INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

ProQuest Information and Learning
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
800-521-0600

UMI®

University of Alberta

Charcoal-based Paleofire History of Christina Lake in the Boreal Forest of Alberta

by

Lana Dee Laird ©

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of Master of Science

Department of Earth and Atmospheric Sciences

Edmonton, Alberta

Spring 2000

0-612-60142-0

University of Alberta

Library Release Form

Name of Author: Lana Dee Laird

Title of Thesis: Charcoal-based Paleofire History of Christina Lake in the Boreal Forest of Alberta

Degree: Master of Science

Year this Degree Granted: 2000

Lana Laird

10626 - 158 Avenue
Edmonton, Alberta
T5X 4H5

April 17, 2000

University of Alberta

Faculty of Graduate Studies and Research

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled Charcoal-based Paleofire History of Christina Lake in the Boreal Forest of Alberta submitted by Lana Dee Laird in partial fulfillment of the requirements for the degree of Master of Science.

Dr. I.D. Campbell

G.P. Kershaw

Dr. G.P. Kershaw

Martin Sharp

Dr. M. Sharp

Ross Wein

Dr. R.W. Wein

April 7, 2000

Abstract

Annually-laminated sediment (spanning ~940 years) from Christina Lake, Alberta was analysed for charcoal, pollen, sediment influx, loss on ignition and vivianite concentrations. The sedimentology suggests a cooler/wetter "Little Ice Age" interval preceded and followed by warmer/drier conditions. Vivianite concentrations were not found to be a useful palaeoenvironmental indicator. The charcoal profile showed large fire return intervals of ~68 years (1083 - 1490 AD), ~29 years (1490 -1723 AD), ~130 years (1723 - 1853 AD), and ~16 years (1853-1949 AD). Vegetation changed little, with the exception of a *Pinus* pollen decline 1797-1853 AD (possibly related to cold/wet climate and/or reduced fire activity) and small *Populus* and *Corylus* pollen increases prior to ~1250 AD (possibly related to the warm/dry "Medieval Warm Period"). This is the first long, high-resolution charcoal record from the boreal forest of north-central Alberta, and confirms that even far from any major ecotone, fire activity and vegetation were affected by climatic fluctuations over the last millennium.

“If we knew what we were doing, it wouldn’t be called research, would it?”

Albert Einstein

Acknowledgements

This thesis could not have been completed without the kind support of the following individuals and organizations. For assistance with field work I thank Amy Reisler, Karen Perronnet, Dr. Ross Wein, Connie Boldt, Michael Liston, Farrah Gilchrist, and personnel from Amoco Petroleum (who also provided snowmobiles). For laboratory analyses I thank M.J.M. Duke for ^{137}Cs analysis, Diane Caird for XRD analysis, Frank Radford for ICP-AES analysis, Farrah Gilchrist for preparing material for DendroScan, and Environment Canada, Environmental Protection Service who allowed me to use their Total Carbon Analyser machine and Cathy Biehn who patiently trained me on it. For research support I thank the Sustainable Forest Management Network of Centres of Excellence, Alberta-Pacific Forest Industries who paid for the plane on one of the field trips, the J. Gordin Kaplin Graduate Student Award who provided a travel bursary, and the Canadian Forest Service, Northern Forestry Centre who provided office and laboratory facilities. NSERC, the Canadian Forest Service, the Walter H. Johns Graduate Fellowship, the Harington Paleoenvironmental Scholarship, and the Sustainable Forest Management Network of Centres of Excellence provided personal funding. Thierry Varem-Sanders wrote the image analysis program for vivianite analysis, taught me how to use DendroScan, built field equipment, kept my computer running, and was helpful in a hundred other ways. For all of the above, I am truly grateful.

I especially thank Dr. Ian Campbell for his cheerful encouragement and assistance on every aspect of this project. Most of all, I am grateful to my family for their love, patience, and unfailing support from start to finish.

Table of Contents

List of Tables

List of Figures

CHAPTER 1

Introduction

1.1 Rationale and Hypothesis

Fire is the primary agent of disturbance in Canada's boreal forest, and the floristic and structural mosaic of this biome exists largely as a result of the fire regime (Johnson 1992; Payette 1992; Rowe and Scotter 1973; Wein and MacLean 1983). Understanding the fire history of the forest and the factors affecting the fire regime is therefore essential to understanding the ecosystem as a whole. Historical records and dendrochronological studies including fire scars and stand origin dates can illuminate recent fire history (e.g., Heinselman 1973; Larsen 1997), but a much longer record (many 100s to 1000s of years) is required to fully understand the complicated interactions among climate, fire and vegetation through time (Campbell and Flannigan 2000; Clark and Robinson 1993). Such long-term information is available only through proxy indicators of fire, such as charcoal deposits in lake sediments, peats, or soils.

In recent years, the interest in paleofire research has increased substantially. This interest has come primarily from three groups: 1) national park and wilderness area managers who want to understand the "natural" fire regime in order to develop appropriate fire management policies; 2) forest managers who want to emulate natural disturbances as much as possible in their harvesting practices; and 3) climate change researchers who need to know how the fire regime and vegetation responded to climate changes in the past in order to model the potential impacts on the boreal forest of various future climate change scenarios. Current research by the latter group suggests that if global climate change occurs as expected, the fire regime of the boreal forest will be altered (Bergeron and Flannigan 1995; Weber and Flannigan 1997; Wotton and Flannigan 1993) and the changed fire regime could have a greater impact on the boreal forest than will the direct effects of the climate change itself (Bergeron and Flannigan 1995; Weber and Flannigan 1997; Wein and de Groot 1996). Thus, at a recent conference on fire activity in the boreal forest ("National Workshop on Increasing Forest Fire Activity in Canada," Edmonton, Alberta, April 1-4, 1996), several speakers (e.g., B.J. Stocks and B. S. Lee) designated the acquisition of long-term fire history data through stratigraphic charcoal studies as a research priority.

To date, most high-resolution long-term paleofire studies have been concentrated in the temperate forests of eastern North America (reviewed by Campbell and Flannigan 2000) and very few such studies have been done in Canada's boreal forest region (e.g., Bergeron et al. 1998; Larsen and MacDonald 1998a, 1998b). The need for research on the long-term paleofire history of the western boreal forest thus provided the impetus for this study.

Annually-laminated (varved) lake sediments provide ideal study sites for long-term paleofire studies based on charcoal (Tolonen 1986). The lack of sediment mixing allows for good temporal resolution of the charcoal signal from which fire events can be determined, and the varves provide a tight chronology for the study. Near the beginning of this project, four lakes in the boreal forest of Alberta were tested for the presence of varves. Only one, Christina Lake (55° 37' N, 110° 57' W), showed evidence of laminations and thus this moderately large (2130 ha) open lake became the study site. (The study site is described in Chapters 2-4 and so will not be described here).

The main objective of this study was to determine the fire history of a mid-boreal area over the last several hundred years using charcoal extracted from the annually-laminated lake sediment. To this end, a ~940-year charcoal record was extracted from the sediments of Christina Lake. Selected samples were also analyzed for pollen to determine if any significant palynologically detectable changes in vegetation occurred over the last 900+ years, and basic geochemical analyses of the sediment (sediment accumulation rate, and the concentrations of organic matter, carbonate and ash) were done to determine if some type of proxy climate signal could be detected. The possibility of using vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$) as a paleoenvironmental indicator was also explored. The main purpose of these corollary investigations was to provide some vegetational and climatic context for the paleofire signal.

Based on low-resolution palynological studies spanning much of the Holocene, the assumption has often been made that the mid-boreal forest has seen little change over the last 3000 or so years (eg., Lichti-Federovich 1970; Vance 1986). It is also generally thought that vegetation responds to climate changes very slowly and with long time lags, and so the climatic fluctuations of the last 1000 years may not have been of sufficient intensity or duration to cause any significant impacts, except perhaps at ecotones (Gajewski 1993). Several high-resolution studies of various types have shown, however, that the climatic changes over the last millennium were sufficient to impact lake hydrology (Campbell 1998; Vance et al. 1992), treeline limits in the Rockies (Luckman et al. 1997), and tree growth near both the northern and subalpine treelines (Jacoby and Cook 1981; Luckman et al. 1997; Szeicz 1996). Several dendrochronology-based studies in the subalpine forests of Alberta and British Columbia also showed changes in fire cycles over the last few hundred years, apparently in response to climate (Johnson et al. 1990; Johnson and Larsen 1991; Johnson and Wowchuk 1993; Masters 1990). It was thought possible, then, that the climatic changes over the last 1000 years may have affected the fire regime and vegetation of the mid-boreal forest as well (although perhaps more subtly than at ecotonal sites), but the changes may have gone undetected due to the low temporal resolution of most palynological studies.

Based on borrowed ideas relevant to site selection for pollen studies, it has also been suggested that small, closed lakes might be best suited for charcoal-based reconstruction of local fire histories while larger lakes would be more appropriate for more regional paleofire studies (Patterson et al. 1987; Tolonen 1986). It was thought, however, that by choosing a method of charcoal analysis that included only large fragments of charcoal which do not travel very far from source (Clark 1988a; Clark et al. 1998; Clark and Patterson 1997; Patterson et al. 1987; Wein et al. 1987), extracting a local fire signal from an open lake as large as Christina Lake, might be possible.

This study thus attempted to disprove the following null hypothesis:

> *The mid-boreal forest is sufficiently stable in the face of minor climate changes that none of the known climate changes over the last 1000 years will be detectable in the pollen, charcoal, or sedimentological records of a moderately large lake in the mid-boreal forest.*

It was hoped that the results of this study would help to establish the sensitivity limits of the fire regime and vegetation of the western boreal forest to climatic changes as this information may be useful to others in predicting the response of the forest to future climate change.

1.2 Organization of Thesis

This thesis is organized as follows. Immediately following is a brief literature review consisting of two parts. Part one gives a summary of what is known about charcoal production and taphonomy, and a brief review of a variety of methods used in charcoal-based paleofire studies. Part two presents the findings of the high-resolution paleofire studies that have been completed to date in the boreal forest of Canada (and selected studies from adjacent biomes). In Chapter 2, I present a comparison of two different methods of charcoal extraction, and compare the results of each to the known fire history near Christina Lake since 1900. The purpose of that investigation was to determine the spatial sensitivity of the paleofire signal derived from each method and by doing so, to determine if either method produced a useable signal for local fire activity near Christina Lake. In Chapter 3, the paleofire signal extracted by the sieving method (which proved to be a more reliable method for extracting a local fire signal) is compared to pollen analysis results and to the results from basic geochemical analyses of the sediment (sediment accumulation rate, and the concentrations of organic matter, carbonates and ash) from which a general proxy paleoclimate signal was inferred. In Chapter 4, the possibility of using vivianite as a proxy indicator of climate is explored. A final summary, discussion, and suggestions for further research are presented in Chapter 5.

As this thesis is organized around three papers, it contains some unavoidable redundancies (such as repetition of introductory material, methodological details and study site descriptions). Each of the three papers also has a different bibliographic style to meet the requirements of the journal to which it was (or will be) submitted. Chapter 2 has been accepted for publication in an upcoming special issue of the journal *Palaeogeography, Palaeoclimatology,* *Palaeoecology* (Laird and Campbell In Press).

All dates refer to year AD unless otherwise noted.

1.3 Literature Review

1.3.1 Stratigraphic Charcoal Theory and Methods

Because paleofire studies based on charcoal analysis is a relatively new branch of paleoecology, no standardized approach to studying sedimentary charcoal has yet been adopted and large knowledge gaps concerning charcoal taphonomy still remain. Below is a brief synopsis of what is known about charcoal production and taphonomy and a brief summary of charcoal quantification methodologies. The latter is intended to be indicative of the great variety in techniques rather than an exhaustive compilation and is biased towards those methods which have been used on lake sediments rather than peats or soils. More detailed reviews can be found in Tolonen (1986), Novokov et al. (1997), and especially Patterson et al. (1987) and Rhodes (1998).

Charcoal is produced by the incomplete combustion of plant material. The amount of charcoal produced depends on the fuel type (Stocks and Kauffman 1997) and more specifically on the density, moisture and lignin content of the plant material (Clark 1984; Patterson et al. 1987; Pyne et al. 1996). Fire intensity is also important. Generally speaking, given the same mass of identical fuel, high intensity fires will produce lower quantities and smaller fragments of charcoal with a higher carbon content while low intensity fires will produce higher quantities and larger fragments of charcoal with lower carbon content (Clark 1984; Patterson et al. 1987; Pyne et al. 1996). Wildfires in the boreal forest burn through a variety of fuels and at different temperatures and so can be expected to produce charcoal fragments of varying sizes and carbon concentrations.

Once produced, the charcoal can be transported to the lake via wind or water. The aerial dispersal of charcoal is dependent on particle size, the height of the thermal plume associated with the fire, wind speed and direction, and atmospheric washing by rain. Theoretical and experimental studies suggest that larger charcoal particles (> ~100 μm in diameter) generally do not travel very far (usually < 1 km) from source (Clark 1988a; Clark et al. 1998; Clark and Patterson 1997; Patterson et al. 1987; Wein et al. 1987). If, however, the thermal plume of the fire interacts with larger scale meteorological conditions (frontal systems, jet streams, etc.), large particles may be transported up to 10s of km while very small particles may potentially travel 100s or 1000s of km (Garstang et al. 1997).

