amount of time represented in each sample. While such values can be estimated from radiocarbon dates, the results can be misleading if few dates are available or if dates were obtained on wide core intervals as was the case for the 1976 Anderson Pond profile. Also, charcoal influx values can be affected by post-fire erosion, which can increase sediment influx over the short term, to values higher than would be interpolated from dated horizons (Swain 1973). Erosion years after a fire with sediment deposition into the lake could give anomalous charcoal peaks. The charcoal to pollen ratio should eliminate false peaks because pollen should be redeposited along with charcoal. Immediately after an actual fire, the amount of charcoal should be higher than the amount of pollen due to the abundance of airborne charcoal and the reduction of the source of pollen (Swain 1973).

Patterson et al. (1987) reviewed studies of microscopic charcoal as a fossil indicator of fire and concluded that vegetation type at a burn site may play an important role in the amount of charcoal that gets deposited at that site. Additionally, if airborne transport of charcoal particles is as effective as water transport, then mires could be as effective as nearby lakes in recording evidence of fires. Patterson et al. (1987) found that microscopic charcoal records can be validated against other proxies, and that quantifying microscopic charcoal is a relatively fast method for collecting data on past fire activity.

According to Patterson and Backman (1988), charcoal to pollen ratios of less than 100 to 200 μm^2/grain likely represent time intervals when few fires occurred. Infrequent fires may be typified by values of 300 to 800 μm^2/grain. Such values may also represent background levels in landscapes that are fire-dominated (Patterson and Backman 1988). In areas that burn often, values of 2000 to 4000 or more μm^2/grain for an individual fire can be expected (Patterson and Backman 1988). In a later study, Patterson et al. (2005) concluded that charcoal to pollen ratios greater than 500–1000 μm^2/pollen grain signify fires that burned within the watershed of lakes, or in the case of wetlands, fires that burned through the wetland.

These interpretations of charcoal:pollen ratios suggest that Anderson Pond was a site that burned frequently from the LGM to the late glacial (average charcoal:pollen ratio of 4196 μm^2/grain). That charcoal:pollen ratios in the Anderson Pond sediments from the LGM to 15,000 cal yr BP consistently exceed 1000 μm^2 charcoal/pollen grain suggests repeated local burning of the conifer-dominated vegetation that then surrounded the site. Charcoal:pollen ratios suggest that areas surrounding Anderson Pond also burned during the middle and late Holocene (average charcoal:pollen ratio of 1223 μm^2/grain for 8200 cal yr to present). The Mid Holocene Warm Period does not show consistently higher charcoal:pollen ratios than the late Holocene, but this interval shows much higher charcoal concentrations than other intervals of the Holocene or Pleistocene (average charcoal area concentration of 1507 mm^2/cm^3 for 8200 cal yr to present). The higher pollen concentrations at Anderson Pond during the Holocene (Delcourt 1979) have the effect of depressing charcoal:pollen ratios.

Charcoal records from Binnewater Pond (Robinson et al. 2005) and Whiteoak Bottoms (Boehm 2012) provided data on charcoal area concentrations during periods of hardwood dominance that can be compared to values at Anderson Pond. At Binnewater Pond, vegetation transitioned from a pine and spruce forest to an oak-dominated forest around 10,000 cal yr BP. The vegetation at Anderson Pond was dominated by oak by 14,000 cal yr BP. Whiteoak Bottoms was dominated by alder, betula, oak and sedge between 14,500 and 12,600 cal yr BP. Despite similar oak pollen percentages between Anderson and Binnewater Ponds (ca. 60%), charcoal concentrations at Anderson Pond were two orders of magnitude higher, with a maximum of 1374 mm^2/cm^3, and were an order of magnitude higher than at Whiteoak Bottoms.

Key Deer Pond (Albritton 2009), Grizzly and Lost Lakes (Tinner et al. 2006), and Binnewater Pond (Robinson et al. 2005) provided charcoal area concentration data for sites dominated by conifers. Albritton (2009) found maximum charcoal values of 863 mm^2/cm^3 for Key Deer Pond in the pine rockland of the Florida Keys. The vegetation here is dominated by South Florida slash pine (*Pinus elliottii* var. *densa)* and shrub and herb species adapted to frequent, low intensity fires that help maintain the pine rockland ecosystem (Harley et al. 2013). Anderson Pond had a maximum charcoal area concentration value of 2730 mm^2/cm^3 during the late glacial interval of conifer dominance, an order of magnitude higher than in the frequently-burned area surrounding Key Deer Pond (Albritton 2009), one to two orders of magnitude higher than values for the two Alaskan boreal forest lakes, and two orders of magnitude higher than values for Binnewater Pond (Robinson et al. 2005).

The hardwood-dominated section of the Anderson Pond record (11,200 cal yr BP to present, and including the MHWP) showed maximum values for charcoal:pollen indices that were an order of magnitude higher than values for Whiteoak Bottoms. The lower charcoal/pollen ratios at Whiteoak Bottoms may reflect better conditions for pollen preservation at this site during the last glacial than at Anderson Pond during the Holocene, when Delcourt found high percentages of damaged and degraded grains in pollen samples. Under conditions of poor pollen preservation, we can expect higher charcoal:pollen ratios as charcoal is more resistant to decomposition than pollen (Bush et al. 2007).

Charcoal:pollen ratios in the conifer-dominated lower interval of the Anderson Pond record (23,000–11,200 cal yr BP) revealed that it had the second highest maximum charcoal value of the four sites, with 16,382 μm^2/grain (at 20,200 cal yr BP), similar to the maximum value of 20,297 μm^2/grain at Key Deer Pond, the site with the highest maximum. That charcoal:pollen ratios during the conifer-dominated interval at Anderson Pond were similar to values at the frequently burned Key Deer Pond site, and charcoal area concentrations higher than found at Key Deer Pond, suggests that fires occurred regularly at Anderson Pond during the LGM and the late glacial.

Comparing microscopic charcoal indices between cores is complicated by differences in processing that can affect charcoal concentrations and pollen:charcoal ratios, for example, whether sediments are sieved during processing and if so, the size of the mesh; whether a vortex stirrer is used, and how many times the sediments are stirred, centrifuged, and decanted during chemical treatments and water rinses (Clark 1984). Microscopic charcoal concentrations and pollen:charcoal ratios are also affected by local and regional wind patterns, size of depositional basins, and sediment mixing, among other factors. We present the above comparisons to put the Anderson Pond charcoal record into the context of other fire history studies in the eastern U.S. Based on suggestions of Patterson and Backman (1988) and Patterson et al. (2005), we interpret charcoal:pollen ratios at Anderson Pond to indicate repeated, probably local fires from the LGM to the late glacial, and during the middle and late Holocene. The fact that ratios are similar to those found at Key Deer Pond in the frequently burned, pine-dominated rockland vegetation supports our interpretation that fires were local and common.

2.7.2 Fire-Vegetation-Relationships

For eastern temperate North America from the LGM into the late glacial, lake-sediment records generally exhibit conifer-dominated pollen spectra, with oaks rising to dominance in the Holocene (Webb 1988, Williams et al. 2004). In Michigan, northern pines displaced spruce during the Younger Dryas (12,800–11,600 cal yr BP), with oaks dominating by the end of the Younger Dryas (Hupy and Yansa 2009). The replacement of spruce by northern pines may have been driven in part by reduced moisture availability, as jack pine has deep roots (Carey 1993), while North American spruce species (black, red, and white) have shallow roots (Blum 1990, Fryer 2014, Nienstaedt and Zasada 2015). The southeastern United States exhibited the same pattern of conifer dominance (northern pines and spruce) until the late glacial (Watts 1980, Williams et al. 2004).

Komarek (1974) stated that the pines and oaks that have covered most of the forested areas of the southeastern U.S. in the past are predominantly fire-adapted species. In particular, jack pine is highly fire-dependent (Carey 1993). Jack pine needs fire for its serotinous cones to open and release seeds. The seeds require a mineral substrate for establishment, which is created by fire. Shade-intolerant, fast-growing jack pine is the dominant species in the southern boreal forest today (Morris and MacDonald 1991). It grows on poorly developed or sandy substrates that are typically nutrient poor; jack pine can persist on the driest, harshest sites (Carey 1993). Jack pine is typically killed by crown fires or moderate-severity surface fires, resulting in evenaged stands (Frissell 1973). Oaks also are well adapted to environments with disturbances, and they have deep roots and can tolerate drought well (Dey 2002).

Delcourt (1979) measured pine pollen grains in the Anderson Pond core, and narrowed the species to jack pine and red pine. She also found needle fragments of a two-needle pine in the sediments, and confirmed through analysis of cross sections that the pine species in the lower portion of the Anderson Pond profile was jack pine. In this section of the core, from the time prior to the Last Glacial Maximum to the late glacial, spanning some 10,000 years, the charcoal dataset clearly shows that fire activity tracked the coniferous pollen record.

The forest assemblage of northern pines, spruce, and fir with 23% pollen of temperate deciduous species (Delcourt 1979) around the LGM corresponds to a cool mixed forest biome (Williams et al. 2004) with enough soil moisture to sustain the forest (Delcourt 1979). The reduction in fire activity at Anderson Pond around 15,000 cal yr BP after thousands of years of conifer dominance suggests major changes in one or more environmental factors that dramatically altered the fire regime. Delcourt (1979) inferred rapid and major ecosystem change at Anderson Pond during the transition from coniferous to deciduous forest between 12,750 and 12,500 ^{14}C yr BP (15,190–14,740 cal yr BP), with rapid infilling of inorganic sediments, and shallowing of the pond. She postulated that the elimination of jack pine may have been due to a shift to milder winters and to lengthening of the growing season, both associated with late glacial warming.

Other researchers have inferred warming at the onset of the Younger Dryas (12,900 cal yr BP) in the southeastern U.S. Flower et al. (2011) discussed the cessation of cold meltwater pulses from the Laurentide Ice Sheet down the Mississippi River to the Gulf of Mexico at the onset of the Younger Dryas, inferred from $\delta^{18}O$ shifts and Mg/Ca ratios in foraminifera in marine sediment cores. Dorale et al. (2010) inferred drought conditions in southwestern Missouri during the Younger Dryas based on stable carbon isotopes in a buried soil profile; their findings suggested that the Younger Dryas was arid as well as warmer. Nordt et al. (2002) inferred a warmer but wetter Younger Dryas in southern Texas from an increase in $\delta\ ^{13}C$ values in a buried soil sequence along the Medina River, and from an increase in $\delta^{18}O$ of foraminifera from a sediment core from the Gulf of Mexico at that time. A warmer but wetter climate was inferred by Grimm et al. (2006) for central Florida from their pollen record from Lake Tulane sediments.

Although milder winters and a longer growing season may have contributed to the decline of jack pine ca. 15,000 cal yr BP, we suggest that eutrophication may also have played a role. In the modern boreal forest, jack pine can outcompete other species on nutrient-poor, mineral-rich substrates, typical of recently glaciated regions on the Canadian Shield (Morris and MacDonald 1991). If organic matter or nutrients increased at Anderson Pond, jack pine would lose its competitive advantage, and other taxa, such as oaks, could displace it (Farmer et al. 1988). Delcourt (1979) attributed the appearance of sugar maple and beech in the Anderson Pond pollen record around 13,000 ^{14}C yr BP (15,550 cal yr BP) to either their migration into the region, or to the availability of the mull humus soil they require, at this time. Whether the development of this mull humus contributed to the decline of jack pine or occurred after the decline is unknown. Lafleur et al. (2015) demonstrated that soil organic accumulation hinders seed germination, suckering, and growth of trembling aspen (*Populus tremuloides)* in boreal forests, but whether jack pine would be harmed by organic accumulation or whether such accumulation could occur with jack pine present is uncertain.

The change in the fire regime at Anderson Pond around 15,000 cal yr BP observed in our charcoal record is strongly associated with the decline of jack pine and spruce, suggesting that the reduction in fire at Anderson Pond was driven by this change in vegetation. Although climate may have influenced these shifts in forest composition, patterns of burning during the late glacial and early Holocene did not follow the pattern identified by Daniau et al. (2012) from a global synthesis of charcoal records of increased fire with climate warming. Rather, at Anderson Pond, fire activity decreased from the late glacial into the Holocene as climate warmed because northern pines and spruces that are adapted to fire and whose flammable needles can promote fire were replaced by deciduous taxa less strongly associated with fire.

The marked increase in populations of hornbeam/hophornbeam (*Ostrya* and *Carpinus*) at the site following the decline of pine and spruce around 15,000 cal yr BP also indicates low fire activity, as both taxa are fire intolerant (Delcourt and Delcourt 1994). Delcourt (1979) interpreted their importance at Anderson Pond from the late glacial period to the early Holocene to indicate a mesic climate similar to that of the modern Allegheny Plateau region of Ohio and West Virginia. Conditions would have been warmer than the climate during the dominance of pine and spruce, but still cool in comparison with the early Holocene.

Renewed fire activity at Anderson Pond during the middle Holocene appears associated with warmer and drier climates during the Mid-Holocene Warm Period (MHWP). The increased fire activity during the MHWP at Anderson Pond matches an increase in *Alnus* and *Cephalanthus*, both wetland taxa. The pollen record of Delcourt (1979) shows that the interior of the Anderson Pond basin became a shrub swamp beginning around 9600 cal yr BP and remained so through the MHWP. The desiccation of ponds results in oxidizing sedimentary environments unfavorable for pollen preservation (Delcourt and Delcourt 1980). From the increase in indeterminate pollen (they used the term ‘indeterminable’), Delcourt and Delcourt (1980) inferred lowered water levels during the MHWP at Anderson Pond. They also noted reduced influx of plant macrofossils during this period, and inferred unfavorable conditions for deposition and preservation, namely desiccation.

The shallowing of Anderson Pond at this time was likely driven by climate but was also a consequence of natural infilling over time. Paleoclimate datasets from other sites in Tennessee (Driese et al. 2008, Driese et al. In Press) and the Great Plains and Rocky Mountains (Dean et al. 1996) suggest dry climate during the MHWP. Recently, Tanner et al. (2014) recovered sediment cores from a wetland in Panthertown Valley, North Carolina, that span the last ca. 9000 years. Their analyses of $\delta^{13}C$ isotopes, pollen, n-alkane biomarkers, and bulk sedimentary C/N ratios revealed warm, dry mid-Holocene conditions. On a larger scale, much of the Northern Hemisphere was apparently dry during the middle Holocene (Mayewski et al. 2004). A drier climate during the MHWP may have been an important factor in the increase in fire activity at Anderson Pond during this interval. Charcoal area concentration values diminish from around 5000 cal yr BP to present (1976, time of coring), indicating a reduction in fire activity probably due to amelioration of climate at Anderson Pond.

2.7.3 Humans as a Possible Source of Fires at Anderson Pond

Fire use by Native populations in temperate eastern North America has been documented historically (Patterson and Sassaman 1988, Brown 2000, Pyne 2000, Williams 2000). Native Americans are considered to have been a primary source of ignition in pre-settlement eastern oak-hickory forests (Abrams 1992, Delcourt and Delcourt 1998). They used fire to clear undergrowth from oak stands to facilitate acorn harvesting and to attract game (Abrams and Nowacki 2008). Anderson et al. (2011) used stone tool evidence to infer population fluctuations in the United States before, during, and after the Younger Dryas stadial. There were several quarries in Kentucky, Tennessee, and South Carolina, suggesting the possibility of human presence at Anderson Pond during the late glacial and early Holocene.

During the MHWP, indigenous populations were actively using plant resources and fire in the Little Tennessee River watershed in eastern Tennessee as evidenced by paleoethnobotanical studies of charred wood, fruit and seed assemblages (Chapman et al. 1982). Ethnobotanical remains have also been found in rock shelters in the Cumberland Plateau of Tennessee and Kentucky (Delcourt et al. 1997, Franklin et al. 2010). Shell middens west of the Appalachian mountains provide additional evidence of human occupation of the southeastern U.S.A. (Gremillion 1996). The archaeological evidence of human presence in Tennessee and surrounding areas during the middle Holocene suggests a possible anthropogenic origin for fires during the MHWP interval of the Anderson Pond charcoal record, when deciduous forest vegetation dominated the surrounding area. Drier climate during the middle Holocene could have facilitated the spread of fires set by people and may have increased the opportunity for lightning to ignite fires. Lightning-set fires are rare today in the southern Appalachians (Harmon 1982, Bratton and Meier 1995, Delcourt and Delcourt 1997), owing to high precipitation. However, lighting strikes do occasionally ignite fires, especially on drier slopes and ridgetops (Delcourt and Delcourt 1997, Whiteman 2000, Lafon et al. 2005, Mitchener and Parker 2005).

Lightning may be a more likely a source of ignition than human-set fires during the boreal forest interval at Anderson Pond (23,000–15,000 cal yr BP), though human-set fires cannot be ruled out. Lightning strikes are recognized as a source of ignition in the boreal forests today (Nash and Johnson 1996), especially during drought intervals.

2.8 Conclusions

Microscopic charcoal stratigraphy—in particular, changing charcoal to pollen ratios—revealed that fire activity at Anderson Pond, central Tennessee, was high from the LGM to ca. 15,000 cal yr BP, when spruce and pine pollen were abundant and jack pine was the dominant species (Delcourt 1979). The sharp reduction in fire activity at ca. 15,000 cal yr BP matches the steep decline in pine pollen percentages, marked reduction in spruce and fir pollen percentages, and an increase in pollen of the fire-intolerant taxa, *Ostrya/Carpinus*. Fire activity remained low from ca. 15,000 to 8200 cal yr BP, during which time oak rose to dominance. Fire activity from the LGM to ca. 15,000 cal yr BP was linked to the presence of conifers, particularly jack pine. The disappearance of jack pine and other conifers signals the end of the high fire activity that characterized this interval. In Alaska, coniferous vegetation is interpreted to have been the driver of past fire (Brubaker et al. 2009, Higuera et al. 2009), and this also seems to be the case for Anderson Pond from the LGM to about 15,000 cal yr BP. During this period, fire activity at Anderson Pond does not follow expectations based on the global charcoal synthesis by Daniau et al. (2012), in which fire was associated with warmer temperatures.

Highest fire activity as indicated by charcoal area concentrations occurred during the Mid-Holocene Warm Period (8200–5000 cal yr BP). A warmer, drier climate with periodic desiccation is indicated by abundant pollen of woody wetland taxa such as buttonbush and alder, and increased indeterminate pollen. With microscopic charcoal to pollen ratios in excess of 4000 μm^2/pollen grains for most of the period from the LGM to ca. 11,200 cal yr BP, and exceeding 1000 μm^2/pollen grains for the interval 8200–444 cal yr BP (excepting the 5562 cal yr BP level), fires must have burned within the watershed, or in the wetland itself during exceptionally dry episodes (Patterson et al. 2005) during the MHWP. Fires in the middle Holocene may have been anthropogenic in origin, or fires may have been set by lightning during droughts. Regardless of ignition source, the higher fire activity during the MHWP is consistent with the findings of Daniau et al. (2012) that fires increase during periods of warmer climate. Declining charcoal area concentration values after ca. 5000 cal yr BP may signal reduced human presence at the site, and/or moister conditions.

Anderson Pond had the highest charcoal area concentrations for both the time of boreal forest and the time of hardwood forest compared with microscopic charcoal records from seven other sites. Key Deer Pond exceeded Anderson Pond for charcoal:pollen ratios for the boreal portion of the record, although values were the same order of magnitude. Anderson Pond had the highest charcoal:pollen ratio for the MHWP hardwood interval. Differences in charcoal indices for the sites with lowest charcoal indices may relate to differences in pollen processing methods. Variations between Anderson Pond and the other sites may be attributed to local and regional wind patterns and basin characteristics.

2.9 Acknowledgements

This project was possible because of the original work on Anderson Pond by Hazel and Paul Delcourt in the 1970s. We thank Scott Meeks for facilitating access to the original Anderson Pond pollen slides and notes. We also thank Steven G. Driese, Chad S. Lane, Yingkui Li, Henri Grissino-Mayer, Roger Horn, Mathew Boehm, Karoline Mikolajewski, Dave Morris, Timothy A. Price, and Thomas Waldrop for helpful discussion or manuscript review. The work of the data contributors and the Neotoma community is gratefully acknowledged (Neotoma Paleoecology Database http://www.neotomadb.org). This research was supported by the National Science Foundation under Grant EAR-0822824 to Zheng-Hua Li and Sally Horn.

2.10 References

Abrams, M.D. 1992. Fire and the development of oak forests. *BioScience* 42(5): 346–353.

Abrams, M.D.; Nowacki, G.J. 2008. Native Americans as active and passive promoters of mast and fruit trees in the eastern U.S.A. *The Holocene* 18(7): 1123–1137.

Agee, J.K. 1998. Fire and pine ecosystems. *In: Ecology and Biogeography of Pinus* (Ed.: Richardson, D.M.), Cambridge University Press, New York, pp. 193–218.

Alaska Fire Service 2015. Alaska Interagency Coordination Center, Incident Information on Alaska fires. [http://fire.ak.blm.gov/incinfo/aklgfire.php Accessed June 2015]

Albritton, J. 2009. *A 1700-Year History of Fire and Vegetation in Pine Rocklands of National Key Deer Refuge, Big Pine Key, Florida: Charcoal and Pollen Evidence from Key Deer Pond.* M.S. Thesis, University of Tennessee.

Anderson, B.; Herz, N.; Hollander, Z. 2015. *Unpredictable Alaska wildfire keeps crews guessing as disaster is declared.* Alaska Dispatch News, June 15, 2015. https://www.adn.com/article/20150615/unpredictable-alaska-wildfire-keeps-crews-guessing-disaster-declared [Accessed June 16, 2015]

Anderson, D.G.; Goodyear, A.C.; Kennett, J., West, A. 2011. Multiple lines of evidence for possible human population decline/settlement reorganization during the early Younger Dryas. *Quaternary International* 242(2): 570–583.

Ballard, J.P. 2009. *A Lateglacial Paleofire Record for East-Central Michigan*. M.S. Thesis, University of Cincinnati.

Blum, B.M. 1990. *Picea rubens* Sarg., red spruce. *In*: *Silvics of North America*, Volume 1, Conifers. Agricultural Handbook 645 (Technical Coordinators: Burns, R.M.; Honkala, B.H.), U.S.D.A. Forest Service, Washington, D.C, pp. 250–259. http://www.na.fs.fed.us/pubs/silvics_manual/Volume_1/picea/rubens.htm [Accessed: July 5, 2015].

Boehm, M.S. 2012. *Late Pleistocene Climate, Vegetation, and Fire History from a Southern Appalachian Bog, Whiteoak Bottoms, Nantahala National Forest, North Carolina, U.S.A* M.S. Thesis, University of Tennessee.

Bratton, S.P.; Meier, A.J. 1995. The natural disturbance history of the Chattooga watershed: written records. United States Forest Service, Chattooga River Demonstration Project, Clemson, South Carolina.

Braun, E.L. 1950. *Deciduous Forests of Eastern North America*. Blakiston, Philadelphia.

Broecker, W.S.; Denton, G.H.; Edwards, R.L.; Cheng, H.; Alley, R.B.; Putnam, A.E. 2010. Putting the Younger Dryas cold event into context. *Quaternary Science Reviews* 29(9): 1078–1081.

Brown, H. 2000. Wildland burning by American Indians in Virginia. *Fire Management Today* 60(3): 29–39.

Brubaker, L.B.; Higuera, P.E.; Rupp, T.S.; Olson, M.A.; Anderson, P.M.; Hu, F.S. 2009. Linking sediment-charcoal records and ecological modeling to understand causes of fire-regime change in boreal forests. *Ecology* 90(7): 1788–1801.

Bush, M.B.; Silman, M.R.; de Toledo, M.B.; Listopad, C.; Gosling, W.D.; Williams, C.; de Oliveira, P.E.; Krisel, C. 2007. Holocene fire and occupation in Amazonia: records from two lake districts. *Philosophical Transactions of the Royal Society* B 362: 209–218.

Carcaillet, C.; Bouvier, M.; Fréchette, B.; Larouche, A.C.; Richard, P.J.H. 2001. Comparison of pollen-slide and sieving methods in lacustrine charcoal analyses for local and regional fire history. *The Holocene* 11(4): 467–476.

Carcaillet, C.; Richard, P.J.H. 2000. Holocene changes in seasonal precipitation highlighted by fire incidence in eastern Canada. *Climate Dynamics* 16(7): 549–559.

Carey, J.H. 1993. *Pinus banksiana. In: Fire Effects Information System* [Online]. U.S.D.A. Forest Service, Rocky Mountain Research Station, Fire Sciences Laboratory. http://www.fs.fed.us/database/feis/plants/tree/pinban/all.html [Accessed: January 6, 2015].

Carey, J.H. 1992a. *Pinus elliottii. In: Fire Effects Information System* [Online]. U.S.D.A. Forest Service, Rocky Mountain Research Station, Fire Sciences Laboratory. http://www.fs.fed.us/database/feis/plants/tree/pinell/all.html [Accessed: February 28, 2015].

Carey, J.H.1992b. *Pinus palustris. In: Fire Effects Information System* [Online]. U.S.D.A. Forest Service, Rocky Mountain Research Station, Fire Sciences Laboratory. http://www.fs.fed.us/database/feis/plants/tree/pinpal/all.html [Accessed: February 28, 2015].

Chapman, J.; Delcourt, P.A.; Cridelbaugh, P.A.; Shea, A.B.; Delcourt, H.R. 1982. Man-land interaction: 10,000 years of American Indian impact on Native ecosystems in the Lower Little Tennessee River Valley, eastern Tennessee. *Southeastern Archaeology* 1(2): 115–121.

Clark, R.L. 1982. Point count estimation of charcoal in pollen preparations and thin sections of sediments. *Pollen et Spores* 24(3–4): 523–535.

Clark, R.L. 1984. Effects on charcoal of pollen preparation procedures. *Pollen et Spores* 26: 559–576.

Clement, R.M.; Horn, S.P. 2001. Pre-Columbian land-use history in Costa Rica: a 3000-year record of forest clearance, agriculture and fires from Laguna Zoncho. *The Holocene* 11(4): 419–426.

Daniau, A.-L.; Bartlein, P.J.; Harrison, S.P.; Prentice, I.C.; Brewer, S.; Friedlingstein, P.; Harrison-Prentice, T.I.; Inoue, J.; Izumi, K.; Marlon, J.R.; Mooney, S.; Power, M.J.; Stevenson, J.; Tinner, W.; Andrič, M.; Atanassova, J.; Behling, H.; Black, M.; Blarquez, O.; Brown, K.J.; Carcaillet, C.; Colhoun, E.A.; Colombaroli, D.; Davis, B.A.S.; D'Costa, D.; Dodson, J.; Dupont, L.; Eshetu, Z.; Gavin, D.G.; Genries, A.; Haberle, S.; Hallett, D.J.; Hope, G.; Horn, S.P.; Kassa, T.G.; Katamura, F.; Kennedy, L.M.; Kershaw, P.; Krivonogov, S.; Long, C.; Magri, D.; Marinova, E.; McKenzie, G.M.; Moreno, P.I.; Moss, P.; Neumann, F.H.; Norström, E.; Paitre, C.; Rius, D.; Roberts, N.; Robinson, G.S.; Sasaki, N.; Scott, L.; Takahara, H.; Terwilliger, V.; Thevenon, F.; Turner, R.; Valsecchi, V.G.; Vannière, B.; Walsh, M.; Williams, N.; Zhang, Y. 2012. Predictability of biomass burning in response to climate changes. *Global Biogeochemical Cycles* 26(GB4007): 1–12.

Dean, W.E.; Ahlbrandt, T.S.; Anderson, R.Y.; Bradbury, J.P. 1996. Regional aridity in North America during the middle Holocene. *The Holocene* 6(2): 145–155.

Delcourt, H.R. 1979. Late Quaternary vegetation history of the Eastern Highland Rim and adjacent Cumberland Plateau of Tennessee. *Ecological Monographs* 49(3): 255–280.

Delcourt, H.R. 1978. *Late Quaternary Vegetation History of the Eastern Highland Rim and Adjacent Cumberland Plateau of Tennessee.* Ph.D. Dissertation, University of Minnesota.

Delcourt, H.R.; Delcourt, P.A.; Spiker, E.C. 1983. A 12,000-year record of forest history from Cahaba Pond, St. Clair County, Alabama. *Ecology* 64(4): 874–887.

Delcourt, H.R.; Delcourt, P.A. 1994. Postglacial rise and decline of *Ostrya virginiana* (Mill.) K. Koch and *Carpinus caroliniana* Walt. in eastern North America: predictable responses of forest species to cyclic changes in seasonality of climates. *Journal of Biogeography* 21(2): 137–150.

Delcourt, H.R.; Delcourt, P.A. 1997. Pre-Columbian Native American use of fire on southern Appalachian landscapes. *Conservation Biology* 11(4): 1010–1014.

Delcourt, P.A.; Delcourt, H.R. 1980. Pollen preservation and Quaternary environmental history in the southeastern United States. *Palynology* 4(1): 215–231.

Delcourt, P.A.; Delcourt, H.R. 1998. The influence of prehistoric human-set fires on oak-chestnut forests in the southern Appalachians. *Castanea* 63(3): 337–345.

Dey, D. 2002. The ecological basis for oak silviculture in eastern North America. *In: Oak Forest Ecosystems: Ecology and Management for Wildlife,* (Eds.: McShea, W.J.; Healy, W.M.). Johns Hopkins University Press, Baltimore, pp 60–79.

Dorale, J.A.; Wozniak, L.A.; Bettis III, E.A.; Carpenter, S.J.; Mandel, R.D.; Hajic, E.R.; Lopinot, N.H.; Ray, J.H. 2010. Isotopic evidence for Younger Dryas aridity in the North American midcontinent. *Geology* 38(6): 519–522.

Driese, S.G.; Li, Z.-H.; McKay, L.D. 2008. Evidence for multiple, episodic, mid-Holocene Hypsithermal recorded in two soil profiles along an alluvial floodplain catena, southeastern Tennessee, USA. *Quaternary Research* 69(2): 276–291.

Driese, S.G.; Li, Z.-H.; Cheng, H.; Harvill, J.L.; Sims, J. In press. High-resolution rainfall records for middle and late Holocene based on speleothem annual UV fluorescent layers integrated with stable isotopes and U/Th dating, Raccoon Mountain Cave, Tennessee, U.S.A. *In: Caves and Karst Across Time,* Geological Society of America Special Paper Volume. (Eds.: Feinberg, J.; Gao, Y.; Alexander Jr., E.C.), Boulder, Colorado, p. 1-37.

Dyke, A.S. 2004. An outline of North American deglaciation with emphasis on central and northern Canada. *In: Quaternary Glaciations: Extent and Chronology*. Volume 2 (Eds.: Ehlers, J.; Gibbard, P.L.; Hughes, P.D.), Elsevier, Amsterdam, pp. 373–424.

Farmer, R.E.; Morris, D.M.; Weaver, K.B.; Garlick, K. 1988. Competition effects in juvenile jack pine and aspen as influenced by density and species ratios. *Journal of Applied Ecology* 25(3): 1023–1032.

Fauria, M.M.; Johnson, E.A. 2008. Climate and wildfires in the North American boreal forest. *Philosophical Transactions of the Royal Society B* 363: 2317–2329.

Fiedel, S.J. 2011. The mysterious onset of the Younger Dryas. *Quaternary International* 242(2): 262–266.

Firestone, R.B.; West, A.; Kennett, J.P.; Becker, L.; Bunch, T.E.; Revay, Z.S.; Schultz, P.H.; Belgya, T.; Kennett, D.J.; Erlandson, J.M.; Dickenson, O.J.; Goodyear, A.C.; Harris, R.S.; Howard, G.A.; Kloosterman, J.B.; Lechler, P.; Mayewski, P.A.; Montgomery, J.; Poreda, R.; Darrah, T.; Hee, S.S.; Smith, A.R.; Stich, A.; Topping, W.; Wittke, J.H.; Wolbach, W.S. 2007. Evidence for an extraterrestrial impact 12,900 years ago that contributed to the megafaunal extinctions and the Younger Dryas cooling. *Proceedings of the National Academy of Sciences of the United States of America* 104(41): 16016–16021.

Flower, B.P.; Williams, C.; Hill, H.W.; Hastings, D.W. 2011. Laurentide Ice Sheet meltwater and the Atlantic meridional overturning circulation during the last glacial cycle: a view from the Gulf of Mexico. *In*: *Abrupt Climate Change: Mechanisms, Patterns, and Impacts* (Eds.: Rashid, H.; Polyak, L.; Mosley-Thompson, E.), American Geophysical Union, Washington, D.C., pp. 39–56.

Franklin, J.D.; Walker, R.; Hays, M.A.; Beck, C.W. 2010. Late Archaic site use at Sachsen Cave Shelter, Upper Cumberland Plateau, Tennessee. *North American Archaeologist* 31(3–4): 447–479.

Frissell Jr., S.S. 1973. The importance of fire as a natural ecological factor in Itasca State Park, Minnesota. *Quaternary Research* 3(3): 397–407.

Fryer, J.L. 2014. *Picea mariana. In: Fire Effects Information System* [Online]. U.S.D.A. Forest Service, Rocky Mountain Research Station, Fire Sciences Laboratory (Producer). http://www.fs.fed.us/database/feis/plants/tree/picmar/all.html [Accessed April 25, 2015].

Garman, R.K.; Taylor, L.C. 1971. Geologic map and mineral resources summary of the Dry Valley 7.5 minute Quadrangle, Tennessee, GM 331-SW. Tennessee Department of Conservation, Division of Geology, Nashville, Tennessee, U.S.A.

Gill, J.L.; Williams, J.W.; Jackson, S.T.; Donnelly, J.P.; Schellinger, G.C. 2012. Climatic and megaherbivory controls on late-glacial vegetation dynamics: a new, high-resolution, multi-proxy record from Silver Lake, Ohio. *Quaternary Science Reviews* 34: 66–80.

Gill, J.L.; Williams, J.W.; Jackson, S.T.; Lininger, K.B.; Robinson, G.S. 2009. Pleistocene megafaunal collapse, novel plant communities, and enhanced fire regimes in North America. *Science* 326: 1100–1103.

Goman, M.; Leigh, D.S. 2004. Wet early to middle Holocene conditions on the upper coastal plain of North Carolina, U.S.A. *Quaternary Research* 61(3): 256–264.

Gremillion, K.J. 1996. The paleoethnobotanical record for the mid-Holocene Southeast. *In: Archaeology of the Mid-Holocene Southeast* (Eds.: Sassaman, K.E.; Anderson, D.G.), University Press of Florida, Gainesville, pp. 99–114.

Grimm, E.C.; Watts, W.A.; Jacobson Jr., G.L.; Hansen, B.C.S.; Almquist, H.R.; Dieffenbacher-Krall, A.C. 2006. Evidence for warm wet Heinrich events in Florida. *Quaternary Science Reviews* 25(17): 2197–2211.

Harley, G.L.; Grissino-Mayer, H.D.; Horn, S.P. 2013. Fire history and forest structure of an endangered subtropical ecosystem in the Florida Keys, USA. *International Journal of Wildland Fire* 22: 394–404

Harmon, M.E. 1982. Fire history of the westernmost portion of the Great Smoky Mountains National Park. *Bulletin of the Torrey Botanical Club* 109: 74–79.

Heyerdahl, E.K.; Card, V. 2000. Implications of paleorecords for ecosystem management. *Trends in Ecology and Evolution* 15(2): 49–50.

Higuera, P.E.; Brubaker, L.B.; Anderson, P.M.; Hu, F.S.; Brown, T.A. 2009. Vegetation mediated the impacts of postglacial climate change on fire regimes in the south-central Brooks Range, Alaska. *Ecological Monographs* 79(2): 201–219.

Horn, S.P. 1993. Postglacial vegetation and fire history in the Chirripó Páramo of Costa Rica. *Quaternary Research* 40: 107–116.

Hu, F.S.; Brubaker, L.B.; Gavin, D.G.; Higuera, P.E.; Lynch, J.A.; Rupp, T.S.; Tinner, W. 2006. How climate and vegetation influence the fire regime of the Alaskan boreal biome: the Holocene perspective. *Mitigation and Adaptation Strategies for Global Change* 11(4): 829–846.

Hupy, C.M.; Yansa, C.H. 2009. The vegetation history of Michigan: the last 17,000 years. *In Michigan: A Geography* (Eds.: Schaetzl, R.S.; Darden, J.; Brandt, D.), Thomson Publishing, Washington D.C., pp. 91–105.

Hussey, T.C. 1993. *A 20,000 Year Record of Vegetation and Climate at Clear Pond, Northeastern South Carolina.* M.S. Thesis, University of Maine.

Juggins. S. 2010. C2 Version 1.5 User guide. Software for ecological and palaeoecological data analysis and visualisation. Newcastle University, Newcastle upon Tyne, the United Kingdom.

Komarek, E.V. 1974. Effects of fire on temperate forests and related ecosystems: southeastern United States. *In: Fire and Ecosystems* (Eds.: Kozlowski, T.T.; Ahlgren, C.E.), Academic Press, San Diego, pp. 251–277.

Lafleur, B.; Cazal, A.; Leduc, A.; Bergeron, Y. 2015. Soil organic layer thickness influences the establishment and growth of trembling aspen (*Populus tremuloides*) in boreal forests. *Forest Ecology and Management* 347: 209–216.

Lafon, C.W.; Hoss, J.A.; Grissino-Mayer, H.D. 2005. The contemporary fire regime of the central Appalachian Mountains and its relation to climate. *Physical Geography* 26(2): 126–146.

LaMoreaux, H.K.; Brook, G.A.; Knox, J.A. 2009. Late Pleistocene and Holocene environments of the southeastern United States from the stratigraphy and pollen content of a peat deposit on the Georgia coastal plain. *Palaeogeography, Palaeoclimatology, Palaeoecology* 280(3): 300–312.

Liu, Y.; Andersen, J.J.; Williams, J.W.; Jackson, S.T. 2013. Vegetation history in central Kentucky and Tennessee (U.S.A.) during the last glacial and deglacial periods. *Quaternary Research* 79(2): 189–198.

Maenza-Gmelch, T.E. 1997. Holocene vegetation, climate, and fire history of the Hudson Highlands, southeastern New York, U.S.A. *The Holocene* 7(1): 25–37.

Marlon, J.R.; Bartlein, P.J.; Daniau, A.-L.; Harrison, S.P.; Maezumi, S.Y.; Power, M.J.; Tinner, W.; Vanniére, B. 2013. Global biomass burning: a synthesis and review of Holocene paleofire records and their controls. *Quaternary Science Reviews* 65: 5–25.