No studies have yet been done on water dispersal of charcoal but Clark and Patterson (1997) suggest that charcoal transport by surface runoff (i.e. slope wash) might be important in areas of steep slopes, heavy precipitation, or impermeable soils, but is probably insignificant in forested areas with porous soils overlying gentle terrain. For lakes with inflowing streams, fluvially-transported charcoal could be very important. The surface area of inflowing streams might be greater than the surface area of the lake and the lower wind velocities over sheltered streams as compared to the lake might mean greater deposition of wind-borne charcoal on the stream surface (Clark 1988a). Also, direct deposits of charcoal into the stream could occur wherever stream bank vegetation was burned. Stream or shoreline erosion of older charcoal deposits would also be possible during periods of high water levels.

Several factors influence the deposition of charcoal particles once they have reached the lake. Due to its porosity, charcoal has an effective specific density of ~0.3 - 0.6 and so floats until it becomes waterlogged (Clark 1988a; Patterson et al. 1987). Thus, some losses may occur in open lakes if the charcoal reaches the outlet before sinking. Wave action may also redistribute charcoal towards the shores where it may become trapped in littoral vegetation. Once the charcoal finally sinks, it may be resuspended and redeposited many times until it is either finally overlain by sufficient sediment to protect it from lake currents or is deposited in a part of the basin that is too deep to be affected by lake currents. Whitlock and her colleagues (Whitlock et al. 1997; Whitlock and Millspaugh 1996) have shown that even 8 years after the 1988 Yellowstone fires, charcoal was still working its way from the sides of the lake basin into the centre. Similarly, Bradbury (1996) found that charcoal was still being reworked from the littoral areas to the profundal sediments of Elk Lake (Minnesota) more than 70 years after the last known fire in the watershed.

Most charcoal studies to date involved quantifying charcoal on microscope slides, often in conjunction with pollen analysis (Patterson et al. 1987; Rhodes 1998). Techniques include areal estimates based on ocular grid counts or point counts, or simply tallying the number of charcoal fragments above and below a certain size threshold (eg., Battson and Cawker 1983; Cwynar 1978; Gajewski et al. 1985; Mehringer et al. 1977; Swain 1973, 1978, 1980; Waddington 1969; Wein et al. 1987). Researchers using an ocular grid to estimate the area of each charcoal fragment often group the data into various size classes as larger particles are thought to be more indicative of local fire. Because counting charcoal particles is very time consuming (especially if each particle has to be measured as well), some researchers have used image analysis software to expedite the process (Earle et al. 1996; Horn et al. 1992; MacDonald et al. 1991; Morrison 1994; Patterson et al. 1987; Terasmae and Weeks 1979). Distinguishing charcoal from other dark objects was the most common problem encountered with the image analysis technique.

Several recent studies have employed methods which focus only on larger charcoal particles which are thought to be a more reliable indicator of local fire activity. In many of Clark's studies, for example, only charcoal particles > 50 μm are counted on petrographic thin sections of varved lake sediments (eg., Clark 1988b; Clark 1990; Clark and Royall 1995). While the thin section method has the advantage of being able to attain annual resolution, thin section preparation is costly in terms of time, money and sediment and several researchers have experienced difficulty in preparing thin sections of suitable quality (C. Carcaillet, pers. comm.). A simpler wet sieving method in which only larger particles (usually > 125 μm) are retained has been used successfully by several researchers (Clark et al. 1998; Long et al. 1998; Millspaugh and Whitlock 1995; Whitlock et al. 1997; Whitlock and Millspaugh 1996). The sieving method will be described in greater detail in Chapters 2 and 3.

Winkler (1985) developed a rapid non-visual method of quantifying the total charcoal content of a sample based on digestion in hot nitric acid followed by ignition at 500 °C. Nitric acid removes non-charred organic material, carbonates and pyrite but does not digest charcoal, coal, or "soot". Subtracting the post-ignition sample weight from the oven-dry post-treatment weight yields the amount of undigested elemental carbon remaining after the acid treatment. This elemental carbon represents the amount of charcoal in the sample if the study site is not contaminated by coal or "soot" from the burning of fossil fuels. This method is discussed in greater detail in Chapter 2.

In some studies the relationship between the charcoal signal and local fire activity is not always clear so other indices are used in conjunction with charcoal to help distinguish true fire events. In charcoal studies which also include pollen analysis, charcoal:pollen ratios have been used based on the rationale that after a fire event charcoal will increase while pollen will decrease (Battson and Cawker 1983; Cwynar 1978; Gajewski et al. 1985; Swain 1973, 1978, 1980). Similarly, conifer:sprouter ratios (or its variants) have been used based on the assumption that "sprouter" taxa which proliferate after a fire will be more abundant than conifers which take longer to regenerate and reach sexual maturity (Cwynar 1978; Swain 1973, 1980). Pollen chronosequences have also been used in which a progression from early successional to late successional species in the pollen record are assumed to reflect post-fire vegetation changes (Larsen and MacDonald 1998a, 1998b). In areas of high relief where post-fire erosion is likely, increases in varve thickness, the magnetic susceptibility of the sediment, or the Al or V content of the sediment have been used in conjunction with charcoal to determine local fire events (Cwynar 1978; Long et al. 1998; Millspaugh and Whitlock 1995; Swain 1973; Tolonen 1986; Whitlock et al. 1997).

To date, only one study has been done which compares the results of various proxy measures of fire activity to each other and to the known fire history of the study site. In Rainbow Lakes, Wood Buffalo National Park, MacDonald et al. (1991) compared microscopic charcoal (using both optical microscopy and an image analysis technique), macroscopic charcoal, elemental carbon (using the Winkler method), pollen, varve thickness, and geochemical analysis of the sediment to the known fire history (based on fire maps, fire scars and stand origin dates). Their results showed that none of the various charcoal measures had consistent correspondence to local fires and none, except microscopic charcoal counted by optical microscopy and image analysis, had any significant correlation to each other. Erosional indices (varve thickness and geochemical analyses) also showed no relationship to fire activity. The authors suggest that variations in fire characteristics (spatial extent, proximity to the lake, fuel type, intensity, and meteorological conditions during and after the fire), inconsistent erosion, and the order of magnitude difference in abundance between microscopic and macroscopic charcoal may be responsible for the poor correlations. Overall, however, macroscopic charcoal had a better correspondence to local fire activity while microscopic charcoal appeared to be strongly influenced by regional fire activity.

As indicated in the preceding review, there is no standardized methodology for paleofire studies based on stratigraphic charcoal. The research to date suggests, however, that choosing a method which focuses on larger charcoal particles may yield the most reliable signal for local fire activity. A method which focuses on the smaller fragments (such as pollen slide counts) or the "total" charcoal content (such as the Winkler method) may, however, be useful for determining a more regional signal which may provide additional valuable information.

1.3.2 High-resolution Paleofire Studies in the Canadian Boreal Forest

The following is a brief review of high-resolution studies concerning the fire history of the boreal forest of Canada over the past 1000 years. These studies are grouped into two broad categories: 1) long-term fire histories extending more than 500 years into the past; and 2) shorter-term fire histories which are limited to the last 500 years or less. The main emphasis is on studies from the western boreal forest and secondarily on the eastern boreal. Selected studies from the Subalpine, Aspen Parkland, and Forest-Tundra areas which show changes in fire activity over the last 1000 years are also included.

In the studies below, "fire return interval" refers to the time between fires (often of unknown size) within the study area (where the study area is usually a stand for dendrochronlogical studies and the charcoal catchment for charcoal-based studies). "Fire cycle" refers to the time it takes to burn an area equivalent in size to the study area (Romme 1980).

1.3.2.1 Long-term Fire Histories

In the western boreal forest of Canada, only three fire history studies have been completed which span more than 500 years and have sufficient resolution to detect possible changes in fire regimes over the last millennium. In Rainbow Lakes, Wood Buffalo National Park, Larsen and MacDonald (1998a) found a mean fire return interval of 69 years over an 840-year time span in this white spruce (*Picea glauca* (Moench)Voss) dominated site. Their data showed shorter mean fire return intervals between 1555 and 1700 (48 years) and longer mean fire return intervals before (56 years) and after (80 years) this period. In the Fariya Lake area (just outside Wood Buffalo National Park), Larsen and MacDonald (1998b) found an average fire return interval of 34 years (over 580 years) in a landscape dominated by black spruce (*Picea mariana* (Mill.)BSP) and jack pine (*Pinus banksiana* Lamb.). Again, their data showed shorter mean fire return intervals between 1552 and 1680 (~26 years) and longer mean fire return intervals before (41 years) and after (~36 years) this period. Both sites showed anomalously low pine pollen abundance from the late 1700s to the mid-1800s which may be related to climate.

The resolution of Campbell and Campbell's (In Press) study in Elk Island National Park, Alberta is not sufficient to determine individual fire events but their pollen and charcoal results showed climate-induced vegetation changes over the last ~1400 years and their effect on the fire regime. The charcoal curve showed much lower charcoal abundance during the Medieval Warm Period ~800 to 1200 AD. The authors suggest that the warm dry climate during this time period caused groundwater levels to drop around a small pond and lead to the replacement of flammable shrub birch (*Betula glandulosa* Michx.) with less flammable aspen (*Populus tremuloides* Michx.) around the fringes of the pond resulting in less fire activity despite the warm dry climate.

In the eastern boreal forest, Bergeron et al. (1998) report preliminary results from a 6700-year charcoal record extracted from the varved sediments of Lake Francis in Quebec. The results showed variable fire return intervals throughout the Holocene but the mean fire return interval was much longer prior to 2100 years ago (332 +/- 195 yr) than in the last 2100 years (99 +/- 53 years). Regional pollen evidence also showed that white cedar (*Thuja occidentalis* L., a late successional species) was much more abundant during the period of longer fire return intervals in the mid-Holocene whereas jack pine (a pioneer species) became more abundant in more recent times when fire return intervals were shorter. All tree species were present throughout the study period (although in varying abundances) suggesting that each of them was able to cope with the variable fire return intervals.

Using pollen and charcoal deposits in humus on the islands of Lake Duparquet, Quebec, Larocque et al. (2000) showed that long fire return intervals lead to the replacement of jack pine by eastern white pine (*Pinus strobus* L.) and black spruce while short fire return intervals lead to the cyclic regeneration of jack pine.

Near the northern tree limit in northern Quebec, Arseneault and Payette (1992) found that a fire in ~1750 lead to a shift from lichen-spruce to lichen-tundra. The lichen-spruce vegetation established on the site ~1700 BP, but severe climate during the Little Ice Age lead to the krummholz spruce being able to reproduce only through layering. Thus, after the fire in 1750, the forest could not be regenerated as the remaining krummholz spruce in unburned areas could not produce viable seed. Similarly, lack of post-fire regeneration, especially during cool periods, has been implicated in the deforestation of many sites in the forest-tundra of northern Quebec over the last 3000 years BP (Filion et al. 1991; Payette 1980; Payette and Gagnon 1985).

In Pine Lake, in the Aspen Parkland region of Alberta, Campbell et al. (In Press) found low-amplitude variation in the charcoal curve for most of the 3000 years of their record. They suggest this typifies a grassland fire regime. A marked change in the charcoal record occurred in the mid-19th century coincident with the time when the modern aspen forest developed. After the mid-19th century, the charcoal curve showed variations of much higher amplitude. The authors suggest that aspen "fire-proofed" the landscape somewhat resulting in less frequent fires. When fires did occur, however, the charcoal peaks were higher due to greater fuel loads.

1.3.2.2 Shorter-term Fire Histories

Larsen (1997) used forest stand age, fire scars, and historical data in Wood Buffalo National Park to compare fire cycles in aspen, jack pine, black spruce, and white spruce stands from the mid-1700s to the present. He found average fire cycles of 39, 39, 78, and 96 years respectively. He also looked at the mean waterbreak distance at each site and concluded that the shorter fire cycles found in aspen and jack pine stands may be partly due to their preference for drier sites which are further away from water bodies which might act as fire breaks. He also noted a decrease in fire frequency after ~1860 which he suggested might be due to increased precipitation which more than offset the increase in temperatures in the last century, or alternatively, to changes in aboriginal burning practices.

Yarie (1981) also estimated fire cycles in different vegetation types in the interior of Alaska and found fire cycles of 105 years in white spruce, 43 years in black spruce, and 30 years in hardwood (poplar and birch) stands based on life table analysis. His results also suggested that the flammability of white spruce stands increases with age, whereas black spruce stands experience a slight decrease in flammability with age due to increased paludification.

Carroll and Bliss (1982) used fire scars and stand origin dates to determine fire return intervals in jack pine stands in six sites in northeastern Alberta and northern Saskatchewan. The average fire return intervals for these sites ranged from 28 to 54 years (overall average 38 years) and increased from west to east.

The charcoal record from Amisk Lake, Alberta shows increased fire activity with increased warming since the mid-1800s, while the charcoal record from Opal Lake, Saskatchewan shows decreasing fire activity over the same period (Campbell and Flannigan 2000). The vegetation around Opal Lake is dominated by open pine and aspen stands on well-drained soils. The authors suggest that the cooler/moister Little Ice Age climate may have promoted more pine than aspen and thus increased the flammability of the landscape whereas the drier conditions since the mid-1800s may have promoted more aspen than pine resulting in a decrease in fire activity despite the general warming trend.

In the eastern boreal, Bergeron and Archambault (1993) compiled a 300-year dendrochronology-based fire history of the Lake Duparquet area in northwestern Quebec. They found that drought and fire were more frequent during the Little Ice Age than during the warming trend from the end of the Little Ice Age ~1850 to the present. Other studies in the Lake Duparquet area have shown that islands in the lake experienced a greater number of fires than the lakeshore due to a higher frequency of lightning strikes on the islands (Bergeron 1991). Many of the island fires were smaller and of non-lethal intensity, however, whereas the lakeshore fires were predominantly large, stand-replacing fires. It was concluded that the lower intensity of most of the island fires has allowed red pine (*Pinus resinosa* Ait.) to continue to exist on the islands whereas it has been eliminated on the mainland (Bergeron 1991; Bergeron and Brisson 1990).

In central Quebec, Cogbill (1985) found fire cycles of 130 years in black spruce - feather moss forests and 70 years in both jack pine and deciduous forests using dendrochronological techniques. Further east in southeastern Labrador, Foster (1983) estimated a 500 year fire cycle based on fire maps and fire scars. He suggested large fires were rare in this area due to high precipitation and a preponderance of lakes and wetlands which act as firebreaks. Lichen-woodlands and birch forests existed only in areas which had burned in the last 110 years. Old black spruce and fir stands occurred in extensive paludified plains with much longer fire cycles (> 500 years).

Several dendrochronology-based fire histories in the subalpine forests of Alberta and British Columbia begin in the 1500s or 1600s and show a substantial increase in fire cycle length from the mid-1700's to the present (eg., Johnson et al. 1990; Johnson and Larsen 1991; Johnson and Wowchuk 1993; Masters 1990). Johnson and Wowchuk (1993) suggest the consistency in the timing of fire cycle changes must be due to large-scale climatic factors and suggest a reduced frequency of blocking upper ridges in the mid-troposphere since the onset of the last phase of the Little Ice Age in the mid-1700s as a possible mechanism. Very long fire cycles between 1780 and 1830 were also noted in the Kananaskis watershed (Johnson and Larsen 1991) and a reduction of Indian-caused fires due to a small-pox epidemic was suggested as a possible cause, although the authors note there is little evidence to support this hypothesis.

In Jasper National Park, Tande (1979; 1980) compared area burned with below average tree-ring growth (which he used as a proxy indicator for below average precipitation) for the period of 1700 to 1913 near the Jasper townsite. He found that 92% of the total area burned was burned during periods of below average precipitation. While human use of the area may have increased the number of fires during certain time periods, climate seemed to be the dominant influence on total area burned. No fires > 500 ha occurred in the study area from 1908 to 1980 which the author attributed to active fire suppression in the Park which began in 1913.

As illustrated in the above review, very few long-term fire histories have been done in the boreal forest as most of the studies are based on dendrochronology and are necessarily limited to the last few hundred years. High-resolution charcoal-based studies spanning a longer time interval are therefore needed to place the results of the shorter-term studies into a broader temporal context. It should also be noted that only the coarsest of comparisons can be made among many of the studies due to the differences in methodology and sizes of the study areas.

1.4 References

Arseneault, D., and Payette, S. 1992. A postfire shift from lichen-spruce to lichen-tundra vegetation at tree line. Ecology **73**: 1067-1081.

Battson, R.A., and Cawker, K.B. 1983. Methodology to determine long term fire histories: an examination of charcoal and pollen from Mashagama Lake, Ontario. *In* Resources and dynamics of the boreal zone. *Edited by* R.W. Wein, R.R. Riewe, and I.R. Methven. Association of Canadian Universities Northern Studies, Ottawa, Ont. pp. 226-248.

Bergeron, Y. 1991. The influence of island and mainland lakeshore landscapes on boreal forest fire regimes. Ecology **72**: 1980-1992.

Bergeron, Y., and Archambault, S. 1993. Decreasing frequency of forest fires in the southern boreal zone of Quebec and its relation to global warming since the end of the 'Little Ice Age'. Holocene **3**: 255-259.

Bergeron, Y., and Brisson, J. 1990. Fire regime in red pine stands at the northern limit of the species' range. Ecology **71**: 1352-1364.

Bergeron, Y., and Flannigan, M.D. 1995. Predicting the effects of climate change on fire frequency in the southeastern Canadian boreal forest. Wat. Air Soil Pollut. **82**: 437-444.

Bergeron, Y., Richard, P.J.H., Carcaillet, C., Gauthier, S., Flannigan, M., and Prairie, Y.T. 1998. Variability in fire frequency and forest composition in Canada's southeastern boreal forest: a challenge for sustainable forest management. Conservation Ecology [online] **2**: 6.

Bradbury, J.P. 1996. Charcoal deposition and redeposition in Elk Lake, Minnesota, USA. Holocene **6**: 339- 344.

Campbell, C. 1998. Late Holocene lake sedimentology and climate change in southern Alberta, Canada. Quat. Res. **49**: 96-101.

Campbell, I.D., and Campbell, C. In Press. Late Holocene vegetation and fire history at the southern boreal forest margin in Alberta, Canada. Palaeogeogr. Palaeoclim. Palaeoecol.

Campbell, I.D., and Flannigan, M.D. 2000. Long-term perspectives on fire-climate-vegetation relationships in the North American boreal forest. *In* Fire, climate change, and carbon cycling in the boreal forest. *Edited by* E.S. Kasischke and B.J. Stocks. Springer, New York. pp. 151-172.

Campbell, I.D., Last, W.M., Campbell, C., Clare, S., and McAndrews, J.H. In Press. The late-Holocene paleohydrology of Pine Lake, Alberta: a multiproxy investigation. J. of Paleolimn.

Carroll, S.B., and Bliss, L.C. 1982. Jack pine - lichen woodland on sandy soils in northern Saskatchewan and northeastern Alberta. Can. J. Bot. **60**: 2270-2282.

Clark, J.S. 1988a. Particle motion and the theory of charcoal analysis: source area, transport, deposition, and sampling. Quat. Res. **30**: 67-80.

Clark, J.S. 1988b. Stratigraphic charcoal analysis on petrographic thin sections: application to fire history in northwestern Minnesota. Quat. Res. **30**: 81-91.

Clark, J.S. 1990. Fire and climate change during the last 750 yr in northwestern Minnesota. Ecol. Monogr. **60**: 135-159.

Clark, J.S., Lynch, J., Stocks, B.J., and Goldammer, J.G. 1998. Relationships between charcoal particles in air and sediments in west-central Siberia. Holocene **8**: 19-29.

Clark, J.S., and Patterson, W.A., III. 1997. Background and local charcoal in sediments: Scales of fire evidence in the paleorecord. *In* Sediment records of biomass burning and global change. *Edited by* J.S. Clark, H. Cachier, J.G. Goldammer, and B.J. Stocks. Springer-Verlag, Berlin. pp. 23-48.

Clark, J.S., and Robinson, J. 1993. Paleoecology of Fire. *In* Fire in the environment: the ecological, atmospheric, and climatic importance of vegetation fires. *Edited by* P.J. Crutzen, and J.G. Goldammer. John Wiley and Sons, Ltd., New York. pp. 193-214.

Clark, J.S., and Royall, P.D. 1995. Particle-size evidence for source areas of charcoal accumulation in late Holocene sediments of eastern North American lakes. Quat. Res. **43**: 80-89.

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

Cogbill, C.V. 1985. Dynamics of the boreal forests of the Laurentian Highlands, Canada. Can. J. For. Res. **15**: 252-261.

Cwynar, L.C. 1978. Recent history of fire and vegetation from laminated sediment of Greenleaf Lake, Algonquin Park, Ontario. Can. J. Bot. **56**: 10-21.

Earle, C.J., Brubaker, L.B., and Anderson, P.M. 1996. Charcoal in northcentral Alaskan lake sediments: relationships to fire and late-Quaternary vegetation history. Rev. Palaeobot. Palynol. **92**: 83-95.

Filion, L., Saint-Laurent, D., Desponts, M., and Payette, S. 1991. The late Holocene record of aeolian and fire activity in northern Quebec, Canada. Holocene **1**: 201-208.

Foster, D.R. 1983. The history and pattern of fire in the boreal forest of southeastern Labrador. Can. J. Bot. **61**: 2459-2471.

Gajewski, K. 1993. The role of paleoecology in the study of global climatic change. Rev. Palaeobot. Palynol. **79**: 141-151.

Gajewski, K., Winkler, M.G., and Swain, A.M. 1985. Vegetation and fire history from three lakes with varved lake sediments in northwestern Wisconsin, U.S.A. Rev. Palaeobot. Palynol. **44**: 277-292.

Garstang, M., Tyson, P.D., and Radke, L. 1997. Atmospheric transports of particulate and gaseous products by fires. *In* Sediment records of biomass burning and global change. *Edited by* J.S. Clark, H. Cachier, J.G. Goldammer, and B.J. Stocks. Springer-Verlag, Berlin. pp. 207-250.

Heinselman, M.L. 1973. Fire in the virgin forests of the Boundary Waters Canoe Area, Minnesota. Quat. Res. **3**: 329-382.

Horn, S.P., Horn, R.D., and R.Byrne. 1992. An automated charcoal scanner for paleoenvironmental studies. Palynology **16**: 7-12.

Jacoby, G.C., and Cook, E.R. 1981. Past temperature variations inferred from a 400-year tree-ring chronology from Yukon Territory, Canada. Arct. Alp. Res. **13**: 409-418.

Johnson, E.A. 1992. Fire and vegetation dynamics: studies from the North American boreal forest. Cambridge University Press, Cambridge, UK.

Johnson, E.A., Fryer, G.I., and Heathcott, M.J. 1990. The influence of man and climate on frequency of fire in the interior wet belt forest, British Columbia. J. Ecol. **78**: 403-412.

Johnson, E.A., and Larsen, C.P.S. 1991. Climatically induced change in fire frequency in the southern Canadian Rockies. Ecology **72**: 194-201.

Johnson, E.A., and Wowchuk, D.R. 1993. Wildfires in the southern Canadian Rocky Mountains and their relationship to mid-tropospheric anomalies. Can. J. For. Res. **23**: 1213-1222.

Laird, L.D., and Campbell, I.D. In Press. High resolution palaeofire signals from Christina Lake, Alberta: a comparison of the charcoal signals extracted by two different methods. Palaeogeogr. Palaeoclim. Palaeoecol.

Larocque, I., Bergeron, Y., Campbell, I.D., and Bradshaw, R.H.W. 2000. Vegetation changes through time on islands of Lac Duparquet, Abitibi, Canada. Can. J. For. Res. **30**: 179-190.

Larsen, C.P.S. 1997. Spatial and temporal variations in boreal forest fire frequency in northern Alberta. J. Biogeogr. **24**: 663-673.

Larsen, C.P.S., and MacDonald, G.M. 1998a. An 840-year record of fire and succession in a boreal white spruce forest. Ecology **79**: 106-118.

Larsen, C.P.S., and MacDonald, G.M. 1998b. Fire and vegetation dynamics in a jack pine and black spruce forest reconstructed using fossil pollen and charcoal. J. Ecol. **86**: 815-828.

Lichti-Federovich, S. 1970. The pollen stratigraphy of a dated section of Late Pleistocene lake sediment from central Alberta. Can. J. Earth Sci. **7**: 938-945.

Long, C.J., Whitlock, C., Bartlein, P.J., and Millspaugh, S.H. 1998. A 9000-year fire history from the Oregon Coast Range,based on a a high-resolution charcoal study. Can. J. For. Res. **28**: 774-787.

Luckman, B.H., Briffa, K.R., Jones, P.D., and Schweingruber, F.H. 1997. Tree-ring based reconstruction of summer temperatures at the Columbia Icefield, Alberta, Canada, AD 1073-1983. Holocene **7**: 375-389.

MacDonald, G.M., Larsen, C.P.S., Szeicz, J.M., and Moser, K.A. 1991. The reconstruction of boreal forest fire history from lake sediments: a comparison of charcoal, pollen, sedimentological, and geochemical indices. Quat. Sci. Rev. **10**: 53-71.

Masters, A.M. 1990. Changes in forest fire frequency in Kootenay National Park, Canadian Rockies. Can. J. Bot. **68**: 1763-1767.

Mehringer, P.J.Jr., Arno, S.F., and Petersen, K.L. 1977. Postglacial history of Lost Trail Pass Bog, Bitterroot Mountains, Montana. Arct. Alp. Res. **9**: 345-368.

Millspaugh, S.H., and Whitlock, C. 1995. A 750-year fire history based on lake sediment records in central Yellowstone National Park, USA. Holocene **5**: 283-292.

Morrison, K.D. 1994. Monitoring regional fire history through size-specific analysis of microscopic charcoal: the last 600 years in south India. J. Arch. Sci. **21**: 675-685.

Novakov, T., Cachier, H., Clark, J.S., Gaudichet, A., Macko, S., and Masclet, P. 1997. Characterization of particulate products of biomass combustion. *In* Sediment Records of Biomass Burning. *Edited by* J.S. Clark, H. Cachier, J.G. Goldammer, and B. Stocks. Springer-Verlag, Berlin. pp. 117-143.

Patterson, W.A., III, Edwards, K.J., and Maguire, D.J. 1987. Microscopic charcoal as a fossil indicator of fire. Quat. Sci. Rev. **6**: 3-23.

Payette, S. 1980. Fire history at the treeline in northern Quebec: a paleoclimatic tool. *In* Proceedings of the fire history workshop, October 20-24, 1980, Tuscon, Arizona. USDA Forest Service, Rocky Mountain Forest and Range Experimental Station, General Technical Report RM-81. pp. 126-131.