Marlon, J.R.; Bartlein, P.J.; Walsh, M.K.; Harrison, S.P.; Brown, K.J.; Edwards,, M.E. ; Higuera, P.E.; Power, M.J.; Anderson, R.S.; Briles, C.; Brunelle, A.; Carcaillet, C.; Daniels, M.; Hu, F.S.; Lavoie, M.; Long, C.; Minckley, T.; Richard, P.J.H.; Scott, A.C.; Shafer, D.S.; Tinner, W.; Umbanhowar Jr., C.E.; Whitlock, C. 2009. Wildfire responses to abrupt climate change in North America. *Proceedings of the National Academy of the Sciences of the United States of America* 106(8): 2519–2524.

Matlack, G.R. 2013. Reassessment of the use of fire as a management tool in deciduous forests of eastern North America. *Conservation Biology* 27(5): 916–926.

Mayewski, P.A.; Rohling, E.E.; Stager, J.C.; Karlén,W.; Maasch, K.A.; Meeker, L.D.; Meyerson, E.A.; Gasse, F.; van Kreveld, S.; Holmgren, K.; Lee-Thorp, J.; Rosqvist, G.; Rack, F.; Staubwasser, M.; Schneider, R.R.; Steig, E.J. 2004. Holocene climate variability. *Quaternary Research* 62(3): 243–255.

Mitchener, L.J.; Parker, A.J. 2005. Climate, lightning, and wildfire in the national forests of the southeastern United States: 1989-1998. *Physical Geography* 26(2): 147–162.

Morris, D.M.; MacDonald, G.B. 1991. Development of a competition index for young conifer plantations established on boreal mixedwood sites. *The Forestry Chronicle* 67(4): 403–410.

Nash, C.H.; Johnson, E.A. 1996. Synoptic climate of lightning caused forest fires in the subalpine and boreal forests. *Canadian Journal of Forest Research* 26: 1859–1874.

Nienstaedt, H.; Zasada, J.C. 1990. *Picea glauca* (Moench) Voss, white spruce. *In: Silvics of North America*, Volume 1, Conifers. Agricultural Handbook 645 (Technical Coordinators: Burns, R.M.; Honkala, B.H.), U.S.D.A. Forest Service, Washington, D.C., pp. 204–226. http://www.na.fs.fed.us/pubs/silvics_manual/Volume_1/picea/glauca.htm [Accessed: July 5, 2015].

Nordt, L.C.; Boutton, T.W.; Jacob, J.S.; Mandel, R.D. 2002. C4 plant productivity and climate-CO_2 variations in south-central Texas during the late Quaternary. *Quaternary Research* 58(2): 182–188.

Olson, D.L.; Cronan, J.B.; McKenzie, D.; Barnes, J.L.; Camp, A.E. 2011. *Compiling, Synthesizing, and Analyzing Existing Boreal Forest Fire History Data in Alaska.* Final Report to the Joint Fire Science Program, Project #06–3–1–26. http://www.firescience.gov/projects/06-3-1-26/project/06-3-1-26_final_report.pdf

Patterson III, W.A.; Backman, A.E. 1988. Fire and disease history of forests. *In*: *Vegetation History*, *Handbook of Vegetation Science,* Volume 7 (Eds.: Huntley, T.; Webb III, T.), Kluwer Academic Publishers, Dordrecht, The Netherlands, pp. 603–632.

Patterson III, W.A.; Edwards, K.J.; Maguire, D.J. 1987. Microscopic charcoal as a fossil indicator of fire. *Quaternary Science Reviews* 6(1): 3–23.

Patterson III, W.A.; Richburg, J.A.; Clark, K.H.; Shaw, S. 2005. Paleoecology of Calf Island in Boston's Outer Harbor. *Northeastern Naturalist* 12(sp3): 31–48.

Patterson III, W.A.; Sassaman, K.E. 1988. Indian fires in the prehistory of New England. *In: Holocene Human Ecology in Northeastern North America* (Ed.: Nicholas, G.P.), Plenum Press, New York, pp. 107–135.

Peteet, D. 1995. Global Younger Dryas? *Quaternary International* 28: 93–104.

Power, M.J.; Marlon, J.R.; Bartlein, P.J.; Harrison, S.P. 2010. Fire history and the global charcoal database: a new tool for hypothesis testing and data exploration. *Palaeogeography, Palaeoclimatology, Palaeoecology* 291(1): 52–59.

Pyne, S.J. 2000. Where have all the fires gone? *Fire Management Today* 60(3): 4–6.

Reimer, P.J.; Bard, E.; Bayliss, A.; Beck, J.W.; Blackwell, P.G.; Ramsey, C.B.; Buck, C.E.; Cheng, H.; Edwards, R.L.; Friedrich, M.; Grootes, P.M.; Guilderson, T.P.; Haflidason, H.; Hajdas, I.; Hatté, C.; Heaton, T.J.; Hoffmann, D.L.; Hogg, A.G.; Hughen, K.A.; Kaiser, K.F.; Kromer, B.; Manning, S.W.; Niu, M.; Reimer, R.W.; Richards, D.A.; Scott, E.M.; Southon, J.R.; Staff, R.A.; Turney, C.S.M.; van der Plicht, J. 2013. INTCAL13 and MARINE13 Radiocarbon age calibration curves 0–50,000 years cal BP. *Radiocarbon* 55(4): 1869–1887.

Reimer, P.J.; Brown, T.A.; Reimer, R.W. 2004. Discussion: reporting and calibration of post-bomb ^{14}C data. *Radiocarbon* 46(3): 1299–1304.

Robinson, G.S.; Burney, L.P.; Burney, D.A. 2005. Landscape paleoecology and megafaunal extinction in southeastern New York State. *Ecological Monographs* 75(3): 295–315.

Swain, A.M. 1973. A history of fire and vegetation in northeastern Minnesota as recorded in lake sediments. *Quaternary Research* 3(3): 383–396.

Stuiver, M.; Reimer, P.J. 1993. Extended ^{14}C database and revised CALIB radiocarbon calibration program. *Radiocarbon* 35(1): 215–230.

Tanner, B.R.; Lane, C.S.; Martin, E.M.; Young, R.; Collins, B. 2014. Sedimentary proxy evidence of a mid-Holocene hypsithermal event in the location of a current warming hole, North Carolina, USA. *Quaternary Research* 83(2): 315–323.

Taylor, B.E.; Rich, F.J.; Brooks, M.J.; Ivester, A.H.; Clement, C.O. 2011. Late Pleistocene and Holocene vegetation changes in the Sandhills, Fort Jackson, South Carolina. *Southeastern Geology* 48(3): 147–163.

Telford, R.J.; Heegaard, E.; Birks, H.J.B. 2004. The intercept is a poor estimate of a calibrated radiocarbon age. *The Holocene* 14(2): 296–298.

Tinner, W.; F.S. Hu. 2001. Responses of fire and vegetation to Little-Ice-Age climatic change in boreal Alaska. *Abstract from The Ecological Society of America 86th Annual Meeting,* August 5–10, 2001, Madison, Wisconsin. Ecological Society of America, Washington, D.C., p. 221.

Tinner, W.; Hu, F.S.; Beer, R.; Kaltenrieder, P.; Scheurer, B.; Krahenbuhl, U. 2006. Postglacial vegetational and fire history: pollen, plant macrofossil, and charcoal records from two Alaskan lakes. *Vegetation History and Archaeobotany* 15(4): 279–293.

Webb III, T. 1988. Glacial and Holocene vegetation history: eastern North America. *In: Vegetation History* (Eds.: Huntley, B.; Webb III, T.), Kluwer Academic Press, Dordrecht, The Netherlands, pp. 385–414.

Western Regional Climate Center 2014. *Sparta, Tennessee (408522) 1981–2010 Monthly Climate Summary*, NCDC 1981-2010 Monthly Normals, http://www.wrcc.dri.edu/cgi-bin/cliMAIN.pl?tn8522 [Accessed 6 December 2014]

Whiteman, C.D. 2000. *Mountain Meteorology: Fundamentals and Applications*. Oxford University Press, New York.

Whitlock, C.; Larsen, C. 2001. Charcoal as a fire proxy. *In: Tracking Environmental Change Using Lake Sediments,* Volume 3 (Eds.: Smol, J.P.; Birks, H.J.B.; Last, W.M.; Bradley, R.S.; Alverson, K.), Kluwer Academic Publishers, Dordrecht, The Netherlands, pp. 75–97.

Whitlock, C.; Moreno, P.I.; Bartlein, P. 2007. Climatic controls of Holocene fire patterns in southern South America. *Quaternary Research* 68(1): 28–36.

Williams, G.W. 2000. Introduction to aboriginal fire use in North America. *Fire Management Today* 60(3): 8–12.

Williams, J.W.; Shuman, B.N.; Webb III, T.; Bartlein, P.J.; Leduc, P.L. 2004. Late-Quaternary vegetation dynamics in North America: scaling from taxa to biomes. *Ecological Monographs* 74(2): 309–334.

Chapter 2 Appendix

Table 2.1 Radiocarbon dates and calibrations for Anderson Pond 1976B (AP-76B) sediment core. Sample depths and uncalibrated ^{14}C ages are from Delcourt (1979).

Lab Number[a]	Core interval (cm)	Depth in profile midpoint (cm)	Depth below mud/water interface midpoint (cm)	Material Dated	Uncalibrated ^{14}C age (^{14}C yr BP)	Calibrated Age yr BP (2-sigma) [b]	Relative Area Under Calibration Curve	Weighted Mean Calibration Age cal yr BP [c]
		25	0		1976 coring			–26
A-1820[d]	59–65	63	38	bulk sediment	–10 ±100	–6 to –2 –1 to 0 152 to 6 280 to 170	0.017 0.001 0.633 0.348	133
A-1821	103.5–108.5	106	81	bulk sediment	5610 ± 110	6659–6204	1.0	6415
A-1869	123.5–128.5	126	101	bulk sediment	8930 ± 160	10,304–9552 10,393–10,312	0.964675 0.035325	9994
A-1870	144–156	150	125	bulk sediment	12,540 ± 180	15,334–14,083	1.0	14,733
A-1871	203–217	210	185	bulk sediment	12,750 ± 220	15,819–14,223	1.0	15,092
A-1872	308–321	314.5	289.5	bulk sediment	15,310 ± 420	19,530–17,604	1.0	18,548
A-1822	421–435	428	403	bulk sediment	16,230 ± 300	20,296–18,881	1.0	19,583
A-1873	595–607	601	576	bulk sediment	18,300 ± 1300	25,133–19,033	1.0	22,051
A-1823	687–700	693.5	668.5	bulk sediment	18,760 ± 320	23,419–21,914	1.0	22,661
A-1874	966–981	973.5	948.5	bulk sediment	25,000 ± 3000	34,997–22,677	1.0	29,026

[a] Analyses were performed by the University of Arizona Laboratory of Geochronology, Tucson.

[b] ^{14}C ages were calibrated using the CALIB 7.0.2 computer program (Stuiver and Reimer, 1993) and the dataset of Reimer et al. (2013).

[c] Weighted mean of the 2 σ calibrated radiocarbon probability distribution

[d] This date was calibrated with CALIBomb.

Tables 2.2 a–d Comparisons of Anderson Pond microscopic charcoal indices with other studies of microscopic charcoal. Summary of maximum, minimum, and mean values, where available.

Table 2.2a Charcoal area concentrations for hardwood intervals of pollen and charcoal records.

Charcoal Area Concentrations: comparison of hardwood intervals in records			
Site	Anderson Pond, Tennessee (11,200 cal yr BP to modern part of core, hardwood dominated)	Whiteoak Bottoms North Carolina (14,500–12,600 cal yr BP interval dominated by *Alnus*, *Quercus*, *Betula*, and Cyperaceae)	Binnewater Pond, southeastern New York State (past 10,000 cal yrs of record dominated by *Quercus*)
Ref.	This study	Boehm 2012	Robinson et al. 2005
Size	35 ha	3 ha	30 ha
	Charcoal (mm^2/cm^3)	Charcoal (mm^2/cm^3)	Charcoal (mm^2/cm^3)
MAX	5448	189	ca. 40
MIN	19	0	ca. 0
MEAN	1374	64	

Table 2.2b Charcoal area concentrations for coniferous sections of pollen and charcoal records.

Charcoal Area Concentrations: Comparison of conifer intervals in records					
Site	Anderson Pond, Tennessee (25,000–11,200 cal yr BP, conifer interval)	Key Deer Pond, South Florida (past 1700 cal yr)	Grizzly Lake, Boreal Alaska (past 9600 cal yr)	Lost Lake, Boreal Alaska, (past 14,700 cal yr)	Binnewater Pond, southeastern New York State (25,000–10,000 cal yr BP, conifer interval)
Ref.	This study	Albritton 2009	Tinner et al. 2006	Tinner et al. 2006	Robinson et al. 2005
Size	35 ha	0.0012 ha	11 ha	31 ha	30 ha
	Charcoal (mm^2/cm^3)	Charcoal (mm^2/cm^3)	Charcoal (mm^2/cm^3)	Charcoal (mm^2/cm^3)	Charcoal (mm^2/cm^3)
MAX	2730	863	157.1	87.5	ca. 75
MIN	14	80	0	0	ca. 0
AVE	759	308			

Table 2.2c Charcoal to Pollen Ratios for hardwood intervals in pollen and charcoal records.

	Charcoal to Pollen Ratios: Comparison of hardwood intervals in records	
Site	Anderson Pond, Tennessee (11,200 cal yr BP to present, upper section of core)	Whiteoak Bottoms North Carolina (14,500–12,600 cal yr BP)
Reference	This study	Boehm 2012
Size	35 ha	3 ha
	Charcoal (μm^2/grain)	Charcoal (μm^2/grain)
MAX	3199	744
MIN	85	9
AVE	1121	188

Table 2.2d Charcoal to pollen ratios for coniferous intervals in pollen and charcoal records.

Charcoal to Pollen Ratios: comparison of conifer intervals in records				
Site	Anderson Pond, Tennessee (lower section of core, 25,000–11,200 cal yr BP)	Calf Island Marsh, Boston's Outer Harbor (past 1200 cal yr)	Key Deer Pond, South Florida (past 1700 cal yr)	Lake of the Clouds, Minnesota (past 1000 cal yr)
Reference	This study	Patterson et al. 2005	Albritton 2009	Swain 1973
Size	35 ha	0.4 ha	0.0012 ha	12.5 ha
	Charcoal (μm^2/grain)	Charcoal (μm^2/grain)	Charcoal (μm^2/grain)	Charcoal (μm^2/grain)
MAX	16,382	6935	20297	10
MIN	136	55	650	near 0
AVE	4196	2326	7413	

Table 2.3 Summary of charcoal intervals comparing Anderson Pond to seven other sites, for hardwood dominated vs. conifer dominated intervals.

			charcoal area concentrations mm^2/cm^3	Site with highest values	No. Sites compared	charcoal: pollen μm^2/grain	Site with highest values	No. Sites compared
Hardwood-dominated interval	11,200 cal yr BP to present for Anderson Pond	max	5448	Anderson Pond	3	3199	Anderson Pond	2
Conifer-dominated interval	23, 000–11,200 cal yr BP for Anderson Pond	max	2730	Anderson Pond	5	20,297	Key Deer Pond	4

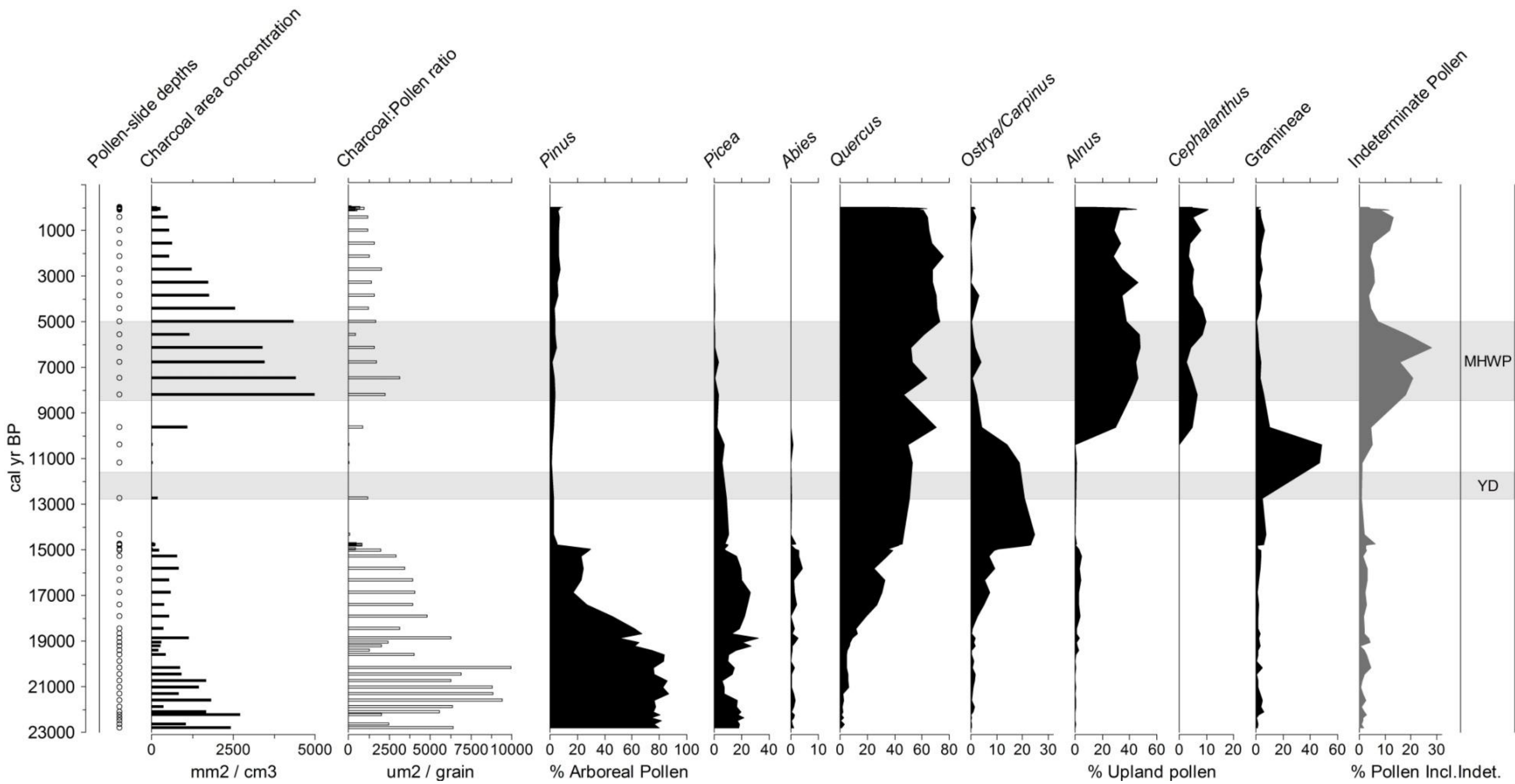

Figure 2.1 Anderson Pond microscopic charcoal with pollen percentages for selected taxa from Delcourt (1979). Microscopic charcoal was quantified on the same slides used for pollen analysis by Hazel Delcourt. MHWP is the Mid-Holocene Warm Period, 8200–5000 cal yr BP. YD is the Younger Dryas stadial, 12,800–11,600 cal yr BP. In the charcoal area concentration graph, the value at 8205 cal yr BP (5448 mm^2/cm^3) is truncated, and in the charcoal:pollen graph, the value at 20,182 cal yr BP (16,382 μm^2/grain) is truncated, in both cases to better display the data.

Chapter 3

Fire-Vegetation Interaction Across the Late Glacial and Holocene: Three New Macroscopic Charcoal Records from the Southeastern U.S.A.

This chapter is in preparation for submission to the journal *Palaeogeography, Palaeoclimatology, Palaeoecology*. My use of "we" in this chapter refers to my co-authors, Sally P. Horn, Zheng-Hua Li, and myself. The revised manuscript will include additional discussion comparing the new charcoal records to other paleofire records from the region.

3.1 Abstract

Few continuous charcoal records exist to understand past fire activity in the southeastern United States. Three high-resolution macroscopic charcoal records were constructed for glacial to recent times using lake sediments from Cahaba Pond, Alabama; Jackson Pond, Kentucky; and Pigeon Marsh, Georgia. We compared charcoal data to vegetation changes inferred from existing pollen data for the sites and to charcoal datasets from Anderson Pond, Tennessee and Slack and Swift Lakes, Michigan. These charcoal datasets provide insights into past fire-climate-vegetation linkages during times of dynamic environmental change. We found peaks in macroscopic charcoal abundance at ca. 14,000 cal yr BP at Jackson Pond and Swift and Slack Lakes, and at ca. 12,400 cal yr BP at these sites and Cahaba Pond. Increased fires occurred during the Mid-Holocene Warm Period at Anderson Pond, Jackson Pond, and Swift and Slack Lakes, a time interval not represented in the Cahaba Pond and Pigeon Marsh profiles due to missing sediments. The higher fire activity during the middle Holocene may reflect both a climate more conducive to fire in temperate forests and greater accidental or purposeful ignition by Native Americans. The late-glacial charcoal record at Pigeon Marsh was composed predominantly of sedge charcoal, indicating low temperature fires that may have been ignited by lightning strikes at this ridge-top location.

3.2 Introduction

Charcoal records developed from lake-sediment profiles provide key information on the history of fires within lake basins and beyond (Whitlock and Larsen 2001, Whitlock and Anderson 2003). When coupled with pollen data, a clearer picture emerges of what may be driving the fire ecology. Establishing fire-climate-vegetation linkages and timing of major vegetational shifts is crucial to understanding abrupt climate and environmental changes such as the Younger Dryas abrupt climate reversal some 12,800 years ago (Peteet 1995, Firestone et al. 2007, Broecker et al. 2010, Fiedel 2011). In addition, these charcoal records can provide land managers with information on natural fire regimes needed for implementing appropriate prescribed burning plans (Komarek 1974, Heyerdahl and Card 2000, Matlack 2013).

Few high-resolution paleofire records exist for eastern North America for the past 15,000 years, a time of dynamic global change in climate and environments (Peteet 1995, Broecker et al. 2010, Fiedel 2011). High-resolution macroscopic charcoal records are available from Binnewater Pond, New York (Robinson et al. 2005); Appleman Lake, Indiana (Gill et al. 2009); Slack, Swift, and Big Fish Lakes, and Lake Sixteen, Michigan (Ballard 2009); and Silver Lake, Ohio (Gill et al. 2012). Paleofire records for the southeastern U.S. for this time frame are scarce. Some coarser-resolution charcoal records exist for Sandy Run Creek, Georgia (LaMoreaux et al. 2009), and Brown's Pond, Virginia (Kneller and Peteet 1993). Hussey (1993) constructed microscopic charcoal and pollen records for Clear Pond, South Carolina. Liu et al. (2013) recently obtained new cores from Anderson Pond, Tennessee and Jackson Pond, Kentucky for pollen analysis and AMS radiocarbon dating. They did not analyze charcoal to reconstruct fire history, but they obtained radiocarbon dates on charcoal macrofossils of ca. 20,000 cal yr BP at Anderson Pond and 18,000 cal yr BP at Jackson Pond. Taylor et al. (2011) also used charcoal from their sediment cores for radiocarbon dating. They recovered cores from a pocosin at Sandhills, Fort Jackson, South Carolina and reported that macroscopic charcoal occurred throughout the sediment profile, from which they developed a 22,000 cal yr pollen record.

Daniau et al. (2012) synthesized charcoal records from the Last Glacial Maximum (LGM) to the present to explore the sensitivity of fire to climate. Their analyses showed that fire increased uniformly with changes in temperature, peaking at intermediate moisture levels. They concluded that changes in fire regimes were predictable from changes in regional climates. and that temperature is the most important driver of shifts in biomass burning during this time interval.

We studied macroscopic charcoal as an indicator of local fire history in sediment cores from Cahaba Pond, Alabama; Jackson Pond, Kentucky; and Pigeon Marsh, Georgia using a combination of old and new cores. At Cahaba and Jackson Ponds, we quantified macroscopic charcoal in cores collected by Hazel and Paul Delcourt and students. These cores had been used for prior pollen analyses (Delcourt et al. 1983, Wilkins et al. 1991). The advantage of using this previously collected core material is the ability to directly link the new paleofire data to prior pollen data for these two study sites. For Pigeon Marsh, we used a new core collected in 2013. Watts (1975) previously cored Pigeon Marsh and described pollen assemblages.

The new macrosocopic charcoal records were compared to a microscopic charcoal record for Anderson Pond, Tennessee (Chapter 2, this dissertation) and to macroscopic charcoal records from Slack and Swift Lakes, Michigan (Ballard 2009) to address three questions: 1) How do the new macroscopic charcoal records from the southeastern U.S. compare with prior pollen reconstructions from the LGM into the Holocene at these sites? 2) To what extent do patterns show similarities with the comparison records from Anderson Pond, Tennessee, and Swift and

Slack Lakes, Michigan? 3) What are the implications of the new records and comparisons for understanding patterns in human and natural fire ignition and linkages between fire, climate, and vegetation across the late glacial and Holocene?

3.2.1 Natural and Anthropogenic Ignition of Fires in Eastern U.S. Forests

The lack of active volcanoes in the eastern U.S. makes lightning the principal natural force that can ignite fires. Komarek (1974) divided the southeastern U.S. into two lightning fire bioclimatic regions because the Appalachian Mountains affect frontal systems coming from the west and consequently the distribution of precipitation. The southern part of the eastern deciduous forest lies west of the Appalachians. Annual rainfall here is well distributed which prevents widespread wildfires except during very unusual conditions (Komarek 1974). The other lightning region is composed of two physiographic regions, the Piedmont Plateau and the Coastal Plain, curving around from the east to the south. The former was classified as the oak-pine forest and the latter as the evergreen forest region by Braun (1950). The pines of the oak-pine region are not as flammable as the southern pines but are more flammable than pines of the eastern deciduous forest (Komarek 1974). Barden (1974) reported an average of six lightning fires per year from 1960 to 1971 for an 800,000-ha region of pine hardwood stands in Great Smoky Mountains National Park and Cherokee, Nantahala, and Pisgah National Forests. He found that the average area burned by lightning fires was 0.8 ha and the largest was 33 ha.

In their review of wildfire ignitions in the Southeast, Long and Prestemon (2013) stated that humans are the ignition source for the majority of fires in the region. They listed the four types of anthropogenic ignition sources on U.S. public lands as: arson, escaped debris burns, campfires, and equipment. Important factors associated with these fires have been daily weather conditions including winds, fuel moisture, fire behavior indices, and duration of an immediately preceding precipitation event. Ignition frequency in many cases increased with warmer, drier, and windier conditions, as expected. Ignition frequency was also affected by vegetation type, fuel load, and topography, likely through interactions with the weather and climate variables (Long and Prestemon 2013).

Native populations used fire for many purposes, which have been documented historically (Patterson and Sassaman 1988, Van Lear and Waldrop 1989, Brown 2000, Pyne 2000, Williams 2000). Abrams (1992) and Delcourt and Delcourt (1998) concluded that Native Americans were a primary source of ignition in pre-settlement oak-hickory forests in the eastern U.S. Native Americans burned vegetation for the purposes of clearing undergrowth from oak stands to facilitate acorn harvesting and to attract game (Abrams and Nowacki 2008). Indigenous populations were actively using plant resources and fire along the Little Tennessee River watershed during the Mid-Holocene Warm Period (MHWP), as evidenced by paleoethnobotanical studies of charred wood, fruit, and seed assemblages (Chapman et al. 1982). In eastern Kentucky, ethnobotanical remains have also been found in rock shelters along the Western Escarpment of the northern Cumberland Plateau (Delcourt et al. 1998). Franklin (2002, 2015) has studied over 200 rock shelters on the Upper Cumberland Plateau of Tennessee, finding evidence of occupation by prehistoric people from Paleoindian to Mississippian times. Human occupation of the southeastern U.S.A. is also evidenced by shell middens on floodplains west of the Appalachians (Gremillion 1996). The evidence of mid-Holocene occupation in the southeastern U.S., and paleoethnobotanical evidence of fire use, makes anthropogenic ignition―purposefully, or by accident―a likely source for fires in this region, at least during the middle and late Holocene.

The comparison sites of Slack and Swift Lakes, Michigan, are in an area in which we can expect human-set fires during the late glacial and early Holocene. Both lakes are located less than 1 km from the Gainey stone tool site (Simons 1997). Gainey fluted points are similar to Redstone points, and date to 12,656–12,455 cal yr BP (Lepper 1999, Lepper and Funk 2006, Goodyear 2010, Anderson et al. 2011). People may have continued to live in this area beyond the time of the Gainey site, perhaps clearing forest undergrowth with fire to facilitate agriculture, hunting, range management, or travel (Brown 2000).

3.3 Study Site and Methods

3.3.1 Study Sites

We analyzed lake sediments from Cahaba Pond in St. Clair County, Alabama (Delcourt et al. 1983); Jackson Pond in Larue County, central Kentucky (Wilkins et al. 1991); and Pigeon Marsh on Pigeon Mountain, Georgia (Figure 3.1).

Cahaba Pond is a 0.2-ha pond located 30 km northeast of Birmingham, Alabama (33.5677 ºN, 86.5342 ºW). It formed in a collapsed sinkhole of Ordovician limestone (Delcourt et al. 1983) at an elevation of 204 m. An aquifer 1–3 m below the surface in the limestone is the source of a spring that feeds Cahaba Pond (Delcourt et al. 1983).

Jackson Pond is a 3-ha, spring-fed sinkhole at the head of a valley underlain by Mississippian limestone (37.4324 ºN, 85.7247 ºW). The site lies on the Interior Low Plateau approximately 1 km from the Dripping Springs Escarpment. The Western Coal Field physiographic subdivision lies to the west, and the boundary of the Mississippian Plateau physiographic subdivision lies to the east (Wilkins et al. 1991).

Pigeon Marsh (34.6640 ºN, 85.4011 ºW) is located at an elevation of 630 m on the crest of the eastern ridge of Pigeon Mountain in northwest Georgia, south of Chattanooga, Tennessee

(Watts 1975). The marsh is about 50 m by 100 m in size, surrounded by steep wooded slopes. Red maple and sweetgum grow around the marsh and mats of sphagnum moss grow under the trees. Sweetgum and buttonbush grow in the marsh with tussocks of sedge (*Carex*). The marsh is located near the point of origin of Allen Creek (Watts 1975) and an overflow ditch has been constructed on the south end. Pine, oak, holly, and beech were growing on the slopes around the marsh in December 2013.

3.3.2 Field Methods

Lake sediments from all these sites were recovered from anchored floating platforms using piston corers. At Cahaba and Jackson Ponds, cores were recovered in 1-m increments using a Livingstone piston corer and extruded and wrapped in plastic and foil in the field before being transferred to the University of Tennessee (Delcourt et al. 1983, Wilkins et al. 1991). At Pigeon Marsh, we used a Colinvaux-Vohnout locking piston corer (Colinvaux et al. 1999) to core the shallow (<1 m) deposits at three locations near the center of the wetland. Core sections were returned to the lab still encased in their original aluminum coring tubes, and opened and described in the lab, where they were stored at 6 °C.

3.3.3 Laboratory Methods—Cahaba and Jackson Pond Macroscopic Charcoal

Archived cores for Cahaba Pond and Jackson Pond were dry at the time of sampling. These cores were initially refrigerated, but later had been stored at room temperature. H. Delcourt had placed cork depth markers in Cahaba Pond core sections where she sampled for pollen and had made depth markings on the Jackson pond core sections. She had also inserted notes in foil where sections were removed to sieve for macrofossils or for radiocarbon dating.

These sampling procedures allowed us to tie our charcoal sampling intervals to the original work on the cores.

We performed macroscopic charcoal analysis (Whitlock and Anderson 2003) using "cookies" cut from the now-dry sediment core sections from Cahaba and Jackson Ponds. Sections from two Cahaba pond cores, CP-79A and B, were available. We focused on CP-79B, the core for which Delcourt et al. (1983) had carried out pollen analysis. We cut core sections using a hacksaw and a mitre box to which we attached a half-cut PVC pipe to hold the core section. Where possible, an expandable parallel caliper tool was used to subdivide the segments between positions marked by corks into interpolated 1 cm (original) thickness; some slices were wider. Where sections had been removed from the CP-79B core for radiocarbon or macrofossil analyses, we cut sections from the CP-79A core, which had been recovered 5 m away (H. Delcourt unpublished field notes). The cores were correlated by depth and stratigraphy, and by matching patterns in stable nitrogen isotope values (this dissertation, Chapter 4) between the two cores. For core CP-79B, all available core sections were cut to construct a charcoal record that begins at the base of the core, about 14,000 cal yr BP, and extends to modern times but with gaps based on sample availability.

From the Jackson Pond JP-83A core, we sampled from two core sections (120–169 cm and 169–267.5 cm, these original core interval notations include water depth), to construct a record that spans from about 14,000 cal yr BP to present. For this core, sections were cut at interpolated 1 cm intervals using a modified 10" (25 cm) compound miter saw with a 1.6 mm continuous masonry blade.

We processed half of each mud cookie for charcoal and archived the other half. We recorded the mass of the half cookie before processing. The samples from the Cahaba core were first treated with boiling water with ca. 0.5 g of baking soda added to about 100 ml deionized water, and allowed to soak for 24 hours. This method was based on protocols for sampling ostracods shared by B. Curry (pers. communication, August 22, 2011). The samples were then sieved and treated with 6% sodium hypochlorite (household bleach) for 24 hours. The Jackson Pond samples were only treated with bleach. When bleach-treatment was complete, the samples were wet-sieved using 3" diameter sieves. The Cahaba Pond samples were sieved with stacked 250 and 125 µm sieves, and the Jackson Pond samples were sieved with only the 125 µm sieve. Samples were transferred to labeled Petri dishes and counted wet on a coaster with guidelines. Counts for the >250 µm and 125–250 µm subsamples from the Cahaba core were combined. Charcoal concentrations were reported on a volumetric basis (particles >125 µm /cm^3) by dividing the charcoal count by an estimated original wet volume for the material sieved. To estimate these volumes, we first oven-dried samples of the archived halves of charcoal samples from the dry cores to determine further water loss. We selected a representative sample for each lithologic unit in the core. The results allowed us to convert our dry core sample masses to oven-dry sample masses. These values were then divided by original bulk density values for core samples in H. Delcourt's unpublished laboratory notes to estimate original volumes.

3.3.4 Laboratory Methods—Pigeon Marsh Macroscopic Charcoal

For Pigeon Marsh, we chose to work with core PM-2013-1, the longest of the three cores. Samples of 2 cm^3 volume were taken at 1-cm contiguous intervals using a rectangular brass sampler. Samples were treated with a 1:1 solution of household bleach and 5% sodium hexametaphosphate to disaggregate the sediments, sieved with a 125 µm sieve, and wet-counted in Petri dishes underlain by a marked coaster. Charcoal concentrations were reported on a volumetric basis (particles >125 µm /cm^3) by dividing the charcoal count in the 2 cm^3 volume by two. Samples of 1 cm^3 volume were taken at 10 cm intervals and processed for loss-on-ignition to determine organic and carbonate percentages (Dean 1974).

3.3.5 Chronology

We obtained AMS radiocarbon dates on macrofossils from four levels of the 2013 Pigeon Marsh core, and for two levels of the 1979 Cahaba Pond cores. We calibrated these new AMS radiocarbon dates and original radiocarbon dates obtained on bulk sediment by Delcourt et al. (1983) and Wilkins et al. (1991) using the radiocarbon calibration software CALIB 7.0.2 (Stuiver and Reimer 1993) and the dataset of Reimer et al. (2013). We used CALIBomb (Reimer et al. 2004) for one recent date in Pigeon Marsh. Ages for each pollen and charcoal sample were interpolated linearly using the weighted means of the probability distributions of the calibrated ages (Telford et al. 2004), with some adjustment needed at Pigeon Marsh, as described below.

3.3.6 Stratigraphic Diagrams

Charcoal concentrations for Jackson Pond, Cahaba Pond, Pigeon Marsh and comparison sites were plotted by calibrated age using C2 software (Juggins 2010). We also plotted selected pollen percentages from the original study by Watts (1975) at Pigeon Marsh that were provided to S. Horn by E. Grimm, and pollen data from Anderson Pond (Delcourt 1979), Cahaba Pond (Delcourt et al. 1983), and Jackson Pond (Wilkins et al. 1991) that we downloaded from the Neotoma database (http://www.neotomadb.org) and cross-checked against data in H. Delcourt (1978) and Wilkins (1985).

3.4 Results

3.4.1 Sediment Core from Pigeon Marsh

The Pigeon Marsh core we analyzed was 54 cm long, and composed of predominantly dark brown sediment. The sediment appeared organic-rich, but loss-on-ignition showed 8% or less organic content through the core together with less than 1% carbonate. Sand-sized quartz grains were abundant in samples sieved for charcoal. A sharp contact was observed angling between 16 cm and 18 cm depth. Above this sharp contact, the sediment was brownish gray (Munsell 10YR 4/1). Below the contact, sediment was dark brown (10YR 3/3). A 2.5 x 2.5 cm angular sandstone rock was present at a depth of 10 cm.

3.4.2 Chronology

The calibrated ages from Cahaba Pond (Table 3.1) and Jackson Pond (Table 3.2) show that the cores extend to ca. 14,000 and 25,000 cal yr BP, respectively. Our charcoal records cover the period from ca. 14,000 years to the present, with a notable gap in the Cahaba Pond record between ca. 8500 and 2500 cal yr BP. The original Cahaba cores contained limited sediment from this time period because of low sedimentation rates and/or hiatuses in the Holocene portion of the cores, and because sections of the core had been used by Delcourt et al. (1983) for bulk radiocarbon and macrofossil analyses.

The calibrated radiocarbon dates for the Pigeon Marsh core (Table 3.3) reveal a major hiatus that we place above the sharp, angled contact at 16–18 cm. We regard the modern stick at 17 cm as out of place and estimate that the material above the sharp contact may cover ca. 200 years. The 2-sigma calibrated ages of the two dates below the modern date overlap. To estimate sedimentation rates, we assumed the sample at 23.5 cm to have a calibrated age 200 years younger than the weighted mean age of the sample at 33 cm, which was 15,058 cal yr BP. This adjusted age of 14,858 cal yr BP is within the 2 sigma calibrated age range of 15,236–14,826 cal yr BP. We interpolated upwards from 23 cm to the inferred position of the hiatus midpoint at 17 cm using the rate estimated between 33 and 23.5 cm. We assumed the sediment from 17 cm to the top of the core corresponded to the last 200 years, and assigned an age of 137 cal yr BP to the sediment above the hiatus. The age model shows a major gap between ca. 14,732 at 17 cm and ca. 200 years just above that point. Based on the radiocarbon dates, our record below 17 cm covers only a portion of the original pollen diagram by Watts (1975). Initial pollen analysis on the new core by S. Horn revealed dominance of conifer (including spruce) pollen and sedges and grasses in the Pigeon Marsh sediment below 17 cm, consistent with the pollen results of Watts and the AMS radiocarbon dates.