Payette, S. 1992. Fire as a controlling process in the North American boreal forest. *In* A systems analysis of the global boreal forest. *Edited by* H. Shugart, R. Leemans, and G.B. Bonan. Cambridge University Press. pp. 144-169.

Payette, S., and Gagnon, R. 1985. Late Holocene deforestation and tree regeneration in the forest-tundra of Quebec. Nature **313**: 570-572.

Pyne, S.J., Andrews, P.L., and Laven, R.D. 1996. Introduction to Wildland Fire. John Wiley & Sons, New York.

Rhodes, A.N. 1998. A method for the preparation and quantification of microscopic charcoal from terrestrial and lacustrine sediment cores. Holocene **8**: 113-117.

Romme, W. 1980. Fire history terminology: report of the ad hoc committee. *In* Proceedings of the fire history workshop, October 20-24, 1980, Tuscon, Arizona. USDA Forest Service, Rocky Mountain Forest and Range Experimental Station, General Technical Report RM-81. pp. 135-137.

Rowe, J.S., and Scotter, G.W. 1973. Fire in the boreal forest. Quat. Res. **3**: 444-464.

Stocks, B.J., and Kauffman, J.B. 1997. Biomass consumption and behavior of wildland fires in boreal, temperate, and tropical ecosystems: parameters necessary to interpret historic fire regimes and future fire scenarios. *In* Sediment records of biomass burning and global change. *Edited by* J.S. Clark, H. Cachier, J. G. Goldammer, and B.J. Stocks. Springer-Verlag, Berlin. pp. 169-188.

Swain, A.M. 1973. A history of fire and vegetation in northeastern Minnesota as recorded in lake sediments. Quat. Res. **3**: 383-396.

Swain, A.M. 1978. Environmental changes during the past 2000 years in north-central Wisconsin; analysis of pollen, charcoal, and seeds from varved lake sediments. Quat. Res. **10**: 55-68.

Swain, A.M. 1980. Landscape patterns and forest history in the Boundary Waters Canoe Area, Minnesota: a pollen study from Hug Lake. Ecology **61**: 747-754.

Szeicz, J.M. 1996. White spruce light rings in northwestern Canada. Arct. Alp. Res. **28**: 184-189.

Tande, G.F. 1979. Fire history and vegetation pattern of coniferous forests in Jasper National Park, Alberta. Can. J. Bot. **57**: 1912-1931.

Tande, G.F. 1980. Interpreting fire history in Jasper National Park, Alberta. *In* Proceedings of the fire history workshop, October 20-24, 1980, Tuscon, Arizona. USDA Forest Service, Rocky Mountain Forest and Range Experimental Station, General Technical Report RM-81. pp. 31-34.

Terasmae, J., and Weeks, N.C. 1979. Natural fires as an index of paleoclimate. Can. Field Nat. **93**: 116- 125.

Tolonen, K. 1986. Charred particle analysis. *In* Handbook of Holocene palaeoecology and palaeohydrology. *Edited by* B.E. Berglund. John Wiley and Sons, New York. pp. 485-496.

Vance, R.E. 1986. Pollen stratigraphy of Eaglenest Lake, northeastern Alberta. Can. J. Earth Sci. **23**: 11-20.

Vance, R.E., Mathewes, R.W., and Clague, J.J. 1992. 7000 year record of lake-level change on the northern Great Plains: a high-resolution proxy of past climate. Geology **20**: 879-882.

Waddington, J.C.B. 1969. A stratigraphic record of the pollen influx to a lake in the Big Woods of Minnesota. Geological Society of America, Special Paper **123**: 263-281.

Weber, M.G., and Flannigan, M.D. 1997. Canadian boreal forest ecosystem structure and function in a changing climate: impact on fire regimes. Environ. Rev. **5**: 145-166.

Wein, R.W., Burzynski, M.P., Sreenivasa, B.A., and Tolonen, K. 1987. Bog profile evidence of fire and vegetation dynamics since 3000 years BP in the Acadian forest. Can. J. Bot. **65**: 1180-1186.

Wein, R.W., and de Groot, W.J. 1996. Fire - climate change hypotheses for the Tiaga. *In* Fire in ecosystems of boreal Eurasia. *Edited by* J.G. Goldammer, and V.V. Furyaev. Kluwer Academic Press, The Netherlands. pp. 505-512.

Wein, R.W., and MacLean, D.A. (*Eds.*). 1983. The role of fire in northern circumpolar ecosystems. John Wiley and Sons, New York.

Whitlock, C., Bradbury, J.P., and Millspaugh, S.H. 1997. Controls on charcoal distribution in lake sediments: case studies from Yellowstone National Park and northwestern Minnesota. *In* Sediment records of biomass burning and global change. *Edited by* J.S. Clark, H. Cachier, J.G. Goldammer, and B.J. Stocks. Springer-Verlag, Berlin. pp. 367-386.

Whitlock, C., and Millspaugh, S.H. 1996. Testing the assumptions of fire-history studies: an examination of modern charcoal accumulation in Yellowstone National Park, USA. Holocene **6**: 7-15.

Winkler, M.G. 1985. Charcoal analysis for paleoenvironmental interpretation: a chemical assay. Quat. Res. **23**: 313-326.

Wotton, B.M., and Flannigan, M.D. 1993. Length of the fire season in a changing climate. For. Chron. **69**: 187-192.

Yarie, J. 1981. Forest fire cycles and life tables: a case study from interior Alaska. Can. J. For. Res. **11**: 554-562.

CHAPTER 2

High-resolution Palaeofire Signals from Christina Lake, Alberta: a Comparison of the Charcoal Signals Extracted by Two Different Methods[1]

2.1 Introduction

The boreal forest of Canada is a fire-dependent biome (Rowe and Scotter, 1973; Wein and MacLean, 1983; Payette, 1992) and understanding the interactions among fire, vegetation and climate is integral to understanding the boreal ecosystem. Palaeofire studies can illuminate past fire regime and vegetation responses to climate changes (Clark and Robinson, 1993; Campbell and Flannigan, 2000). This information is increasingly important as concern over future global climate change escalates. Current climate change models suggest that global warming may dramatically alter the fire regime of the boreal forest, especially in those areas where an increase in drought is predicted (Weber and Flannigan, 1997). If so, the changed fire regime is expected to have a much greater impact on the boreal forest than will the direct effects of climate warming alone (Wein and de Groot, 1996; Weber and Flannigan, 1997).

Palaeofire studies necessarily depend on proxy indicators of fire such as charcoal found in lake sediments, peat, and soils. Adequate dating control allows for the interpretation of the charcoal signal through time but it is difficult to interpret the spatial aspect of the signal. The source area of a particular signal may depend on both the methodology used and the characteristics of the sampling site.

The methodologies employed to extract and quantify stratigraphic charcoal vary widely and include sieving methods, thin sections, chemical assays, and an array of pollen slide counting methods (for reviews, see Tolonen (1986), Patterson et al. (1987), Novakov et al. (1997), and Rhodes (1998)). Each of these methods focuses on a particular size fraction of charcoal except for chemical assays which quantify all size fractions. Aerial dispersal models and limited experimental research suggest that larger charcoal fragments (> 100 μm) are not aerially transported very far from source (at most, 10s of km if entrained in a thermal plume) while smaller particles may be aerially transported 100s to 1000s of km (Clark and Patterson, 1997; Garstang et al., 1997). It is therefore assumed that charcoal quantification methods which focus on larger particles, such as thin sections and sieving methods, extract a more "local" charcoal signal, while pollen slide counts which focus on smaller charcoal particles may reflect a more "regional" fire signal (Clark and Patterson, 1997). It is not clear what sort of signal

---

[1] A version of this chapter has been accepted for publication in *Palaeogeography, Palaeoclimatology, Palaeoecology* as "High-resolution palaeofire signals from Christina Lake, Alberta: a comparison of the charcoal signals extracted by two different methods" by L.D. Laird and I.D. Campbell.

chemical assay methods reflect since particles of all sizes are included, but Winkler (1985) suggests her chemical assay method is comparable to pollen slide counts so the charcoal signal obtained by this method may be predominantly regional as well. There have been very few studies which compare the charcoal signals obtained via different methods (eg. MacDonald et al., 1991 and Clark and Patterson, 1997) so it is not yet clear how widely the above assumptions may apply. Also, these assumptions are based on aerial dispersal only as no quantitative research has been done on charcoal transport in surface runoff and streams.

The sampling site characteristics may also affect the size of the charcoal catchment. If the same factors affecting pollen dispersal hold true for charcoal as well (at least for very small particles), charcoal deposits found in sediments of small closed lakes and peat deposits in forest hollows would be expected to reflect dominantly local fire activity while the charcoal in large open lakes might be more representative of regional fire activity (Jacobson and Bradshaw, 1981; Sugita, 1994).

Since both local and regional fire signals have the potential to yield valuable information, an attempt was made to extract both types of signals from annually-laminated sediment retrieved from Christina Lake in the boreal forest of northern Alberta. Constraints of time and sediment availability precluded the use of Clark's thin section method or pollen slide counts for this study. Two methods of charcoal extraction were chosen based on their ease of use and cost effectiveness in terms of both time and money. The sieving method described by Whitlock and Millspaugh (1996) was chosen to extract the "local" charcoal signal. Winkler's (1985) chemical assay method based on nitric acid digestion was chosen to extract what was hoped would be a more "regional" signal. The charcoal curve from each of these methods was then compared to the known recent fire history near the lake to determine the spatial sensitivity of each signal.

Digestion in nitric acid has often been used to distinguish charcoal from other dark organic material and to remove excess organics (eg. Swain, (1973); Singh (1981)). The use of nitric acid digestion in combination with loss on ignition as a method of quantifying charcoal (or black carbon) as described by Winkler (1985) has, however, sometimes been problematic and thus has not been widely adopted. One of the major drawbacks attributed to this method has been the imprecision inherent in gravimetric techniques which makes it difficult to reproduce results especially in small samples with very low levels of charcoal (Novakov et al., 1997; Rhodes, 1998). Another disadvantage is that the resulting "charcoal" signal may include not only charcoal but also coal, carbon from the by-products of fossil fuel combustion (Winkler, 1985) and clay water losses, and such "noise" may obscure the true charcoal signal (MacDonald et al., 1991; Novakov et al., 1997). Some researchers have also experienced problems with inadequate digestion in materials with very high organic content such as peat (Rhodes, 1998).

Given the various problems encountered with this technique, some testing and modifications were done to improve the precision and suitability of this method for sediments containing low levels of charcoal. First, the ability of nitric acid digestion to remove different types of organic material and the effect of nitric acid on charcoal and different types of clastic material was tested. Secondly, the use of a Total Carbon Analyser apparatus rather than standard loss on ignition was explored. The methodology and results of these experiments are outlined below. The remainder of the paper focuses on a comparison of the charcoal signals extracted by sieving and nitric acid digestion/Total Carbon Analyser quantification and their relationship to each other and to known fire activity near the lake.

2.2 Study Site

Christina Lake (55° 37' N 110° 57' W) is located in northern Alberta, Canada (Figure 2-1). The lake is large (2130 ha) with six permanent inflowing streams and a drainage basin of 1250 km^2. The morphology of the lake is long and narrow reaching a maximum length and width of approximately 13 km and 2 km respectively. The deepest basin reaches a maximum depth of 33 m and here the sediments are laminated. Most of the lake basin has steeply sloping sides and there are only isolated pockets of littoral areas (Bradford, 1990).

The lake lies within the Central Mixedwood Subregion of the Boreal Forest Natural Region (Alberta Environmental Protection, 1994). This subregion is characterized by a mosaic of deciduous and coniferous trees (often occurring in mixed stands) and extensive peatlands. Predominant soils are Gray Luvisols and Eutric Brunisols on upland sites and Organic and Gleysolic soils in poorly drained areas. The climate is subhumid continental with short cool summers (average May-September temperature is 12° C) and long cold winters. Average annual precipitation is 380 mm.

The drainage basin of the lake consists of level to gently rolling terrain overlying a thick (up to 150 m) mantle of glacial till and channel fill materials. Although no known outcrops of potentially coal-bearing bedrock occur in the basin, the till may contain a small amount of coal derived from ice-scoured bedrock to the northeast of the study area.

Vegetation in the drainage basin is largely dominated by peatlands with black spruce (*Picea mariana*) and larch (*Larix laricina*) as the dominant trees. Vegetation on upland areas is composed of trembling aspen (*Populus tremuloides*), white spruce (*Picea glauca*), jack pine (*Pinus banksiana*), birch (*Betula papyrifera*) and balsam poplar (*Populus balsamifera*).

Human impact on the area was minimal until oil and gas exploration began in the region in the mid 1980s. Although it has been accessible by rail since 1919, the lake has been accessible by an all-weather road only since 1986. The hamlet of Conklin is located immediately west of the lake but other than a recreational lodge and campground on the north shore at the western end of the lake, there is no other shoreline development. The nearest large population centre is Fort McMurray 125 km to the north. Contamination in the core due to fossil fuel combustion should therefore be minimal.

2.3 Methodology

2.3.1 Core Retrieval and Sampling

A core of laminated sediment was retrieved using a box-type freeze-corer (Swain, 1973) at a water depth of approximately 30 m. The core included the water/sediment interface and penetrated to a depth of 100 cm. Judged on the basis of crust thickness and regularity of laminations, the best face was selected for sampling. The sediment was cut into contiguous 1 cm strips parallel to the plane of deposition.

2.3.2 Core Dating

The laminations were examined under a stereoscope at 50x magnification and were found to be similar to those described from Swedish lakes (Petterson, 1996) and consistent with the successional deposition of material over one year. Typically, a thicker (1-1.5 mm) light-coloured layer consisting of a mixture of silt, diatoms, and organic material (representing spring to autumn) alternated with a thinner (< 1 mm) dark layer consisting of very fine organic material (deposited while the lake was frozen over in winter). The light layer sometimes included a white layer of pure diatoms representing an algal "bloom" in the spring or autumn. Each couplet of a light layer (with or without a diatom bloom) and a dark layer was assumed to be a true varve (i.e. to represent one year of deposition) and the cores were dated by varve counting.

Independent confirmation of the annual nature of the laminations was given by ^{137}Cs dating (see Appendix 1). Contiguous 1 cm samples from the upper 20 cm of core 1 were analysed for radioactive cesium content. The greatest cesium activity occurred in the sample containing sediment deposited in the years 1963 to 1967 as determined by the varve count. This is consistent with the peak in ^{137}Cs fallout in the northern hemisphere (due to the atmospheric testing of nuclear weapons) in 1963 (Walling and He, 1993).

2.3.3 Determination of Near Shore Fire Activity

Recent fire activity near the lake was determined mainly from Delisle and Hall's (1987) study of fires > 200 ha occurring beween 1931 and 1983 in Alberta. The first fire reported in this study for the Christina Lake region occurred in 1940 but the authors caution that fires occurring in more remote areas were under-reported in the early years of their study period. For this study, the information obtained from Delisle and Hall was assumed to be a fair representation of fires > 200 ha in the Christina Lake area from 1940 to 1983. These data were supplemented by fire records (1961- 1995) from the Conklin Fire Tower located 8 km immediately west of Christina Lake to obtain information on fires > 200 ha since 1983 (Rick Strickland, pers. comm.;

Peter Englefield, pers. comm.).

To obtain information on older fires, fire scars were collected from jack pine (*Pinus banksiana*) trees within 5.5 km of the lake shore. Disks, wedges or cores were collected from scarred trees (Arno and Sneck, 1977) at 30 cm above the ground. A total of 30 fire scars were obtained from fourteen different sites. Fire scars were dated using DendroScan (Varem-Sanders and Campbell, 1996) to count the annual tree rings. Samples too fragile to survive processing for DendroScan were planed with a razor blade and the rings were counted under a stereo microscope at 50x magnification.

2.3.4 Charcoal Extraction via Sieving

The "Oregon Sieving Method" developed by Whitlock and Millspaugh (1996; Millspaugh and Whitlock, 1997) was used. Known volumes of sediment (in most cases 2 ml) were soaked in a sodium polyphosphate-based water softening agent (i.e., Calgon) for several days to deflocculate the sediment. Each sample was then very gently washed through nested sieves with mesh openings of 125 μm and 250 μm. The material retained on each screen was washed onto filter paper and examined under a stereo microscope at 25x to 50x magnification. All charcoal particles were tallied. Although separating the sediment into two size fractions facilitated counting, very few charcoal particles > 250 μm were found. Totals from both size fractions were added together and expressed in terms of number of fragments > 125 μm per cc of sediment. The results were then divided by the number of varves in that 1 cm segment of the core to obtain the influx (number of charcoal fragments per cm^2 per year) or divided by the oven-dry weight per cc of sediment (determined from a separate series of samples) to obtain concentration (number of charcoal fragments per g of oven-dry sediment). Number of fragments rather than areal estimates of charcoal were tallied to remain true to the method outlined by Whitlock and Millspaugh (1996). Also, areal estimates of charcoal are usually done so that larger fragments of charcoal (presumably representing more local fire activity) are given more weight than very small fragments (which are presumed to represent a more "regional" background signal of less importance) (Patterson et al., 1987). Because only the large (and presumably "local") fragments of charcoal are extracted by this method, the extra time involved in measuring each particle was deemed unnecessary.

2.3.5 Nitric Acid Digestion Trials

2.3.5.1 Organics

Various types of oven-dry organic material (alfalfa sprouts, spruce needles, aspen leaves, grass, sawdust, peat, and algae) were ground with a mortar and pestle and passed through a #35 sieve with openings of 500 μm. Dried insects (small beetles) were used whole. Approximately 0.5 ml of oven-dried sample was added to tared Pyrex test tubes and weighed.

Approximately 3 ml of concentrated nitric acid was added to each test tube and all were placed in a hot water bath (temperatures within the test tubes averaged ~ 75°C). Once the initial rapid reaction subsided (about 15 - 20 minutes) an additional 7 ml of acid was added and timing began. Every half hour, the samples were stirred and any material stuck to the sides of the tube above the acid level was washed down with a small amount of additional acid. Once the prescribed length of time had elapsed, test tubes were removed, centrifuged for 10 minutes and decanted through glass filter paper. Any residue caught on the filter paper was washed back into the tube with distilled water. Two distilled water rinses were centrifuged and decanted (again through glass filter paper). The test tubes were then oven-dried at 105°C overnight, cooled in a desiccator and weighed again. Timed trials of 1, 2, 4 and 8 hours of acid digestion were done to determine the optimal duration for treatment.

A replicate series of oven-dried organic samples were also ignited at 550°C for one hour to ascertain how nitric acid digestion compared with common loss on ignition methods for determining organic content.

2.3.5.2 Charcoal, Clay, Sand, and Sediments

Charcoal (completely charred spruce wood), clay (kaolinite), sand, lake sediment from two different lakes, and synthetic sediments made up of known amounts of charcoal, clay, sand, and organic material (ground dried spruce needles) were digested in nitric acid for the optimal time period resulting from the above experiment (two hours). After processing, oven-dried samples were weighed, ignited in a muffle furnace for one hour at 550°C, cooled in a desiccator and reweighed as suggested by Winkler (1985). As a control, a series of the same sample types were processed as above but omitting the nitric acid treatment.

2.3.6 Total Carbon Analyser Tests

A series of test samples were processed in nitric acid as above. Sub-samples of oven-dried material were then analysed for total carbon using an ASTRO 2001 Total Organic Carbon Analyser. In this technique, the carbon in the CO_2 given off during ignition (at 850° C) is measured using a non-dispersive infrared detector and results were expressed in $\mu g\ C\ g^{-1}$ (equivalent to ppm). Depending on the sample size, this apparatus is capable of detecting carbon values as low as 1 ppm. The Carbon Analyser was calibrated using a potassium hydrogen phthalate standard, and a blank and a dextrose standard were used as a quality control after every tenth sample. As a control, a series of test samples that had not undergone nitric acid treatment was also analysed as above.

2.3.7 Nitric Acid/Total Carbon Analysis of Christina Lake Sediment

A known volume of sediment from each 1 cm interval of the core was oven-dried and treated in nitric acid for 2 hours as above and oven-dried. Sub-samples were then analysed in the Total Carbon Analyser as above. The carbon analyser portion of the analysis required several days to complete and the machine was calibrated anew each day. As a test of the precision of this method, a small set of duplicate samples was analysed on separate days and was found to be satisfactory (Figure 2-2). Because each day's calibration might vary slightly, a small selection of samples from each day's run was processed again on a single day so that the results from all samples could be standardized to a single calibration.

2.4 Results and Discussion

2.4.1 Experimental Results

The results of the nitric acid digestion timed trials and loss on ignition of a variety of organic materials are given in Table 2-1. A one hour treatment in hot nitric acid did not appear to be sufficient to remove all digestible material. Increasing the digestion period to two hours, however, provided good results as it removed about the same amount of material as loss on ignition. There was no significant improvement with four or eight hours of treatment. Thus a two hour digestion period was chosen as satisfactory and was used in the remaining analyses.

Two hour nitric acid and ignition treatments of charcoal, clay, sand, and various sediments showed some expected and unexpected results (Table 2-2). The biggest surprise was that charcoal actually gained over 10% of its oven-dry weight with nitric acid treatment. The fine fragments of charcoal used in the experiment may have behaved as an activated charcoal filter and adsorbed nitric acid. The strong acrid smell of the samples even after six distilled water rinses and vigorous stirring tends to support this hypothesis. Why this should have occurred in our tests but not in Winkler's (1985) tests in unclear. Clay may also adsorb a small amount of nitric acid as the samples treated in nitric acid showed slightly higher losses on ignition than did untreated samples (Table 2-2). The problems caused by clay water losses on ignition, on the other hand, came as no surprise. Treated samples of pure clay showed a 6.35% loss on ignition which would be counted as "charcoal" in Winkler's method (1985). The importance of this can be seen by comparing the results of synthetic sediment samples 1 and 2. Although the percentage of charcoal added to both of these samples was exactly the same, the "charcoal" results of Synthetic 2 (which contained 10% more clay than Synthetic 1) were 0.5% higher. This small change would be quite significant in sediments containing only 1 or 2% charcoal but with large changes in clay content as the increase in clay water losses would result in an erroneous "charcoal" peak.

Overall, however, if the digestion time is increased to 2 hours, Winkler's method worked very well on charcoal-rich materials. Although the resulting number given as "charcoal" was inaccurate due to clay water losses (and perhaps unknown matrix effects as well (Novakov et al., 1997)), as long as the sediment type and the proportion of clay remained consistent, Winkler's method accurately tracked changes in charcoal abundance. For example, the loss on ignition result for the Amisk Lake sediment sample to which 4% of charcoal was added was almost exactly 4% higher than the result for the unadulterated Amisk Lake sample (Table 2-2).

The Total Carbon Analyser results for treated and untreated samples are shown in Table 2-3. The results for the treated synthetic sediments were particularly good with the calculated charcoal values matching predicted values. Treated sand and clay samples also showed results very close to predicted values. The only disturbing results were the ones for the lake sediment samples to which charcoal had been added. One would expect the result for the charcoal-enhanced Christina Lake sample to be ~ 7.69% (1.69 + 6) and the Amisk Lake sample to be ~ 5.74% (1.74 + 4), but results obtained were 2.14% and 0.87% higher. A possible explanation for this discrepancy is that the charcoal added to the sample again acted as an activated carbon filter and adsorbed some of the dissolved carbon during the nitric acid treatment. The fact that the greater error occurred in the sample with the greater amount of added charcoal tends to support this view. It might be wondered, however, why the same effect did not occur in the synthetic sediment samples, but perhaps the charcoal preferentially reacted with particular carbon compounds found in the lake sediment but not in the synthetic samples. Despite this rather puzzling phenomenon, the TCA results were considered promising enough to warrant pursuing this method on the entire Christina Lake core.

2.4.2 Christina Lake Results

A map of documented recent fire activity in the Christina Lake region since 1940 and the fire scar collection sites is shown in Figure 2-3. A summary of fire scar information for fires prior to 1940 is given in Table 2-4. Known fire activity since 1900 is compared with both the sieved charcoal curve and the TCA carbon curve in Figure 2-4. The greatest area burned by documented fires in the Christina Lake watershed occurred in the1940s. Fire-scar evidence suggests other pulses of near-shore fire activity from 1901-1905, 1913-1916, and 1928-31, although the sizes of these fires cannot be determined. The close timing of several of the known fires prevented their isolation as separate events in the charcoal curves given the sampling interval of the study (each 1 cm sample contained 1.5 to 5 years of sediment, avg. 3.5 years) and the fact that charcoal from a single fire event may be deposited over several years (Whitlock and Millspaugh, 1996). However, in spite of these limitations, a comparison of the known fire activity with each of the charcoal curves yielded some interesting results.

Peaks in the sieved charcoal curve corresponded well with known fire activity within 100 m of the shore (Figure 2-4 and Table 2-4). The larger shore fires of 1942 and 1949 produced a much stronger response than the smaller 1988 shore fire. The response of this curve to fires that are not known to have burned to the shore was less consistent. The 1941 fire which came to within 3.2 km of the east shore showed clearly (although this peak may correspond to the 1942 shore fire if the chronology established by the varve count is in error by 0.5 years). Response to the 1980 fire 1.7 km west of the lake is weak as is the response to the 1990 fire (which may be indistinguishable from continued influx from the 1988 fire). The 1971 fire went totally undetected in the sieved charcoal curve despite the fact that it burned to within 3.8 km of the shore, straddled one of the inflowing streams, and was much larger in area than either the 1980, 1988, or 1990 fires. The sieved charcoal curve thus shows a very local signal most strongly representing near-shore fire activity.

The known large fires of 1941, 1942 and 1949 are also evident on the TCA carbon curve (Figure 2-4) but the peak from the 1949 fire is delayed by at least one year. The peak from the 1980 fire was also delayed by at least 4.5 years. This suggests that it takes several seasons to transport the bulk of the charcoal from the burned watershed to the final deposition site in the lake. This is consistent with the results of Whitlock and Millspaugh's (1996) research on the fires in Yellowstone National Park which showed that the peak in charcoal deposition in the sediment may occur several years after the fire. The delay in response also suggests that charcoal transport by runoff and stream inputs into the lake are very important to this signal. This hypothesis is further supported by the very high correlation between the TCA carbon curve and the sediment influx curve for the core (r= .92, p=.01). Limited evidence suggests that the TCA carbon curve is more responsive than the sieved charcoal curve to watershed fires that do not burn near the shore. The 1971 fire which went undetected in the sieved charcoal curve is reflected in a broad weak peak over several samples in the TCA carbon curve. The TCA curve also had a stronger response to the 1903 fires than did the sieved charcoal curve. This suggests that the TCA curve may have responded to not only the near shore fire but also to another fire in the same year burning near Birch Creek (Figure 2-3 and Table 2-4).