3.4.3 Charcoal

The three charcoal records provide evidence of fire occurrences across the late glacial and Holocene at Jackson Pond, but with gaps in the record at Pigeon Marsh (after 14,500 cal yr BP) and Cahaba Pond (middle and late Holocene) (Figure 3.2).

At Cahaba Pond, the highest charcoal concentrations, 53 to 148 fragments/cm^3 occur during the interval 1370–640 cal yr BP. These fires occurred in association with deciduous forests in the late Holocene (Figure 3.4). A small peak in charcoal occurs around 12,400 cal yr BP (13 particles/cm^3), also at a time when deciduous taxa dominated the forest, coincident with a decline in beech (*Fagus*) and hornbeam/hophornbeam (*Ostrya/Carpinus*) (Figure 3.4). Overall, the charcoal record is sparse except for the late Holocene.

At Jackson Pond, charcoal is low throughout the record except for closely-spaced peaks of 41 and 36 fragments/cm^3 at ca. 5350 and 5170 cal yr BP respectively, when pollen shows that forests were dominated by oaks. Small peaks were found around 14,000 cal yr BP (7 fragments/cm^3); 12,400 cal yr BP (5 fragments/cm^3), and 11,110 cal yr BP (10 fragments/cm^3). A slightly larger peak (14 fragments/cm^3) occurred at 6790 cal yr BP (Figure 3.4).

The high charcoal concentrations from 16,500 to 14,500 cal yr BP at Pigeon Marsh match the interval of high conifer pollen in the pollen diagram produced by Watts (1975). Oak and sedge pollen are also abundant in this interval, based on comparison with Watts (Figure 3.3) and initial pollen analysis by S. Horn of slides prepared from our 2013 core. We did not attempt systematic identification of charcoal in our core samples, but most of the charcoal in the Pigeon Marsh record has a morphology that suggests sedge (Cyperaceae) leaves. The maximum charcoal value at Pigeon Marsh is 140 fragments/cm^3 at 15,797 cal yr BP. The Pigeon Marsh charcoal record indicates relatively high fire activity from 16,500 to ca. 14,500 cal yr BP with a range of 68–140 fragments/cm^3.

3.5 Discussion

3.5.1 Interpretations of the Three New Charcoal Records

The charcoal record at Cahaba Pond is largely a record of fires during the latest Holocene, a time for which Delcourt et al. (1983) inferred from pollen and plant macrofossil analysis that sweetgum (*Liquidambar styraciflua*) increased in importance; oak (*Quercus*), hickory (*Carya*), chestnut or chinkapin (*Castanea*), and white pine (*Pinus strobus*) dominated the slopes; and buttonbush (*Cephalanthus*), arrowhead or wapato (*Sagittaria*), and watershield (*Brasenia*) grew in the pond itself. The fires burned close to the pond or perhaps on the surface of the dried pond during exceptionally dry years. Given high indigenous populations in Alabama at this time, these fires may have been set by people (Walthall 1990).

Earlier in the record, the smaller peak in charcoal at ca. 12,400 cal yr BP occurs during a time of vegetation transition that may have been related to fire. Cahaba Pond vegetation was dominated by beech (*Fagus*), and hornbeam/hophornbeam (*Ostrya*/*Carpinus*) from inception of the pond around 14,000 cal yr BP to about 12,400 cal yr BP. Beech and hornbeams are fire-intolerant taxa (Tubbs and Houston 1990, Delcourt and Delcourt 1994); around 12,400 cal yr BP, both declined dramatically, replaced by magnolia and pine (Figure 3.4; Delcourt et al. 1983), followed by oak dominance. At this time, aquatic plant assemblages also shifted from submerged to emergent taxa as the pond shallowed (Delcourt et al. 1983). The extent to which fire at this time contributed to changes in hydrology and vegetation remains uncertain, but the coincidence of the charcoal peak and these other shifts is intriguing. Delcourt et al. (1983) noted that sedimentation slowed dramatically after 8400 BP (9419 cal yr BP) and considered a possible hiatus between 5750 and 3000 BP (6551–3184 cal yr BP), resulting from desiccation of the pond. They argued instead, however, that the aquatic plant assemblages and sediment lithology indicated rising water levels after 8400 BP (9419 cal yr BP). They speculated that a larger pond area would have distributed sediment influx across a larger area, thus reducing the rate of sediment accumulation at the core site. They also speculated that shrubs growing at the margins of the pond may have trapped sediments. However, Whitehead and Sheehan (1985) argued against this interpretation. They pointed to evidence of a sharp change in sediment type in the Cahaba Pond core at 220 cm and unusually sharp changes in pollen percentages, such as in oak (*Querucs*) and tupelo or blackgum (*Nyssa*), at 8400 BP (9419 cal yr BP). They also noted that the radiocarbon dates suggested that portions of the record were missing: 242–245 cm was dated as 8190 ±90 ^{14}C years BP, 210–214 cm dated to 5750 ±90 ^{14}C years BP, and 200–207 cm dated to 2990 ±80 ^{14}C years BP. Comparing the pollen record of Cahaba Pond to one of their sites, B.L. Bigbee in western Alabama, they viewed the expansion of *Nyssa*, *Liquidambar*, and *Pinus* as more recent developments involving modern taxa, and suggested that it was placed too early at 8400 cal yr BP at Cahaba Pond (Whitehead and Sheehan 1985).

Jackson Pond had the lowest macroscopic charcoal concentrations of all sites considered. The two relatively large charcoal peaks at ca. 5000 cal yr BP may be associated with a warmer and drier climate during the Mid-Holocene Warm Period. Wilkins et al. (1991) inferred that Jackson Pond had become a shallow pond surrounded by shrub thickets by 8100 cal yr BP; the macroscopic charcoal may indicate the burning of these thickets, perhaps in fires ignited by Native Americans to clear the thickets, or for hunting. No evidence of agricultural activity was found in the pollen analysis (Wilkins et al. 1991), but the relatively flat slopes surrounding the pond certainly could have been cultivated. The Jackson Pond cores extend back in time to ca. 25,000 cal yr BP, further than our analysis of macroscopic charcoal. Pollen assemblages from the late glacial and the LGM show higher conifer pollen percentages, and possibly the sediments in this unstudied part of the core would reveal more fires associated with conifers, as found for macroscopic charcoal at Pigeon Marsh and microscopic charcoal at Anderson Pond (this dissertation, Chapter 2). However, spot-checking for charcoal in a few samples from the conifer-dominated interval of the Jackson Pond core studied by Wilkins et al. (1991) revealed very low charcoal concentrations. That there is low charcoal when conifers are present may indicate long distance transport of coniferous pollen, which seems to be supported by evidence in the plant-macrofossil diagram developed by Wilkins et al. (1991) for the 1983 Jackson Pond cores. For *Picea*, no macrofossils were found above 400 cm (ca. 18,230 cal yr BP) in the core, and for

Pinus, no macrofossils were found at any depth. However, Liu et al. (2013) did find some conifer macrofossils in their new core from Jackson Pond. They also found small macroscopic charcoal in one sample from the lower part of their core; they AMS-dated this charcoal, together with uncharred plant remains, to ca. 18,000 cal yr BP.

The Pigeon Marsh charcoal record indicates relatively high fire activity from 16,500 to ca. 14,500 cal yr BP, when the record is truncated. During this interval, pine dominated the pollen spectra, along with oak and sedge, based on Watts (1975). That the charcoal below the sharp contact at 17 cm appeared sedge-like is consistent with the dominance of sedge pollen among herbs (Figure 3.3), and initial pollen counts on our 2013 core. In addition, during picking for macrofossils for radiocarbon dating in the 32–34 cm sample (interpolated age 15,058 cal yr BP), a charcoaled *Sagittaria* embryo was observed. These findings suggest that fires burned at a time of low water level in the marsh, when these aquatic plants dried enough to carry a fire. The pollen record (Watts 1975) also includes *Ostrya/Carpinus* during this time of active fires. Because *Ostrya* and *Carpinus* are fire-intolerant taxa (Delcourt and Delcourt 1994), their presence at this time suggests that fires were of low intensity, or that fires did not burn areas that supported these trees. Given the ridgetop location of Pigeon Marsh, we can expect some pollen to blow upslope from forests at lower elevation not subjected to fire.

Watts (1975) suggested that the treeline may have been depressed below the elevation of Pigeon Marsh during the Pleistocene, but this hypothesis seems inconsistent with regional treeline reconstructions. Based on evidence of pollen and macrofossils of spruce and fir from several lowland bog deposits in the southern U.S., Shelton (1981) estimated that the treeline in the Great Smoky Mountains was at an elevation of between 900 and 1500 m during the last glacial period. Patterned ground, a periglacial feature, was reported at 1500 m in the southernmost portion of the Appalachian Highlands (Delcourt and Delcourt 1985, Mills and Delcourt 1991). The elevation of Pigeon Marsh is 630 m, which falls well below this estimate for a site farther north, so Pigeon Mountain is not expected to have been above treeline during glacial times. However, the stands of conifers and oaks indicated by the pollen assemblages may have been relatively open, with enough herbaceous understory to carry fires. The ridgetop position of the marsh suggests lightning strikes as a possible source of fires (Delcourt and Delcourt 1997, Bratton and Meier 1998, Whiteman 2000, Lafon et al. 2005, Mitchener and Parker 2005).

3.5.2 Comparisons of Fire Histories with Anderson Pond, Slack and Swift Lakes

The presence of abundant charcoal prior to 14,000 cal yr BP in the Pigeon Marsh record matches the microscopic charcoal evidence from Anderson Pond, Tennessee (Figure 3.4; this dissertation, Chapter 2). At Anderson Pond, jack pine and spruce carried fires; at Pigeon Marsh, fires may have burned primarily herbaceous vegetation, perhaps on a dried marsh surface as well as in the forest understory.

Around 14,000 cal yr BP, slightly too early for the Cahaba Pond record and during a gap in the Pigeon Marsh record, a slight peak exists at Jackson Pond (7 fragments/cm^3), and large peaks at Slack and Swift Lakes in Michigan (118 and ca. 196 fragments/cm^3, respectively). Charcoal is low at this time in the microscopic record for Anderson Pond, but sample density is low in this part of the record, which has a very low sedimentation rate or a hiatus (Webb and Webb 1988). Around 12,400 cal yr BP, broadly contemporaneous fires may have occurred at four sites. Peaks in charcoal concentration occur at Cahaba Pond (27 fragments/cm^3), Jackson

Pond—slight (5 fragments/cm^3), Slack Lake (212 fragments/cm^3) and Swift Lake (169 fragments/cm^3). The peak at Slack Lake is the highest peak in the record.

The largest charcoal peaks at Jackson Pond, in the middle Holocene, match in time a peak near the top of the Slack Lake record (Ballard 2009) and also coincide with peaks at Anderson Pond (Figure 3.4). Both Slack and Swift have abundant charcoal in the Holocene, and the highest charcoal levels at Swift Lake occur during the Mid-Holocene Warm Period. We have no charcoal samples from Cahaba Pond and Pigeon Marsh during this time interval; the gaps in the records at these sites may be partly associated with drier climate conditions at this time.

3.5.3 Linkages Between Fire, Vegetation, and Climate Across the Late Glacial and Holocene

Conifers, with their flammable resins, are more combustible than deciduous trees (Agee 1998). Of the six sites, all but Cahaba Pond had conifers present during the period between the Late Glacial Maximum and the Younger Dryas (ca. 12,900–11,600 cal yr BP), based on prior published studies and on our initial pollen analysis of a core section from Slack Lake that spans 14,000–11,000 cal yr BP. We extrapolate pollen data from Slack to nearby Swift Lake. Fire activity was high at Anderson Pond from the LGM to 15,000 cal yr BP, when pine and spruce dominated local forests. Fire activity was high at Slack and Swift Lakes from 14,000 to the end of the Younger Dryas around 11,600 cal yr BP when conifers were present. These late-glacial fires may have been ignited by humans, given contemporaneous archaeological evidence of human occupation at the nearby Gainey stone tool site. At the Michigan lakes, fire activity remained high into the Holocene, with different vegetation burning. Based on Hupy and Yansa (2009), we expect that Holocene fires burned vegetation dominated by deciduous taxa. These fires may also have been ignited by people, though we lack evidence of nearby occupation during the Holocene. Schaetzl (2015) reported that the population of the southern half of the Lower Peninsula of Michigan was about 12,000 when Etienne Brule, the first European, arrived in A.D. 1620. Algonquin Indians occupied Lower Michigan for at least a century before Europeans arrived; the presence of mound sites in Michigan suggests that southern Moundbuilder Indians preceded the Algonquins (Halsey 1999, Kingsley 1999; Schaetzl 2015).

Although conifers were present from the LGM to Younger Dryas at Jackson Pond, the charcoal record shows little fire activity, suggesting that few fires burned close to the lake. For fire to ignite, fuel must be sufficiently warm and dry, yet the cool period of the LGM to late glacial had abundant evidence of fire activity at Anderson Pond, Pigeon Marsh, and Slack and Swift Lakes. Climate is inferred to have been somewhat cooler than present from the LGM to the late glacial at Anderson Pond and Pigeon Marsh based on the interpretations of Delcourt (1979) and Watts (1975). For Slack and Swift Lakes, climate is interpreted by Hupy and Yansa (2009) also to have been somewhat cooler. Based on the global synthesis of Daniau et al. (2012), we should expect fires to increase with warming.

At Cahaba Pond, Delcourt et al. (1983) interpreted the late-glacial presence of mountain maple (*Acer spicatum*), striped maple (*Acer pensylvanicum*), Atlantic white-cedar (*Chamaecyparis thyoides*), and baldcypress (*Taxodium distichum*) along with numerous temperate mixed hardwood taxa to indicate a cool, moist stable temperate climate. They also inferred long frost-free periods, lack of severely cold winters, and low fire frequency. The charcoal record for Cahaba Pond supports this interpretation. That a small peak in charcoal at around 12,400 cal yr BP is coincident with declines in the fire-intolerant taxa American beech

(*Fagus grandifolia*) and hornbeam/hophornbeam (*Carpinus caroliniana, Ostrya virginiana*) suggests a fire event that may have contributed to a change in vegetation.

Drought is another aspect of climate that exerts an important control on fire. Burned aquatic vegetation was observed in samples from Pigeon Marsh for 15,000 cal yr BP, suggesting desiccation of the marsh at that time. Charcoaled *Najas* and sedge seeds, along with charcoaled spruce needles, were observed in Swift Lake ca. 14,000 cal yr BP (Ballard 2009), which suggests spruce may have been growing in the shallow developing pond as the ice melted in this kettle lake. Burned aquatic vegetation was also observed in Swift Lake at 6500 cal yr BP (Ballard 2009), suggesting a lower lake level.

Pollen records show that spruce-sedge parkland dominated in the region of Slack and Swift Lakes, Michigan from 13,000 to 11,000 cal yr BP (Hupy and Yansa 2009). Jack and/or red pine (*Pinus banksiana* and *P. resinosa*) first appeared 13,000 years ago in the southwestern Lower Peninsula during the spruce phase. By 11,000 years ago, several species of pine dominated many of the forests of the southern Lower Peninsula (Manny et al. 1978, Kapp 1999).

At Jackson Pond, Wilkins et al. (1991) inferred dieback of coniferous trees during the late glacial, when coniferous forests became more open . Pollen of deciduous trees was minor until ca. 13,000 cal yr BP, after which time mixed conifer-hardwood forests became established. Wilkins et al. (1991) interpreted Jackson Pond to have been a relatively deep, clear-water pond that transitioned to a shallow, productive pond with cattails and water lilies by 10,000 ^{14}C yr BP [11,700 cal yr BP]. By 7300 ^{14}C yr BP [8000 cal yr BP], it had become a shallow pond fringed by shrub thickets and upland vegetation was dry oak-hickory forest. Higher charcoal indices were expected for the coniferous part of the record, but fire activity was low. Lack of macroscopic charcoal when coniferous pollen is present in the record suggests that conifers in the watershed were not burning or possibly that conifers were not present and that the conifer pollen was from long distance transport. Liu et al (2013) reported needles of jack pine and other pines in glacial-age sediments from their 2007 Jackson Pond core, but not from late glacial sediments. Only wildfires burning within or very close to the watershed would be expected to deposit macroscopic charcoal in Jackson Pond (Whitlock and Larsen 2001).

3.6 Conclusions

Pigeon Marsh had the highest charcoal abundances of the three new records, probably driven by its location on a ridgetop, a site more likely to receive lightning strikes than more sheltered sites. Charcoaled aquatic macrofossils at Pigeon Marsh suggest periodic desiccation of the marsh from 16,500 to 14,500 cal yr BP. Jackson Pond had relatively low charcoal abundances except for mid-Holocene peaks likely related to warming at that time. The presence of conifers with very low charcoal during the late glacial may indicate that the coniferous pollen is from long distance transport; if so, wildfires associated with the coniferous forest would have produced charcoal outside the Jackson Pond watershed.

At Cahaba Pond, low late-glacial charcoal concentrations are consistent with the presence of fire-intolerant beech and hornbeam, until around 12,400 cal yr BP. High fire activity occurred in the latest Holocene, perhaps from people burning vegetation on a desiccated pond bottom. Water level at time of coring October 19-20, 1979 was 127 cm (Delcourt et al. 1983). Wells in the area have been reported to fluctuate by 2.1 m seasonally (Causey 1963). At Anderson Pond, another collapsed sinkhole pond, Delcourt (1979) reported that water levels varied through the year by 2 to 3 m. Lowest water levels occurred in the early autumn. At Cahaba Pond, Delcourt et al. (1983) inferred rising water after 8400 BP (9490 cal yr BP) from the aquatic vegetation, but it is not unreasonable to consider that fluctuations in the water levels of 1–3 m—particularly during a time of drought—may have exposed the bottom of the pond.

At Anderson Pond, high microscopic charcoal indices are observed in the Mid-Holocene Warm Period, and Slack and Swift Lakes show high macroscopic charcoal in the part of the MHWP these records include. Hiatuses in the Pigeon Marsh and Cahaba Pond records preclude comparisons of middle Holocene fire patterns at these sites.

Comparing the three new macroscopic charcoal records with prior data from Swift and Slack Lakes, and with microscopic charcoal data from Anderson Pond, suggests possibly contemporaneous fires at four of the six sites (Cahaba, Jackson, Slack, Swift) around 12,400 cal yr BP, although charcoal peaks at Cahaba Pond and Jackson Pond are minor. Anderson Pond showed high fire activity from 23,000–15,000 cal yr BP, driven by flammable coniferous vegetation at that site. When conifers declined, so did fire activity. Slack and Swift lakes also showed high fire activity during the late glacial and into the Holocene, with fires likely driven by both fuel availability and by post-Younger Dryas human occupation of the nearby Gainey stone tool site. At Anderson Pond, the middle Holocene was a time of high charcoal abundances, probably linked to climate warming. The apparent shallowing of Anderson, Cahaba, and Jackson Ponds around the beginning of the Holocene (Delcourt 1979, Delcourt et al. 1983, Wilkins et al. 1991) would have made these sites more susceptible to water level fluctuations in the middle Holocene and possibly to fires on the dried pond surfaces during droughts. At Cahaba Pond, dry mid-Holocene conditions may account for very low sedimentation rates and/or hiatuses in the record (Whitehead and Sheehan 1985, Webb and Webb 1988, Jackson and Whitehead 1993).

Overall, fire histories for the the six eastern U.S. charcoal records are variable due to differences in topographic position; vegetation; climate (temperature, drought, lightning-producing storms); human activity; and unknown factors. More than one factor may have influenced fire at any given site. High fire activity was likely linked to vegetation type at Anderson Pond, and Swift and Slack Lakes, particularly to the presence of conifers from the LGM to the late glacial. Drought was probably an important factor during the middle Holocene at several sites. Anthropogenic burning likely explains some patterns, particularly in the late Holocene for Cahaba Pond, around the middle Holocene at Anderson and Jackson Ponds, and during the late glacial at Swift and Slack Lakes. Contemporaneous wildfires may have occurred around 14,000 cal yr BP at Jackson Pond, Slack and Swift Lakes, and around 12,400 cal yr BP at Cahaba and Jackson Ponds, and Slack and Swift Lakes.

3.7 Acknowledgements

We acknowledge and appreciate the previous sediment coring and pollen work performed by Hazel Delcourt, Paul Delcourt, Gary Wilkins, and William Watts, which enabled the charcoal-vegetation comparisons at Cahaba and Jackson Ponds and Pigeon Marsh. We also thank Scott Meeks for making available original sediment cores and notes for Cahaba and Jackson Ponds. We thank Eric Grimm for providing access to the original pollen data from Pigeon Marsh and for sharing his age model for the site. We also thank Henri Grissino-Mayer, Yingkui Li, Chad Lane, Steven Driese, Roger Horn, Mathew Boehm, Paul Lemieux III, Elizabeth MacLennan, Bryson Patrick, and Timothy Price for laboratory assistance, helpful discussion, or manuscript review. The work of the data contributors and the Neotoma community is gratefully acknowledged (Neotoma Paleoecology Database http://www.neotomadb.org). This research was supported by the National Science Foundation under Grant EAR-0822824 to Zheng-Hua Li and Sally Horn.

3.8 References

Abrams, M.D. 1992. Fire and the development of oak forests. *BioScience* 42(5): 346–353.

Abrams, M.D.; Nowacki, G.J. 2008. Native Americans as active and passive promoters of mast and fruit trees in the eastern U.S.A. *The Holocene* 18(7): 1123–1137.

Agee, J.K. 1998. Fire and pine ecosystems. *In: Ecology and Biogeography of Pinus* (Ed.: Richardson, D.M.), Cambridge University Press, New York, pp. 193–218.

Anderson, D.G.; Goodyear, A.C.; Kennett, J., West, A. 2011. Multiple lines of evidence for possible human population decline/settlement reorganization during the early Younger Dryas. *Quaternary International* 242(2): 570–583.

Ballard, J.P. 2009. *A Lateglacial Paleofire Record for East-Central Michigan*. M.S. Thesis, University of Cincinnati.

Barden, L.S. 1974. *Lightning Fires in Southern Appalachian Forests.* Ph.D. Dissertation, University of Tennessee.

Bratton, S.P.; Meier, A.J. 1998. The recent vegetation disturbance history of the Chattooga River Watershed. *Castanea* 63(3): 372–381.

Braun, E.L. 1950. *Deciduous Forests of Eastern North America*. Blakiston, Philadelphia.

Broecker, W.S., Denton, G.H., Edwards, R.L., Cheng, H., Alley, R.B., Putnam, A.E. 2010. Putting the Younger Dryas cold event into context. *Quaternary Science Reviews* 29(9): 1078–1081.

Brown, H. 2000. Wildland burning by American Indians in Virginia. *Fire Management Today* 60(3): 29–39.

Causey, L.V. 1963. Geology and ground-water resources of St. Clair County, Alabama. *Geological Survey of Alabama Bulletin* 73:1–84.

Chapman, J.; Delcourt, P.A.; Cridelbaugh, P.A.; Shea, A.B.; Delcourt, H.R. 1982. Man-land interaction: 10,000 years of American Indian impact on Native ecosystems in the Lower Little Tennessee River Valley, eastern Tennessee. *Southeastern Archaeology* 1(2): 115–121.

Colinvaux, P.A.; De Oliveira, P.E.; Moreno, J.E. 1999. *Amazon Pollen Manual and Atlas*. Harwood Academic Publishers, Amsterdam.

Daniau, A.-L.; Bartlein, P.J.; Harrison, S.P.; Prentice, I.C.; Brewer, S.; Friedlingstein, P.; Harrison-Prentice, T.I.; Inoue, J.; Izumi, K.; Marlon, J.R.; Mooney, S.; Power, M.J.; Stevenson, J.; Tinner, W.; Andrič, M.; Atanassova, J.; Behling, H.; Black, M.; Blarquez, O.; Brown, K.J.; Carcaillet, C.; Colhoun, E.A.; Colombaroli, D.; Davis, B.A.S.; D'Costa, D.; Dodson, J.; Dupont, L.; Eshetu, Z.; Gavin, D.G.; Genries, A.; Haberle, S.; Hallett, D.J.; Hope, G.; Horn, S.P.; Kassa, T.G.; Katamura, F.; Kennedy, L.M.; Kershaw, P.; Krivonogov, S.; Long, C.; Magri, D.; Marinova, E.; McKenzie, G.M.; Moreno, P.I.; Moss, P.; Neumann, F.H.; Norström, E.; Paitre, C.; Rius, D.; Roberts, N.; Robinson, G.S.; Sasaki, N.; Scott, L.; Takahara, H.; Terwilliger, V.; Thevenon, F.; Turner, R.; Valsecchi, V.G.; Vannière, B.; Walsh, M.; Williams, N.; Zhang, Y. 2012. Predictability of biomass burning in response to climate changes. *Global Biogeochemical Cycles* 26(GB4007): 1–12.

Dean, W.E. 1974. Determination of carbonate and organic matter in calcareous sediments and sedimentary rocks by loss on ignition: comparison with other methods. *Journal of Sedimentary Petrology* 44(1): 242–248.

Delcourt, H.R. 1978. *Late Quaternary Vegetation History of the Eastern Highland Rim and Adjacent Cumberland Plateau of Tennessee.* Ph.D. Dissertation, University of Minnesota.

Delcourt H.R. 1979. Late Quaternary vegetation history of the eastern Highland Rim and adjacent Cumberland Plateau of Tennessee. *Ecological Monographs* 49(3): 255–280.

Delcourt, H.R.; Delcourt, P.A.; Spiker, E.C. 1983. A 12,000-year record of forest history from Cahaba Pond, St. Clair County, Alabama. *Ecology* 64(4): 874–887.

Delcourt, H.R.; Delcourt, P.A. 1985. Quaternary palynology and vegetational history of the southeastern United States. *In: Pollen Records of late-Quaternary North American Sediments* (Eds.: Bryant Jr., V.M.; Holloway, R.G.), American Association of Stratigraphic Palynologists Foundation, Nottingham, the United Kingdom, pp. 1–37.

Delcourt, H.R.; Delcourt, P.A. 1997. Pre-Columbian Native American use of fire on southern Appalachian landscapes. *Conservation Biology* 11(4): 1010–1014.

Delcourt, H.R.; Delcourt, P.A. 1994. Postglacial rise and decline of *Ostrya virginiana* (Mill.) K. Koch and *Carpinus caroliniana* Walt. in eastern North America: predictable responses of forest species to cyclic changes in seasonality of climates. *Journal of Biogeography* 21: 137–150.

Delcourt, P.A.; Delcourt, H.R. 1998. The influence of prehistoric human-set fires on oak-chestnut forests in the southern Appalachians. *Castanea* 63(3): 337–345.

Delcourt, P.A.; Delcourt, H.R.; Ison, C.R.; Sharp, W.E.; Gremillion, K.J. 1998. Prehistoric human use of fire, the Eastern Agricultural Complex, and Appalachian oak–chestnut forests: paleoecology of Cliff Palace Pond, Kentucky. *American Antiquity* 63: 263–278.

Dyke, A.S. 2004. An outline of North American deglaciation with emphasis on central and northern Canada. *In: Quaternary Glaciations: Extent and Chronology,* Volume 2 (Eds.: Ehlers, J.; Gibbard, P.L.; Hughes, P.D.), Elsevier, Amsterdam, pp. 373–424.

Fiedel, S.J., 2011. The mysterious onset of the Younger Dryas. *Quaternary International* 242(2): 262–266.

Firestone, R.B.; West, A.; Kennett, J.P.; Becker, L.; Bunch, T.E.; Revay, Z.S.; Schultz, P.H.; Belgya, T.; Kennett, D.J.; Erlandson, J.M.; Dickenson, O.J.; Goodyear, A.C.; Harris, R.S.; Howard, G.A.; Kloosterman, J.B.; Lechler, P.; Mayewski, P.A.; Montgomery, J.; Poreda, R.; Darrah, T.; Hee, S.S.; Smith, A.R.; Stich, A.; Topping, W.; Wittke, J.H.; Wolbach, W.S. 2007. Evidence for an extraterrestrial impact 12,900 years ago that contributed to the megafaunal extinctions and the Younger Dryas cooling. *Proceedings of the National Academy of Sciences of the United States of America* 104(41): 16016–16021.

Franklin, J.D. 2002. The Prehistory of Fentress County, Tennessee: An Archaeological Survey. Ph.D. Dissertation, University of Tennessee.

Franklin, J.D. 2015. Rock shelters of the Upper Cumberland Plateau of Tennessee. http://faculty.etsu.edu/franklij/ucp_shelter_page.htm [Accessed July 7, 2015].

Gill, J.L.; Williams, J.W.; Jackson, S.T.; Lininger, K.B.; Robinson, G.S. 2009. Pleistocene megafaunal collapse, novel plant communities, and enhanced fire regimes in North America. *Science* 326: 1100–1103.

Gill J.L.; Williams J.W.; Jackson S.T.; Donnelly, J.P.; Schellinger, G.C. 2012. Climatic and megaherbivory controls on late-glacial vegetation dynamics: a new, high-resolution, multi-proxy record from Silver Lake, Ohio. *Quaternary Science Reviews* 34: 66–80.

Goodyear III, A.C. 2010. Instrument-assisted fluting as a technochronological marker among North American Paleoindian points. *Current Research in the Pleistocene* 27: 86–88.

Gremillion, K.J. 1996. The paleoethnobotanical record for the mid-Holocene Southeast. *In: Archaeology of the Mid-Holocene Southeast* (Eds.: Sassaman, K.E.; Anderson, D.G.), University Press of Florida, Gainesville, pp. 99–114.

Halsey, J.R., 1999. Late Woodland Burial Practices. *In: Retrieving Michigan's Buried Past: The Archaeology of the Great Lakes State* (Ed.: Halsey, J.R.), Cranbrook Institute of Science, Bloomfield Hills, Michigan pp. 234–248.

Heyerdahl, E.K.; Card, V. 2000. Implications of paleorecords for ecosystem management. *Trends in Ecology and Evolution* 15(2): 49–50.

Hupy, C.M.; Yansa, C.H. 2009. The vegetation history of Michigan: the last 17,000 years. *In: Michigan: A Geography* (Eds.: Schaetzl, R.S.; Darden, J.; Brandt, D.), Thomson Publishing, Washington, D.C., pp. 91–105.

Hussey, T.C. 1993. *A 20,000 Year History of Vegetation and Climate at Clear Pond, Northeastern South Carolina.* M.S. Thesis, University of Maine.

Jackson, S.T.; Whitehead, D.R. 1993. Pollen and macrofossils from Wisconsinan interstadial sediments in northeastern Georgia. *Quaternary Research* 39: 99–106.

Juggins. S. 2010. C2 Version 1.5 User guide. Software for ecological and palaeoecological data analysis and visualisation. Newcastle University, Newcastle upon Tyne, the United Kingdom.

Kapp, R.O. 1999. Michigan Late Pleistocene, Holocene and presettlement vegetation and climate. *In*: *Retrieving Michigan's Buried Past: The Archaeology of the Great Lakes State*. (Eds.: Halsley, J.R.; Stafford, M.D.), Cranbrook Institute of Science, Bloomfield Hills, Michigan, pp. 30–58.

Kingsley R.G. 1999. The Middle Woodland period in southern Michigan. *In: Retrieving Michigan's Buried Past: the Archaeology of the Great Lakes State* (Ed.: Halsey, J.R.), Cranbrook Institute of Science, Bloomfield Hills, Michigan, pp. 148–172.

Komarek, E.V. 1974. Effects of fire on temperate forests and related ecosystems: southeastern United States. *In: Fire and Ecosystems* (Eds.: Kozlowski, T.T.; Ahlgren, C.E.), Academic Press, San Diego, pp. 251–277.

Lafon, C.W.; Hoss, J.A.; Grissino-Mayer, H.D. 2005. The contemporary fire regime of the central Appalachian Mountains and its relation to climate. *Physical Geography* 26(2): 126–146.

Kneller, M.; Peteet, D. 1993. Late-Quaternary climate in the Ridge and Valley of Virginia, U.S.A.: changes in vegetation and depositional environment: a contribution to the 'North Atlantic Seaboard Programme' of IGCP–253, Termination of the Pleistocene. *Quaternary Science Reviews* 12: 613–628.

LaMoreaux, H.K.; Brook, G.A.; Knox, J.A. 2009. Late Pleistocene and Holocene environments of the southeastern United States from the stratigraphy and pollen content of a peat deposit on the Georgia coastal plain. *Palaeogeography, Palaeoclimatology, Palaeoecology* 280: 300–312.

Lepper, B.T. 1999. Pleistocene peoples of midcontinental North America. *In: Ice Age Peoples of North America: Environments, Origins, and Adaptations of the First Americans* (Eds.: Bonnichsen, R.; Turnmire, K.L.), Oregon University Press, Corvallis, pp. 362–394.

Lepper, B.T.; Funk, R.E. 2006. Paleo-indian: east. *In: Handbook of North American Indians,* Volume 3. Environment, Origins and Population (Ed.: Ubelaker, D.H.), Smithsonian Institution, Washington, D.C., pp. 171–193.

Liu, Y.; Andersen, J.J.; Williams, J.W.; Jackson, S.T. 2013. Vegetation history in central Kentucky and Tennessee (U.S.A.) during the last glacial and deglacial periods. *Quaternary Research* 79(2): 189–198.

Long, A.; Prestemon, J. 2013. Wildfire ignitions: state of the science in the Southeast. Southern Fire Exchange Fact Sheet 2013-1, Joint Fire Science Program. U.S.D.A. Forest Service, Southern Research Station.

Matlack, G.R. 2013. Reassessment of the use of fire as a management tool in deciduous forests of eastern North America. *Conservation Biology* 27(5): 916–926.

Manny, B.A.; Wetzel, R.G.; Bailey, R.B. 1978. Paleolimnological sedimentation of organic carbon, nitrogen, phosphorus, fossil pigments, pollen and diatoms in a hypereutrophic, hardwater lake: a case history of eutrophication. *Polskie Archiwum Hydrobiologii* 25: 243–267.

Mills, H.H.; Delcourt, P.A. 1991. Quaternary geology of the Appalachian Highlands and Interior Low Plateaus. *In: Quaternary Nonglacial Geology: Conterminous U.S.* (Ed.: Morrison R.B.), The Geology of North America, volume K-2. The Geological Society of America, Boulder, Colorado.

Mitchener, L.J.; Parker, A.J. 2005. Climate, lightning, and wildfire in the national forests of the southeastern United States: 1989–1998. *Physical Geography* 26(2): 147–162.

Patterson III, W.A.; Sassaman, K.E. 1988. Indian fires in the prehistory of New England. *In: Holocene Human Ecology in Northeastern North America* (Ed.: Nicholas, G.P.), Plenum Press, New York, pp. 107–135.

Peteet, D. 1995. Global Younger Dryas? *Quaternary International* 28: 93–104.

Pyne, S.J. 2000. Where have all the fires gone? *Fire Management Today* 60(3): 4–6.

Reimer, P.J.; Bard, E.; Bayliss, A.; Beck, J.W.; Blackwell, P.G.; Ramsey, C.B.; Buck, C.E.; Cheng, H.; Edwards, R.L.; Friedrich, M.; Grootes, P.M.; Guilderson, T.P.; Haflidason, H.; Hajdas, I.; Hatté, C.; Heaton, T.J.; Hoffmann, D.L.; Hogg, A.G.; Hughen, K.A.; Kaiser, K.F.; Kromer, B.; Manning, S.W.; Niu, M.; Reimer, R.W.; Richards, D.A.; Scott, E.M.; Southon, J.R.; Staff, R.A.; Turney, C.S.M.; van der Plicht, J. 2013. INTCAL13 and MARINE13 Radiocarbon age calibration curves 0–50,000 Years Cal BP. *Radiocarbon* 55(4): 1869–1887.

Reimer, P.J.; Brown, T.A.; Reimer, R.W. 2004. Discussion reporting and calibration of post-bomb ^{14}C data. *Radiocarbon* 46(3): 1299–1304.

Robinson, G.S.; Burney, L.P.; Burney, D.A. 2005. Landscape paleoecology and megafaunal extinction in southeastern New York State. *Ecological Monographs* 75(3): 295–315.

Schaetzl, R. 2015. Native Americans in the Great Lakes region. http://geo.msu.edu/extra/geogmich/paleo-indian.html [Accessed July 7, 2015].

Shelton, N. 1981. *Great Smoky Mountains National Park.* National Park Handbook 112. United States National Park Service, Division of Publications, Washington D.C.

Simons, D.B. 1997. The Gainey and Butler Sites as focal points for caribou and people. *In: Caribou and Reindeer Hunters of the Northern Hemisphere* (Eds.: Jackson, L.J.; Thacker, P.T.), Avebury, Brookfield, Vermont, pp. 105–131.

Stuiver, M.; Reimer, P. J. 1993. Extended ^{14}C database and revised CALIB radiocarbon calibration program. *Radiocarbon* 35(1): 215–230.

Taylor, B.E.; Rich, F.J.; Brooks, M.J.; Ivester, A.H.; Clement, C.O. 2011. Late Pleistocene and Holocene vegetation changes in the Sandhills, Fort Jackson, South Carolina. *Southeastern Geology* 48(3): 147–163.

Telford, R.J.; Heegaard, E.; Birks, H.J.B. 2004. The intercept is a poor estimate of a calibrated radiocarbon age. *The Holocene* 14(2): 296–298.

Tubbs, C.H.; Houston, D.R. 1990. *Fagus grandifolia* Ehrh. American beech. *In: Silvics of North America,* Volume 2, Hardwoods. Agricultural Handbook 654 (Technical Coordinators: Burns, R.M.; Honkala, B.H.), U.S.D.A. Forest Service, Washington D.C., pp 324–332. http://www.na.fs.fed.us/pubs/silvics_manual/volume_2/fagus/grandifolia.htm [Accessed: July 5, 2015].

Van Lear, D.H.; Waldrop, T.A. 1989. History, uses, and effects of fire in the Appalachians. General Technical Report SE-54, U.S.D.A. Forest Service, Southeastern Forest Experiment Station, Asheville, North Carolina.

Walthall, J.A. 1990. *Prehistoric Indians of the Southeast: Archaeology of Alabama and the Middle South*. University of Alabama Press, Tuscaloosa.

Watts, W.A. 1975. Vegetation record for the last 20,000 years from a small marsh on Lookout Mountain, Northwestern Georgia. *Geological Society of America Bulletin* 86(3): 287–291.

Webb, R.S.; Webb III, T. 1988. Rates of sediment accumulation in pollen cores from small lakes and mires of eastern North America. *Quaternary Research* 30: 284–297.

Whitehead, D.R.; Sheehan, M.C. 1985. Holocene vegetational changes in the Tombigbee River Valley, eastern Mississippi. *American Midland Naturalist* 113(1): 122–137.

Whiteman, C.D. 2000. *Mountain Meteorology: Fundamentals and Applications*. Oxford University Press, New York.

Whitlock, C.; Anderson, R.S. 2003. Fire history reconstructions based on sediment records from lakes and wetlands. *In: Fire and Climatic Change in Temperate Ecosystems of the Western Americas* (Eds: Veblen, T.T.; Baker, W.L.; Montenegro, G.; Swetnam, T.W.), Springer-Verlag, New York, pp. 3–31.

Whitlock, C.; Larsen, C. 2001. Charcoal as a fire proxy. *In: Tracking Environmental Change Using Lake Sediments,* Volume 3 (Eds: Smol, J.P.; Birks, H.J.B.; Last, W.M.; Bradley, R.S.; Alverson, K.), Kluwer Academic Publishers, Dordrecht, The Netherlands, pp. 75–97.

Wilkins, G.R. 1985. *Late-Quaternary Vegetational History at Jackson Pond, Larue County, Kentucky*. M.S. Thesis, University of Tennessee.

Wilkins, G.R.; Delcourt, P.A.; Delcourt, H.R.; Harrison, F.W.; Turner, M.R. 1991. Paleoecology of central Kentucky since the Last Glacial Maximum. *Quaternary Research* 36(2): 224–229.

Williams, G.W. 2000. Introduction to aboriginal fire use in North America. *In*: *Fire Management Today* 60(3): 8–12.

Chapter 3 Appendix

Table 3.1 Radiocarbon dates and calibrations for sediment core from Cahaba Pond, Alabama (CP-79B), collected in 1979.

Lab Number[a]	Core interval (cm)	Depth in profile midpoint (cm)	Depth below mud/water interface midpoint (cm)	Material Dated	$\delta^{13}C$ (‰)	Uncalibrated ^{14}C age (^{14}C yr BP)	Calibrated Age yr BP (2–sigma) [b]	Relative Area Under Calibration Curve	Weighted Mean Calibration Age cal yr BP [c]
		127	0			cored in 1979			–29
W–4770	134–145	139.5	12.5	bulk sediment		840 ±50	804–677 831–808 905–853	0.82345 0.045265 0.131285	767
W–4784	165–171	168	41	bulk sediment		1750 ± 50	1430–1423 1455–1442 1872–1521	0.003262 0.00736 0.989378	1672
W–4780	200–207	203.5	76.5	bulk sediment		2990 ±80	3370–2952	1.0	3161
W–4906	210–214	212	85	bulk sediment		5750 ± 90	6371–6322 6742–6392	0.035396 0.964604	6550
W–4910	242–245	243.5	116.5	bulk sediment		8190 ± 90	8825–8810 8878–8872 9442–8978	0.004349 0.001739 0.993912	9165
W–4771	245–250	247.5	120.5	bulk sediment		8710 ± 80	9936–9531 10004–9995 10120–10064	0.965498 0.003145 0.031357	9729
W–4773	345–351	348	221	bulk sediment		9680 ± 100	11245–10733	1.0	11007
W–4775	445–451	448	321	bulk sediment		9960 ± 90	11772–11208 11792–11789	0.999284 0.000716	11472

Table 3.1 Continued.

Lab Number[a]	Core interval (cm)	Depth in profile midpoint (cm)	Depth below mud/water interface midpoint (cm)	Material Dated	$\delta^{13}C$ (‰)	Uncalibrated ^{14}C age (^{14}C yr BP)	Calibrated Age yr BP (2–sigma) [b]	Relative Area Under Calibration Curve	Weighted Mean Calibration Age cal yr BP [c]
W–4778	**540–550**	**545**	**418**	**bulk sediment**		**10190 ± 80**	**11569–11404** **11576–11572** **12160–11591**	**0.061117** **0.001038** **0.937845**	**11861**
Beta–379635	539–540	539.5	412.5	plant macrofossils	–24.8	10360 ±40	12398–12039	1.0	12226
Beta–379636	590–591	590.5	463.5	plant macrofossils	–27.7	10890 ±40	12791–12689	1.0	12734
W–4782	**560–570**	**565**	**438**	**bulk sediment**		**10980 ± 100**	**13049–12712**	**1.0**	**12871**
W–4781	640–650	645	518	bulk sediment		11270 ± 130	13382–12824	1.0	13124
W–4783	720–730	725	598	bulk sediment		11780 ± 120	13852–13344 13936–13903	0.989852 0.010148	13615
QL–1486	750–766	758	631	bulk sediment		11960 ± 70	14008–13586	1.0	13814

[a] Beta-379635 and Beta-379636 are AMS dates obtained for this study. Other dates are standard dates from Delcourt et al. (1983). These new AMS dates were used in place of the standard dates in bold in our age model. Analyses were performed by Beta Analytic, University of Washington (QL); and USGS Radiocarbon Laboratory, Reston, Virginia.

[b] Calibrations were calculated using CALIB 7.0.2 (Stuiver and Reimer, 1993) and the dataset of Reimer et al. (2013).

[c] Weighted mean of the 2 σ calibrated radiocarbon probability distribution.

Table 3.2 Radiocarbon dates and calibrations for sediment cores from Jackson Pond, Kentucky (JP-83B), collected in 1983

Lab Number[a]	Core interval (cm)	Depth in profile midpoint (cm)	Depth below mud/water interface midpoint (cm)	Material Dated	Uncalibrated ^{14}C age (^{14}C yr BP)	Calibrated Age yr BP (2–sigma) [b]	Relative Area Under Calibration Curve	Weighted Mean Calibration Age cal yr BP [c]
		93	0		cored in 1983			–33
A–3870	128–138	133	40	bulk sediment	120 ± 50	151–7 280–171	0.602548 0.397452	140
A–3871	155–166	160.5	67.5	bulk sediment	940 ± 80	980–690	1.0	849
A–3872	215–226	220.5	127.5	bulk sediment	10040 ± 190	12251–11138 12388–12259	0.970363 0.029637	11651
A–3873	263–277	270	177	bulk sediment	11860 ± 250	14490–13134	1.0	13769
A–3874	505–515	510	417	bulk sediment	17750 ± 270	22188–20758	1.0	21459
A–3875	700–710	705	612	bulk sediment	20330 ± 630	25830–23025	1.0	24461

[a] All radiocarbon dates are from Wilkins et al. (1991). Analyses were performed by the University of Arizona Laboratory of Geochronology, Tucson.

[b] Calibrations were calculated using CALIB 7.0.2 (Stuiver and Reimer, 1993) and the dataset of Reimer et al. (2013).

[c] Weighted mean of the 2 σ calibrated radiocarbon probability distribution.

Table 3.3 Radiocarbon dates and calibrations for lake-sediment cores from Pigeon Marsh, Georgia (PM-2013-1) collected in 2013.

Lab Number[a]	Core interval (cm)	Depth below mud/water interface midpoint (cm)	Material Dated	$\delta^{13}C/^{12}C$ (‰)	Uncalibrated ^{14}C age (^{14}C yr BP)	Calibrated Age yr BP (2–sigma) [b]	Relative Area Under Calibration Curve	Weighted Mean Calibration Age cal yr BP [c]
		0						–63
Beta–396124[d]	16–18	17	wood	–27.0	154.8 ± 0.3 pMC	–13.30 to –13.22 –18.53 to –18.25 –20.01 to –18.77 –20.83 to –20.22 –22.06 to –21.99	0.040 0.103 0.617 0.229 0.012	–21
Beta-408513	22.5–24.5	23.5	charcoal, plant fragments	–28.0	12700 ± 60	14841–15315	1.0	15110
Beta–402430	32–34	33	leaf fragments	–27.9	12660 ± 40 BP	15236–14826	1.0	15058
Beta–382660	51.5–53.5	52.5	leaf fragments	–27.4	13630 ±40	16639–16238	1.0	16430

[a] All dates are from this study. Analyses were performed by Beta Analytic.

[b] Calibrations were calculated using CALIB 7.0.2 (Stuiver and Reimer, 1993) and the dataset of Reimer et al. (2013).

[c] Weighted mean of the 2 σ calibrated radiocarbon probability distribution.

[d] Calibrations were calculated using CALIBomb (Reimer et al. 2004).

Figure 3.1 Map of eastern North America with the three study sites and the comparison sites Anderson Pond and Slack and Swift Lakes indicated with stars. The line represents the maximum extent of the Laurentide Ice Sheet (LIS) roughly 20,000 years ago. Ice sheet reconstruction after Dyke (2004)

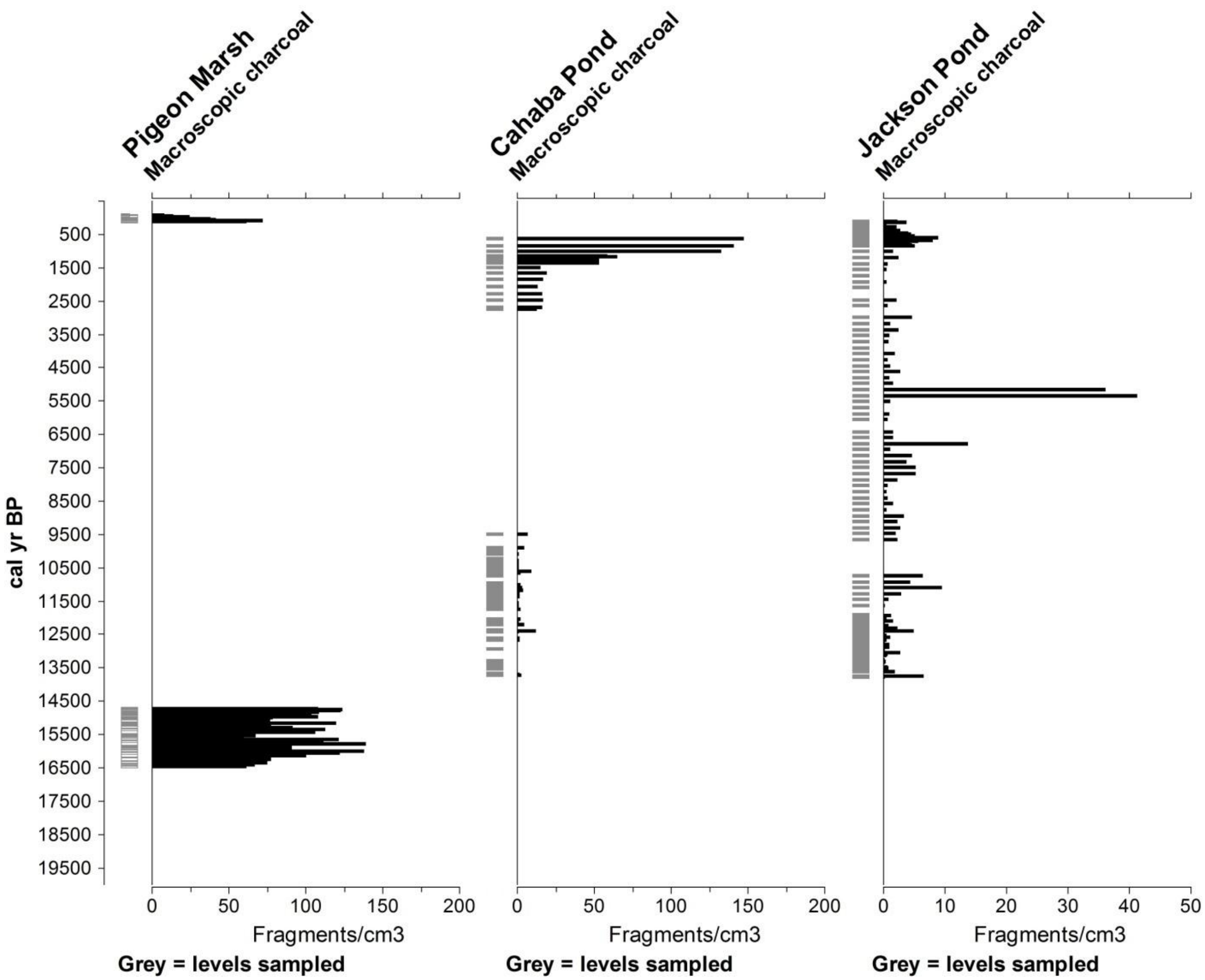

Figure 3.2 Macroscopic charcoal data graphed as fragments/cm^3 (black bars) for Pigeon Marsh, Georgia; Cahaba Pond, Alabama; and Jackson Pond, Kentucky. Gray lines are sample levels and indicate gaps in data or hiatuses in the records. Note different scale for the Jackson Pond profile, in which charcoal is less abundant.

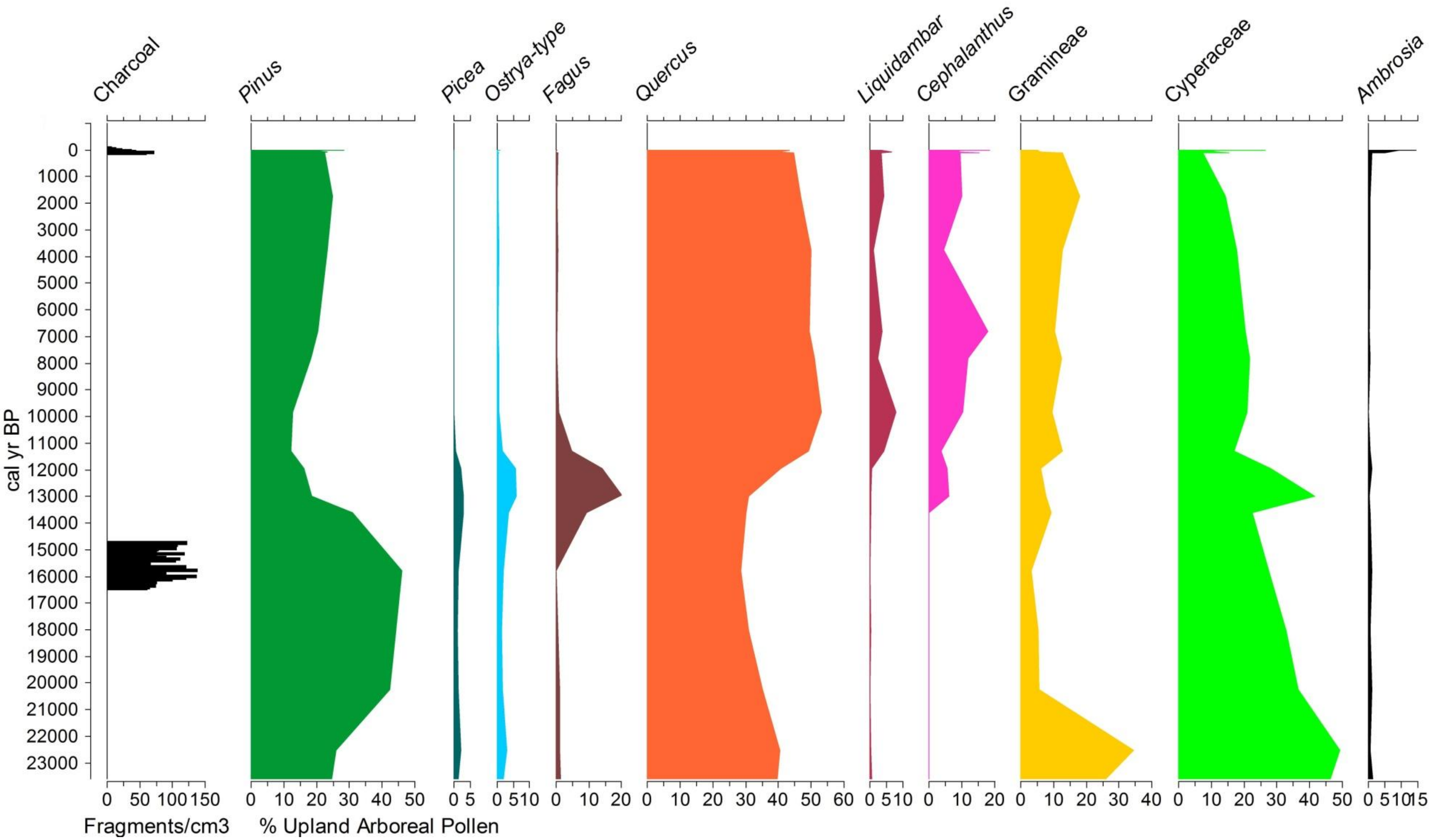

Figure 3.3 Pigeon Marsh macroscopic charcoal concentrations shown together with pollen data from Watts (1975). Pollen percentage data and the age model used to plot them are both courtesy of E Grimm. All pollen types are shown as the percentage of upland arboreal pollen, excluding *Cephalanthus*, other swamp shrubs, and all herbaceous taxa. The age model for the pollen is based on the original radiocarbon dates obtained by Watts (1975), his *Ambrosia* peak, and the dating of the late-glacial *Fagus* peak at Clear Pond, South Carolina (E. Grimm, pers. communication to S. Horn, June 3, 2015).

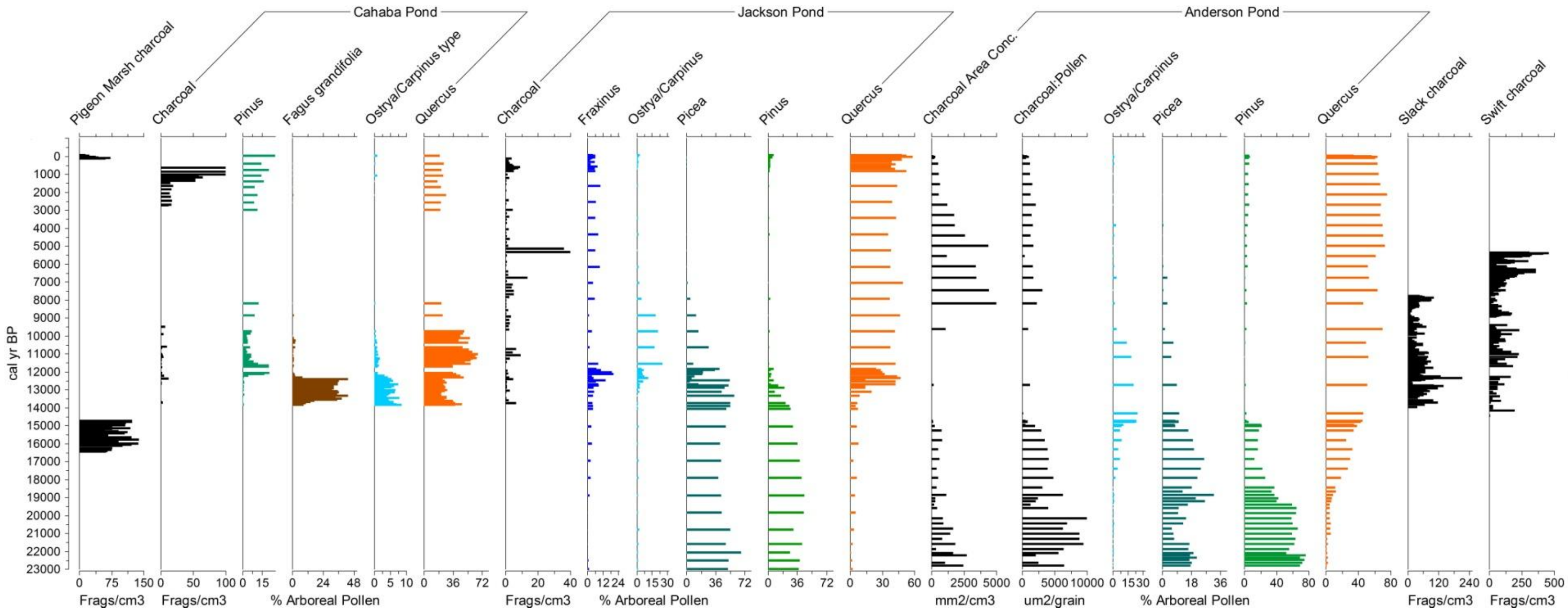

Figure 3.4 Charcoal and pollen comparisons. Pigeon Marsh macroscopic charcoal; Cahaba Pond macroscopic charcoal and selected pollen taxa, as percent arboreal pollen; Jackson Pond charcoal and selected pollen taxa; Anderson Pond microscopic charcoal as charcoal area concentrations (mm^2/cm^3) and charcoal:pollen ratios (μm^2/grain), with selected pollen taxa; and Swift and Slack Lake macroscopic charcoal. All macroscopic charcoal is graphed as charcoal fragments/cm^3. Some high charcoal values in the Cahaba and Jackson pond charcoal graphs are truncated to better show the lower values.

Chapter 4

Siliceous Aggregates in Late Glacial Lake Sediments in the Eastern U.S.: Markers for Ash from Wildfire Events

This chapter is in preparation for submission to a peer-reviewed geology journal. My co-authors are Steven G. Driese, Sally P. Horn, Chad S. Lane, and Zheng-Hua Li.

4.1 Abstract

Thin-section analysis of late-glacial sediments from five lacustrine sites in the eastern U.S. revealed an unusual grain type, here designated as "siliceous aggregates." Siliceous aggregates are grains that consist of very fine to medium silt-sized monocrystalline quartz grains, cemented primarily with amorphous silica from dissolved phytoliths, and are 50–200 μm in diameter. Based on previous findings, mainly from studies at archaeological sites, the hypothesis that siliceous aggregate grains originate from wood ash was tested in the laboratory using an experimental design involving different combinations of beech and mixed hardwood ash, different solution chemistries ("natural" and low pH rainfall), presence/absence of detrital very fine to medium quartz silt (simulating loessal silts), and the presence/absence of organic matter. The results of the experiments showed that siliceous aggregates form from wood ash, independent of acidity and algae, but require the presence of loessal quartz silt grains and an aqueous solution to develop. Very little is known about the silica component of wood ash; the experiments in this study provides needed insight into this area. Stacked datasets of siliceous aggregate occurrences by calibrated ages in five lake-sediment cores, together with charcoal concentrations, total nitrogen and $\delta^{15}N$, sedimentary calcium (in a suite of elements that occur in wood ash), selected pollen percentages showing major vegetation shifts, and combustion markers in the GISP2 and GRIP ice cores suggest that during the late glacial period, two—possibly more—large-scale wildfire events occurred in eastern North America. Ca, K, and Mg in the GISP2 ice core may link to wood ash produced by such wildfires. Siliceous aggregates in lake-sediment cores appear to be a good indicator of wood ash generated by paleofires, and may occur in the absence of a charcoal peak.

4.2 Introduction

In this study, siliceous aggregate grains discovered in sediment cores from lakes and wetlands in the eastern U.S. are described and interpreted genetically. Siliceous aggregates are composed of very fine- to medium-silt-sized monocrystalline quartz grains cemented primarily with amorphous silica, and typically range from 50–200 μm in diameter. They sometimes contain organic inclusions and calcite. They are rare in the sediment record, occurring at only three times since the Last Glacial Maximum (at ca. 19,250, 14,000 and 12,400 cal yr BP) for six sites investigated along a roughly north-south transect across the interior eastern U.S. region. Our interpretations are supported by results from laboratory experiments that were designed to test the hypothesis that these grains are genetically related to wood ash produced by wildfires. Siliceous aggregates form diagenetically by wetting of wood ash after a fire. They require the input of loess; phytoliths in the wood ash are dissolved by highly alkaline ash and the amorphous silica nucleates around the loess when pH is lowered. Weiner (2010), working in archaeological settings, previously postulated that siliceous aggregates are indicators of fire.

Weiner (2010) studied siliceous aggregates in Hayonim and Kebara caves in Israel, and characterized the matrix silica in the siliceous aggregates as complex and having soil minerals embedded in it. He further stated that the silica was synthesized by the tree, primarily in the bark. Schiegl et al. (1996) reported that siliceous aggregates had been found in the ash from the heartwood of recently cut trees, and thus must have formed within the tree, although how they formed and why, was unknown. Schiegl et al. (1996) also studied siliceous aggregates in the Israeli cave environments and reported that they could undergo diagenesis in an acidic environment.

The concrete industry may also provide useful insights into the production and geochemical behavior of amorphous silica. Wood ash is used as a raw material for Portland cement, and an expanding gel forms in concrete exposed to constant moisture if the alkali content (Na_2O+K_2O) is too high, leading to an alkali-silica reaction (Øye 2012).

Diagenesis and formation of siliceous aggregates at open landscape sites must take place on land with secondary transport into lakes because of the presence of organic terrestrial inclusions in some aggregates. Biogenic silica dissolves at pH >9.8 (Maynard 2015) at 25 ºC (Dove et al. 2008). In wood ash with typical pH of 13.0, phytoliths dissolve when the wood ash is rained upon. When the pH drops below 9.8, the amorphous silica will precipitate onto any silt-sized quartz grains in the wood ash. Dove et al. (2008) studied the kinetics of amorphous silica dissolution, since the mechanisms by which amorphous silica dissolves are poorly understood.

In this study, thin-section examination of the lake sediments revealed that siliceous aggregates are rare from 23,000 cal yr BP to recent time. Occurrences clustered around three times: once around the Last Glacial Maximum, and twice during late glacial time. Their rarity may indicate that they formed under specific and unusual paleoenvironmental conditions. Because siliceous aggregates occur at about the same two times in five of six sites examined in the eastern U.S., it is reasonable to infer that they could represent distinctive large-scale events that occurred possibly contemporaneously across this region. We address the following research questions:

1. Does the timing of the occurrences of siliceous aggregates in sediment records from lakes in the eastern U.S. show a relationship to peaks in total nitrogen and $\delta^{15}N$ in these records?

2. Can siliceous aggregates be produced in the laboratory in samples of wood ash?

3. Do siliceous aggregates require rainwater, nitric acid rain, or organic acids from e.g. algae, to form?

4. How much time is required for siliceous aggregates to form?

5. Is silt important for the formation of siliceous aggregates?

6. Are the occurrences of siliceous aggregates in the lake-sediment records examined contemporaneous, suggesting the possibility of large-scale events?

7. Is there evidence in ice cores of large-scale biomass burning at the time of siliceous aggregate occurrences?

4.3 Study Sites and Methods

Lake sediments from six sites in eastern North America (Figure 4.1) were analyzed using petrographic thin sections together with analyses of sedimentary charcoal, nitrogen isotopes, and elemental composition. The 2-m long core from Anderson Pond analyzed in this study was collected by Stephen Jackson and Jack Williams in 2007 and is parallel to the 7.5-m long core in which they analyzed pollen and obtained AMS radiocarbon dates (Liu et al. 2013). Sediment cores from Cahaba Pond, Alabama were collected in 1979 by Delcourt et al. (1983). The Jackson Pond, Kentucky sediment core was collected in 1983 by Wilkins et al. (1991). Pigeon Marsh cores were collected in December 2013 by J.Ballard and S. Horn; prior work by Watts (1975) guided the field work. Slack and Swift lake-sediment cores were collected by J. Ballard, Thomas V. Lowell, and students in 2008 (Ballard 2009).

4.3.1 Thin-Section Micromorphology

Micromorphological analyses using petrographic thin sections focused on identifying spatial and temporal distributions of siliceous aggregates. A total of 42 thin sections was prepared from the six study sites, comprising a total coverage of 229 cm of strata examined microscopically (Table 4.1). Because Anderson Pond, Tennessee was the first site studied and was exploratory, sampling on the core was across a wider depth interval than on the other lake-sediment cores. The core from Pigeon Marsh also was sampled along its entire length. For other sites and cores, sampling was targeted on major pollen shifts or charcoal intervals, with radiocarbon age control also as a guide. Samples were also obtained from both above and below target depths to place the results in context. Core samples from already-dried cores were cut to size with a hacksaw, marked, and wrapped for shipment. These cores were from Cahaba and Jackson Ponds. All moist core samples were first air-dried and then surface-impregnated with low-viscosity epoxy to stabilize them for shipment to a commercial lab for subsequent preparation into standard (30 μm thick) thin sections. Samples were examined at Baylor University using an Olympus BX51 research microscope equipped with a Leica 6.5 Mpx digital camera and Leica image processing software, using both standard plane-polarized (PPL) and cross-polarized (XPL) light, as well as with UV fluorescence (UVf).

4.3.2 Nitrogen Isotopes

Nitrogen isotope data ($\delta^{15}N$ and total nitrogen contents) were determined for dried, ground, non-acidified bulk sediments in N analyses from five of the six sites following the suggestion of Brodie et al. (2011), who advised against using acidified bulk sediment samples prepared for stable carbon isotope analysis for nitrogen isotope analysis. They considered that acidification may alter the nitrogen isotope signal, and advised preparing separate samples if both C and N isotopes are to be analyzed. For Swift Lake, nitrogen isotope data were only available for acidified samples that we had prepared for stable C analyses in other research, but our comparison of nitrogen isotope data between acidified and non-acidified samples at the other study sites showed nearly indistinguishable values, leading us to feel confident in our use here of values on acidified samples for Swift Lake. The late glacial into early Holocene interval was targeted for sampling, because siliceous aggregates were found around 14,000 cal yr BP during the initial extensive analysis of the Anderson Pond 2007 core. For cores that had experienced shrinkage from original core lengths, calculations were made to adjust to original lengths. Uniform shrinkage across the length of core sections was assumed, unless specific stratigraphic markers were present. The Anderson Pond (AP) 2007 and Cahaba Pond (CP-79B) cores were sampled at ca. 10 cm intervals for nitrogen isotope analysis. The Cahaba Pond (CP-79A), Jackson Pond (JP-83A), Pigeon Marsh (PM 2013), Slack (SLK), and Swift Lake (SW) cores were sampled at high-resolution (1 cm contiguous) to aid in identification of discrete peaks in $\delta^{15}N$ values. Samples were analyzed on a Costech 4010 elemental analyzer interfaced with a Thermo Delta V Plus mass spectrometer at the Center for Marine Science at the University of North Carolina Wilmington. Precision was generally better than 0.2 or 0.3 ‰ based on repeated analyses of USGS 40 and USGS 41 standards. Isotope values were reported in delta notation, where $\delta^{15}N$ (‰ versus atmospheric N_2) = ($^{15}N/^{14}N_{sample} \div {}^{15}N/^{14}N_{air}$-$N_2$ - 1) x 1000 (Hastings et al. 2013). $\delta^{15}N_{air}$ is expected to be 0 ‰ (Talbot 2002). Talbot (2002) gave expected values for the $\delta^{15}N$ of atmospheric NO_3^- as +7 to +10 ‰, while Hastings et al. (2013) gave a range of -15 to +5‰. In the past, the nitrogen isotope composition of sediment organic matter has not been widely used in paleoenvironmental reconstruction, but it is particularly useful as a proxy to identify changes in past availability of nitrogen to aquatic primary producers (Talbot 2002).

4.3.3 XRF Elemental Analysis

XRF analyses were performed contiguously across sections of lake-sediment cores from the six sites to obtain data for elements found in wood ash, which can be 22–92% $CaCO_3$ and contain Ca, K, Al, Mg, Fe, P, Mn, Na, N, and Zn (Risse and Gaskin 2002) (Table 4.2). The purpose was to test for evidence of wood ash inputs to the lake sediments, and measurements were made using a handheld energy-dispersive TRACeR III-V+ portable XRF (Bruker AXS Company) in the Department of Anthropology at the University of Tennessee (UT). Areas under the elemental lines were obtained by means of Gaussian curve fitting, which allows for a semi-quantitative evaluation of the spectral data (Bow 2012). Spectra were deconvoluted and converted to raw data using Spectra ARTAX software 7.2.0.0 (Bow 2012). Data for the Bruker gun was plotted as area under the curve. Elemental data were also obtained from selected depths for the Anderson Pond 2007 core, the Cahaba Pond CP-79B core, and the Swift Lake core using a benchtop BTX Profiler (Olympus) in the UT Department of Geography. The BTX Profiler was also used for XRF analysis of beech wood ash and oven-dried leachate from the pH 1.0 treatment in the wood ash experiments. These data were reported in percent or ppm.

4.3.4 Comparisons with Charcoal and Pollen Data

Microscopic charcoal data from a core collected in 1976 from Anderson Pond (Delcourt, 1979; this dissertation, chapter 2); macroscopic charcoal data from Cahaba Pond, Jackson Pond, and Pigeon Marsh (this dissertation, chapter 3), and macroscopic charcoal records from Slack and Swift Lakes (Ballard 2009) were compared with siliceous aggregate occurrences. Siliceous aggregate occurrences were also compared with the timing of major shifts in vegetation inferred from prior pollen analyses (Delcourt 1979, Delcourt et al. 1983, Wilkins et al. 1991). These pollen data were obtained from the dissertations for Anderson Pond (Delcourt 1978) and Jackson

Pond (Wilkins 1985), laboratory notebooks for Anderson Pond, Cahaba Pond, and Jackson Ponds, and Neotoma (Neotoma Paleoecology Database http://www.neotomadb.org) and cross-checked with Delcourt (1978) and Wilkins (1985).

4.3.5 Wood Ash Experimental Design and Methods

Experiments were conducted at the University of Tennessee in an attempt to produce siliceous aggregates in the lab. A basic assumption was that the process required existence of wood ash, generated by fire. Macro- and microelements found in wood ash are somewhat variable (Demeyer et al. 2001), but calcium carbonate is the largest component, along with K, Mg, P, Fe, Al, and Zn (Table 4.2). We prepared our own ash for the experiments, as described below.

For sample containers, 125 ml round polypropylene Nalgene® bottles were modified by cutting off the base of each bottle. The bottle was inverted, with the mouth down, and 30 micron PEEK high temperature mesh was fused to the mouth of each Nalgene bottle using a hot plate. This mesh served the purpose of allowing throughflow of "rain" leachate, while retaining any >30 µm siliceous aggregates that might form.

To determine if siliceous aggregates required an acidic environment to form, experiments were conducted with sets of samples treated with simulated acid rain with low pH values of 1.0 and 2.0, in conjunction with control sets of samples treated with simulated "natural" rain of pH 5.7. A second part of the experiments tested the biological component, to assess whether algae or microbes play a role in siliceous aggregate formation (Figure 4.1.1). A set of two trays of samples was placed in a greenhouse and run parallel to the experiment in the lab.

Experiment 1 consisted of a set of four trays of eight samples each of ash of beech wood (*Fagus grandifolia*). Two greenhouse trays (approximately 25 x 50 cm) were set up in a fume hood, one for pH 5.7 ("natural" weakly acidic rainfall) as a control and another for pH 2.0 ("nitric acid rain"). The trays served as a catchment for the leachate draining through the wood ash samples. Another pair of greenhouse trays (the control and pH 2.0 nitric acid rain) was located in the greenhouse to test whether algae may promote the formation of siliceous aggregates. The greenhouse samples were seeded with cyanobacteria that occurred in the greenhouses, to evaluate whether cyanobacteria, algae, or some other types of microbiota may play a role in siliceous aggregate formation. Taxa included *Euglena*, *Microcystis*, *Chlorococcus* (green algae), and single-celled and filamentous cyanobacteria, including *Lingbya* (Ken McFarland, pers.communication, April 30, 2015).

Beech wood was selected for ash production to simulate the environment at Cahaba Pond, where beech was the dominant taxa until around the time of siliceous aggregate occurrence. Wood was cut up, oven-dried, and burned to ash outdoors in a metal tub. Charcoal was still abundant after cooling and examination, so ash was combusted in large ceramic crucibles (volume ca. 250 cm^3) in a muffle furnace for 1 hr at 500 ºC following methods by Úbeda et al. (2009) and Stoof et al. (2010). Large charcoal pieces persisted, so these were removed by dry sieving with a 2 mm mesh, and separately combusted for two hours at 550 ºC to ash.

Because of the corollary hypothesis that the silt-sized grains in the siliceous aggregates originated either from the wood itself, or from loessal quartz silt, fluvial sediment from the Tennessee River was mechanically sieved to obtain a silt-sized fraction. This sediment was treated with 37% hydrochloric acid to remove yellow iron oxide coatings of silica grains. This treatment was used to control for iron reacting with silica. After washing, the silt fraction was air dried. The fluvial silt-sized sediment included quartz and non-quartz silt.

Each wood ash sample container was filled to a depth of 50 mm with wood ash. Eight sample containers were prepared for each of the four sample sets, which were placed into racks on the greenhouse trays (Figure 4.1.1). As Experiment 1 was exploratory, samples were subjected to eight different treatments in parallel for the four sets. Experiment 1 independent variables were as follows: (1) A control, to which nothing was added — if the silt-sized quartz originates in the wood itself, one might expect siliceous aggregate formation; (2) White quartz silt, to simulate loess, in case the siliceous aggregate formation depends on the presence of loessal silt; (3) Orsa clay (bentonite), because it is a possible source of silica (hydrated aluminosilicate); (4) Iron oxide, because it is known to accelerate dissolution of silica; (5) Iron and white silt; (6) Yellow quartz silt (iron oxide coatings); (7) Very fine quartz sand; and (8) Fine quartz sand.

Experiment 1 was run for a period of 122 days and samples were watered a total of 93 days. Each sample was watered by filling the head space to the rim of the Nalgene bottle and allowing the simulated rain to percolate down through the ash sample and collect in the leachate tray. The pH of the leachate was measured three times the following day, and the leachate poured off into a dedicated collection bucket for that set of samples. Air and sediment temperatures were recorded for samples in the fume hood environment and the greenhouse environment.

Experiment 2 was set up with mixed hardwood ash samples, also burned outdoors in a metal tub. Experiment 2 consisted of two trays in the fume hood, with 12 Nalgene bottles in each, with white silt added to every sample (Figure 4.1.1). The larger sample size was used to facilitate statistical analysis of results. One set of samples was watered with the “natural” pH 5.7 rain, and the other was watered with pH 1.0 simulated nitric acid rain for a period of 32 days, and then switched to pH 2.0 simulated nitric acid rain for the remaining 62 days of the experiment.

Experiment 1 was launched November 5, 2014. Experiment 2 was launched December 3, 2014. Both experiments were stopped on March 6, 2015. Experiments were watered for six out of seven days in a week, with a 12 day period of no rain December 18–30, which was 44 days after the start of Experiment 1 and 13 days after the start of Experiment 2. During this period, trays were wrapped with saran wrap to avoid complete desiccation. The laboratory fume hood was a drier environment than the humid greenhouse.

For thin-section analysis for Experiment 1, samples 1 and 2 were selected from each of the four trays that contained eight samples per tray (no additions; white silt additions). This resulted in a subtotal of eight thin-section samples from Experiment 1. For thin section analysis for Experiment 2, four samples were randomly selected from each of the two trays, which had 12 per set. Thus a subtotal of eight thin section samples was available from Experiment 2. Drying and sample preparation procedures for the 16 samples were identical to those described previously for the natural samples, and preparation of samples into thin sections and thin section analyses were also the same as described previously.

Following thin section analyses, two-tailed Fisher exact tests were used to separately test the interdependence between 1) the addition of silt and the formation of siliceous aggregates, and 2) acid rain and the formation of siliceous aggregates.