There is no evidence for a "regional" charcoal signal in the results obtained by either the sieving or the TCA method. In 1980, a fire consuming 137, 313 ha occurred just 17 km east of the lake shore and just 2.5 km outside the drainage basin (Figure 2-3). Several other large fires in the region also occurred in 1981, 1982, and 1990. Despite their magnitude and proximity, none of these fires elicited any noticeable response in either the charcoal curve or the TCA carbon curve.

The fact that both palaeofire signals are so strongly local is somewhat surprising. Aerial dispersal models for charcoal (Clark, 1988; Clark and Patterson, 1997; Garstang et al., 1997) and pollen dispersal theories (Jacobson and Bradshaw, 1981; Sugita, 1994) suggest that such a large open lake should serve as a catchment for aerially transported charcoal from outside the drainage basin. Perhaps the east-west orientation of this narrow lake limits its exposure to airborne charcoal transported on prevailing westerly winds. Alternatively, the pattern of deposition of airborne charcoal is such that while some fine charcoal does travel long distances, its importance as a component of the signal is minor compared to the influx of charcoal from a local fire.

2.5 Conclusions

Modifications to Winkler's chemical assay method of charcoal quantification (Winkler, 1985) by increasing the duration of the nitric acid treatment and using a Total Carbon Analyser (TCA) rather than loss on ignition removed some of the problematic aspects of this method of charcoal quantification. The sieved charcoal curve most strongly reflected large fires reaching the shore. The TCA carbon curve detected shore fires as well as fires within the drainage basin that did not burn to the lake edge. Very large fires occurring just outside the drainage basin were not detected by either method suggesting that stream transport may be critical for the representation of fires that do not reach the shoreline at this site.

The sieving method proved to be useful for detecting a local fire signal. The TCA method is somewhat less strongly local and it's greater sensitivity to non-shore fires made it useful for assessing the extent of fire disturbance in the watershed as a whole. Because the TCA method is able to detect very low levels of carbon, it may be useful in determining a regional airborne charcoal signal in small closed lakes or hollows where stream inputs will not swamp the regional signal.

Table 2-1: Effects of nitric acid treatments of various durations on different types of organic materials.

Sample Type	Average weight loss with nitric acid treatment (% oven-dry weight)				loss on ignition (% oven-dry wt.)
	1 hour	2 hours	4 hours	8 hours	
alfalfa sprouts	88.01 ± 0.92 n=3	95.99 ± 0.87 n=3	95.21 ± 0.56 n=3	98.54 ± 0.09 n=3	95.30
spruce needles	92.17 ± 1.63 n=3	95.93 ± 0.69 n=3	95.08 ± 0.64 n=3	97.86 ± 0.17 n=3	95.82
aspen leaves	91.25 ± 0.69 n=3	94.16 ± 0.14 n=3	95.58 ± 0.67 n=3	94.83 ± 0.59 n=3	95.09
grass	91.56 ± 0.32 n=3	92.90 ± 0.19 n=2	95.85 ± 0.82 n=3	95.85 ± 0.06 n=2	91.04
sawdust	88.55 ± 1.85 n=3	96.52 ± 0.27 n=3	97.01 ± 0.57 n=3	97.50 ± 0.79 n=3	97.95
peat	74.21 ± 1.98 n=3	86.39 ± 0.19 n=3	85.19 ± 0.30 n=3	85.77 ± 0.58 n=3	83.68
insects	64.76 ± 12.76 n=3	97.39 ± 0.68 n=3	95.38 ±0.51 n=2		
algae		98.17 ± 0.23 n=2		98.28 ± 0.10 n=2	92.49
overall average	**84.36**	**94.68**	**94.19**	**95.52**	**93.05**

Table 2-2: Results of nitric acid and ignition treatments on clastics and sediments.

Sample Type	Weight Loss (% oven-dry weight)		Predicted Charcoal (% oven-dry weight)
	Nitric Acid Treatment "Organics and Carbonates"	Loss on Ignition at 550° C "Charcoal"	
clay	3.96 ± 0.23 n=3	6.35 ± 0.03 n=3	0
clay (untreated)		5.55 ± 0.084 n=3	
sand	20.76 ± 0.18 n=3	0.67 ± 0.11 n=3	~0
sand (untreated)		0.79 ± 0.073 n=3	
charcoal	-10.83 ± 0.32 n=3	109.09 ± 0.20 n=3	100
charcoal (untreated)		96.54 ± 0.097 n=3	
Christina Lake	35.40 ± 0.28 n=4	5.63 ± 0.07 n=4	?
Christina Lake (untreated)		25.32 ± 0.151 n=3	
Amisk Lake	38.96 ± 0.22 n=4	5.04 ± 0.12 n=4	?
Amisk Lake (untreated)		28.48 ± 0.159 n=3	
peat	86.08 ± 1.20 n=4	2.92 ± 0.12 n=4	?
peat (untreated)		83.68 ± 0.761 n=3	
Synthetic 1[a] (45-20-30-5)	39.24 ± 0.19 n=4	7.57 ± 0.13 n=4	~5
Synthetic 2 (45-30-20-5)	30.35 ±0.35 n=4	8.08 ± 0.12 n=4	~5
Synthetic 3 (47-21-32-0)	41.54 ± 0.43 n=4	2.37 ± 0.13 n=4	~0
Synthetic 4[b] (45-20-30-5)	39.27 ± 0.49 n=4	7.62 ± 0.24 n=4	~5
Synthetic 4[b] (untreated)		34.35 ± 0.737 n=3	
Christina Lake + 6% charcoal	33.29 ± 0.55 n=4	11.53 ± 0.35 n=4	? + 6
Amisk Lake + 4% charcoal	37.41 ± 0.49 n=4	9.12 ± 0.20 n=4	? + 4
peat + 10% charcoal	78.57 ± .043 n=4	13.90 ± 0.43 n=4	? + 10

[a] Numbers refer to the proportions of sand, clay, organic material, and charcoal respectively (expressed as % of oven-dry weight). Exact proportions were added to each individual sample.

[b] Proportions were mixed into one large sample which was later divided into smaller samples.

Table 2-3: Total Carbon Analyser results for treated and untreated samples.

Sample Type	TCA Carbon (% oven-dry weight)	Charcoal [c] (% oven-dry weight)	Predicted Charcoal (% oven-dry weight)
clay	0.16 ± 0.015 n=5	0.18	0
clay (untreated)	0.07 ± 0.006 n=4		
sand	0.26 ± 0.014 n=5	0.30	~0
sand (untreated)	2.78 ± 0.243 n=3		
charcoal	79.66 ± 1.742 n=7	92.63	100
charcoal (untreated)	85.97 ± 3.399 n=6		
Christina Lake	1.46 ± 0.097 n=4	1.69	?
Christina Lake (untreated)	11.29 ± 0.127 n=4		
Amisk Lake	1.49 ± 0.089 n=7	1.74	?
Amisk Lake (untreated)	14.30 ± 0.375 n=4		
peat	0.71 n=1	0.83	?
peat (untreated)	47.40 ± 0.742 n=2		
Synthetic 1* (45-20-30-5)	4.33 ± 0.320 n=13	5.03	~5
Synthetic 2 (45-30-20-5)	4.50 ± 0.363 n=10	5.23	~5
Synthetic 3 (47-21-32-0)	0.76 ± 0.111 n=11	0.88	~0
Synthetic 4** (45-20-30-5)	4.40 ± 0.291 n=9	5.11	~5
Christina Lake + 6% charcoal	8.45 ± 0.490 n=6	9.83	? + 6
Amisk Lake + 4% charcoal	5.69 ± 0.126 n=6	6.61	? + 4

---

[a] Numbers refer to the proportions of sand, clay, organic material, and charcoal respectively (expressed as % of oven-dry weight). Exact proportions were added to each individual sample.

[b] Proportions were mixed into one large sample which was later divided into smaller samples.

[c] Calculated by dividing the carbon result by 0.86 (untreated charcoal contains an average of %85.97 carbon as indicated).

Table 2-4: Fire activity in the Christina Lake region between 1900 and 1940 as determined by fire scars.

Year	Distance from shore	Comments
1939	5.5 km	outside watershed
1936	900 m	
1933	5.5 km	outside watershed
1931	1 km	
1929	< 100 m	near Sunday Creek
1928	300 m	
1919	3 km	400 m from Birch Creek
1916	< 100 m	
1915	< 100 m	near Sunday Creek
1913	< 100 m	
1911	3 km	400 m from Birch Creek
1905	< 100 m	
1903	< 100 m	
1903	3 km	400 m from Birch Creek
1901	< 100 m	

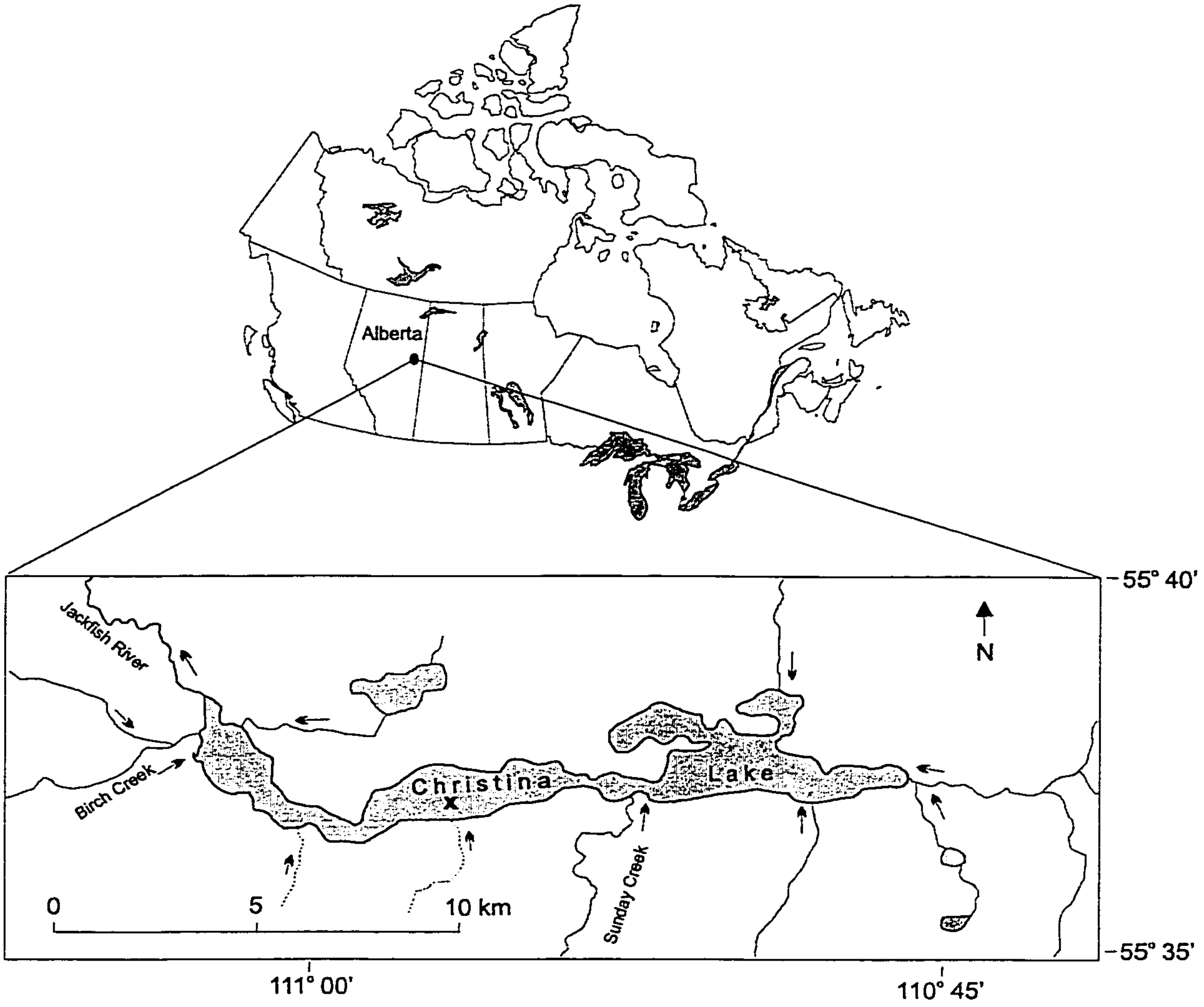


Figure 2-1: Location of Christina Lake in the boreal forest of Alberta, Canada. The location of the coring site is marked with an "x".

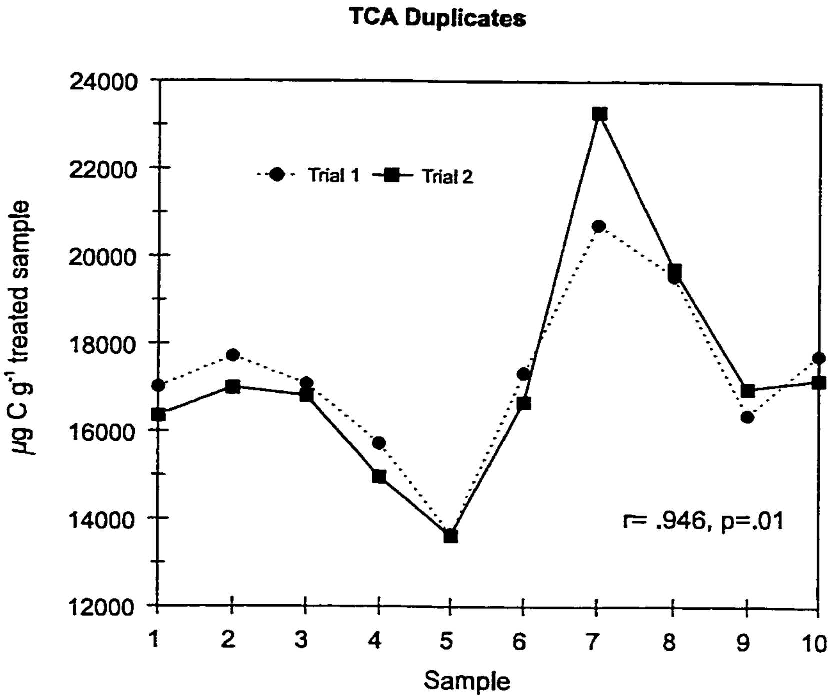
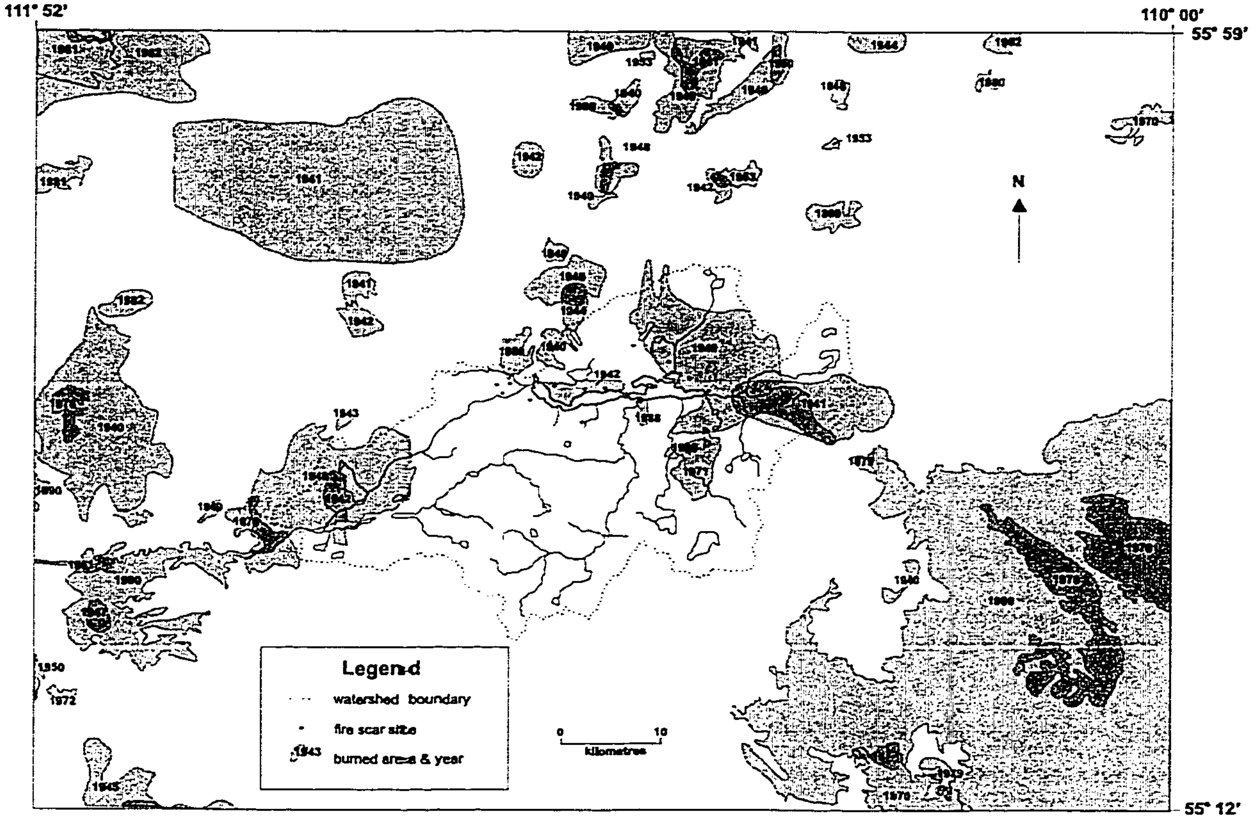


Figure 2-2: Total Carbon Analyzer (TCA) results for a duplicate series of samples analysed on different days.

Figure 2-3: Fire activity since 1940 in the Christina Lake region. Fires > 200 ha are mapped (Delisle and Hall, 1987; Rick Strickland, pers.comm.; Peter Englefield, pers. comm.) and fire scar collection sites are marked.



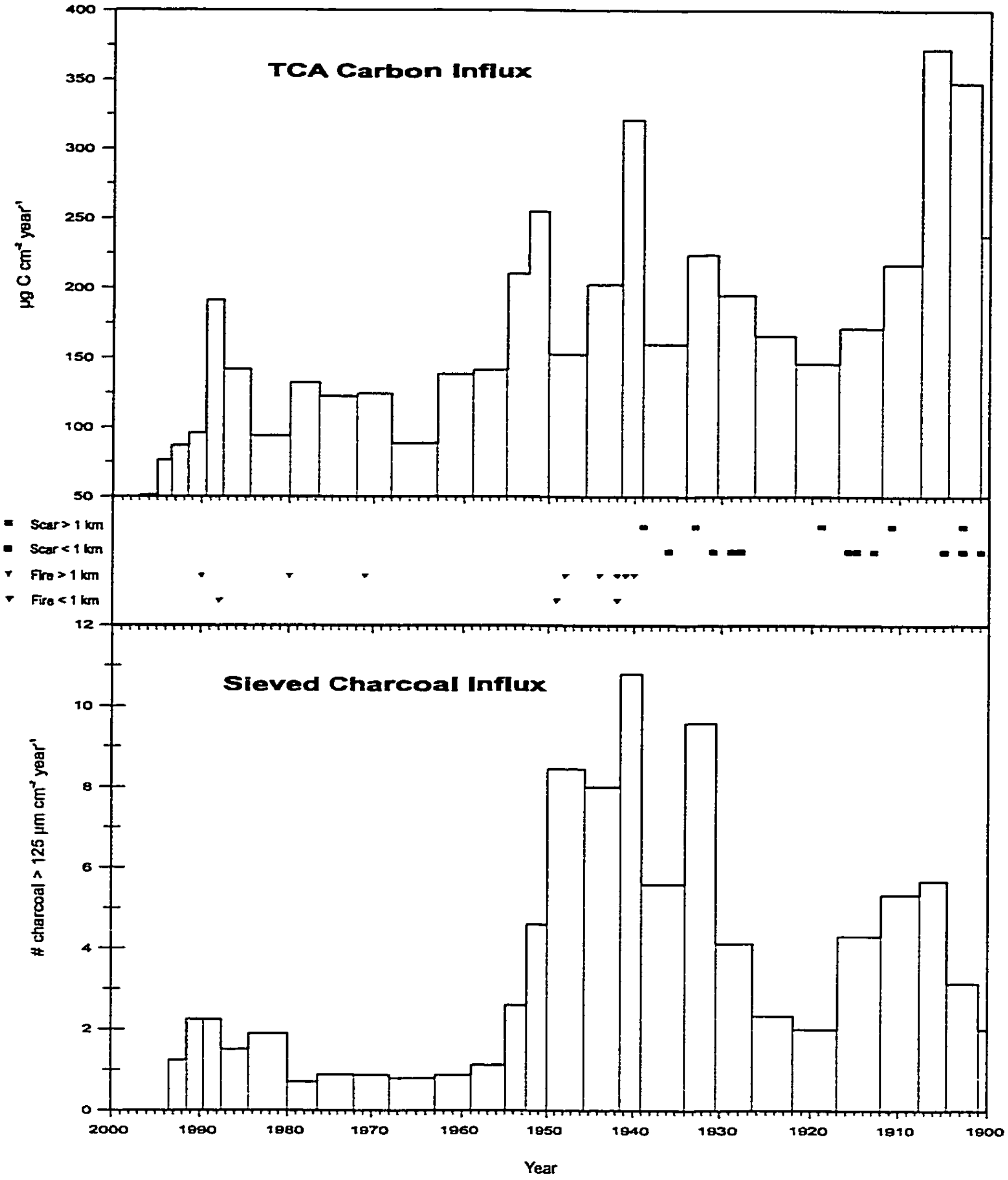


Figure 2-4: Known fire activity since 1900 compared with the charcoal curve extracted by the sieving method and the carbon curve extracted by the TCA method.

2.6 References

Alberta Environmental Protection, 1994. Natural regions and subregions of Alberta: summary. Alberta Environmental Protection, Edmonton.

Arno, S.F., Sneck, K.M., 1977. A method for determining fire history in coniferous forests of the mountain west. USDA Forest Service General Technical Report INT-42.

Bradford, M.E., 1990. Athabasca River Basin: Christina Lake. In: Mitchell, P., Prepas, E. (Eds.), Atlas of Alberta lakes. University of Alberta Press, Edmonton, pp. 136-139.

Campbell, I.D., and Flannigan, M.D. 2000. Long-term perspectives on fire-climate-vegetation relationships in the North American boreal forest. In: Kasischke, E.S., Stocks, B.J. (Eds.), Fire, climate change, and carbon cycling in the boreal forest. Springer, New York, pp. 151-172.

Clark, J.S., 1988. Particle motion and the theory of charcoal analysis: source area, transport, deposition, and sampling. Quaternary Research, 30: 67-80.

Clark, J.S., Patterson, W.A., III, 1997. Background and local charcoal in sediments: Scales of fire evidence in the paleorecord. In: Clark, J.S., Cachier, H., Goldammer, J.G., Stocks, B.J. (Eds.), Sediment records of biomass burning and global change. NATO ASI Series. Series I: Global Environmental Change. Springer-Verlag, Berlin, pp. 23-48.

Clark, J.S., Robinson, J., 1993. Paleoecology of Fire. In: Crutzen, P.J., Goldammer, J.G. (Eds.), Fire in the environment: the ecological, atmospheric, and climatic importance of vegetation fires. John Wiley and Sons, Ltd., New York, pp. 193-214.

Delisle, G.P., Hall, R.J., 1987. Forest fire history maps of Alberta, 1931-1983. Canadian Forestry Service, Northern Forestry Centre, Edmonton, Alta.

Garstang, M., Tyson, P.D., Radke, L., 1997. Atmospheric transports of particulate and gaseous products by fires. In: Clark, J.S., Cachier, H., Goldammer, J.G., Stocks, B.J. (Eds.), Sediment records of biomass burning and global change. NATO ASI Series. Series I: Global Environmental Change. Springer-Verlag, Berlin, pp. 207-250.

Jacobson, G.L., Jr., Bradshaw, R.H.W., 1981. The selection of sites for paleovegetational studies. Quaternary Research, 16: 80-96.

MacDonald, G.M., Larsen, C.P.S., Szeicz, J.M., Moser, K.A., 1991. The reconstruction of boreal forest fire history from lake sediments: a comparison of charcoal, pollen, sedimentological, and geochemical indices. Quaternary Science Reviews, 10: 53-71.

Millspaugh, S., Whitlock, C., 1997. The Oregon Sieving Method. Unpublished material given out to participants of a charcoal workshop held in June, 1997, University of Oregon.

Novakov, T., Cachier, H., Clark, J.S., Gaudichet, A., Macko, S., Masclet, P., 1997. Characterization of particulate products of biomass combustion. In: Clark, J.S., Cachier, H., Goldammer, J.G., Stocks, B. (Eds.), Sediment Records of Biomass Burning. NATO ASI Series I: Global Environmental Change. Springer-Verlag, Berlin, pp. 117-143.

Patterson, W.A., III, Edwards, K.J., Maguire, D.J., 1987. Microscopic charcoal as a fossil indicator of fire. Quaternary Science Reviews, 6: 3-23.

Payette, S., 1992. Fire as a controlling process in the North American boreal forest. In: Shugart, H., Leemans, R., Bonan, G.B. (Eds.), A systems analysis of the global boreal forest. Cambridge University Press, pp. 144-169.

Petterson, G., 1996. Varved sediments in Sweden: a brief review. In: Kemp, A.E.S. (Ed.), Palaeoclimatology and palaeoceanography from laminated sediments. Geological Society Special Publication No. 116. The Geological Society, London, pp. 73-77.

Rhodes, A.N., 1998. A method for the preparation and quantification of microscopic charcoal from terrestrial and lacustrine sediment cores. The Holocene, 8(1): 113-117.

Rowe, J.S., Scotter, G.W., 1973. Fire in the boreal forest. Quaternary Research, 3: 444-464.

Singh, G., Kershaw, A.P., Clark, R., 1981. Quaternary vegetation and fire history in Australia. In: Gill, A.M., Groves, R.H., Noble, I.R. (Eds.), Fire and the Australian Biota. Australian Academy of Science, Canberra, pp. 23-54.

Sugita, S., 1994. Pollen representation of vegetation in Quaternary sediments: theory and method in patchy vegetation. Journal of Ecology, 82: 881-897.

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

Tolonen, K., 1986. Charred particle analysis. In: Berglund, B.E. (Ed.), Handbook of Holocene palaeoecology and palaeohydrology. John Wiley and Sons, New York, pp. 485-496.

Varem-Sanders, T.M.L., Campbell, I.D., 1996. DendroScan: a tree-ring width and density measurement system, Canadian Forest Service, Northern Forestry Centre.