4.3.6 Geochronology and Stratigraphic Diagrams

We developed age models primarily using radiocarbon dates obtained by previous researchers: Delcourt (1979) for the Anderson Pond 1976 core; Liu et al. (2013) for the Anderson Pond 2007 core; Delcourt et al. (1983) for the Cahaba cores; and Wilkins et al. (1991) for the Jackson Pond core. From the Cahaba Pond CP-79B core we obtained two AMS dates on organic macrofossils. We also obtained AMS dates on our new core from Pigeon Marsh. Radiocarbon dates were calibrated using the radiocarbon calibration software Calib 7.0.2 (Stuiver and Reimer 1993) and the dataset of Reimer et al. (2013), and CALIBomb (Reimer et al. 2004) for one modern date. Ages for sample depths in all datasets were interpolated linearly using the weighted means of the probability distributions of the calibrated ages (Telford et al. 2004). Stratigraphic diagrams were produced using C2 Software (Juggins 2010).

4.4 Results

4.4.1 Siliceous Aggregates Identified in Lake-Sediment Thin Sections

Siliceous aggregates were identified in thin-sections prepared from late glacial sediments from Anderson Pond (2007 core, Liu et al. 2013), Cahaba Pond, Jackson Pond, Slack Lake and Swift Lake (Figures 4.2, 4.3). The grains are generally 100–200 μm in diameter, but range to as small as 50 μm. They consist of angular grains of very fine silt- to fine-silt-sized, monocrystalline quartz that are cemented by a mainly amorphous to cryptocrystalline silica matrix. In some instances, small amounts of organic matter (visible with UVf) are included within the grains, and organic grains are abundant within the enclosing sediment matrix. Slack and Swift Lake siliceous aggregates were slightly different from those observed at the other sites in that they also contained detrital calcite silt grains, and in some cases iron oxides or oxyhydroxides (Figure 4.3). No siliceous aggregates were identified in thin-sections prepared from Pigeon Marsh sediments. Visual comparison of these natural grains with experimentally produced siliceous aggregate grains (Figures 4.4–4.7) shows that they are similar.

Siliceous aggregate occurrences at each site are compared with total nitrogen and $\delta^{15}N$ data, elemental XRF data, charcoal, and pollen assemblages, as well as Greenland ice core data (Yang et al. 1995, Mayewski et al. 1997). Comparing all five sites (Figure 4.8), siliceous aggregate occurrences cluster at two intervals in the late glacial. At Anderson Pond, Jackson Pond and Slack Lake, they cluster around 14,000 cal yr BP, and at Cahaba Pond and Swift Lake, siliceous aggregates cluster around 12,400 cal yr BP. Siliceous aggregates were found at a third level, around 19,250 cal yr BP in Jackson Pond; sediments of this age were not sampled in the other cores. The 14,000 cal yr BP occurrence level is coincident with small peaks in Ca and a spike in NH_4 in the GISP2 ice cores. The occurrences of siliceous aggregates around the 12,400 cal yr BP level are roughly contemporaneous with increases in Ca, K, and Mg in the GISP2 ice cores.

Comparing siliceous aggregate occurrences to the nitrogen data (Figure 4.9), for the 14,000 cal yr BP level, small peaks exist for total nitrogen (TN) and $\delta^{15}N$ in Anderson Pond and a small peak in TN exists for Swift Lake. At the 12,400 cal yr BP level of siliceous aggregate occurrences, a major shift in both the TN and $\delta^{15}N$ can be observed for Cahaba Pond, and a small peak in TN is seen for Slack Lake. $\delta^{15}N$ for Swift Lake drops across the 12,400 cal yr BP level where a gap occurs between core sections. Data is lacking for the 12,400 cal yr BP level at Anderson Pond, possibly due to low sedimentation rates or a hiatus. No discernable nitrogen peaks are evident in Jackson Pond for the 12,400 cal yr BP level of siliceous aggregate occurrences, and data are lacking for the 14,000 cal yr BP depth. Peaks in NO3 and NH4 occur in the GISP2 ice cores that may be contemporaneous with both levels of siliceous aggregate occurrences.

At Anderson Pond, comparing siliceous aggregate occurrences in the 2007 core with pollen and charcoal data from the 1976 core (Figure 4.10) shows that siliceous aggregates at 14,000 cal yr BP occur at a time when fire activity had declined, and a major shift in vegetation from coniferous to deciduous took place. The XRF data from the 2007 core show steadily increasing Ca values rather than a discrete peak for the time of siliceous aggregate occurrences.

At Cahaba Pond, siliceous aggregates at ca. 12,400 cal yr BP also occur at a time of major transitions in vegetation, when the once-dominant beech declined dramatically and oak became the dominant arboreal taxon (Figure 4.11). At the same time, a major shift in $\delta^{15}N$ and TN occurs, and XRF analysis shows peaks in Ca, K, Fe, and Zn around 12,400 cal yr BP. A small peak in macroscopic charcoal exists at ca. 12,400 cal yr BP.

For Jackson Pond, siliceous aggregates occur at ca. 14,000 cal yr BP, somewhat preceding the major change in pollen (Figure 4.12). Charcoal analysis began just above the 14,000 cal yr BP level but spot checking in lower portions of the core revealed little charcoal. XRF analysis with the Bruker gun shows some small peaks in Ca, K, Mn, Fe, and Al preceding the siliceous aggregates.

At Slack and Swift Lakes, siliceous aggregates in each lake co-occur with large charcoal peaks (Figure 4.13). For Slack Lake, $CaCO_3$ peaks from loss-on-ignition (LOI) coincide with siliceous aggregates found at 14,000 cal yr BP. At Swift, $CaCO_3$ peaks from LOI and XRF at 14,000 also match the time of siliceous aggregates in Slack Lake. Also at ca. 14,000 cal yr BP at Swift, a slight peak in TN occurs. At the 12,400 cal yr BP level at Slack Lake, peaks in TN and

$CaCO_3$ from LOI occur at at the same time as siliceous aggregates in Swift Lake, with a drop in $\delta^{15}N$ at Swift.

Comparing the two markers for fire, charcoal and the by-product of wood ash, siliceous aggregates, reveals that while charcoal peaks are present with siliceous aggregate occurrences at Slack and Swift Lakes, they are absent at Anderson Pond, the only microscopic charcoal record, and only small peaks occur for Cahaba and Jackson Ponds with siliceous aggregates (Figure 4.14).

We compared siliceous aggregrate occurrences with GISP2 (Yang et al. 1995, Mayewski et al. 1997) and GRIP (Legrand et al. 1992, De Angelis et al. 1997, Fuhrer and Legrand 1997) ice core data to look for global biomass burning signals (Figure 4.15). For the cluster of siliceous aggregates at the 14,000 cal yr BP level (Anderson Pond, Jackson Pond, and Slack Lake), peaks occur in the following ions associated with combustion: NO_3, NH_4 (GISP2); NO_3, NH_4, and oxalate (GRIP). For the 12,400 cal yr BP level of siliceous aggregate occurrences (Cahaba Pond and Swift Lake), the following ions associated with burning match: NO_3, NH_4 (GISP2); NO_3, and sharp peaks in NH_4, acetate, formate, and oxalate (GRIP). Distinctive peaks in Ca, K, and Mg occur at the 14,000 cal yr BP level and rounded peaks in the same ions for 12,400 cal yr BP in the GRIP ice core. It must be noted that the sampling intervals in the GISP2 core are of a much higher resolution than in the GRIP core.

4.4.2 Nitrogen Isotopes

Comparing total nitrogen and $\delta^{15}N$ data with siliceous aggregate occurrences for the five sites (Figure 4.9), at Anderson Pond a small peak in $\delta^{15}N$ exists at the time of siliceous aggregate occurrence. At Cahaba Pond, a major change in total nitrogen (TN) and $\delta^{15}N$ occur at the time of siliceous aggregate occurrence. Analysis of a sediment sample from this interval revealed the presence of cyanins (pers. communication Jamey Fulton to S.Driese, 30 May 2014), which are present in cyanobacteria. For Jackson Pond, we had insufficient sampling depth to compare. At Slack Lake, two slight peaks in TN are observed at the time of siliceous aggregate occurrences for Swift Lake. At Swift Lake, siliceous aggregates occur when there is a drop in $\delta^{15}N$ across a gap between core sections. We extrapolate the nitrogen records between these two lakes because sampling levels for siliceous aggregates do not cover the same time span. Slack and Swift Lakes are less than 2 km apart, so we expect a similar vegetation and climate history at both sites.

NO_3 and NH_4 data from the GISP2 Greenland ice core is compared for a large scale signal for nitrogen. (Figure 4.9). A peak in ammonium occurs at the time of the 14,000 cal yr BP siliceous aggregate occurrences. Peaks in nitrate and ammonium occur around the time of the 12,400 cal yr BP siliceous aggregate occurrences. A small peak in nitrate occurs around the time of the siliceous aggregates at 19,250 cal yr BP in Jackson Pond.

4.4.3 XRF Analyses

XRF elemental analyses for each site are shown together with GISP data (Figures 4.10–4.13) to compare possible wood ash input to the lakes with a global signal. High resolution analyses using the Bruker Xray gun were inconsistent with results from the benchtop Olympus BTX Profiler, and only the data from the profiler are shown here. For Anderson Pond, high-resolution BTX Profiler data showed small peaks in Ca K, Fe, Al, Si, Zn, and P at around the time of occurrence of siliceous aggregates ca. 14,000 cal yr BP. For the Cahaba Pond CP-79B core, coarse-resolution data from the BTX Profiler revealed increases in Ca, K, Fe, Al, and Zn around the time of occurrences in siliceous aggregates in the Cahaba Pond CP-79A core at ca.

12,400 cal yr BP. For the Jackson Pond core, we have XRF data only from the Bruker Xray gun. These data revealed possible increases in Ca, K, Fe, and Al at the time of siliceous aggregate occurrence around 14,000 cal yr BP. The BTX Profiler data from Swift Lake exhibit peaks in Ca and Fe for the time of siliceous aggregate occurrence at nearbly Slack Lake, ca. 14,000 cal yr BP. XRF data were not available for the interval of Swift Lake siliceous aggregates around 12,400 cal yr BP.

4.4.4 Charcoal

Observed occurrences of siliceous aggregates during the late glacial do not coincide with the highest charcoal abundances at Anderson Pond, Cahaba Pond, or Jackson Pond. However, at Slack and Swift Lakes, fire activity is high when siliceous aggregates occur (Figure 4.14).

From the Last Glacial Maximum to ca. 15,000 cal yr BP, the Anderson Pond and Pigeon Marsh records are comparable, with high fire activity at both sites but no siliceous aggregates at Pigeon Marsh, and no charcoal evidence at the time of siliceous aggregates at Anderson Pond. From around 14,000 cal yr BP into the Holocene, Slack and Swift Lakes show high fire activity. Peaks in charcoal exist around 14,000 and 12,400 cal yr BP for both sites.

4.4.5 Wood Ash Experiments

Of the 16 thin sections prepared from the wood ash experiments, nine had siliceous aggregates present (Tables 4.3, 4.4). The size of the experimentally produced siliceous aggregates ranged from ca. 100 µm in diameter to as large as 500 µm in diameter (Figures 4.4–4.7), and hence, the experimental aggregates were larger overall than the natural siliceous aggregates observed in sediment cores (Figures 4.2, 4.3). The experimentally produced aggregates generally had spheroidal shapes; however some were attached to laterally discontinuous, discrete quartz silt lenses and layers. A micromass “cement” of calcite and calcium oxalate appeared to bind the grains, along with very minor cryptocrystalline silica and Fe oxides and oxyhydroxides (Figures 4.4–4.7).

For Experiment 1, only two of the eight thin sections contained aggregates, and both were in samples to which loessal silt was introduced (Table 4.3; Figures 4.4, 4.5). It is noteworthy that no samples lacking introduced silt produced siliceous aggregates. For Experiment 2, all four thin sections with pH 5.7, and three of four thin sections with pH 1.0/pH 2.0 acid rain treatment, contained siliceous aggregates (Tables 4.3, 4.4; Figures 6.6, 6.7).

Based on these experimental results, the formation of siliceous aggregates is promoted by having a source of very fine- to fine-silt-sized quartz as a “seed” around which aggregates appear to have nucleated. A two-tailed Fisher Exact test yielded a p-value of 0.0192, indicating that the null hypothesis of interdependence between the addition of silt and the formation of siliceous aggregates can be rejected (Table 4.5). Another two-tailed Fisher Exact test was executed to evaluate the significance of nitric acid rain in the formation of siliceous aggregates. This test yielded a p-value of 1.000, indicating that the null hypothesis of interdependence between acidity and the formation of siliceous aggregates may not be rejected. The p-value was 1.000 regardless of whether results from Experiment 2 alone were calculated, or whether all samples with silt added were considered.

4.4.6 Geochronology

The Pigeon Marsh and new Cahaba radiocarbon dates are shown along with prior dates and calibrations (Table 4.6–4.11). The new Pigeon Marsh core preserves mainly late glacial-age sediments, based on the radiocarbon results. This finding is in keeping with initial pollen analyses, which match with late-glacial pollen assemblages found by Watts (1975) at the site. The new Cahaba AMS dates improve the chronology for the *Fagus* decline at this site (Figure 4.11). In our age model, we substituted the two new AMS dates for nearby standard dates on bulk sediment (Table 4.7) that Delcourt et al. (1983) had averaged together in their original age model. The new AMS dates result in an age model similar to the initial model based on the averaging of two dates.

4.5 Interpretations and Discussion

4.5.1 General Interpretations

The association between experimental siliceous aggregate formation and additions of loessal silt is not surprising because mineral host grains can serve as substrates upon which precipitates can nucleate by essentially lowering the thermodynamic "threshold" (Blatt et al. 1980). It is noteworthy that the effects of extremely low pH (1.0–2.0) solutions appear negligible as far as promoting siliceous aggregate formation, and thus do not support the initial hypothesis of an event producing nitric acid rain as necessary for their formation. In fact, from thin-section studies it is apparent that the very best examples of siliceous aggregates actually occur in the Experiment 2 series with a "natural"weakly acidified rainfall with pH of 5.7 and silt added (Figures 4.4, 4.6). For the more heavily acidified samples, there was a different matrix appearance that seems to suggest wholesale removal or redistribution of calcite, as well as calcium oxalates derived from the wood ash, to the extent that the matrix appears more enriched in charcoal and other wood fragments (Figures 4.5, 4.7). Additionally, the samples from Experiment 2, which used mixed hardwood as a source of wood ash, had better developed siliceous aggregate grains compared to grains developed with Experiment 1, where the source of wood ash was beech. It is possible that Experiment 2 was more realistic of natural systems because the wood ash derived from combustion of a variety of wood types rather than from a single taxon. The fact that siliceous aggregates are rare in the sediment record makes an origin from limestone unlikely, which is relatively common in the environment. The experiments established that siliceous aggregates form from wood ash.

4.5.2 Similarities Between Natural and Experimental Grains

The experimentally produced grains are morphologically similar to the naturally occurring siliceous aggregates in that they are spheroidal to ovoid in shape, are composed of aggregations of angular detrital, fine- to medium-silt-sized quartz grains, and are bound together by a micromass that appears to be either very finely crystalline or amorphous (compare Figures 4.2 and 4.3 natural grains with experimental grains shown in Figures 4.4–4.7). Some of the grains have occluded bits of organic matter that have also been observed in natural aggregates. There might be evidence for some chemical etching and dissolution on the monocrystalline quartz silt within both the experimental and natural grains, but this requires assessment using an SEM and knowing the surface characteristics of the quartz silt before it was introduced in the experiments. Finally, the association of the siliceous aggregate grains in the natural environment with surrounding organic material such as hackberry carpels, diatoms, and charcoal (in varying states of alteration leading to wood ash formation) argues for the diagenetic alteration of silica in the wood ash to cement these particles and the loessal silt. In other words, the siliceous aggregates in this study did not form within the tree.

4.5.3 Dissimilarities Between Natural and Experimental Grains

The siliceous aggregates produced in the experiments are of a larger size (100–200+ μm diameter) than the natural grains observed in the cores from all the sites. Slack Lake and Swift Lake generally had aggregates of coarse silt size (50–60 μm diameter) or smaller (compare Figures 4.2 and 4.3 natural grains with experimental grains shown in Figures 4.4–4.7). The siliceous aggregates produced in the experiments are composed of larger silt-sized quartz (20–50 μm) than that comprising the natural aggregate grains in Anderson Pond, Jackson Pond, and Cahaba Pond, which are generally very fine silt-size (10–20 μm diameter). This might relate to the overall large size of the experimental aggregates. In addition, the siliceous aggregates produced in the experiments are cemented by an amorphous calcite-oxalate micromass that might contain a silica (quartz) component that is not visible optically, whereas the natural aggregates in Anderson Pond, Jackson Pond, and Cahaba Pond are cemented by a pure siliceous micromass that occasionally contains included organic matter. This is especially apparent in images using UVf (Figures 4.2, 4.3). The siliceous aggregates from Slack Lake and Swift Lake, in contrast, contain a significant carbonate component (Figure 4.3). The differences in diagenetic state between the natural and experimental aggregates could be a product of the short duration of the experiments versus the longer time of the natural systems during which diagenesis can affect the aggregates. For example, silica in phytoliths, wood ash, sponge spicules, and diatoms in some natural samples was likely mobilized and redistributed as micromass "cement." The natural alkalinity of the wood ash, around pH 13, promotes silica dissolution and mobility within the sediments. At pH <9.8, the amorphous silica will precipitate out (Maynard 2015) and nucleate around silt-sized grains. Leachates checked daily for all experiments were around pH 8.0 for all but the initial week of the experiments.

Whereas siliceous aggregates have been reported at archaeological sites, within wood, and in concrete, to our knowledge they have not been identified previously in lake sediments. The siliceous aggregates identified here in late glacial sediments from five of six lakes in a north-south transect across the interior eastern U.S., although associated with wood ash, may actually be a different type than those found in the Israeli caves, especially if aqueous transport from terrestrial surfaces containing wood ash into lake basins was required for formation of lake-sediment siliceous aggregates.

4.5.4. Nitrogen Isotopes and The Nitric Acid Rain Aspect of the Experiments

Total nitrogen and $\delta^{15}N$ analyses on bulk sediment of lake cores from the study sites (Figure 4.9) showed small late-glacial peaks (Slack and Swift Lakes, Anderson Pond) in the total nitrogen, and shifts (Cahaba Pond) that were roughly contemporaneous with siliceous aggregate occurrences. At Cahaba Pond, a major shift is evident in TN and $\delta^{15}N$ at the time of the major shift in vegetation during the late glacial. This crossover pattern is typical of cyanobacteria. Cyanins were found in sediment from this interval (pers. communication Jamey Fulton to S.Driese, 30 May 2014), confirming the presence of cyanobacteria, which prefer an alkaline environment.

The nitrogen isotope patterns of Kolesnikov et al. (1998), who researched nitric acid rain associated with the 1908 Tunguska impact, were compared to patterns of $\delta^{15}N$ and TN in this study. $\delta^{15}N$ values for Cahaba Pond, Anderson Pond, and Swift Lake showed perturbations at the time of siliceous aggregate occurrences. Many records exist in Europe and Greenland for expansion of diatoms and other algae in lakes around the onset of the Younger Dryas. These include records from Knapowka near Wloszczowa, South Poland (Kaczmarska et al.1973); Loch Sionascaig in northern Scotland (Haworth 1976); Hirschenmoor and Rotmeer in the Black Forest region of Germany (Lotter and Birks 1993); Holzmaar, Germany (Lotter et al. 1995); Meerfelder Maar, Germany (Brauer et al. 1999); Petrašiunai and Juodonys in northeastern Lithuania (Stančikaité et al. 2009); Lake Brazi in the south Carpathian Mountains, Romania (Buczkó et al. 2013) and five lakes in southern Greenland (Björck et al. 2002). Peaks exist in ammonium and nitrates in the GISP2 ice core record for this time. To explain the disturbances in the lacustrine nitrogen records, the work of Prinn and Fegley (1987) on nitric acid rain for the K/T impact and the work of Kolesnikov et al. (1998) was used to hypothesize a global scale nitric acid rain event for the onset of the YD, triggered by the shock wave of the extraterrestrial event postulated by Firestone et al. (2007)

While the solubility of silica certainly increases at high pH, it is also possible that the solubility may increase at low pH by the reaction of $Si(OH)_4$ with acids (Alexander 1954). Therefore, the idea that nitric acid rain might play a role in dissolution of the phytoliths in the wood ash was considered.

The experiments showed that siliceous aggregates formed whether the simulated rain was pH 5.7, pH 2.0, or pH 1.0. The strongest acidic rain may have increased throughput of dissolved silica, by more vigorous reaction with the carbonate in the ash. The experiments demonstrated that the siliceous aggregates formed independent of nitric acid rain.

4.5.5. Lack of Association of Charcoal Peaks with Some Siliceous Aggregate Occurrences

Low-severity fires produce a thin layer (< 1 cm) of black ash containing mostly char particles (Balfour 2007), while high-severity fires can produce up to 20 cm of fine white ash (Ulery et al. 1993, Demeyer et al. 2001, Goforth et al. 2005, Gabet and Sternberg 2008, Woods and Balfour 2008). The lack of clear association of siliceous aggregates with high charcoal counts in sediment cores from three of the five sites (Figure 4.14) was unexpected, since both are by-products of fire. The study of the severe Tarkio fire by Woods and Balfour (2008) may provide an explanation. This wildfire in western Montana in 2005 resulted in a <1 to 3.5-cm layer of light grey ash on the soil surface, which provided additional rainfall storage capacity and protection from runoff after the fire. Woods and Balfour (2010) conducted a follow up study and determined that with thicker ash layers (2–5 cm), the effects of water storage increasingly delayed and reduced the runoff response to the point where no overland flow was produced regardless of any pore clogging effect in the underlying soil. Thus, a layer of wood ash with thickness of 2–5 cm could effectively retain charcoal on the landscape and prevent or slow down transport and deposition into the lake.

Alternately, or in addition to this interpretation of landscape stabilization by wood ash, the lack of charcoal peaks when siliceous aggregates occur in sediment profiles could be related to more intense fires with more complete combustion to white ash (Bodí et al. 2014, Pereira et al. 2014). The most extreme type of intense fire is the firestorm. A firestorm is a storm of wind induced by fire, characteristically wind of high velocity, in many cases reported to be of hurricane force (Beaufort scale ≥11, 100 ft/s or 30.5 m/s), capable of uprooting trees and tearing off rooftops (Baldwin and North 1967). During wildfires, dust devils and whirlwinds frequently appear under a strongly tilted convection column (Countryman 1964). During a test fire, Countryman (1964) reported that in the later stages of the fire, whirls extended more than 200 feet up, heavily loaded with dust, ashes, and smoke. An intense wildfire with strong winds is expected to result in more complete combustion, and thus, less remaining charcoal and more ash. The high winds associated with intense wildfires would result in deposition of more silt-sized particles suitable for nucleation sites for siliceous aggregates.

4.5.6. In the Sediment Record Since the LGM, Why do Siliceous Aggregates Rarely Occur?

In this study, we found that siliceous aggregates only occurred at three times since the LGM: ca. 19,250 cal yr BP, ca. 14,000 cal yr BP, and around 12,400 cal yr BP. The occurrence at 19,250 cal yr BP is limited to Jackson Pond; sediments of this age were not available for the other sites (Anderson Pond 2007, Cahaba, Swift, Slack). Siliceous aggregates were found at14,000 cal yr BP in three sites (Anderson Pond, Jackson Pond and Slack Lake). Siliceous aggregates were also found around 12,400 cal yr BP at two sites (Cahaba Pond and Swift Lake).

Standard errors in radiocarbon dates, wide calibrated ranges, and the reliance on dates mostly on bulk sediment make it reasonable to infer contemporaneous events, but further study is needed.

Because siliceous aggregates are rare in the sediment record since the LGM, they must require specific conditions to form and to then be transported and preserved in lake sediments. They require the action of water on wood ash; the presence of silt-sized grains to nucleate around, and a source for amorphous silica such as dissolved phyoliths from the wood ash. Perhaps ash depth is an important factor. A sufficient amount of wood ash may be necessary for siliceous aggregates to form. A depth of five cm of ash was used in the siliceous aggregate experiments. More ash could be generated by a firestorm with high winds providing oxygenation and entraining silt-sized particles. Evidence of such large-scale wildfires might be evident in Greenland ice cores.

4.5.7 Evidence of Large-Scale Northern Hemisphere Fires in Ice Cores

Ice cores from Greenland and Antarctica provide global signals of past atmospheric changes. Legrand and Mayewski (1997) provide a review of the glaciochemistry of polar ice cores. Distinctive organic markers associated with vegetation emissions from biomass burning in boreal forests and elsewhere are recorded in ice cores worldwide and provide information on long-term fire history (Kehrwald et al. 2010). These markers of biomass burning include ammonium and light carboxylic acids such as oxalic and formic acids (Legrand et al. 1992, Dibb et al. 1996), oxalate, levoglucosan (Kehrwald et al. 2012), and nitrates (Savarino and Legrand 1998), although the latter can have other sources such as nitric acid rain from an extraterrestrial shock wave (Hastings et al. 2013). Other particulates used as markers for biomass burning are black carbon (Zennaro et al. 2014) and polycyclic aromatic hydrocarbons (Conedera et al. 2009). Potassium has also been used as evidence of wildfires in ice cores (Andreae 1983, Echalar et al. 1995**,** Savarino and Legrand 1998, Gao et al 2003) and Echalar et al. (1995) observed higher K emissions from flaming fires vs. smoldering fires. Also, non-combustion K sources exist (De Angelis 1997). Other potential biomass indicators and their caveats are discussed by Zennaro et al. (2014). Some of these aerosols may have sources other than biomass burning. Levoglucosan can only be produced by combustion of cellulose at temps >300 ºC (Kehrwald et al. 2012). Levoglucosan and oxalate were considered to be the most definitive markers of combustion by Kehrwald et al. (2012).

The experiments in this research have confirmed that siliceous aggregates are a by-product of wildfire. Because we found them in lake sediments transecting the eastern U.S. around 14,000 cal yr BP and around 12,400 cal yr BP, they may tentatively be considered signatures of two large-scale wildfires. Wildfires of such magnitude should be detectable in the Greenland ice core record. Comparing the timing of siliceous aggregate occurrences with combustion markers in the GISP2 ice core record (Yang et al. 1995, Mayewski et al. 1997) and the GRIP ice core record (Legrand et al. 1992, De Angelis et al. 1997, Fuhrer and Legrand 1997) reveals aerosol peaks that match with siliceous aggregate occurrences (Figure 4.15). The GISP2 ice core is a higher resolution record than the GRIP core. Peaks in nitrate and ammonia are evident in both records for the two late glacial levels, marked with grey lines. In addition, peaks in other combustion markers, acetate, formate, and oxalate, are evident in the GRIP core at the same time as siliceous aggregates at ca.12,400 cal yr BP. Peaks in oxalate and acetate match siliceous aggregate occurrences around 14,000 cal yr BP. Calcium, potassium and magnesium are considered to be dust markers (De Angelis et al. (1997). They are plotted here because they are also conmponents of wood ash. It seems unlikely that wood ash would circulate globally to deposit these signals in the Greenland ice. However, if large-scale wildfires occurred at these times, resulting in destruction of forests, then increased windiness could follow, due to the lack of obstructions to wind flow, and a wood ash signal might be captured in ice cores at these times.

Comparing the occurrences of lake-sediment siliceous aggregates to combustion aerosols in the Greenland ice cores suggests large-scale wildfires during the late glacial around 14,000 and 12,400 cal yr BP. However, this is a preliminary study of siliceous aggregates as a new possible marker for severe wildfires in lake sediments. Further research on siliceous aggregates will be required to constrain the extent and the reproducibility of this wildfire signal in the eastern U.S. and beyond.

4.6 Conclusions

In our XRF analysis of lake sediments to identify calcium peaks with co-occuring K, Mg Al, Si, Fe, Zn, and/or P linked to wood ash inputs to the lake sediments, results are supportive in the case of Cahaba Pond, Slack, and Swift Lakes but ambiguous for Anderson and Jackson Ponds. Other sources of calcium carbonate such as limestone may complicate interpretations. More XRF analyses of lake sediments need to be conducted at high resolution to assess the usefulness of this analysis in detecting past wood ash evidence in lake sediments. The BTX Profiler is a more effective device than the Bruker Gun for determining representative elements in the bulk sediments.

The presence of late-glacial-age siliceous aggregates in lake sediments from 5 of 6 sites suggests the occurrence of contemporaneous wildfires across eastern North America around 14,000 and 12,400 cal yr BP. The fact that they were created from wood ash in the lab demonstrates that they are a by-product of wildfires. The fact that they are rare in the sediment record makes an origin from limestone unlikely, as limestone is common in many environments. Chemical markers of biomass burning in the Greenland ice cores show evidence of peaks at the times of siliceous aggregate occurrences.

This interdisciplinary study of sediment cores from six lake/wetland sites transecting the eastern U.S. revealed occurrences of siliceous aggregates in thin-sections from 5 of the 6 cores during late glacial time. The discovery of approximately contemporaneous siliceous aggregates across such a large region suggests the possibility of very large wildfire events. If indeed they are contemporaneous occurrences across the region, the origin of the fires may be catastrophic in nature. Siliceous aggregates were experimentally produced with beech and mixed hardwood ash, using treatments of low pH (1.0, 2.0) and also weakly acidic pH (5.7) simulated rain, over a period of four months. They formed as a result of acid and non-acid rains in both fume hood and greenhouse environments. Additions of fine quartz silt to experiments were necessary for siliceous aggregate formation; samples that lacked additions of fine quartz silt resulted in no siliceous aggregate formation. Based on the experimental results, the formation of siliceous aggregates requires a source of fine quartz silt as a "seed" around which aggregates nucleate. Dust influxes may have been high during the wildfires that produced the late glacial siliceous aggregates, or more broadly, during the late glacial period. The fact that siliceous aggregates occurred in lake sediments at some sites without a matching peak in charcoal may indicate that the wood ash following severe wildfires can substantially reduce runoff and erosion (Woods and Balfour 2010), thus limiting the transport of charcoal into the lake. Siliceous aggregates may be a new proxy for paleoenvironmental researchers to use as an indicator for severe wildfires.

4.7 Acknowledgements

The authors sincerely thank the following people who contributed to the success of this project: Edward Schilling and Ken McFarland, David Pratt and his crew in the Biology Services Facility at UT, Groundskeeper Jason Cottrell and his crew, Andre Bijkerk, Mathew Boehm, Latisha Brengman, Chris Fedo, Henri Grissino-Mayer, Roger Horn, Carol Harden, Stephen T. Jackson, Matthew and Jacquelyn Kerr, Jim Kocis, Yanan Li, Yingkui Li, J. Barry Maynard, Dr. Jean-Luc Mercier, Bryson Patrick, Timothy A. Price, Benjamin Sheridan, and John W. (Jack) Williams. This research was supported by the National Science Foundation under Grant EAR-

0822824 awarded to Zheng-Hua Li and Sally Horn and Grant EAR-0823131 awarded to Steven Driese.

4.8 References

Alexander, G.B.; Heston, W.M.; Iler, R.K. 1954. The solubility of amorphous silica in water. *The Journal of Physical Chemistry* 58(6): 453–455.

Andreae, M.O. 1983. Soot carbon and excess fine potassium: long-range transport of combustion-derived aerosols. *Science* 220(4602): 1148–1151.

Baldwin, R.; North, M.A. 1967. The firestorm-its size and importance. *Fire Safety Science* 645: 1–32.

Balfour, V.N. 2007. *The Effects of Forest Fires on Runoff Rates: the Role of Duff Removal and Surface Sealing by Vegetative Ash, Western Montana*. Ph.D. Dissertation, University of Montana.

Ballard, J.P. 2009. *A Lateglacial Paleofire Record for East-Central Michigan*. M.S. Thesis, University of Cincinnati.

Björck, S.; Bennike, O.; Rosén, P.; Andresen, C.S.; Bohncke, S.; Kaas E.; Conley D. 2002. Anomalously mild Younger Dryas summer conditions in Southern Greenland. *Geology* 30(5): 427–430.

Blatt, H.; Middleton, G.V.; Murray, R.C. 1980. *Origin of Sedimentary Rocks*. Prentice Hall, Upper Saddle River, New Jersey.

Bodí, M.B.; Martin, D.A.; Balfour, V.N.; Santín, C.; Doerr, S.H.; Pereira, P.; Cerdà , A.; Mataix-Solera, J. 2014. Wildland fire ash: production, composition and eco-hydro-geomorphic effects. *Earth-Science Reviews* 130: 103–127.

Bow, S.M. 2012. *A Tale of Two Shelters: Using XRF Analysis to Assess Compositional Variability of Pottery from Two sites in Franklin County, Tennessee.* M.S. Thesis, University of Tennessee.

Brauer, A.; Endres, C.; Negendank, J.F.W. 1999. Lateglacial calendar year chronology based on annually laminated sediments from Lake Meerfelder Maar, Germany. *Quaternary International* 61: 17–25.

Brodie, C.R.; Casford, J.S.L.; Lloyd, J.M.; Leng, M.J.; Heaton, T.H.E.; Kendrick, C.P.; Yongqiang, Z. 2011. Evidence for bias in C/N, $\delta^{13}C$ and $\delta^{15}N$ values of bulk organic matter, and on environmental interpretation, from a lake sedimentary sequence by pre-analysis acid treatment methods. *Quaternary Science Reviews* 30: 3076–3087.

Buczkó, K.; Magyari, K.; Braun, M.; Bálint, M. 2013. Diatom-inferred Late Glacial and Holocene climatic variability in the south Carpathian Mountains (Romania). *Quaternary International* 293: 123–135.

Campbell, A.G. 1990. Recycling and disposing of wood ash. *Tappi Journal* 9: 141–145.

Conedera, M.; Tinner, W.; Neff, C.; Meurer, M.; Dickens, A.F.; Krebs, P. 2009. Reconstructing past fire regimes: methods, applications, and relevance to fire management and conservation. *Quaternary Science Reviews* 28(5): 555–576.

Countryman, C.M. 1964. Mass fires and fire behavior. U.S.D.A. Forest Service Research Paper PSW-19, Pacific Southwest Forest and Range Experiment Station.

De Angelis, M.; Steffensen, J.P.; Legrand, M.R.; Clausen, H.B.; Hammer, C.U. 1997. Primary aerosol (sea salt and soil dust) deposited in Greenland ice during the last climatic cycle: comparison with east Antarctic records. *Journal of Geophysical Research* 102: 26681–26698.

Delcourt, H.R. 1978. *Late Quaternary Vegetation History of the Eastern Highland Rim and Adjacent Cumberland Plateau of Tennessee.* Ph.D. Dissertation, University of Minnesota.

Delcourt H.R. 1979. Late Quaternary vegetation history of the Eastern Highland Rim and adjacent Cumberland Plateau of Tennessee. *Ecological Monographs* 49(3): 255–280.

Delcourt, H.R.; Delcourt, P.A.; Spiker, E.C. 1983. A 12,000-year record of forest history from Cahaba Pond, St. Clair County, Alabama. *Ecology* 64(4): 874–887.

Demeyer, A.; Nkana, J.C.V.; Verloo, M.G. 2001. Characteristics of wood ash and influence on soil properties and nutrient uptake: an overview. *Bioresource Technology* 77: 287–295.

Dibb, J.E.; Talbot, R.W.; Whitlow, S.I.; Shipham, M.C.; Winterle, J.; McConnell, J.; Bales, R. 1996. Biomass burning signatures in the atmosphere and snow at Summit, Greenland: an event on 5 August 1994. *Atmospheric Environment* 30(4): 553–561.

Dove, P.M.; Han, N.; Wallace, A.F.; De Yoreo, J.J. 2008. Kinetics of amorphous silica dissolution and the paradox of the silica polymorphs. *Proceedings of the National Academy of the Sciences of the United States of America* 105(29): 9903–9903.

Dyke, A.S. 2004. An outline of North American deglaciation with emphasis on central and northern Canada. *In: Quaternary Glaciations: Extent and Chronology.* Volume 2 (Eds.: Ehlers, J.; Gibbard, P.L.; Hughes, P.D.), Elsevier, Amsterdam, pp. 373–424.

Echalar, F.; Gaudichet, A.; Cachier, H.; Artaxo, P. 1995. Aerosol emissions by tropical forest and savanna biomass burning: characteristic trace elements and f luxes. *Geophysical Research Letters* 22(22): 3039–3042, Firestone, R.B.; West, A.; Kennett, J.P.; Becker, L.; Bunch, T.E.; Revay, Z.S.; Schultz, P.H.; Belgya, T.; Kennett, D.J.; Erlandson, J.M.; Dickenson, O.J.; Goodyear, A.C.; Harris, R.S.; Howard, G.A.; Kloosterman, J.B.; Lechler, P.; Mayewski, P.A.; Montgomery, J.; Poreda, R.; Darrah, T.; Hee, S.S.; Smith, A.R.; Stich, A.; Topping, W.; Wittke, J.H.; Wolbach, W.S. 2007. Evidence for an extraterrestrial impact 12,900 years ago that contributed to the megafaunal extinctions and the Younger Dryas cooling. *Proceedings of the National Academy of Sciences of the United States of America* 104(41): 16016–16021.

Fuhrer, K.; Legrand, M.R. 1997. Continental biogenic species in the Greenland Ice Core Project ice core: tracing back the biomass history of the North American continent. *Journal of Geophysical Research* 102: 26735–26745.

Gabet, E.J.; Sternberg, P. 2008. The effects of vegetative ash on infiltration capacity, sediment transport, and the generation of progressively bulked debris flows. *Geomorphology* 101(4): 666–673.

Gao, S.; Hegg, D.A.; Hobbs, P.V.; Kirchstetter, T.W.; Magi, B.I.; Sadilek, M. 2003. Water-soluble organic components in aerosols associated with savanna fires in southern Africa: identification, evolution, and distribution. *Journal of Geophysical Research Atmospheres* 108(D13): 1–16.

Goforth, B.R.; Graham, R.C.; Hubbert, K.R.; Zanner, C.W.; Minnich, R.A. 2005. Spatial distribution and properties of ash and thermally altered soils after high-severity forest fire, Southern California. *International Journal of Wildland Fire* 14: 343–354.

Hastings, M.G.; Casciotti, K.L.; Elliott, E.M. 2013. Stable isotopes as tracers of anthropogenic nitrogen sources, deposition, and impacts. *Elements* 9: 339–344.

Haworth, E.Y. 1976. Two late-glacial (late Devensian) diatom assemblage profiles from Northern Scotland. *New Phytologist* 77(1): 227–256.

Huang, H., Campbell, A.G.; Folk, R.; Mahler, R.L. 1992. Wood ash as a soil additive and liming agent for wheat: field studies. *Communications in Soil Science and Plant Analysis* 23(1–2): 25–33.

Juggins. S. 2010. C2 Version 1.5 User guide. Software for ecological and palaeoecological data analysis and visualisation. Newcastle University, Newcastle upon Tyne, the United Kingdom.

Kaczmarska, I. 1973. Late-glacial diatom flora at Knapówka near Wloszczowa (South Poland). *Acta Palaeobotanica* 14(3): 179–193.

Kehrwald, N.; Zangrando, R.; Gabrielli, P.; Jaffrezo, J-L.; Boutron,C.; Barbante, C. 2012. Levoglucosan as a specific marker of fire events in Greenland snow. *Tellus B* 64: 1–9.

Kehrwald, N.; Zangrando, R.; Gambaro, A.; Cescon, P.; Barbante, C. 2010. Specific molecular markers in ice cores provide large-scale patterns in biomass burning. *PAGES* 18(2): 59–61.

Kolesnikov, E.M.; Kolesnikova, N.V.; Boettger, T. 1998. Isotopic anomaly in peat nitrogen is a probable trace of acid rain caused by 1908 Tunguska bolide. *Planetary Space Science* 46(2/3): 163–167.

Legrand, M.R.; De Angelis, M.; Staffelbach, T.; Neftel, A.; Stauffer, B. 1992. Large perturbations of ammonium and organic acids content in the Summit-Greenland ice core. Fingerprint from forest fires? *Geophysical Research Letters* 19: 473–475.

Legrand, M.; Mayewski, P A. 1997. Glaciochemistry of polar ice cores: a review. *Reviews of Geophysics* 35(3): 219–243.

Liu, Y.; Andersen, J.J.; Williams, J.W.; Jackson, S.T. 2013. Vegetation history in central Kentucky and Tennessee (U.S.A.) during the last glacial and deglacial periods. *Quaternary Research* 79(2): 189–198.

Lotter, A.E.; Birks, H.J.B. 1993. The impact of the Laacher See Tephra on terrestrial and aquatic ecosystems in the Black Forest, southern Germany. *Journal of Quaternary Science* 8(3): 263–276.

Lotter, A.E.; Birks, H.J.B.; Zolitschka, B. 1995. Late-glacial pollen and diatom changes in response to two different environmental perturbations: volcanic eruption and Younger Dryas cooling. *Journal of Paleolimnology* 14: 23–47.

Mayewski, P.A.; Meeker, L.D.; Twickler, M.S.; Whitlow, S.I.; Yang, Q.; Lyons, W.B.; Prentice, M. 1997. Major features and forcing of high-latitude Northern Hemisphere atmospheric circulation using a 110,000-year-long glaciochemical series. *Journal of Geophysical Research* 102: 26345–26366.

Maynard, J. B. 2015. Chapter 5. Mineral-water interactions: silicates and alumino-silicates. http://homepages.uc.edu/~maynarjb/Frontpage520sites/603/GeochemWater/chapter_5.htm [Accessed June 16, 2015]

Muse, J.K.; Mitchell, C.C. 1995. Paper mill boiler ash and lime by-products as soil liming materials. *Agronomy Journal* 87(3): 432–438.

Naylor, L.M.; Schmidt, E.J. 1986. Agricultural use of wood ash as a fertilizer and liming material. *Tappi Journal* 10: 114–119.

Øye, B. 2012. Wood ash as raw material for Portland cement. *ASH 2012*, Ashes in a Sustainable Society Conference, Stockholm, Sweden January 25–27, 2012.

Pereira, P.; Jordán, A.; Cerdà, A.; Martin, D. 2014. Editorial: the role of ash in fire-affected ecosystems. *Catena*, In Press, Corrected Proof, Available 5 January 2015, pp. 1–3.

Prinn, R.G.; Fegley Jr., B. 1987. Bolide impacts, acid rain, and biospheric traumas at the Cretaceous-Tertiary boundary. *Earth and Planetary Science Letters* 83: 1–15.

Reimer, P.J.; Brown, T.A.; Reimer, R.W. 2004. Discussion reporting and calibration of post-bomb ^{14}C data. *Radiocarbon* 46(3): 1299–1304.

Reimer, P.J.; Bard, E.; Bayliss, A.; Beck, J.W.; Blackwell, P.G.; Ramsey, C.B.; Buck, C.E.; Cheng, H.; Edwards, R.L.; Friedrich, M.; Grootes, P.M.; Guilderson, T.P.;Haflidason, H.; Hajdas, I.; Hatté, C.; Heaton, T.J.; Hoffmann, D.L.; Hogg, A.G.; Hughen, K.A.; Kaiser, K.F.; Kromer, B.; Manning, S.W.; Niu, M.; Reimer, R.W.; Richards, D.A.; Scott, E.M.; Southon, J.R.; Staff, R.A.; Turney, C.S.M.; van der Plicht, J. 2013. INTCAL13 and MARINE13 radiocarbon age calibration curves 0–50,000 years cal BP. *Radiocarbon* 55(4): 1869–1887.

Risse, M.; Gaskin, J. 2002. *Best management practices for wood ash as agricultural soil amendment.* The University of Georgia Cooperative Extension Bulletin 1142, pp 1–4. http://extension.uga.edu/publications/files/pdf/B%201142_3.PDF [Accessed April 14, 2015].

Savarino, J.; Legrand, M. 1998. High northern latitude forest fires and vegetation emissions over the last millennium inferred from the chemistry of a central Greenland ice core. *Journal of Geophysical Research: Atmospheres* 103(D7): 8267–8279.

Schiegl, S.; Goldberg, P.; Bar-Yosef, O.; Weiner, S. 1996. Ash deposits in Hayonim and Kebara Caves, Israel: macroscopic, microscopic and mineralogical observations, and their archaeological Implications. *Journal of Archaeological Science* 23(5): 763–781.

Stančikaité, M.; Kisieliene, D.; Moe, D.; Vaikutiené, G. 2009. Late glacial and early Holocene environmental changes in northeastern Lithuania. *Quaternary International* 207: 80–92.

Stoof, C.R.; Wesseling, J.G.; Ritsema, C.J. 2010. Effects of fire and ash on soil water retention. *Geoderma* 159(3): 276–285.

Stuiver, M.; Reimer, P.J. 1993. Extended ^{14}C database and revised CALIB radiocarbon calibration program. *Radiocarbon* 35(1): 215–230.

Talbot, M.R. 2002. Nitrogen isotopes in palaeolimnology. *In: Tracking Environmental Changes Using Lake Sediments,* Volume 2 (Eds.: Last, W.M.; Smol, J.P.), Kluwer Academic Publishers, Dordrecht, the Netherlands.

Telford, R.J.; Heegaard, E.; Birks, H.J.B. 2004. The intercept is a poor estimate of a calibrated radiocarbon age. *The Holocene* 14(2): 296–298.

Úbeda, X.; Pereira, P.; Outeiro, L.; Martin, D.A. 2009. Effects of fire temperature on the physical and chemical characteristics of the ash from two plots of cork oak (*Quercus suber*). *Land Degradation and Development* 20: 589–608.

Ulery, A.L.; Graham, R.C.; Amrhein, C. 1993. Wood-ash composition and soil pH following intense burning. *Soil Science* 156(5): 358–364.

Watts, W.A. 1975. Vegetation record for the last 20,000 years from a small marsh on Lookout Mountain, northwestern Georgia. *Geological Society of America Bulletin* 86(3): 287–291.

Weiner, S. 2010. *Microarchaeology, Beyond the Visible Archaeological Record.* Cambridge University Press, the United Kingdom.

White, R.K.; Rice, J.S. 1993. Wood ash treated sludge for agricultural use. Presented at the *1993 International Summer Meeting of the ASAE*, Paper No. 936058. American Society of Agricultural Engineers.

Wilkins, G.R. 1985. *Late-Quaternary Vegetational History at Jackson Pond, Larue County, Kentucky*. M.S. Thesis, University of Tennessee.

Wilkins, G.R.; Delcourt, P.A.; Delcourt, H.R.; Harrison, F.W.; Turner, M.R. 1991. Paleoecology of central Kentucky since the Last Glacial Maximum. *Quaternary Research* 36: 224–229.

Woods, S.; Balfour, V.N. 2008. The effect of ash on runoff and erosion after a severe forest wildfire, Montana, USA. *International Journal of Wildland Fire* 17(5): 535–548.

Woods, S.W.; Balfour, V.N. 2010. The effects of soil texture and ash thickness on the post-fire hydrological response from ash-covered soils. *Journal of Hydrology* 393(3–4): 274–286.

Yang, Q.; Mayewski, P.A.; Whitlow, S.I.; Twickler, M.S.; Morrison, M.C.; Talbot, R.W.; Dibb, J.E.; Linder, E. 1995. Global perspective of nitrate flux in ice cores. *Journal of Geophysical Research* 100: 5113–5121.

Zennaro, P.; Kehrwald, N.; McConnell, J.R.; Schüpbach, S.; Maselli, O.J.; Marlon, J.; Vallelonga, P.; Leuenberger, D.; Zangrando, R.; Spolaor, A.; Borrotti, M.; Barbaro, E.; Gambaro, A.; Barbante, C. 2014. Fire in ice: two millennia of boreal forest fire history from the Greenland NEEM ice core. *Climate of the Past* 10(5): 1905–1924.

Chapter 4 Appendix

Table 4.1 Summary of lake-core sediment thin sections for the six study sites, comparing total number of thin sections analyzed and their inclusive depth ranges in cm.

Site and Core	Total thin sections analyzed	Total depth range analyzed (cm)	Notes
Anderson Pond 2007	18	85	
Cahaba Pond 79A&B	9	17	
Pigeon Marsh 2013	5	35	15–50 cm contiguous
Jackson Pond 83A	4	33	
Slack Lake	3	33	
Swift Lake	3	26	
Totals	42	229	

Table 4.2 Macroelements in wood ash compared to limestone (after Risse and Gaskin 2002).

Element	Wood Ash*	Limestone**
Macroelements	**Concentration in %**	
Calcium	15 (2.5–33)	31
Potassium	2.6 (0.1–13)	0.13
Aluminum	1.6 (0.5–3.2)	0.25
Magnesium	1.0 (0.1–2.5)	5.1
Iron	0.84 (0.2–2.1)	0.29
Phosphorus	0.53 (0.1–1.4)	0.06
Manganese	0.41 (0–1.3)	0.05
Sodium	0.19 (0–0.54)	0.07
Nitrogen	0.15 (0.2–0.77)	0.01
Microelements	**Concentration in mg/kg**	
Arsenic	6 (3–10)	–
Boron	123 (14–290)	–
Cadmium	3 (0.2–26)	0.7
Chromium	57 (7–386)	6.0
Copper	70 (37–207)	10
Lead	65 (16–137)	55
Mercury	1.9 (0–5)	–
Molybdenum	19 (0–123)	–
Nickel	20 (0–63)	20
Selenium	0.9 (0–11)	–
Zinc	233 (35–1250)	113
Other Chemical Properties		
$CaCO_3$ (%)	43 (22–92)	100
pH	10.4 (9–13.5)	9.9
Total solids (%)	75 (31–100)	100

*Mean and (Range) from analysis of 37 ash samples from studies of Campbell 1990; White and Rice 1993; Naylor and Schmidt 1986; Muse and Mitchell 1995; Huang et al. 1992

**Limestone analysis from Campbell 1990

Table 4.3 Summary of results of nitric acid rain experiments with wood ash samples.

Description of thin section	Total No. in set	No. Samples selected	Presence of siliceous aggregates	Absence of siliceous aggregates
Experiment 1-Lab-pH5.7	8	2	1	1
Experiment 1-Lab-pH2.0	8	2		2
Experiment 1-Greenhouse-pH5.7	8	2		2
Experiment 1-Greenhouse-pH2.0	8	2	1	1
Experiment 2-Lab-pH5.7	12	4	4	
Experiment 2-Lab-pH1.0	12	4	3	1
Totals	56	16	9	7

Table 4.4 Summary of results comparing ash samples from the nitric acid rain experiments, between those with silt added vs. no silt added.

	No. with silt added	No. with no silt added
Absence of siliceous aggregates	3	4
Presence of siliceous aggregates	9	0
Total	12	4
% Presence of siliceous aggregates	75	0
% Absence of siliceous aggregates	25	100

Table 4.5 Statistical Analysis of the data for the Nitric Acid Rain Experiment on Wood Ash. Yellow indicates silt added. Pink indicates acid rain of pH 1.0 or 2.0. Blue indicates "natural" rain of pH 5.7.

Experiments 1 and 2	Does the formation of siliceous aggregates depend on the presence of silt? YES		
	Silt added	no silt added	Totals
Absence of siliceous aggregates	3	4	7
Presence of siliceous aggregates	9	0	9
Total	12	4	16
% presence	75	0	
% absence	25	100	
Fisher's Exact two-tailed test, p-value = 0.0192			

Experiment 2 Silt added to all Samples randomly selected	Does the formation of siliceous aggregates depend on nitric acid rain? NO		
	pH 1.0/2.0	pH 5.7	Totals
Absence of siliceous aggregates	1	0	1
Presence of siliceous aggregates	3	4	7
Totals	4	4	8
% presence	75	100	
% absence	25	0	
Fisher's Exact two-tailed test, p-value = 1.000			

Experiments 1 and 2 Silt added	Does the formation of siliceous aggregates depend on nitric acid rain? NO		
	pH 1.0/2.0 or pH 2.0	pH 5.7	Totals
Absence of siliceous aggregates	2	1	3
Presence of siliceous aggregates	4	5	9
Totals	6	6	12
% presence of siliceous aggregates	67	83	
% absence of siliceous aggregates	33	17	
Fisher's Exact two-tailed test, p-value = 1.000			

Table 4.6 Radiocarbon dates and calibrations for sediment core from Anderson Pond, Tennessee (AP-76B), collected in 1976.

Lab Number[a]	Core interval (cm)	Depth in profile midpoint (cm)	Depth below mud/water interface midpoint (cm)	Material Dated	Uncalibrated ^{14}C age (^{14}C yr BP)	Calibrated Age yr BP (2–sigma) [b]	Relative Area Under Calibration Curve	Weighted Mean Calibration Age cal yr BP [c]
		25	0		cored in 1976			–26
A-1820[d]	59–65	63	38	bulk sediment	-10 ±100	-6 to -2 -1 to 0 152 to 6 280 to 170	0.017 0.001 0.633 0.348	133
A–1821	103.5–108.5	106	81	bulk sediment	5610 ± 110	6659–6204	1.0	6415
A–1869	123.5–128.5	126	101	bulk sediment	8930 ± 160	10304–9552 10393–10312	0.964675 0.035325	9994
A–1870	144–156	150	125	bulk sediment	12540 ± 180	15334–14083	1.0	14733
A–1871	203–217	210	185	bulk sediment	12750 ± 220	15819–14223	1.0	15092
A–1872	308–321	314.5	289.5	bulk sediment	15310 ± 420	19530–17604	1.0	18548
A–1822	421–435	428	403	bulk sediment	16230 ± 300	20296–18881	1.0	19583
A–1873	595–607	601	576	bulk sediment	18300 ± 1300	25133–19033	1.0	22051
A–1823	687–700	693.5	668.5	bulk sediment	18760 ± 320	23419–21914	1.0	22661
A–1874	966–981	973.5	948.5	bulk sediment	25000 ± 3000	34997–22677	1.0	29026

[a] All radiocarbon dates are from Delcourt (1979). Analyses were performed by the University of Arizona Laboratory of Geochronology, Tucson.
[b] Calibrations were calculated using CALIB 7.0.2 (Stuiver and Reimer, 1993) and the dataset of Reimer et al. (2013).
[c] Weighted mean of the 2 σ calibrated radiocarbon probability distribution.
[d] This date was calibrated with CALIBomb (Reimer et al. 2004).

Table 4.7 Radiocarbon dates and calibrations for sediment cores from Anderson Pond, Tennessee (AP-2007), collected in 2007.

	Depth below mud/water interface (cm)	Material Dated	$\delta^{13}C$ (‰)	Uncalibrated ^{14}C age (^{14}C yr BP)	Calibrated Age yr BP (2–sigma) [b]	Relative Area Under Calibration Curve	Weighted Mean Calibration Age cal yr BP [c]
	0			cored in 2007			–57
OS–77549	67	*Scirpus* seed and trigonous Polygonaceae seed		115 ± 35	150–11 176–175 271–186	0.659106 0.001724 0.33917	136
Beta–282459	80.5	Charcoal	–27.2	5340 ± 40	6214–5997 6269–6242	0.936696 0.063304	6117
OS–82720	110	Cyperaceae seeds		12050 ± 60	14068–13755	1.0	13904
OS–77548	118	*Picea* needles and Cyperaceae achene		12050 ± 70	14088–13748	1.0	13906
OS–77356	174	*Picea* needle		12550 ± 150	15266–14163	1.0	14750
OS–79477	209	*Scirpus* achene, *Picea* seed, *Picea* needles		12850 ± 75	15623–15110	1.0	15349

[a] All radiocarbon dates are from Liu et al. (2013) except for Beta–282459, which is from this study. Date Beta-282459 is on the parallel core that we analyzed; other dates are on the core analyzed by Liu et al. (2013). For our age model, we used a depth of 57 cm for the OS-77549 date based on comparison of photographs of the upper sections of the two parallel cores. Analyses were performed by Beta Analytic; Woods Hole Oceanographic Institute, and the University of Georgia.

[b] Calibrations were calculated using CALIB 7.0.2 (Stuiver and Reimer, 1993) and the dataset of Reimer et al. (2013).

[c] Weighted mean of the 2 σ calibrated radiocarbon probability distribution.

Table 4.8 Radiocarbon dates and calibrations for sediment core from Cahaba Pond, Alabama (CP-79B), collected in 1979.

Lab Number[a]	Core interval (cm)	Depth in profile midpoint (cm)	Depth below mud/water interface midpoint (cm)	Material Dated	$\delta^{13}C$ (‰)	Uncalibrated ^{14}C age (^{14}C yr BP)	Calibrated Age yr BP (2–sigma) [b]	Relative Area Under Calibration Curve	Weighted Mean Calibration Age cal yr BP [c]
		127	0			cored in 1979			–29
W–4770	134–145	139.5	12.5	bulk sediment		840 ±50	804–677 831–808 905–853	0.82345 0.045265 0.131285	767
W–4784	165–171	168	41	bulk sediment		1750 ± 50	1430–1423 1455–1442 1872–1521	0.003262 0.00736 0.989378	1672
W–4780	200–207	203.5	76.5	bulk sediment		2990 ±80	3370–2952	1.0	3161
W–4906	210–214	212	85	bulk sediment		5750 ± 90	6371–6322 6742–6392	0.035396 0.964604	6550
W–4910	242–245	243.5	116.5	bulk sediment		8190 ± 90	8825–8810 8878–8872 9442–8978	0.004349 0.001739 0.993912	9165
W–4771	245–250	247.5	120.5	bulk sediment		8710 ± 80	9936–9531 10004–9995 10120–10064	0.965498 0.003145 0.031357	9729
W–4773	345–351	348	221	bulk sediment		9680 ± 100	11245–10733	1.0	11007
W–4775	445–451	448	321	bulk sediment		9960 ± 90	11772–11208 11792–11789	0.999284 0.000716	11472

Table 4.8 Continued.

Lab Number[a]	Core interval (cm)	Depth in profile midpoint (cm)	Depth below mud/water interface midpoint (cm)	Material Dated	$\delta^{13}C$ (‰)	Uncalibrated ^{14}C age (^{14}C yr BP)	Calibrated Age yr BP (2–sigma) [b]	Relative Area Under Calibration Curve	Weighted Mean Calibration Age cal yr BP [c]
W–4778	**540–550**	**545**	**418**	**bulk sediment**		**10190 ± 80**	**11569–11404** **11576–11572** **12160–11591**	**0.061117** **0.001038** **0.937845**	**11861**
Beta–379635	539–540	539.5	412.5	plant macrofossils	–24.8	10360 ±40	12398–12039	1.0	12226
Beta–379636	590–591	590.5	463.5	plant macrofossils	–27.7	10890 ±40	12791–12689	1.0	12734
W–4782	**560–570**	**565**	**438**	**bulk sediment**		**10980 ± 100**	**13049–12712**	**1.0**	**12871**
W–4781	640–650	645	518	bulk sediment		11270 ± 130	13382–12824	1.0	13124
W–4783	720–730	725	598	bulk sediment		11780 ± 120	13852–13344 13936–13903	0.989852 0.010148	13615
QL–1486	750–766	758	631	bulk sediment		11960 ± 70	14008–13586	1.0	13814

[a] Beta-379635 and Beta-379636 are AMS dates obtained for this study. Other dates are standard dates from Delcourt et al. (1983). These new AMS dates were used in place of the standard dates in bold in our age model. Analyses were performed by Beta Analytic, University of Washington (QL); and USGS Radiocarbon Laboratory, Reston, Virginia.

[b] Calibrations were calculated using CALIB 7.0.2 (Stuiver and Reimer, 1993) and the dataset of Reimer et al. (2013).

[c] Weighted mean of the 2 σ calibrated radiocarbon probability distribution.

Table 4.9 Radiocarbon dates and calibrations for sediment cores from Jackson Pond, Kentucky (JP-83B), collected in 1983

Lab Number[a]	Core interval (cm)	Depth in profile midpoint (cm)	Depth below mud/water interface midpoint (cm)	Material Dated	Uncalibrated ^{14}C age (^{14}C yr BP)	Calibrated Age yr BP (2–sigma) [b]	Relative Area Under Calibration Curve	Weighted Mean Calibration Age cal yr BP [c]
		93	0		cored in 1983			–33
A–3870	128–138	133	40	bulk sediment	120 ± 50	151–7 280–171	0.602548 0.397452	140
A–3871	155–166	160.5	67.5	bulk sediment	940 ± 80	980–690	1.0	849
A–3872	215–226	220.5	127.5	bulk sediment	10040 ± 190	12251–11138 12388–12259	0.970363 0.029637	11651
A–3873	263–277	270	177	bulk sediment	11860 ± 250	14490–13134	1.0	13769
A–3874	505–515	510	417	bulk sediment	17750 ± 270	22188–20758	1.0	21459
A–3875	700–710	705	612	bulk sediment	20330 ± 630	25830–23025	1.0	24461

[a] All radiocarbon dates are from Wilkins et al. (1991). Analyses were performed by the University of Arizona Laboratory of Geochronology, Tucson.

[b] Calibrations were calculated using CALIB 7.0.2 (Stuiver and Reimer, 1993) and the dataset of Reimer et al. (2013).

[c] Weighted mean of the 2 σ calibrated radiocarbon probability distribution.

Table 4.10 Radiocarbon dates and calibrations for lake-sediment cores from Pigeon Marsh, Georgia (PM-2013-1), collected in 2013.

Lab Number[a]	Core interval (cm)	Depth below mud/water interface midpoint (cm)	Material Dated	$\delta^{13}C/^{12}C$ (‰)	Uncalibrated ^{14}C age (^{14}C yr BP)	Calibrated Age yr BP (2–sigma) [b]	Relative Area Under Calibration Curve	Weighted Mean Calibration Age cal yr BP [c]
		0						–63
Beta-396124[d]	16–18	17	wood	–27.0	154.8 ± 0.3 pMC	-13.30 to -13.22 -18.53 to -18.25 -20.01 to -18.77 -20.83 to - 20.22 -22.06 to -21.99	0.040 0.103 0.617 0.229 0.012	–21
Beta-408513	22.5–24.5	23.5	charcoal, plant fragments	–28.0	12700 ± 60	14841–15315	1.0	15110
Beta-402430	32–34	33	leaf fragments	–27.9	12660 ± 40	15236–14826	1.0	15058
Beta-382660	51.5–53.5	52.5	leaf fragments	–27.4	13630 ±40	16639–16238	1.0	16430

[a] All dates are from this study. Analyses were performed by Beta Analytic.

[b] Calibrations were calculated using CALIB 7.0.2 (Stuiver and Reimer, 1993) and the dataset of Reimer et al. (2013).

[c] Weighted mean of the 2 σ calibrated radiocarbon probability distribution.

[d] Calibrations were calculated using CALIBomb (Reimer et al. 2004).

Table 4.11 Radiocarbon dates and calibrations for sediment cores from Slack and Swift Lakes, Michigan, collected in 2008.

Lab Number[a]	Site	Depth below mud/water interface (cm)	Depth in profile from platform (cm) (thrust: thrust interval, cm)	Material Dated	$\delta^{13}C$ (‰)	Uncalibrated ^{14}C age (^{14}C yr BP)	Calibrated Age yr BP (2–sigma) [b]	Relative Area Under Calibration Curve	Weighted Mean Calibration Age cal yr BP [c]
	Slack	0	945						-58
OS–71334	Slack	714	1659 (A3:58–60)	organics	–24.95	9630 ± 25	10853–10793 10962–10860 11023–11004 11170–11066	0.110718 0.452766 0.022183 0.414334	10984
OS–70592	Slack	811	1756 (A4: 51)	wood	–24.25	12050 ± 110	13685–13603 14172– 13690	0.036082 0.963918	13913
	Swift	0	975						-58
OS– 71335	Swift	707	1682 (A5:67–71)	organics and seeds	–27.26	8050 ± 30	8833–8779 8922–8860 8943–8932 9027–8948	0.187043 0.152146 0.011972 0.648839	8944
OS–107200	Swift	783.5	1758.5 (A6:58.5)	*Populus deltoides* leaf	–29.11	9490 ± 50	10871–10587 11072–10948	0.724094 0.275906	10810
OS–70562	Swift	882	1857 (A7:57)	wood	–24.41	12200 ± 65	14315–13832	1.0	14095

[a] All radiocarbon dates are from Ballard (2009) except for OS-107200, which is from the present study. Analyses were performed by National Ocean Sciences AMS Facility, Woods Hole Oceanographic Institute

[b] Calibrations were calculated using CALIB 7.0.2 (Stuiver and Reimer, 1993) and the dataset of Reimer et al. (2013).

[c] Weighted mean of the 2 σ calibrated radiocarbon probability distribution.

Figure 4.1 Map showing locations of the six late-glacial sample sites in eastern North America: Anderson Pond, Tennessee; Cahaba Pond, Alabama; Jackson Pond, Kentucky; Pigeon Marsh, Georgia, and Slack and Swift Lakes, Michigan. LIS = Laurentide Ice Sheet maximum extent (after Dyke 2004).

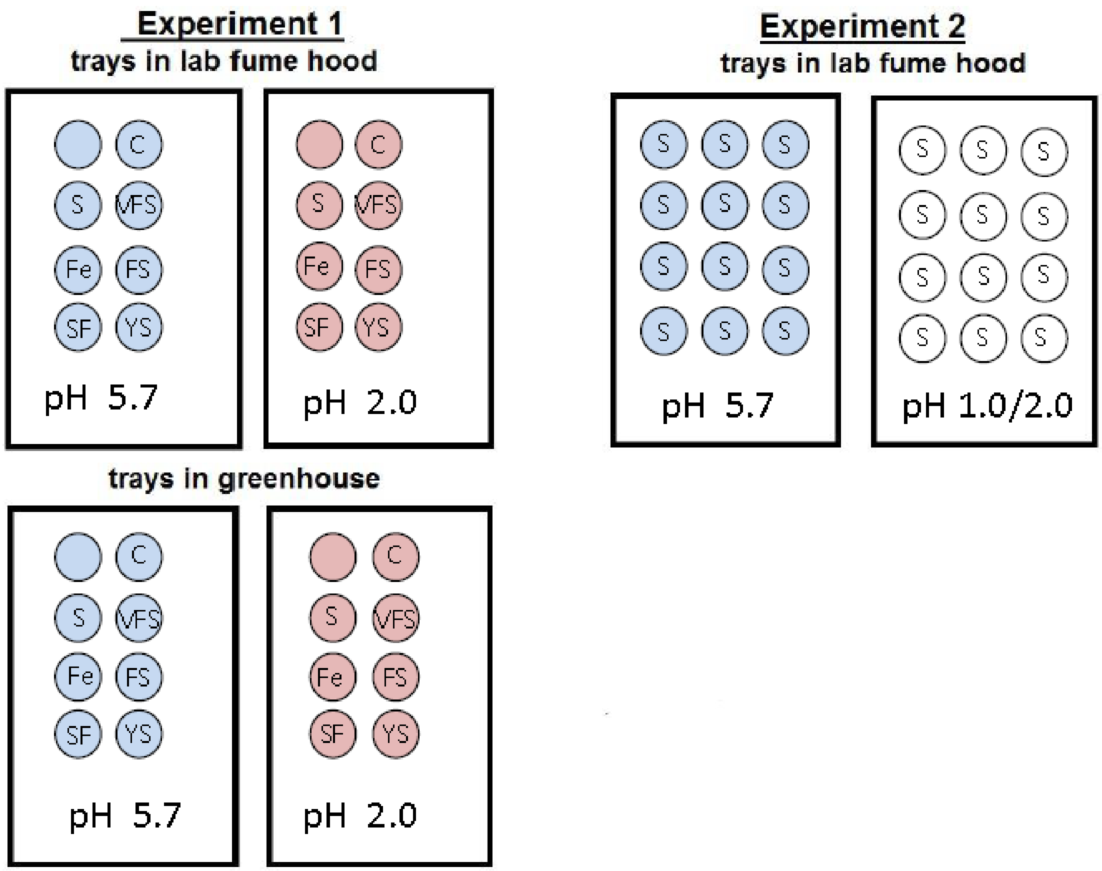

Figure 4.1.1 Diagram of the nitric acid rain experiments. Rectangles represent sample trays; circles represent individual samples. Blue indicates sample containers treated with pH 5.7 "natural" rain, pink indicates samples that were treated with pH 2.0 nitric acid rain, and white indicates samples that were treated with pH 1.0 nitric acid rain for a month, and then treated with pH 2.0 nitric acid rain for the remaining 64 days. Letters on samples indicate additions of silt-sized quartz (S); iron (Fe); silt-sized quartz and iron (SF); bentonite clay (C); very fine quartz sand (VFS); fine quartz sand (FS); and yellow silt-sized quartz (YS). No letter indicates no addition of material.

Figure 4.2 (A, B) Anderson Pond 2007 core, siliceous aggregate grain that is composed of angular grains of monocrystalline fine to very fine silt cemented by amorphous to very finely crystalline silica, 121–124 cm depth, A is in plane-polarized light, PPL; B is in cross-polarized light, XPL). (C-E) Cahaba Pond CP-79A-15, siliceous aggregate grain, 532.3 cm depth, spanning the Pleistocene-Holocene transition (PPL, XPL, UV fluorescence, UVf). (F-H) Cahaba Pond CP-79A-13 siliceous aggregate grain, 536 cm depth, spanning the Pleistocene-Holocene transition (PPL, XPL, UVf). (I-K) Jackson Pond 1983 core, siliceous aggregate grain, 285–293 cm depth (PPL, XPL, UVf). Note brightly fluorescing organic grains visible in UVF photos in (E) and (H). Depths follow original publications as cited in Table 1, and include water depths at all sites other than Anderson Pond 2007.

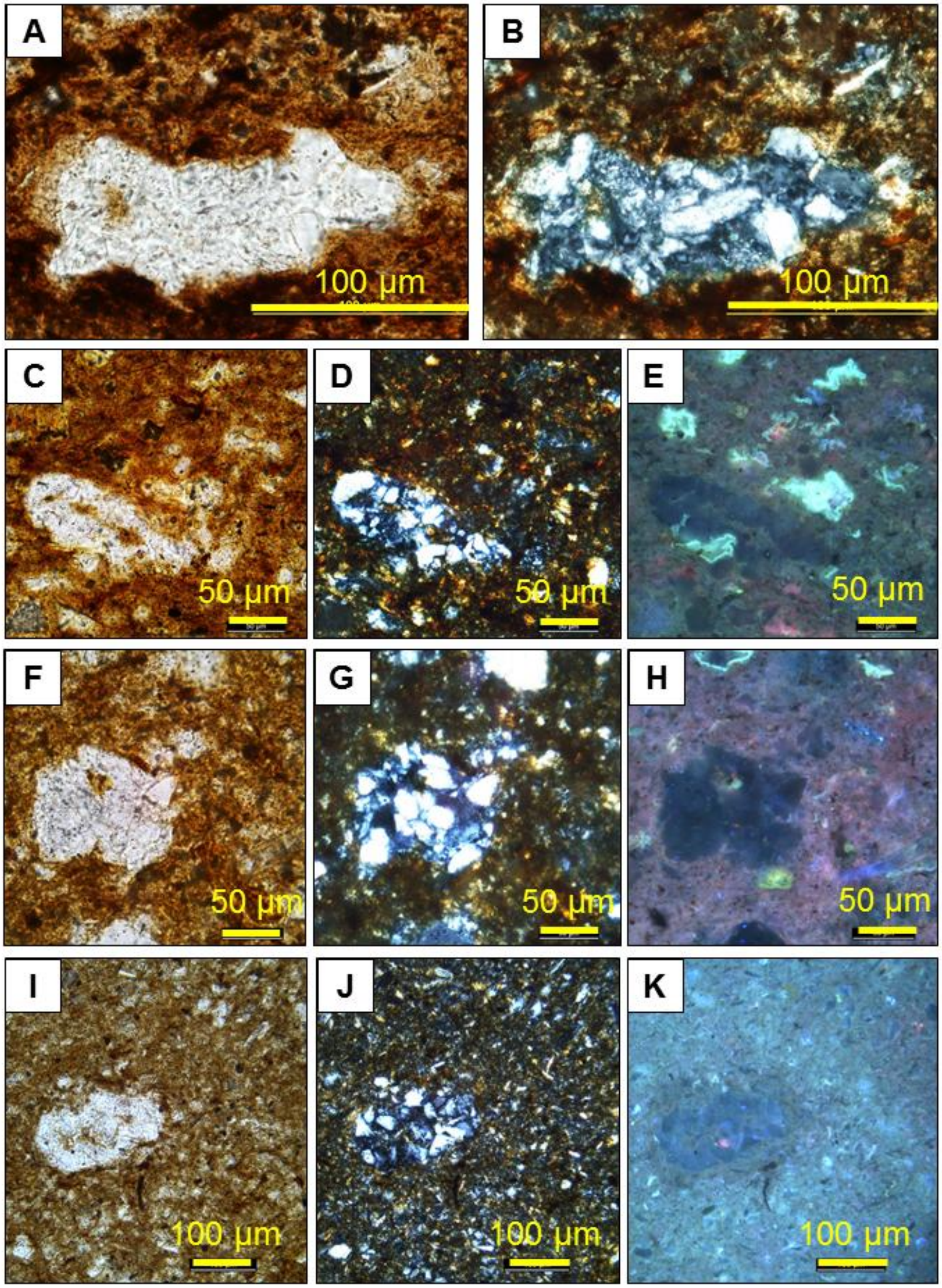
A
100 µm
B
100 µm
C
50 µm
D
50 µm
E
50 µm
F
50 µm
G
50 µm
H
50 µm
I
100 µm
J
100 µm
K
100 µm

Figure 4.2

Figure 4.3 (A, B) Jackson Pond 1983 core, 435–449 cm depth from platform. Siliceous microaggregate grain composed of very fine, monocrystalline angular quartz silt grains cemented by a siliceous micromass (A: PPL and B: XPL). (C-H) Slack Lake core A4, 1749.6–1760.6 cm depth from platform. Spheroidal, siliceous microaggregate grain that resembles those observed in sediment cores from Jackson Pond, Anderson Pond and Cahaba Pond; note reddish Fe-oxide (or oxyhydroxide) center of grain. (C- E, and F-H): (PPL, XPL and UVf) Spheroidal, siliceous microaggregate grain that resembles those observed in sediment cores from Jackson Pond, Anderson Pond and Cahaba Pond, but different in that it includes admixed calcite silt together with quartz component. (I-K) Swift Lake core A6, 1776-1783.5 cm depth from platform. Details of bright red-colored organic matter with mat-like morphology intercalated with siliceous microaggregate grains (yellow arrows) that contain very fine quartz silt and amorphous silica in center and detrital calcite (?) around exterior: this is a different form than that which was observed in Jackson Pond, Anderson Pond and Cahaba Pond.

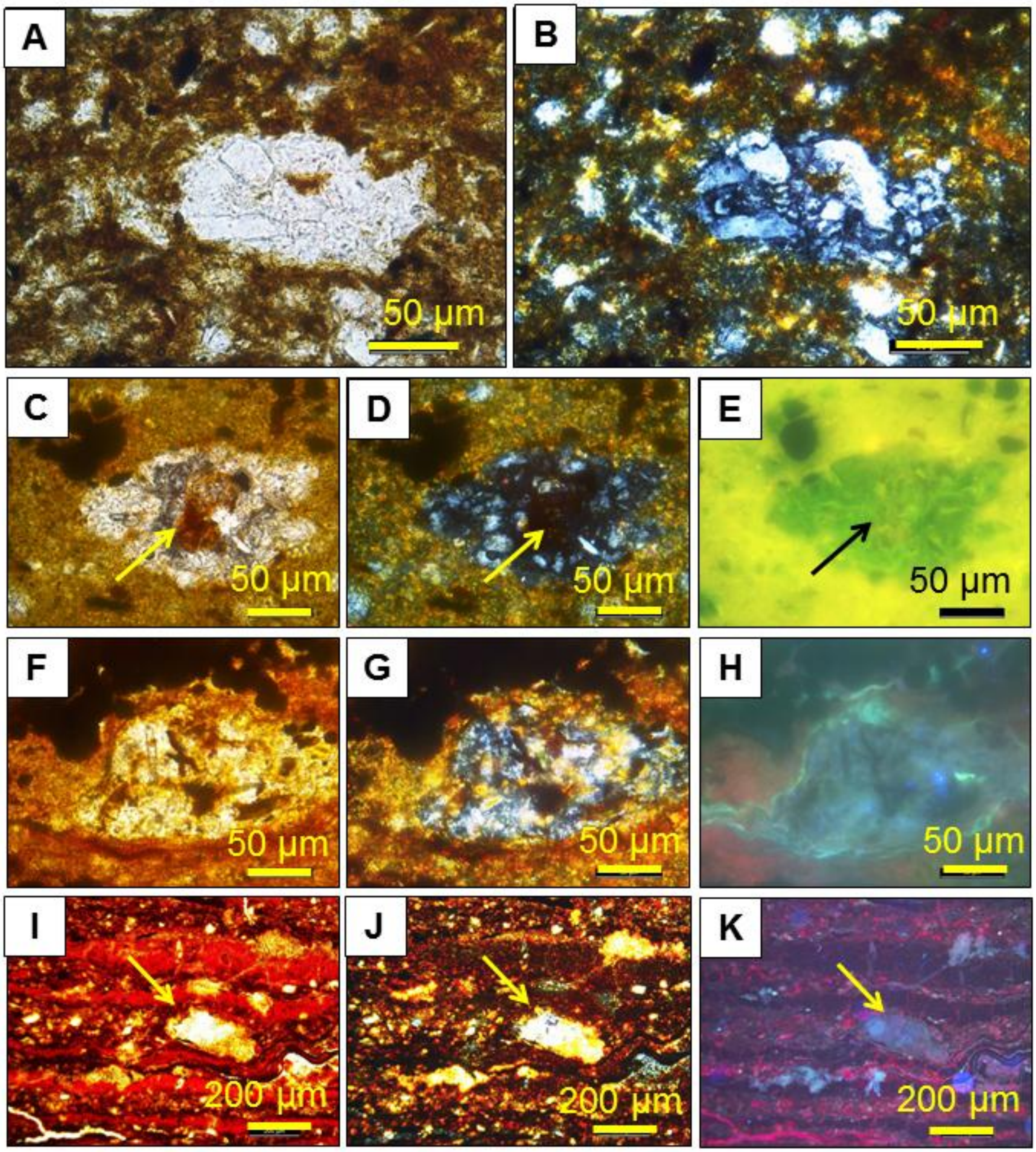
A
50 µm
B
50 µm
C
50 µm
D
50 µm
E
50 µm
F
50 µm
G
50 µm
H
50 µm
I
200 µm
J
200 µm
K
200 µm

Figure 4.3

Figure 4.4 L2-5.7-S: Experiment 1—Lab pH = 5.7—less biological inputs, cooler and drier conditions—Silt added—American beech branches and leaves as source of ash: (A) Scan of whole thin section: Note large pieces of charcoal (yellow arrows). (B, C) yellow box is shown in detail in accompanying photomicrographs where (B) is taken in plane-polarized light, PPL, and (C) is taken in cross-polarized light, XPL. Siliceous aggregate grain is about 300 μm in diameter and is composed of angular grains of fine- to medium-quartz silt. (B, C) Siliceous aggregate grain (yellow dashed box) in charcoal and calcite-oxalate-rich wood-ash sediment. (D-F) Enlarged views of siliceous aggregate grain (outlined) shown in (B, C) where (D) is PPL, (E) is XPL, and (F, G) are in UV fluorescence (UVf). Quartz silt grains appear etched in PPL, and are cemented by calcite-oxalate micromass that has bright gold birefringence in XPL and bright fluorescence much higher than epoxy autofluorescence as seen in NU (F) and NB (G) wavelengths of UVf.

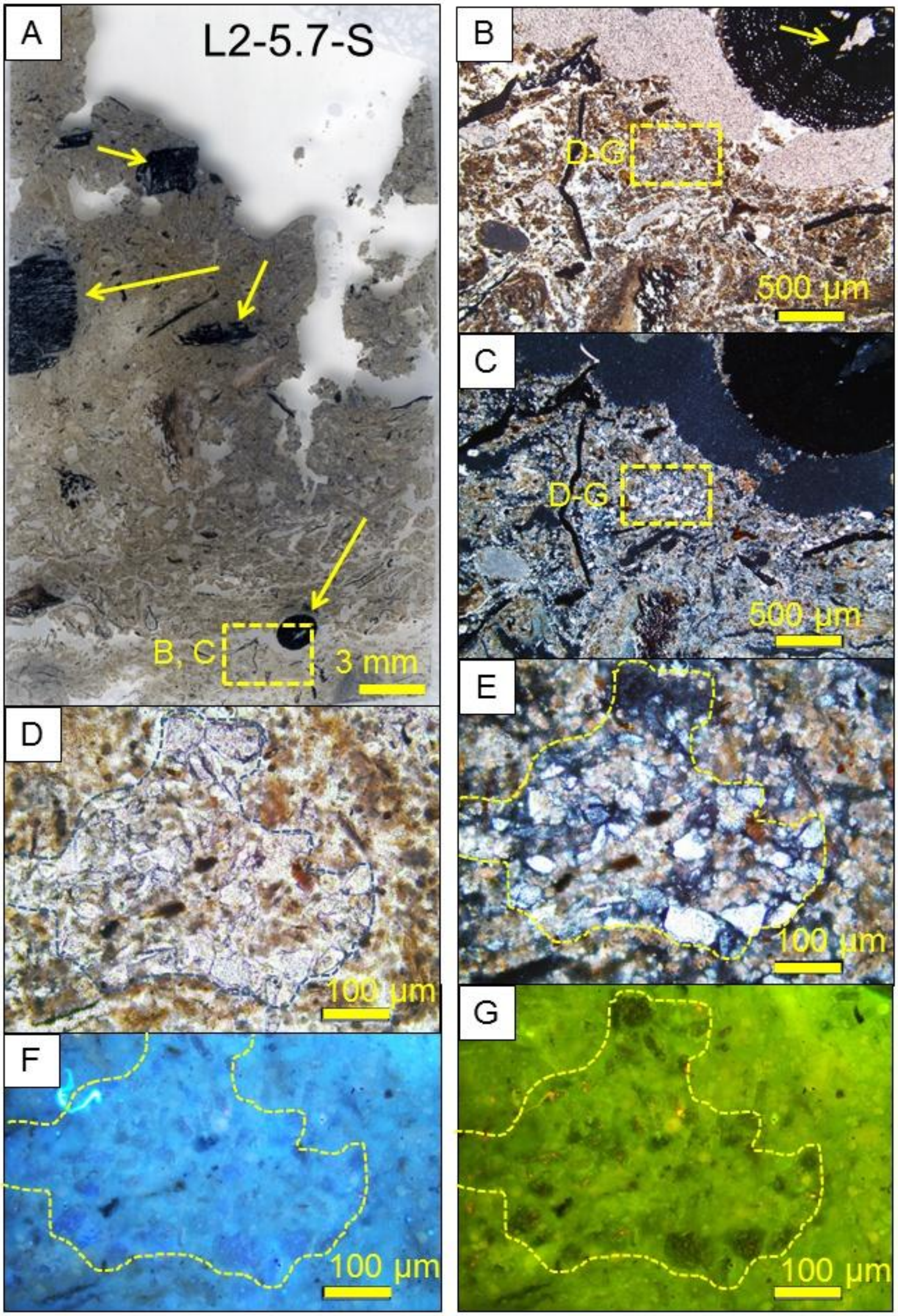
A
L2-5.7-S
B, C
3 mm
B
D-G
500 µm
C
D-G
500 µm
D
100 µm
E
100 µm
F
100 µm
G
100 µm

Figure 4.4

Figure 4.5 G2-2.0-S: Experiment 1—Greenhouse pH = 2.0—cyanobacteria introduced, warmer and humid conditions- Silt added—American beech branches and leaves as source of ash: (A) Scan of whole thin section: Note large pieces of charcoal (yellow arrows). (B, C) yellow box is shown in detail in accompanying photomicrographs where (B) is taken in plane-polarized light, PPL, and (C) is taken in cross-polarized light, XPL). Two siliceous aggregate grains are about 200-300 μm in diameter and are composed of angular grains of fine- to medium-quartz silt. (B, C) Siliceous aggregate grain (yellow dashed box) in charcoal and calcite-oxalate-rich wood-ash sediment. (D-F) Enlarged views of siliceous aggregate grain (outlined) shown in (B, C) where (D) is PPL, (E) is XPL, and (F, G) are in UV fluorescence (UVf). Quartz silt grains appear etched in PPL, and are cemented by calcite-oxalate + silica (?) micromass that has gold to gray birefringence in XPL and bright fluorescence as seen in NU (F) and NB (G) wavelengths of UVf.

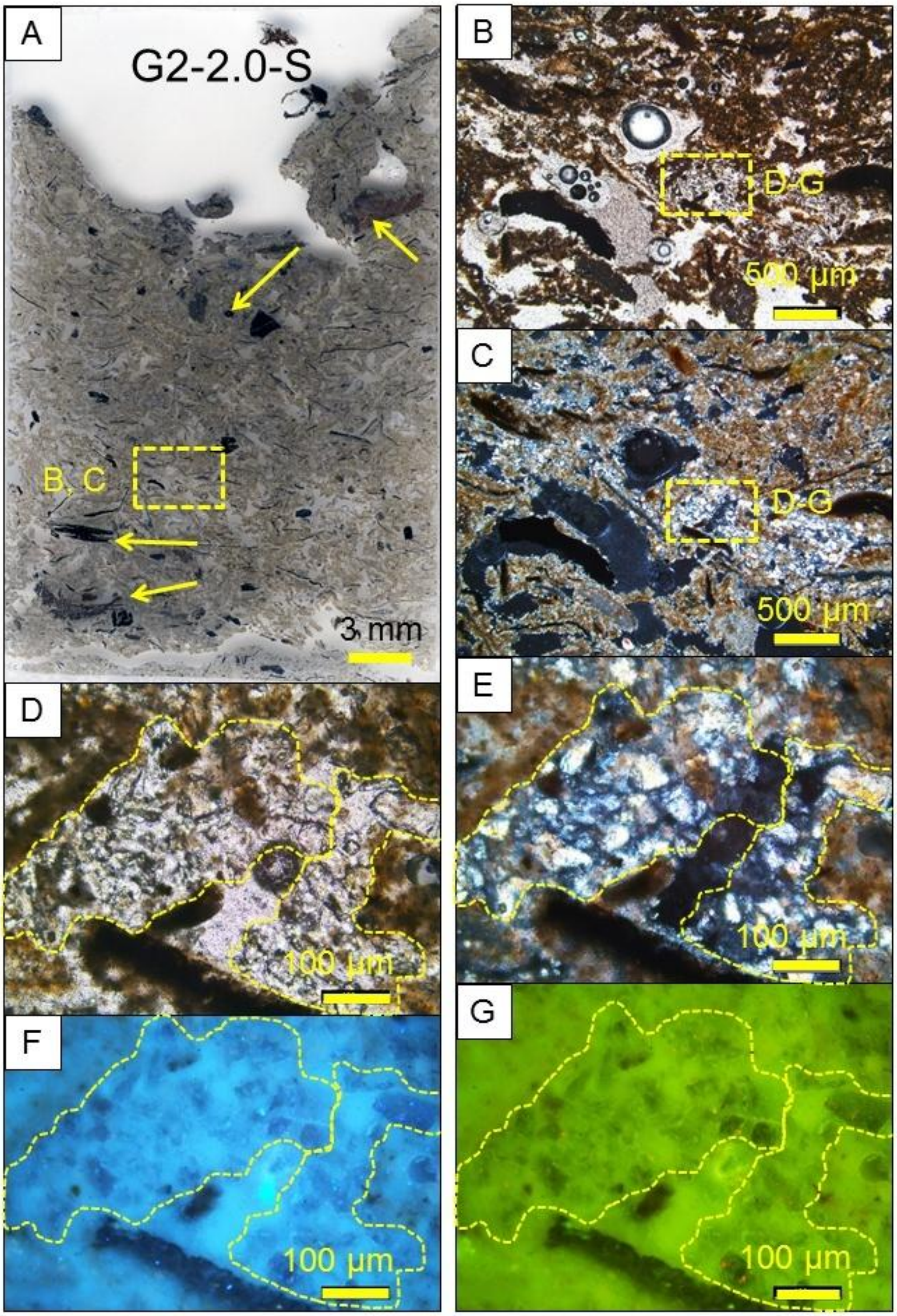
A
G2-2.0-S
B, C
3 mm
B
D-G
500 µm
C
D-G
500 µm
D
100 µm
E
100 µm
F
100 µm
G
100 µm

Figure 4.5

Figure 4.6 DL-3-5.7: Experiment 2—Lab pH = 5.7—no cyanobacteria or green algae introduced, cooler and drier conditions than the humid greenhouse- Silt added—Mixed hardwoods as source of ash: (A) Scan of whole thin section: Note large pieces of charcoal (yellow arrows). (B, C) yellow box is shown in detail in accompanying photomicrographs where (B) is taken in plane-polarized light, PPL, and (C) is taken in cross-polarized light, XPL). Spheroidal siliceous aggregate grain is about 200 μm in diameter and is composed of angular grains of fine- to medium-quartz silt. (B, C) Siliceous aggregate grain (yellow outlined) in fine charcoal and calcite-oxalate-rich wood-ash sediment. (D-F) Enlarged views of siliceous aggregate grain (yellow outlined) shown in (B, C) where (D) is PPL, (E) is XPL, and (F, G) are in UV fluorescence (UVf). Quartz silt grains appear etched in PPL, and are cemented by calcite-oxalate + silica (?) micromass that has pale gold to gray birefringence in XPL and bright fluorescence as seen in NU (F) and NB (G) wavelengths of UVf.

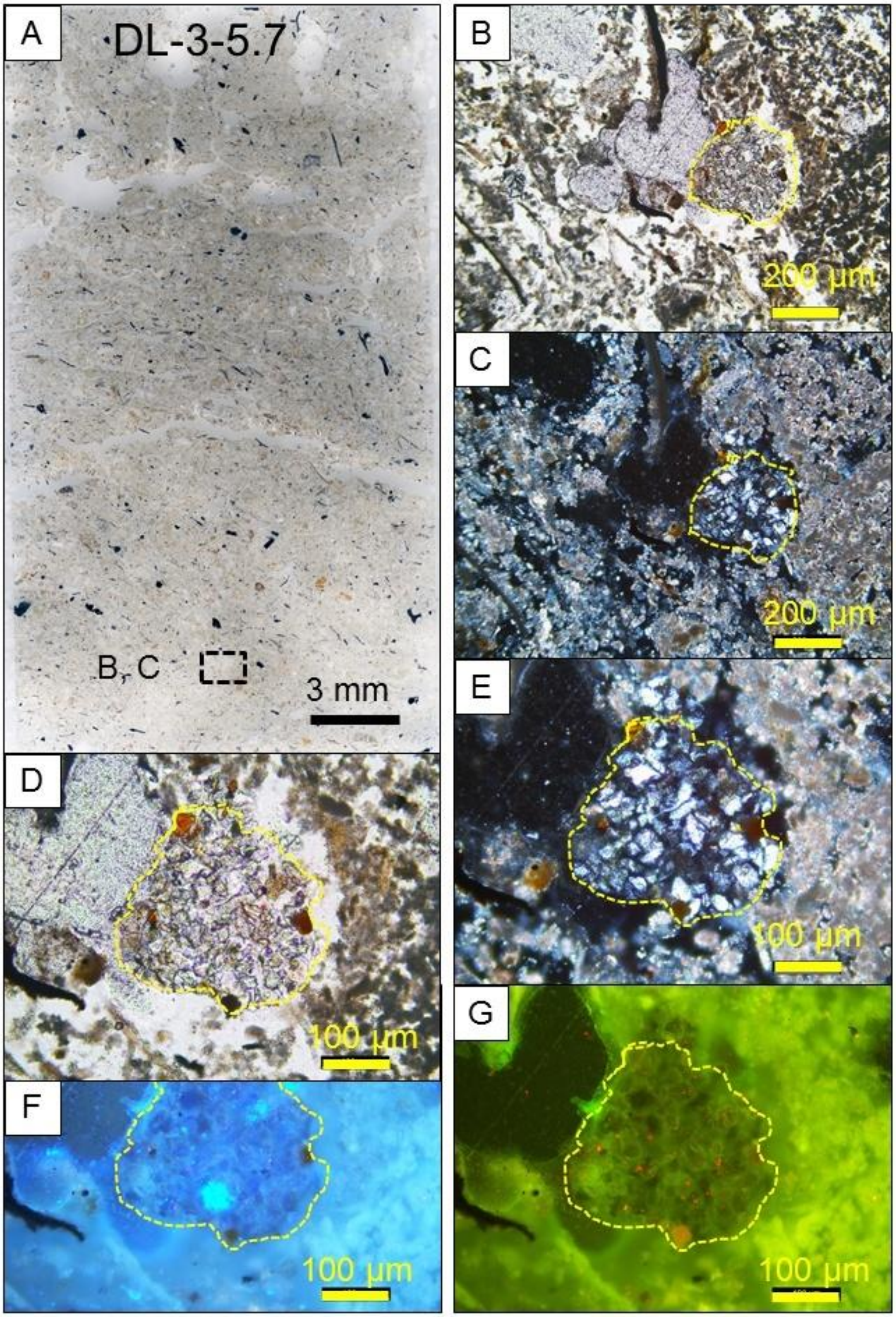

Figure 4.6

Figure 4.7 DL-9-1.0: Experiment 2—Lab pH = 1.0—no cyanobacteria or green algae added, cooler and drier conditions than humid greenhouse- Silt added—Mixed hardwoods as source of ash:(A) Scan of whole thin section: Note development of graded bedding at top, with breakage of layers towards top of deposit forming intraclasts, as well as coarse to fine pieces of charcoal (black grains). (B, C) black box is shown in detail in accompanying photomicrographs where (B) is taken in plane-polarized light (PPL), and (C) is taken in cross-polarized light (XPL). Three spheroidal siliceous aggregate grains, ranging from 75–150 μm in diameter, which are composed of angular grains of fine- to medium-quartz silt. (B, C) Siliceous aggregate grains (yellow outlined) in fine charcoal and calcite-oxalate-rich wood-ash sediment that are most similar to natural grains in terms of size. (D-F) Enlarged views of three siliceous aggregate grains (yellow outline) shown in (B, C) where (D) is PPL, (E) is XPL, and (F, G) are in UV fluorescence (UVf). Quartz silt grains appear etched in PPL, and are cemented by calcite-oxalate + silica (?) with pale gold to gray birefringence in XPL and bright fluorescence as seen in NU (F) and NB (G) wavelengths of UVf. Note pieces of bright fluorescing organic matter, non-fluorescing microcharcoal grains, and Fe-Ti oxide grains (prominent red to reddish orange inclusions within aggregates).

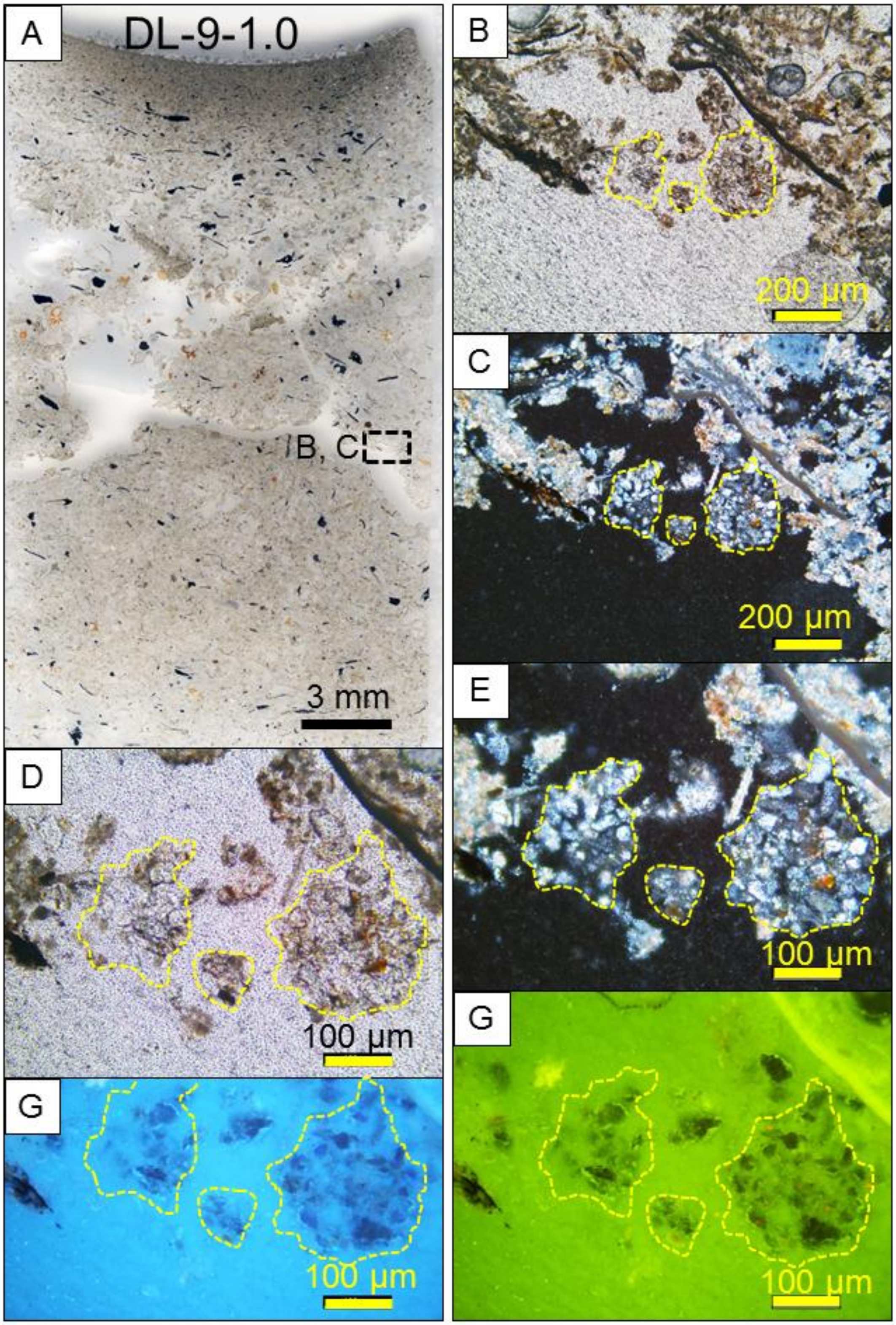

Figure 4.7

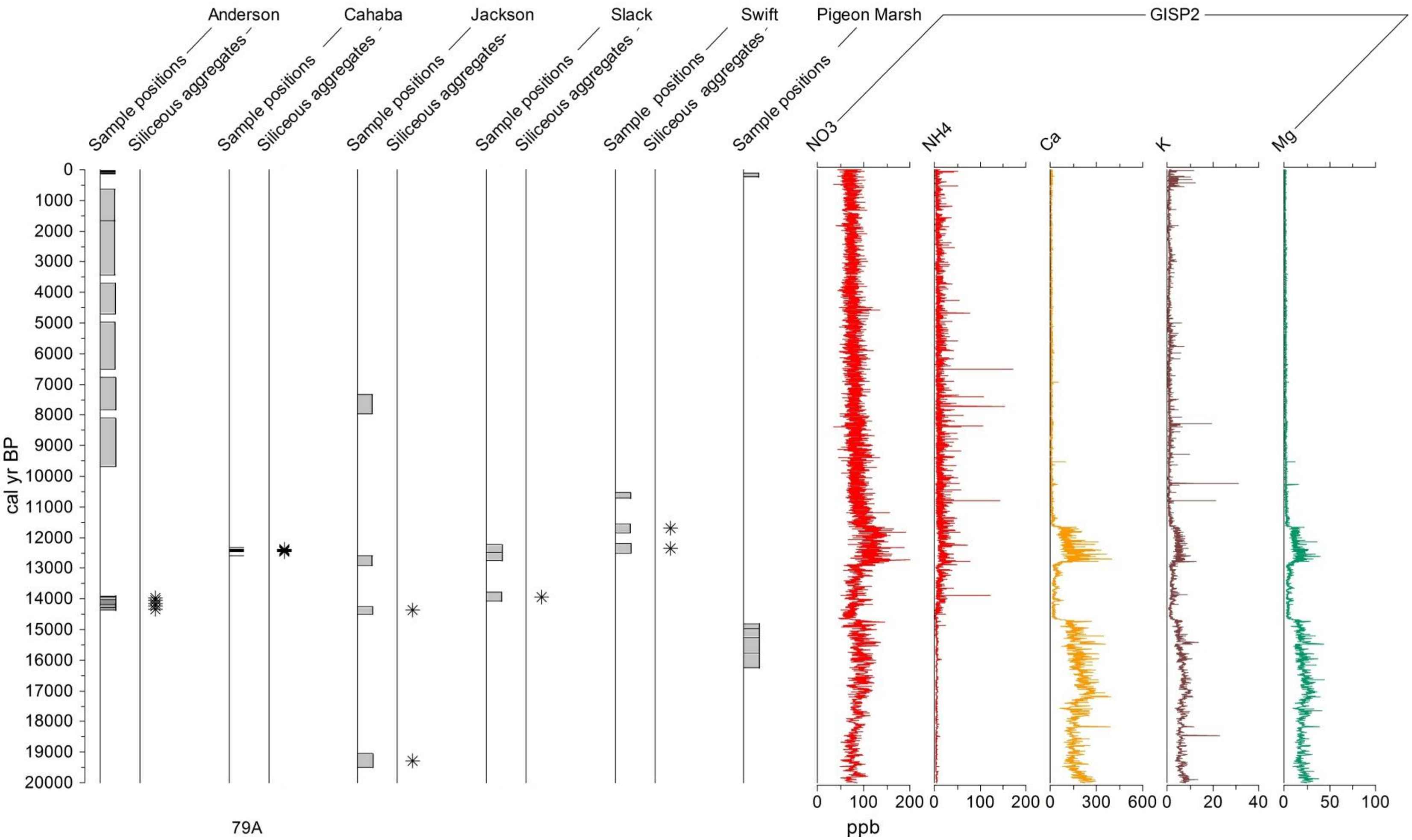

Figure 4.8 Summary of siliceous aggregate occurrences in lake sediments identified using thin section analysis, compared by interpolated calibrated ages for the six sampled sites. Shaded blocks or lines denote the intervals of thin-section analysis; stars indicate presence of siliceous aggregates (none were found at any depth in Pigeon Marsh). Nitrate and ammonium data from the GISP2 Greenland ice core record (Yang et al. 1995, Mayewski et al. 1997) and GISP2 chemical markers that are typically found in plant ash (Ca, K, and Mg) are graphed for comparison; however, these may have originated from sources other than wood ash. Nitrate and ammonium can be markers of biomass burning.

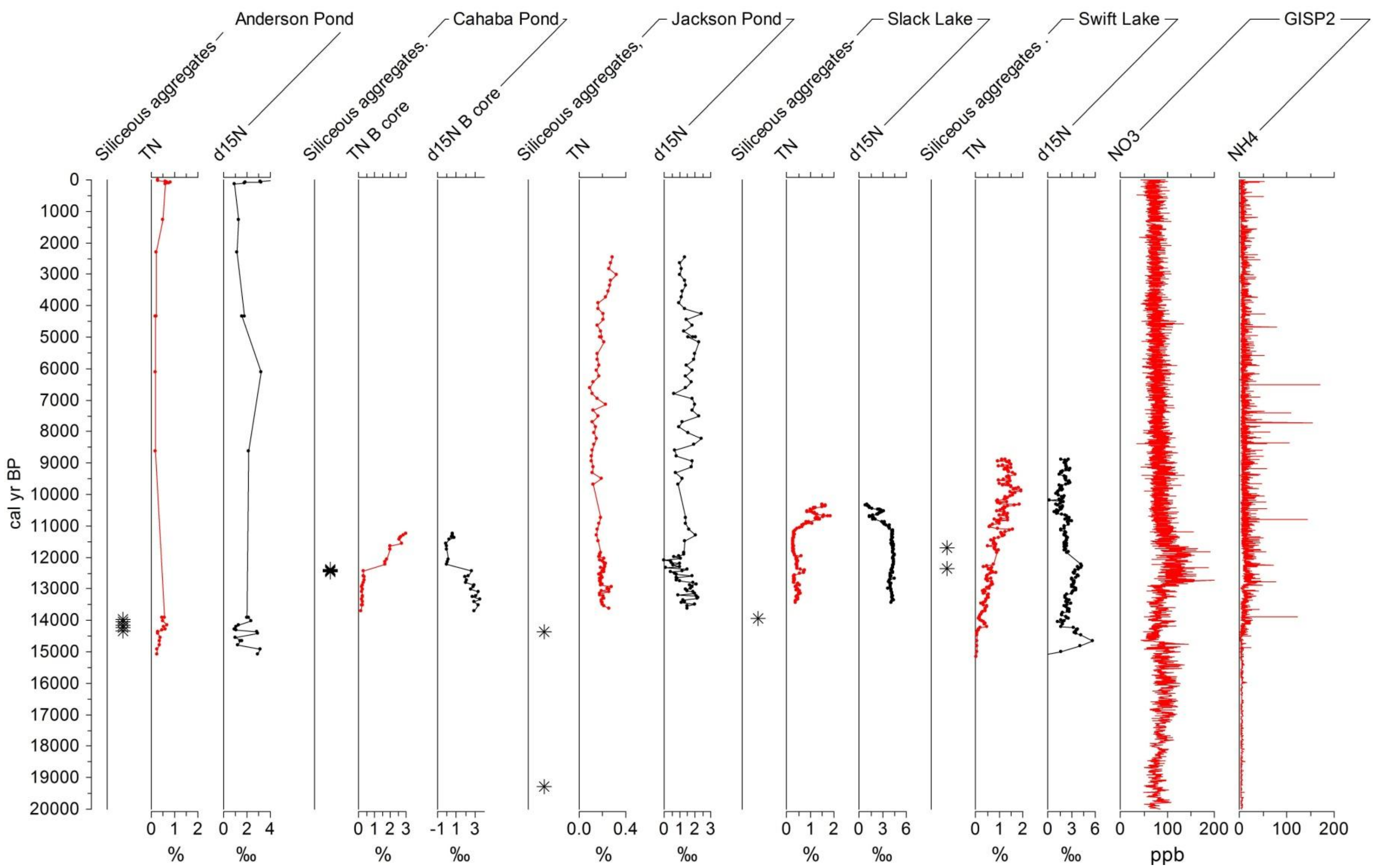

Figure 4.9 Comparison of siliceous aggregate occurrences, total nitrogen (TN), and $\delta^{15}N$ measured in sediments from Anderson Pond 2007, Cahaba Pond 79A and 79B, Jackson Pond 83A, and Slack and Swift Lake cores, together with GISP2 NO_3 and NH_4 (Yang et al. 1995, Mayewski et al. 1997). Siliceous aggregates co-occur with shifts in nitrogen at Cahaba Pond (TN and $\delta^{15}N$) and Swift Lake ($\delta^{15}N$) at ca. 12,400 cal yr BP, and Anderson Pond ($\delta^{15}N$) at ca. 14,000 cal yr BP. Data are lacking for comparisons at Jackson Pond and Slack Lake. Uppermost portion of Anderson Pond $\delta^{15}N$ is truncated to better show the late glacial data.

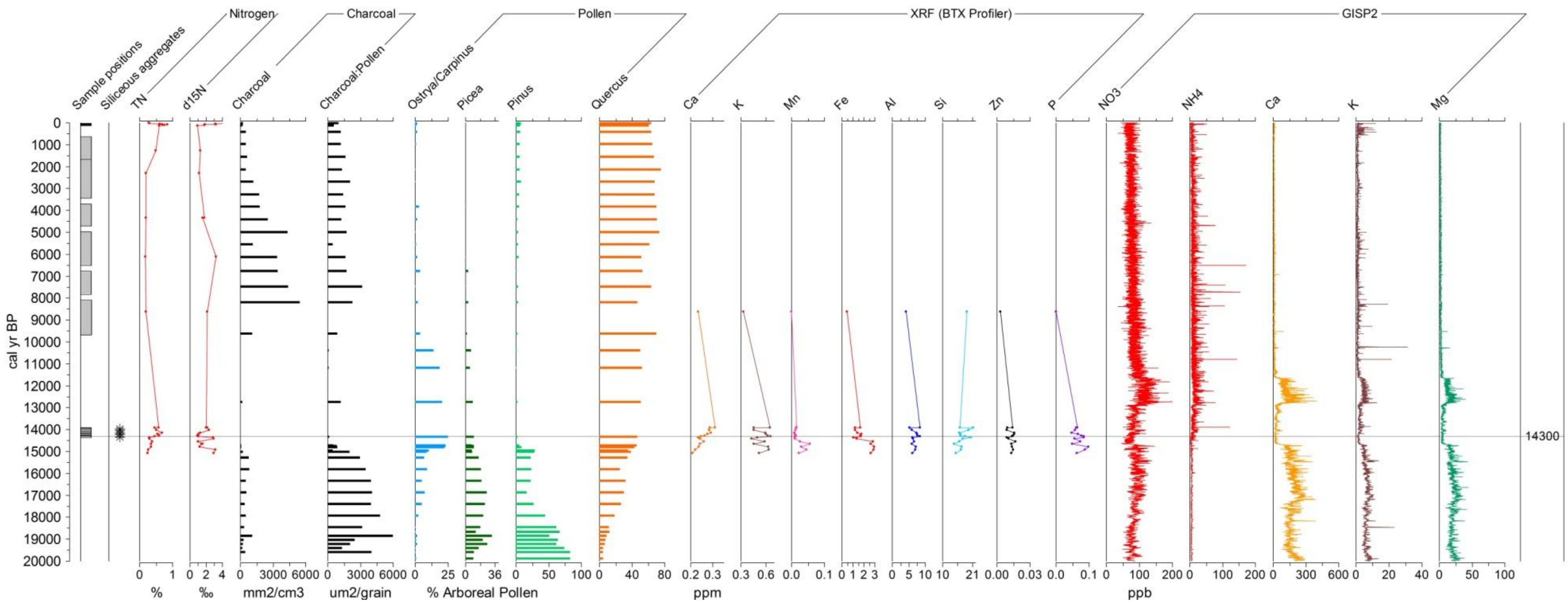

Figure 4.10 Anderson Pond datasets, compared by calibrated age. Shaded boxes represent sample depths for thin sections and asterisks indicate presence of siliceous aggregates, which occur around the time of a peak in δ^{15}N, and when charcoal is relatively low. A major shift in vegetation occurs at the time of siliceous aggregates. High resolution XRF analysis for elements typical of wood ash show a gradual increase in Ca, and small peaks in K, Fe, Al, Zn, and P. Siliceous aggregates may co-occur with a spike in ammonium (NH_4), and peaks in Ca, K, and Mg recorded in the GISP2 ice core, considering that the calibration ranges for radiocarbon dates for the 2007 core include 14,000 cal yr BP. Pollen and microscopic charcoal data are based on analyses of the 1976 core (Delcourt 1979, and this dissertation, chapter 2), while data for thin sections, nitrogen isotopes and XRF data were collected from the 2007 core.

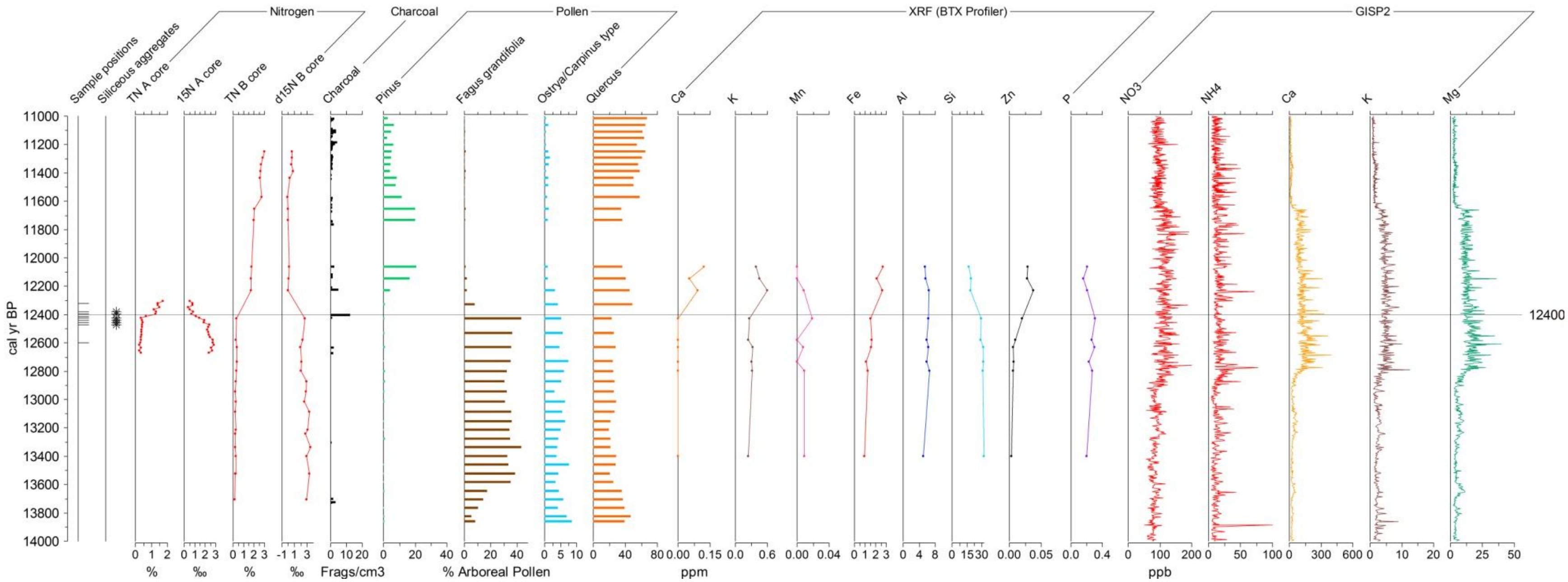

Figure 4.11 Cahaba Pond 79A and 79B datasets for the late glacial interval (14,000–11,000 cal yr BP). Sample depths for thin sections from the CP-79A core are marked with lines; siliceous aggregate occurrences are marked with asterisks. Major changes in TN and $\delta^{15}N$ occur at the time of siliceous aggregates, with TN increasing while $\delta^{15}N$ decreased. This is a signature of cyanobacteria fixing nitrogen from the atmosphere, supported by unpublished data on cyanins found in a sample from this interval (pers. communication Jamey Fulton to S.Driese, 30 May 2014). A small charcoal peak occurs at the time of siliceous aggregates. A major shift in vegetation occurred at the time of siliceous aggregates, with the dramatic decline of the fire-intolerant taxa beech and hornbeam/hophornbeam. Coarse-resolution XRF analysis shows increases in Ca, K, Fe, and Zn around the time of siliceous aggregates. No clear peaks occur in the GISP2 ice core nitrogen or dust ions.

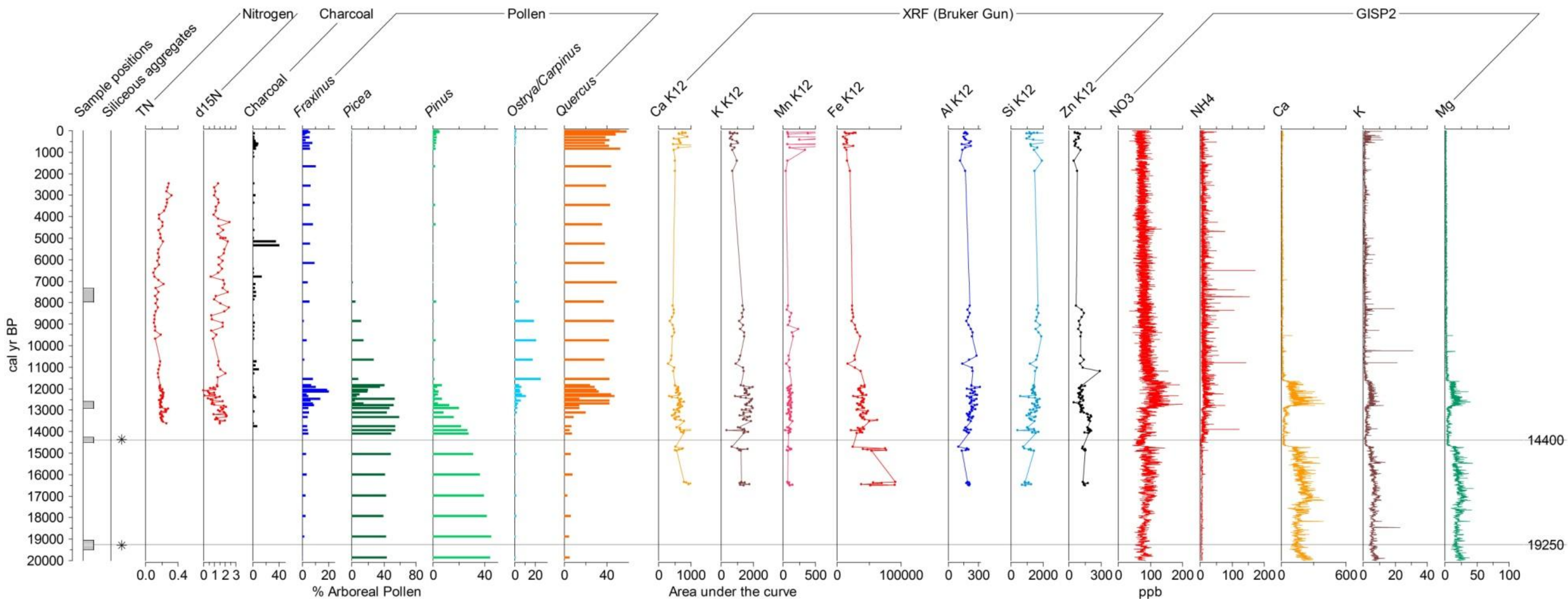

Figure 4.12 Jackson Pond 83A datasets compared by calibrated ages. Sample depths for thin sections are shown with shaded boxes; siliceous aggregate occurrences are designated with asterisks. The major changes in vegetation at Jackson Pond ca. 13,000 cal yr BP post-dates the upper occurrence of siliceous aggregates (pollen data from Wilkins 1985). XRF analysis reveals peaks pre-dating the siliceous aggregate occurrence we found. Charcoal is low at the time of siliceous aggregate occurrence. GISP2 peaks in ammonium(NH_4), Ca, K, and Mg may be contemporaneous with the siliceous aggregates, given the range in calibration of radiocarbon dates.

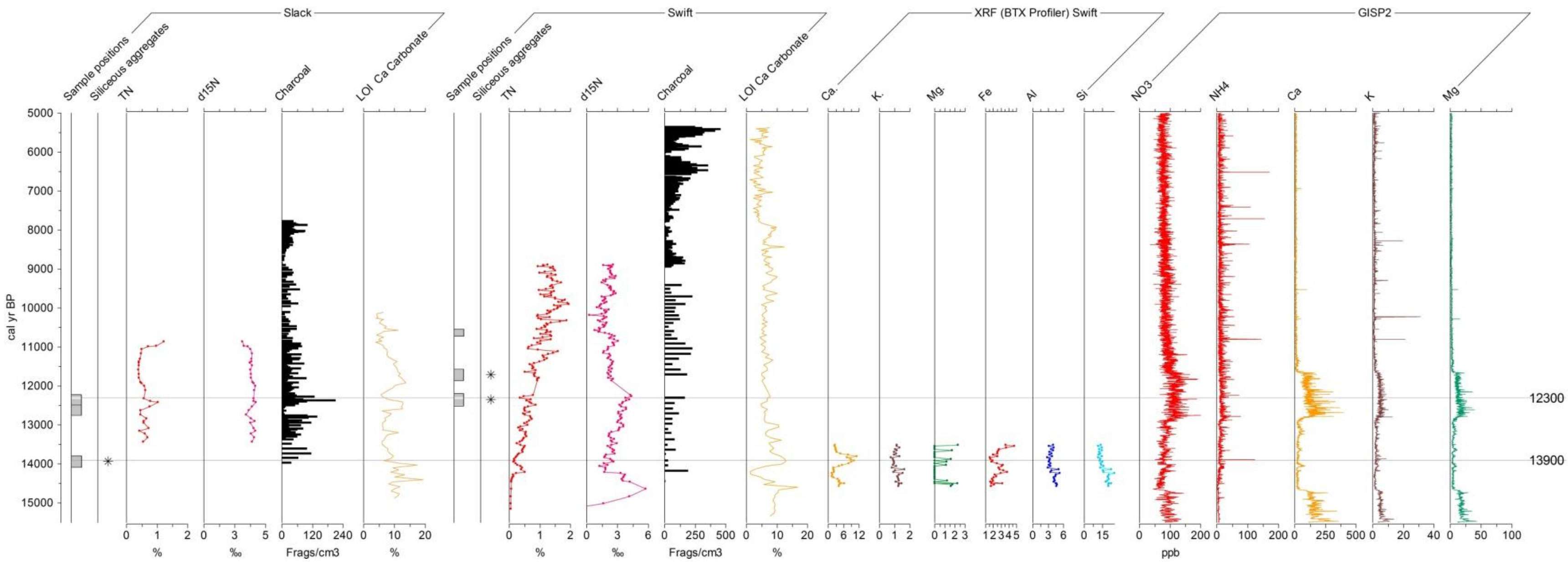

Figure 4.13 Slack and Swift Lake datasets graphed by calibrated ages. Sample depths for thin sections are marked with shaded boxes; siliceous aggregate occurrences are marked with asterisks. For Slack Lake, siliceous aggregates at ca. 14,000 cal yr BP occur near a peak in TN at nearby Swift Lake and near peaks in loss-on-ignition calcium for Slack and Swift Lakes and XRF Ca, K, and Mg for Swift Lake. GISP2 peaks in ammonium (NH_4), Ca, K, and Mg co-occur with Slack Lake siliceous aggregates. Fire activity is high around the time of siliceous aggregates at both Slack and Swift Lakes. At Swift Lake, siliceous aggregates occur when there is a obvious drop in $\delta^{15}N$, high fire activity (charcoal), and peaks in NO_3 and NH_4 in the GISP2 ice core. The nitrate and ammonium may represent a global combustion signal. Ca, K, and Mg in the lake sediments and the ice core may represent dust and/or wood ash inputs.

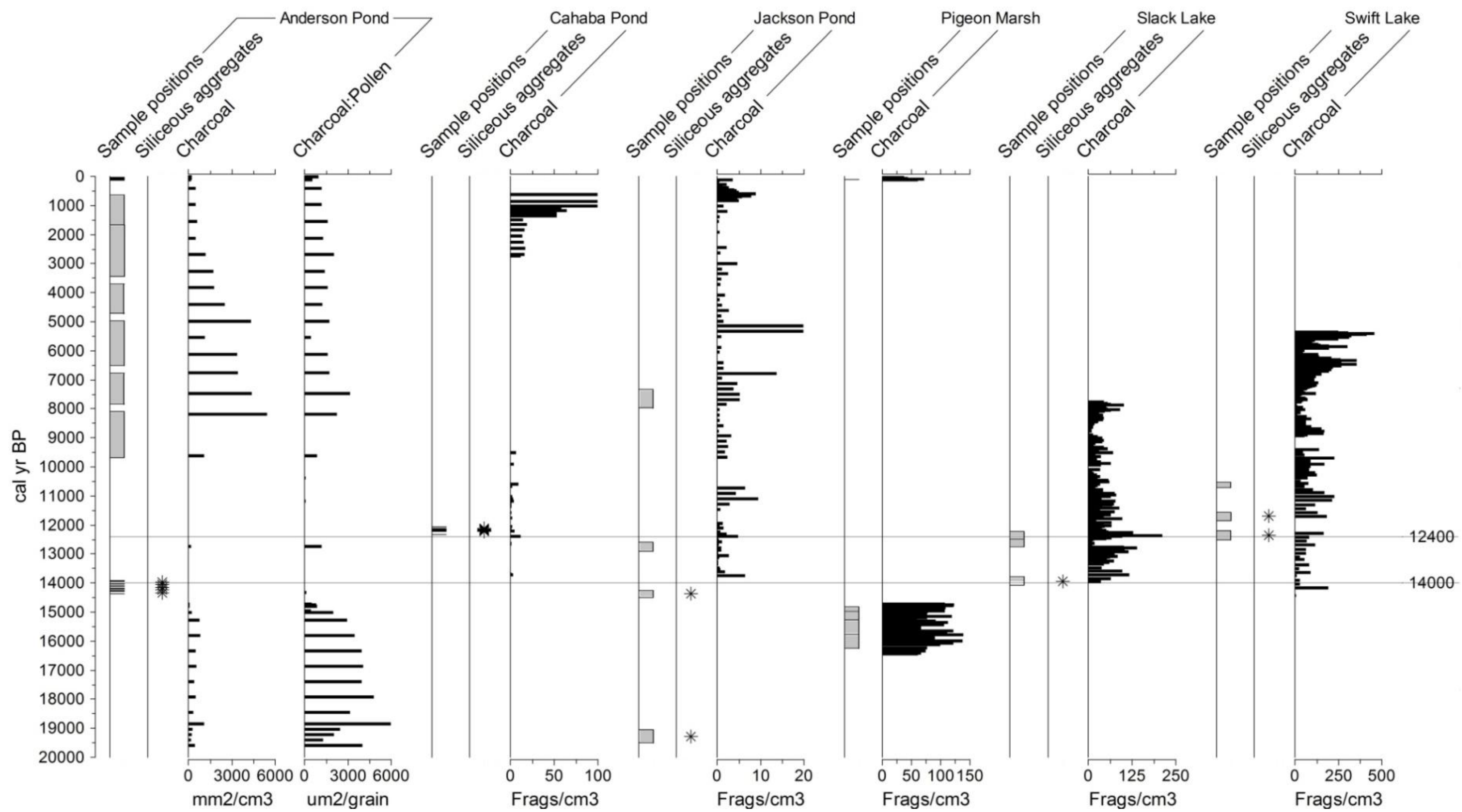

Figure 4.14 Charcoal and siliceous aggregate occurrences compared for the five sites. Note that scales differ. The Pigeon Marsh core has a hiatus between ca. 14,000 cal yr BP and modern times. The Cahaba charcoal record has a gap from 8500–2500 cal yr BP. The highest charcoal peaks in the Cahaba and Jackson Pond charcoal records are truncated to better show the lesser peaks. Slack and Swift Lake cores (Ballard 2009) begin at ca. 14,000 cal years and extend into the early (Slack) and middle (Swift) Holocene; the uppermost charcoal bars indicate the top of the records. Gray lines highlight the levels where siliceous aggregates cluster around 14,000 and 12,400 cal yr BP. At 14,000 cal yr BP, siliceous aggregates do not co-occur with charcoal peaks at Anderson Pond, but do co-occur with a small peak at Jackson Pond, and with a large peak at Slack Lake. At 12,400 cal yr BP, siliceous aggregates occur with a small charcoal peak at Cahaba Pond, and with a large peak at Swift Lake.

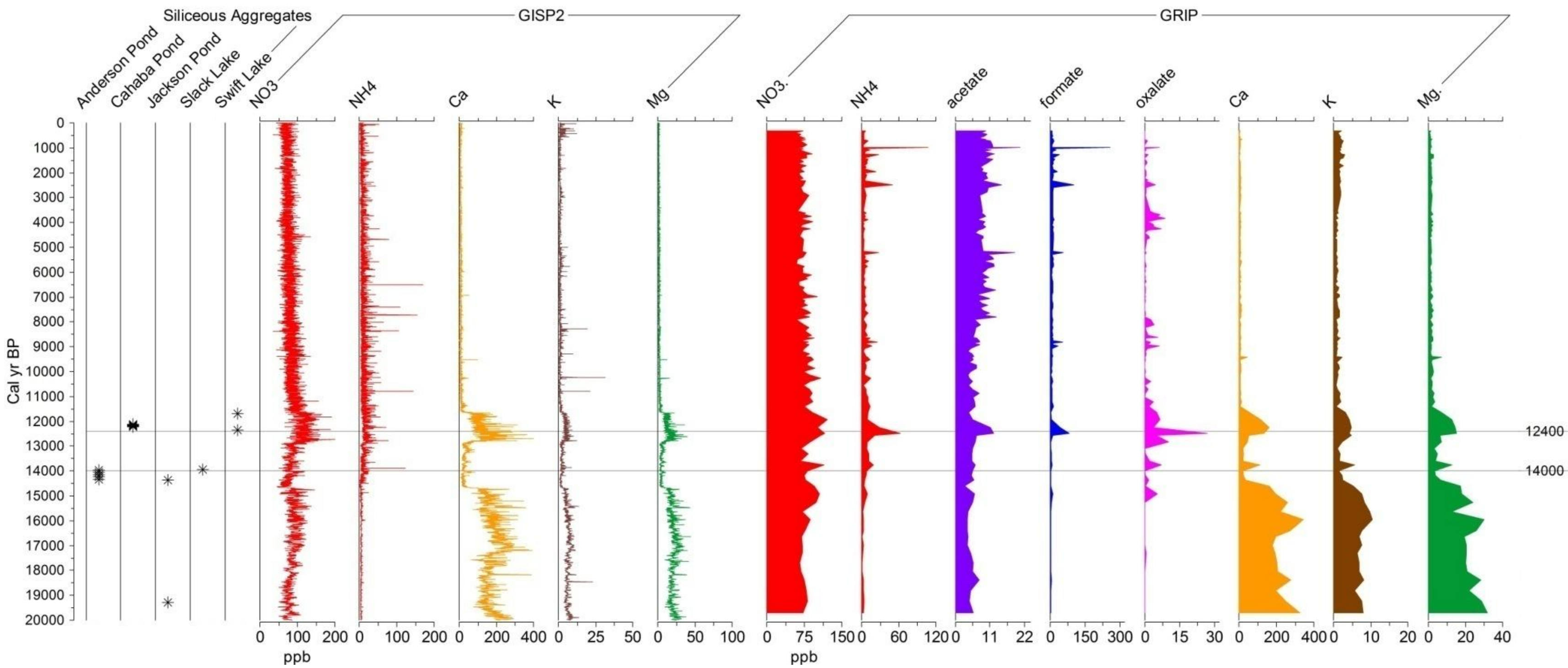

Figure 4.15 The occurrences of siliceous aggregates compared to combustion markers in the Greenland ice cores. GRIP data is coarser than GISP2 data. The siliceous aggregates appear to coincide with peaks in nitrates and ammonium in both ice cores around 14,000 yrs and ca. 12,400 yrs. Siliceous aggregates in Cahaba Pond and Swift Lake seem to be contemporaneous with other combustion markers, acetate, formate, and oxalate in the GRIP core at around 12,400 yrs. The Ca, K, and Mg are interpreted as dust markers by De Angelis et al (1997). Large-scale combustion signals in GISP2 and GRIP ice core records occur around 14,000 and around 12,400 yrs BP, contemporaneously with the lake-sediment occurrences of of siliceous aggregates in eastern North America.

Chapter 5

Summary and Conclusions

5.1 Summary and Conclusions

In this dissertation research, I produced new charcoal records for Anderson Pond, Tennessee; Cahaba Pond, Alabama; Jackson Pond, Kentucky; and Pigeon Marsh, Georgia to contribute to our understanding of fire history in the eastern U.S. I was able to build on the results of previous pollen analyses at these sites (Delcourt 1979, Delcourt et al. 1983, Wilkins et al. 1991, and Watts 1975, respectively) to investigate how vegetation, fire, and climate have interacted through the late glacial and Holocene. Gaps in the sediment records and differences in the time periods covered complicate comparisons of the four charcoal records, but some trends are shared, including evidence of high fire activity at two sites during the late-glacial period. Differences in vegetation, climate, the presence of humans, and topographic setting may all contribute to the diversity of patterns of fire history revealed by the records.

In addition to carrying out traditional charcoal analyses of lake sediments to build long-term fire histories, I explored indicators of wood ash, a by-product of fires, in sediment cores as proxies for past fires. This work involved thin-section analyses of lake sediments led by my committee member, Steven Driese, along with geochemical analyses of sediments and laboratory experiments that I performed. We discovered siliceous aggregates, an unusual grain type, in sediments from three of the four southeastern study sites and in sediment cores from Slack and Swift Lakes, Michigan. Through experimental work I showed that siliceous aggregates derive from wood ash from fires. Because the occurrences of the siliceous aggregates at the five sites are penecontemporaneous, and possibly contemporaneous, I examined markers of large-scale biomass burning in Greenland ice cores and found peaks at the times of siliceous aggregate occurrences during the late glacial. Tentatively, this analysis appears to signal two or more major fire events across the eastern U.S. around 14,000 and 12,400 cal yr BP. This is a pilot study for a new proxy of fire, though, and further work is needed to test initial results and interpretations.

The microscopic charcoal record from Anderson Pond revealed that the fire regime from the Last Glacial Maximum (LGM) to the late glacial was driven primarily by the flammable coniferous vegetation. Fire activity drastically diminished when jack pine was replaced by oak as the dominant taxon during the late glacial. The trend of decreasing fires as climate warmed is in contrast to the results of a global synthesis of charcoal records that found fire to be associated with increasing temperatures (Daniau et al. 2012). Fire activity remained low until the Mid-Holocene Warm Period, when Native Americans in the region may have been setting fires. This is an interval when climate in North America seems to have become generally warmer and drier.

Microscopic charcoal analyses of sediments from Anderson Pond revealed that the site had higher charcoal concentrations and charcoal to pollen ratios than found at seven comparison sites, with one exception. Maximum charcoal to pollen ratios at Anderson Pond during the conifer-dominated LGM to late-glacial period were higher than values found at boreal forest sites, but slightly lower than values found at Key Deer Pond in the frequently burned pine rocklands of the Florida Keys (Albritton 2009). Maximum charcoal concentrations and charcoal to pollen ratios during the middle and late Holocene, when deciduous forest surrounded Anderson Pond, exceeded values from all comparison sites. These comparisons indicate relatively high fire activity at Anderson Pond during the LGM to the late glacial, and during the middle to late Holocene. Fires of low intensity produce more particulate matter (Whitlock and Larsen 2001), and the high charcoal indices at Anderson Pond may additionally indicate that low-intensity fires were more prevalent at Anderson Pond than at the other sites. Differences in pollen processing methods also may have contributed to the differences in charcoal indices between Anderson Pond and the comparison sites.

Cahaba Pond vegetation had been dominated by fire-intolerant American beech for at least 1000 years until around 12,400 cal yr BP, when beech dramatically declined. Beech was replaced by magnolia and pine, followed by oak dominance, while aquatic plant assemblages shifted from submerged to emergent taxa as the pond shallowed. At the same time as the major shift in vegetation, siliceous aggregates formed and were deposited in the sediments, along with a small peak in charcoal. The nitrogen data showed a crossover pattern between the $\delta^{15}N$ and the total nitrogen beginning around 12,400 cal yr BP, consistent with blooms of cyanobacteria (Talbot 2002), which fix nitrogen from the air. Cyanins were found in a sample from Cahaba Pond for this interval that support this interpretation (J. Fulton, pers. communication to S. Driese). The largest charcoal peaks at Cahaba Pond occurred during the interval 1370–640 cal yr BP, perhaps due to people setting brush fires on a dried pond bed. The Cahaba Pond charcoal record is interrupted between ca. 8500 and 2500 cal yr BP due to gaps in material available, which is exacerbated by very low sedimentation rates and/or hiatuses in the Holocene portion of the core. The incomplete record during the middle and late Holocene may be related to warmer and drier conditions at the site during the middle Holocene.

Jackson Pond had the lowest macroscopic charcoal concentrations of all sites in this study. The two largest charcoal peaks occurred around 5,000 cal yr BP, a time of oak-dominated pollen spectra. The charcoal record I developed begins at around 14,000 cal yr BP, at a depth of about 4.5 m above the bottom of the core. Whether charcoal concentrations might be higher below this level, at the time when spruce and pine were the dominant pollen types, awaits further study. The fact that coniferous pollen was present during the late glacial at Jackson Pond with little to no charcoal suggests long-distance transport of pollen, which is supported by macrofossil analyses by Wilkins et al. (1991) on the original Jackson Pond cores and by work on new cores by Liu et al. (2013), neither of which revealed late-glacial conifer macrofossils. Any fires associated with the conifers may have taken place outside the Jackson Pond watershed. Siliceous aggregates occurred around 19,250 cal yr BP and ca. 14,000 cal yr BP at Jackson Pond.

At Pigeon Marsh, fire activity was relatively high across the late glacial (16,500–14,500 cal yr BP) when pine and oak were the dominant arboreal taxa. Charcoal in this core had a distinctive sedge-like morphology. This suggests periodic lowering of the water levels in the marsh, allowing the dried aquatic vegetation to burn. At this ridge-top location, lightning strikes may be the source of the frequent fires indicated by the charcoal record.

To identify peaks in Ca and elements that make up wood ash (K, Mg, Fe, P, Si, Al, and/or Zn), I used XRF analysis of lake sediments. Peaks in some of these elements were observed but results were inconclusive. More high-resolution XRF analyses of lake sediments are needed to identify potential specific pulses of wood ash in the past.

I originally hypothesized that late-glacial-age peaks in total nitrogen in many of the sediment isotope records were evidence of a nitric acid rain event or events. This hypothesis seemed plausible given the late-glacial-age peaks in nitrates in the Greenland ice core record, and the expansion of algae and diatoms at the onset of the Younger Dryas in many lakes in Europe and Greenland. However, I had to reject the hypothesis that nitric acid rain is required for the formation of siliceous aggregates from wood ash based on the results of my laboratory experiments treating wood ash with simulated natural and nitric acid rain to create siliceous aggregates.

Siliceous aggregates are a by-product of combustion, as evidenced by my experiments and the work of archaeological researchers in Israel (Schiegl et al. 1996, Weiner 2010). Siliceous aggregates were experimentally produced with treatments of nitric acid rain and "natural" rain over a period of four months. They formed in low-humidity fume hood conditions and in a humid greenhouse environment. Additions of fine quartz silt to experiments proved to be a key factor for siliceous aggregate formation; samples lacking additions of fine quartz silt showed no siliceous aggregate formation. Dust influxes may have been high during the severe wildfires that produced the late-glacial siliceous aggregates, or more broadly, during the late-glacial period.

Siliceous aggregates are a product of diagenesis from the alkali-silica reaction of wood ash and phytoliths. With the action of rainwater, the high pH of wood ash dissolves the phytoliths from plant material, resulting in an amorphous silica gel. As leaching progresses, pH is lowered, and the amorphous silica precipitates around the loessal silt and any adjacent organic matter. The presence of cemented terrestrial organic particles in siliceous aggregates demonstrates that they formed in the terrestrial environment and were later transported into the lake.

Siliceous aggregates are rare in the sediment record but found at two levels during late glacial time and once near the LGM at sites roughly transecting the eastern U.S. north to south. They occurred around 19,250 cal yr BP in Jackson Pond; ca. 14,000 cal yr BP in Anderson Pond, Jackson Pond, and Slack Lake; and they were found ca. 12,400 cal yr BP in Cahaba Pond and Swift Lake. Siliceous aggregates were found in sediments from five of the six lake sites. Standard errors in radiocarbon dates, wide calibrated ranges, and the reliance on dates mostly on bulk sediment make it reasonable to infer contemporaneous events, but further study is needed.

That they occur in two lakes in close proximity (Slack and Swift) at different times suggests two events.

The presence of siliceous aggregates was not associated with major charcoal peaks in all records examined. Research by Woods and Balfour (2008, 2010) may suggest a partial explanation. They found that the ash from severe fires stabilized the landscape, and erosion was much reduced. Ash has a greater water retention capacity than soil (Woods and Balfour 2008), and the action of water is necessary for formation of siliceous aggregates. A stabilizing mantle of wood ash on the landscape would effectively reduce transport of charcoal into the lake, thus suppressing the charcoal signal of a wildfire in the sediment record.

Siliceous aggregates may therefore be a new tool for paleoenvironmental researchers to use as a proxy for severe wildfires. They appear to have occurred around the LGM in one site, and at two times during the late glacial, around 14,000 and 12,400 cal yr BP, possibly contemporaneously at sites in eastern North America. Widespread firestorms are suggested by the findings of this research, and the oxalate and other biomass burning markers in the GRIP ice core record (Legrand et al. 1992, De Angelis et al. 1997, Fuhrer and Legrand 1997) for 14,000 and 12,400 cal yr BP seem to support this interpretation.

5.2 Future Work

This study demonstrated the value of thin-section analysis of lake sediments. Researchers who study the late-glacial transition may want to add thin-section analyses to their toolkit to look for possible occurrences of siliceous aggregates. These components in cores may provide a new proxy for wildfires, and their presence in cores examined here may suggest some possible widespread ashing events during the late glacial. More work is needed on this topic using the cores included in this study and from other sites.

Xray fluorescence (XRF) and other analyses to detect wood ash inputs to lakes should be conducted in parallel with thin-section analyses of lake sediments. Ideally, the XRF analyses should be carried out at high resolution (1 cm increments) to detect possible spikes in wood ash elements. In this study, analyses of ground, dried sediment using the BTX profiler appeared to provide more representative data for a given stratigraphic level than XRF spot analyses on moist sediment with an XRF gun, although the former method involves more work and is destructive in that sediment used to fill the XRF cells is not available for other purposes. Researchers should look for peaks in Ca occurring with a suite of peaks of elements that are found in wood ash: K, Al, Mg, Fe, P, Mn Si, Na, and Zn (Risse and Gaskin 2002, Bodí et al. 2014).

The “migration” of the boreal forest northwards during the late glacial is generally attributed to climate change. In addition to warming, the eutrophication of ecosystems at the start of the Younger Dryas and again at the end of the Younger Dryas deserves further investigation. Nutrient influx has been shown to cause a decline in dominance of jack pine in the modern boreal forest by removing the advantage for this species, which thrives on nutrient-poor substrates. My dissertation research has raised questions about nutrient inputs during the late glacial from wood ash (Ca, K, Mg, Fe, P, and Zn) and nutrient inputs from nitrogen. Nitrogen-focused nutrient studies need to be conducted on late-glacial sediments together with diatom analyses to understand changes in pH and nutrient influx. Also, additional pollen analyses would provide insights into vegetation shifts occurring at this time, which may be related to nutrient shifts.

Whether the nitrate peaks in the GISP2 ice core record at the beginning of the Younger Dryas were caused by wildfires or shock waves or both could be established by using ^{17}O analysis of the NO_3 in ice core records, if sufficient ice were available for the analysis (Hastings et al. 2013). This is because NO_3 from a shock wave event derives its oxygen from the ozone layer, which is enriched in ^{17}O (Hastings et al. 2013).

At sites of major historic ash-producing wildfires that contain lakes, cores could be collected and analyzed for siliceous aggregates. Some examples of known historical fires in recent history are the Peshtigo Fire that destroyed that city in Wisconsin in 1871 (Pernin 1971), the Rattlesnake Fire in southeastern Arizona which burned 10,330 ha of Madrean oak-pine forest in 1994 (Barton 2002), and the Black Saturday Fire in Australia on Februrary 7, 2009 (Santín et al. 2012). These studies would require dating techniques relying on short-lived radioisotopes such as Pb-210 to precisely date the sediments, and the recovery of cores with minimal disturbance of near-surface sediments, which would contain the intervals of interest.

Finally, freshwater dinoflagellates and freshwater sponges should receive more attention as paleoenvironment proxies. *Peridinium limbatum*, a dinoflagellate, was common at Cahaba Pond and was also found at Pigeon Marsh (Watts 1975). Thousands of resting cysts of dinoflagellates were observed on pollen slides from Cahaba Pond at the time of the major vegetational shift, but dinoflagellates were beyond the scope of this study. Freshwater sponges were thriving during the late glacial at Swift Lake, Michigan (Ballard 2009); Jackson Pond, Kentucky (Wilkins et al. 1991); Cupola Pond, Missouri (Jiang 1990); and Pigeon Marsh, Georgia (Watts 1975); and were observed in thin-sections from Anderson Pond, Tennessee.

Regarding the discovery of siliceous aggregates in lake sediments from the eastern U.S., and their implications together with the GRIP biomass burning markers for possibly contemporaneous widespread firestorms since the LGM, additional studies are needed to refine the timing and extent of these events. Geochemical analyses to understand nutrient flow in lakes could help assess wood ash inputs and nitrogen inputs to environments. Even though nitric acid rain was not required for formation of siliceous aggregates, the possibility still exists that late-glacial nitrogen peaks in lake sediments and ice cores could be explained by nitric acid rain from an airburst shockwave. This hypothesis awaits further study.

5.3 References

Albritton, J. 2009. *A 1700-Year History of Fire and Vegetation in Pine Rocklands of National Key Deer Refuge, Big Pine Key, Florida: Charcoal and Pollen Evidence from Key Deer Pond.* M.S. Thesis, University of Tennessee.

Ballard, J.P. 2009. *A Lateglacial Paleofire Record for East-Central Michigan.* M.S. Thesis, University of Cincinnati.

Barton, A.M. 2002. Intense wildfire in southeastern Arizona: transformation of a Madrean oak–pine forest to oak woodland. *Forest Ecology and Management* 165(1): 205–212.

Bodí, M.B.; Martin, D.A.; Balfour, V.N.; Santín, C.; Doerr, S.H.; Pereira, P.; Cerdà , A.; Mataix-Solera, J. 2014. Wildland fire ash: production, composition and eco-hydro-geomorphic effects. *Earth-Science Reviews* 130: 103–127.

Daniau, A.-L.; Bartlein, P. J.; Harrison, S P.; Prentice, I.C.; Brewer, S.; Friedlingstein, P.; Harrison-Prentice, T.I.; Inoue, J.; Izumi, K.; Marlon, J.R.; Mooney, S.; Power, M.J.; Stevenson, J.; Tinner, W.; Andrič, M.; Atanassova, J.; Behling, H.; Black, M.; Blarquez, O.; Brown, K.J.; Carcaillet, C.; Colhoun, E.A.; Colombaroli, D.; Davis, B.A.S.; D'Costa, D.; Dodson, J.; Dupont, L.; Eshetu, Z.; Gavin, D.G.; Genries, A.; Haberle, S.; Hallett, D.J.; Hope, G.; Horn, S.P.; Kassa, T.G.; Katamura, F.; Kennedy, L.M.; Kershaw, P.; Krivonogov, S.; Long, C.; Magri, D.; Marinova, E.; McKenzie, G.M.; Moreno, P.I.; Moss, P.; Neumann, F.H.; Norström, E.; Paitre, C.; Rius, D.; Roberts, N.; Robinson, G.S.; Sasaki, N.; Scott, L.; Takahara, H.; Terwilliger, V.; Thevenon, F.; Turner, R.; Valsecchi, V.G.; Vannière, B.; Walsh, M.; Williams, N.; Zhang, Y. 2012. Predictability of biomass burning in response to climate changes. *Global Biogeochemical Cycles 26* (GB4007): 1–12.

De Angelis, M.; Steffensen, J.P.; Legrand, M.R.; Clausen, H.B.; Hammer, C.U. 1997. Primary aerosol (sea salt and soil dust) deposited in Greenland ice during the last climatic cycle: comparison with east Antarctic records. *Journal of Geophysical Research* 102: 26681–26698.

Delcourt H.R. 1979. Late Quaternary vegetation history of the eastern Highland Rim and adjacent Cumberland Plateau of Tennessee. *Ecological Monographs* 49(3): 255–280.

Delcourt, H.R.; Delcourt, P.A.; Spiker, E.C. 1983. A 12,000-year record of forest history from Cahaba Pond, St. Clair County, Alabama. *Ecology* 64(4): 874–887.

Fuhrer, K.; Legrand, M.R. 1997. Continental biogenic species in the Greenland Ice Core Project ice core: tracing back the biomass history of the North American continent. *Journal of Geophysical Research* 102: 26735–26745.

Hastings, M.G.; Casciotti, K.L.; Elliott, E.M. 2013. Stable isotopes as tracers of anthropogenic nitrogen sources, deposition, and impacts. *Elements* 9(5): 339–344.

Jiang, L. 1990. *Paleoecological Reconstructions Utilizing Freshwater Sponge Spicule Distributions in Sediments of Cupola Pond and Powers Fort Swale in Missouri and Hood Lake in Arkansas.* M.S. Thesis, Western Carolina University.

Legrand, M.R., De Angelis, M.; Staffelbach, T.; Neftel, A.; Stauffer, B. 1992. Large perturbations of ammonium and organic acids content in the Summit-Greenland ice core. Fingerprint from forest fires? *Geophysical Research Letters* 19: 473–475.

Liu. Y.; Andersen, J.J.; Williams, J.W.; Jackson, S.T. 2013. Vegetation history in central Kentucky and Tennessee (U.S.A.) during the last glacial and deglacial periods. *Quaternary Research* 79(2): 189–198.

Pernin, P. 1971. The Great Peshtigo Fire: an eyewitness account. *The Wisconsin Magazine of History* 54(4): 246–272.

Risse, M.; Gaskin, J. 2002. *Best management practices for wood ash as agricultural soil amendment.* The University of Georgia Cooperative Extension Bulletin 1142, pp 1-4. http://extension.uga.edu/publications/files/pdf/B%201142_3.PDF [Accessed April 14, 2015].

Santín, C.; Doerr, S.H.; Shakesby, R.A.; Bryant, R.; Sheridan, G.J.; Lane, P.N.J.; Smith, H.G.; Bell, T.L. 2012. Carbon loads, forms and sequestration potential within ash deposits produced by wildfire: new insights from the 2009 'Black Saturday' fires, Australia. *European Journal of Forest Research* 131(4): 1245–1253.

Schiegl, S.; Goldberg, P.; Bar-Yosef, O.; Weiner, S. 1996. Ash deposits in Hayonim and Kebara Caves, Israel: macroscopic, microscopic and mineralogical observations, and their archaeological implications. *Journal of Archaeological Science* 23: 763–781.

Talbot, M.R. 2002. Nitrogen isotopes in palaeolimnology. *In: Tracking Environmental Change Using Lake Sediments,* Volume 2 (Eds.: Last, W.M.; Smol, J.P.), Kluwer Academic Publishers, Dordrecht, The Netherlands, pp. 401–439.

Watts, W.A. 1975. Vegetation record for the last 20,000 years from a small marsh on Lookout Mountain, northwestern Georgia. *Geological Society of America Bulletin* 86(3): 287–291.

Weiner, S. 2010. *Microarchaeology, Beyond the Visible Archaeological Record.* Cambridge University Press, the United Kingdom.

Whitlock, C.; Larsen, C. 2001. Charcoal as a fire proxy. *In: Tracking Environmental Change Using Lake Sediments.* Volume 3 (Eds: Smol, J.P.; Birks, H.J.B.; Last, W.M.), Kluwer Academic Press, Dordrecht, The Netherlands, pp. 75–97.

Wilkins, G.R.; Delcourt, P.A.; Delcourt, H.R.; Harrison, F.W.; Turner, M.R. 1991. Paleoecology of central Kentucky since the Last Glacial Maximum. *Quaternary Research* 36: 224–229.

Woods, S.W.; Balfour, V.N. 2008. The effect of ash on runoff and erosion after a severe forest wildfire, Montana, USA. *International Journal of Wildland Fire* 17(5): 535–548.

Woods, S.W.; Balfour, V.N. 2010. The effects of soil texture and ash thickness on the post-fire hydrological response from ash-covered soils. *Journal of Hydrology* 393(3–4): 274–286.

APPENDIX I

Charcoal Point Counting Calculations

Calculations below are based on Clark (1982), with modifications in some cases by S. Horn. This appendix is based on an unpublished laboratory handout by S. Horn prepared February 8, 2005 and modified May 3, 2006.

Areal density of charcoal on the slide (P) (e.g., the estimated probability that a random point will fall on charcoal):

$$P = C/N$$

The accuracy, or relative error, of the estimate of P (S_p/P):

$$(S_p/P) = \sqrt{(1-P)/C}$$

Area of charcoal (total) in mm^2 in all fields of view examined (Af):

$$Af = P \times Fat$$

Estimated area of charcoal in mm^2 in the entire pollen sample (Aps):

$$Aps = \frac{M \times Af}{Mc}$$

Charcoal area in mm^2 expressed on the basis of volume of wet sediment (Acc):

$$Acc = Aps/V$$

Charcoal area in mm^2 expressed on the basis of wet sediment mass (Awm):

$$Awm = Aps/W$$

Charcoal area in mm^2 expressed on the basis of annual influx (Acy):

$$Acy = Acc * \text{sedimentation rate expressed in cm/yr}$$

Charcoal:Pollen ratio (C:P) expressed as mm^2 charcoal per pollen grain:

$$C:P = \frac{Mpo \times Af}{Mc \times Popc}$$

Charcoal:Pollen ratio (C:P) expressed as μm^2 charcoal per pollen grain:

$$C:P = \frac{Mpo \times Af \times 10^6}{Mc \times Popc}$$

Po = points applied in each field of view
F = the number of fields of view examined

N = total number of points applied (equal to Po x F)

Fa = area in mm^2 of each field of view

Fat = total area in mm^2 on slide examined for charcoal (equal to Fa x F)

C = the number of applied points that "touched" charcoal

V = volume in cm^3 of original wet sediment sample processed for pollen

W = mass in g of original wet sediment processed for pollen

Pw = percent water in the wet LOI sample from the same level as pollen sample

M = number of *Lycopodium* marker spores added to original sample processed for pollen

Mc = number of *Lycopodium* marker spores counted in the fields of view that were examined for charcoal by point counting

Mpo = number of *Lycopodium* marker spores counted in the pollen count from the same level

Popc = the total number of pollen grains (excluding spores and indeterminate) counted in the pollen count from the same level

VITA

Joanne P. Ballard was born Joanne P. Sheridan in Isleworth, England on July 8, 1958. She moved to the United States in 1966 and settled with her family in Corydon, Indiana. She attended Purdue University and earned an A.A.S. in Industrial Illustration Technology in 1978. She worked for Philip Morris USA as an Engineering Technician for five years and then started a family. She managed a greenhouse and home-schooled her children. Then she served as Science Fair Coordinator, Parent Teacher Organization President, and substitute taught at West Washington Elementary School, Campbellsburg, Indiana.

In 2004, she returned to college, and earned a B.A. in Geoscience under Dr. Glenn M. Mason at Indiana University Southeast. Joanne received the Outstanding Geoscience Student Award at graduation in 2007. Joanne's interests include the causation for the extinction of the megafauna some 13,000 years ago. At the University of Cincinnati, advised by Dr. Thomas V. Lowell, her thesis research aimed to determine if there was evidence of a catastrophic wildfire around 12,900 cal yr BP, as hypothesized by Firestone and his collaborators. She earned a M.S. in Geology in 2009.

Joanne worked as a Cartographic Technician on the 2010 Decennial at the United States Census Bureau. She was awarded the Annual Customer Service Award in the Geography Branch in 2010. In August 2011, Joanne entered the Ph.D. program in the Department of Geography at the University of Tennessee in Knoxville, under the direction of Dr. Sally P. Horn. She worked as a Graduate Research Assistant and then a Graduate Teaching Assistant, providing instruction for introductory geography lab sessions and lectures. Her specializations are Biogeography and Quaternary environments.