Walling, D.E., He, Q., 1993. Towards Improved Interpretation of 137Cs profiles in lake sediments. In: McManus, J., Duck, R.W. (Eds.), Geomorphology and sedimentology of lakes and reservoirs. John Wiley & Sons Ltd., Toronto, pp. 31-53.

Weber, M.G., Flannigan, M.D., 1997. Canadian boreal forest ecosystem structure and function in a changing climate: impact on fire regimes. Environmental Reviews, 5: 145-166.

Wein, R.W., de Groot, W.J., 1996. Fire - climate change hypotheses for the Tiaga. In: Goldammer, J.G., Furyaev, V.V. (Eds.), Fire in ecosystems of boreal Eurasia. Kluwer Academic Press, The Netherlands, pp. 505-512.

Wein, R.W., MacLean, D.A. (Eds.), 1983. The role of fire in northern circumpolar ecosystems. John Wiley and Sons, New York.

Whitlock, C., Millspaugh, S.H., 1996. Testing the assumptions of fire-history studies: an examination of modern charcoal accumulation in Yellowstone National Park, USA. The Holocene, 6(1): 7-15.

Winkler, M.G., 1985. Charcoal analysis for paleoenvironmental interpretation: a chemical assay. Quaternary Research, 23: 313-326.

CHAPTER 3

~940-year fire history from Christina Lake, Alberta[1]

3.1 Introduction

Canada's boreal forest is a fire-dependent biome (Johnson 1992; Payette 1992; Rowe and Scotter 1973; Wein and MacLean 1983) and understanding the interactions among fire, vegetation and climate is integral to understanding the boreal ecosystem. Palaeofire studies can provide information about past fire regimes which is important to forest managers and park personnel who wish to implement policies and practices which emulate natural disturbances in their efforts to manage the forest in a sustainable manner or to conserve the forest in a "natural" condition. Palaeofire studies can also indicate fire and vegetation responses to past climate changes (Campbell and Flannigan 2000; Clark and Robinson 1993). This information is increasingly important as concern over future global climate change escalates. Current climate change models suggest that global warming may dramatically alter the fire regime of the boreal forest (Bergeron and Flannigan 1995; Weber and Flannigan 1997; Wotton and Flannigan 1993). If so, the changed fire regime is expected to have a much greater impact on the boreal forest than will the direct effects of climate warming alone (Weber and Flannigan 1997; Wein and de Groot 1996).

Proxy indicators of palaeofire include fire-scarred trees, stand origin dates, and charcoal deposits in lake sediments, peats, or soils. Dendrochronological fire studies based on stand origin dates and fire-scars provide excellent temporal and spatial resolution but are limited by the longevity of trees. In the western boreal, for example, most fire scars are found on jack pine (*Pinus banksiana* Lamb.) trees which have a maximum life span of ~150 years (Farrar 1995). A much longer time span (100s to 1000s of years) is required to study the response of fire regimes to past climate changes. For such long-term studies, annually-laminated (varved) lake sediments provide ideal study sites for palaeofire histories based on stratigraphic charcoal (Clark 1990; Cwynar 1978; Patterson et al. 1987; Swain 1973,1978; Tolonen 1986). These sites not only provide a chronology for the study, but the lack of sediment mixing allows good temporal resolution in the charcoal signal from which fire events can be determined.

To date, very few high-resolution palaeofire studies spanning long time scales have been done in the boreal forest of Canada (eg., Bergeron et al. 1998; Larsen and MacDonald 1998a, 1998b). In the western boreal, a number of studies spanning most or all of the Holocene have been done on lake sediments or peat and several of these also included charcoal analysis (Earle et al. 1996; Hickman et al. 1990; Hu et al. 1993, 1996; Kuhry 1994; MacDonald 1987; Nicholson and Vitt 1990). The temporal resolution of these studies, however, is too low to illuminate changes in fire regimes over the last millennium. Several high-resolution shorter-term fire history studies have also been completed in the western boreal forest (Campbell and

Flannigan 2000; Carroll and Bliss 1982; Larsen 1997; Weir and Johnson 1998) and adjacent biomes (Johnson and Fryer 1987; Johnson and Larsen 1991; Johnson and Wowchuk 1993; Masters 1990). These studies, however, only illuminate the fire regimes of the last few hundred years. The only high-resolution palaeofire studies in the western boreal forest which extend more than 500 years into the past are those done by Larsen and MacDonald (1998a, 1998b) in and near Wood Buffalo National Park and Campbell and Campbell (In Press) in Elk Island National Park, which lies in the transition zone from Aspen Parkland to Boreal Forest. A multi-proxy study from Pine Lake, Alberta (in the Aspen Parkland) has also recently been completed (Campbell et al. In Press), and a charcoal-based study is currently underway by Zutter, Schindler and Campbell in the subalpine forest of Jasper National Park.

The past millennium included fluctuations in regional climate which may have impacted the fire regime of the western boreal forest. A generally cool period (with intervals of warmer climate) often called the "Little Ice Age" occurred from approximately 1550-1850 (Bradley and Jones 1992; Lamb 1977). Regional evidence based on tree-ring studies from the Rocky Mountains (Luckman et al. 1997) and the northern tree-line (Jacoby and D'Arrigo 1989; Overpeck et al. 1997) shows that, in Canada, the coldest phase of this period occurred during the early to mid-1800s which coincides with maximum glacier advances in the Rocky Mountains (Luckman 1997). Sedimentological evidence also suggests wetter conditions in Alberta during the Little Ice Age (Campbell 1998; Vance et al. 1992). There is also regional evidence for a warmer drier period often called the "Medieval Warm Period" or the Little Climatic Optimum (Hughes and Diaz 1994) which preceded the Little Ice Age from ~900-1300 AD. Campbell (1998) found evidence for relatively dry conditions from ~800-1300 AD in Pine Lake, Alberta. Further to the south, Vance et al.(1992) found evidence for prolonged periods of severe drought alternating with wetter intervals from 1000 to 600 years B.P at Chappice Lake, Alberta. Luckman (1994; 1997) also reports evidence for a higher treeline in the Rocky Mountains from the 14th to 17th centuries and ~1000 AD and warmer temperatures 1073-1110 AD and 1350-1440 AD.

Here, we present a 937-year palaeofire study based on charcoal extracted from the annually laminated sediment of Christina Lake in the boreal forest of Alberta. The palaeofire signal is compared with pollen results and to basic geochemical analysis of the sediment. The objectives of the study were: 1) to determine fire return intervals over the last millennium; 2) to ascertain whether the climatic shifts of the last millennium were sufficient to impact the fire regime; 3) to determine whether vegetation changed significantly over the last millennium; and 4) to determine whether a proxy climate signal could be extracted from basic geochemical characteristics of the sediment.

3.2 Study Site

Christina Lake (55° 37' N, 110° 57' W) is located in northern Alberta, Canada (Figure 3-1). The lake is large (2130 ha) with six permanent inflowing streams and a drainage basin of 1250 km^2. The morphology of the lake is long and narrow reaching a maximum length and width of approximately 13 km and 2 km respectively. The eastern and western basins are joined by a narrow (~97 m) shallow (< 2 m) constriction. The western basin is the deepest reaching a maximum depth of ~33 m and here the sediments are laminated. Most of the lake basin has steeply sloping sides and there are only isolated pockets of littoral areas (Bradford 1990) which may potentially trap charcoal before it reaches the profundal sediments.

The lake lies within the Central Mixedwood Subregion of the Boreal Forest Natural Region (Alberta Environmental Protection 1994). This subregion is characterized by a mosaic of deciduous and coniferous trees (occurring in pure or mixed stands) and extensive peatlands. Dominant soils are Gray Luvisols and Eutric Brunisols on upland sites and Organic and Gleysolic soils in poorly drained areas. The climate is subhumid continental with short cool summers (average May-September temperature is 12 °C) and long cold winters. Average annual precipitation is 380 mm. Most precipitation occurs in June and July and winters are relatively dry (Alberta Environmental Protection 1994).

The drainage basin of the lake consists of level to gently rolling terrain overlying a thick mantle (up to 150 m) of glacial till and channel fill materials. The underlying bedrock consists of deltaic to marine sandstone, siltstone and mudstone of the Mannville Group to a depth of ~400 m. Paleozoic carbonates occur below ~400 m (Van Horne, 1998). Vegetation in the watershed is largely dominated by peatlands with black spruce (*Picea mariana* (Mill.) BSP) and larch (*Larix laricina* (Du Roi) Koch) as the dominant trees. Vegetation on upland sites includes trembling aspen (*Populus tremuloides* Michx.), white spruce (*Picea glauca* (Moench) Voss), jack pine (*Pinus banksiana* Lamb.), birch (*Betula papyrifera* Marsh) and balsam poplar (*Populus balsamifera* L.).

Human impact on the area was minimal until oil and gas exploration began in the region in the mid-1980s. The hamlet of Conklin (population 205) is located immediately west of the lake but other than a recreational lodge and campground on the north shore at the western end of the lake, there is no other shoreline development (Bradford 1990). The lake has been accessible by an all-weather road only since 1986. The nearest large population centres are Fort McMurray 125 km to the north and Lac La Biche 110 km to the south.

3.3 Methodology

3.3.1 Core Retrieval and Sampling

Two cores of laminated sediment were retrieved using a box-type freeze-corer (Swain 1973) at a water depth of approximately 30 m. One core included the water/sediment interface and penetrated to a depth of ~100 cm while the other core was buried below the water/sediment interface and retrieved sediment from ~57 cm to ~174 cm depth. The two cores were correlated using several distinct marker horizons consisting of unusually thick white diatomaceous laminae. Judged on the basis of crust thickness and regularity of laminations, the best faces of each core were selected for sampling. Two faces of core 1 were sampled (the upper 79 cm of face "A" and the lower 21 cm of face "B") and a single face of core 2. The sediment was cut into contiguous 1 cm strips parallel to the plane of deposition and stored in a freezer in airtight plastic bags. Before sub-sampling for various analyses, the sediment was thawed and homogenized by gently stirring with a glass rod.

3.3.2 Core Dating

The laminations were examined under a stereoscope at 50x magnification and were found to be similar to those described from other varved lake sediments (O'Sullivan 1983; Petterson 1996) and consistent with an annual deposition cycle. Typically, a thicker (1-1.5 mm) light-coloured layer consisting of a mixture of silt, diatoms, and organic material (representing spring to autumn) alternated with a thinner (< 1 mm) dark layer consisting of very fine organic material (deposited while the lake was frozen over in winter). The light layer sometimes included a white band of pure diatoms representing an algae "bloom" in the spring or autumn. Each couplet of a light layer (with or without a diatom bloom) and a dark layer was assumed to be a true varve (i.e. to represent one year of deposition) and the cores were dated by varve counting. The number of varves in each 1 cm interval ranged from 1 to 10 with an average of ~4.5.

Independent confirmation of the annual nature of the laminations was given by ^{137}Cs dating (Laird and Campbell In Press)(see Appendix 1). Contiguous 1 cm samples from the upper 20 cm of core 1 were analysed for radioactive cesium content. The greatest cesium activity occurred in the sample containing sediment deposited in the years 1963 to 1967 as determined by the varve count. This is consistent with the peak in ^{137}Cs fallout in the northern hemisphere (due to the atmospheric testing of nuclear weapons) in 1963 (Walling and He 1993).

3.3.3 Basic Geochemical Analyses

3.3.3.1 Sediment Influx

Samples of known volume were oven-dried overnight at 105 °C in tared crucibles. These were removed to a dessicator, cooled to room temperature and reweighed. The oven-dry weight for each sample was divided by the number of varves counted in the 1 cm interval from which the sample was taken to obtain the total sediment influx in g cm^{-2} yr^{-1}.

3.3.3.2 Organics, Carbonates, and Ash

Following the procedure described by Dean (1974), oven-dry samples of known volume were weighed then ignited at 550 °C in a muffle furnace for 1 hour, removed to a dessicator, cooled and reweighed. The difference between oven-dry weight and post-ignition weight represents the organic matter in the sediment. The same samples were ignited again at 1000 °C for 1 hour, cooled in a dessicator and reweighed. The difference between the post-550 °C weight and the post-1000 °C weight represents mainly the CO_2 evolved from carbonates, which when divided by .44 (the fraction of CO_2 in calcium carbonate) represents the amount of carbonate in the sediment (assuming all carbonate is calcium carbonate). The remaining ash is dominantly silicates, including non-carbonate clastic materials and diatom frustules.

3.3.4 Determination of Near Shore Fire Activity

Recent fire activity near the lake was determined mainly from Delisle and Hall's (1987) study of fires > 200 ha occurring between 1931 and 1983 in Alberta. The first fire reported in this study for the Christina Lake region occurred in 1940 but the authors caution that fires occurring in more remote areas were under-reported in the early years of their study period. For this study, the information obtained from Delisle and Hall was assumed to be accurate in the Christina Lake area only from 1940 to 1983. These data were supplemented by fire records (1961- 1995) from the Conklin Fire Tower located 8 km immediately west of Christina Lake to obtain information on fires > 200 ha since 1983 (Rick Strickland, pers. comm.; Peter Englefield, pers. comm.).

To obtain information on older fires, fire scars were collected from jack pine trees in accessible stands within 5.5 km of the lake shore. Disks, wedges or cores were collected from scarred trees at 30 cm above the ground (Arno and Sneck 1977). A total of 30 fire scars were obtained from fourteen different sites. Fire scars were dated using DendroScan software (Varem-Sanders and Campbell 1996) to count and, where necessary, cross date the annual tree rings. Samples too fragile to survive processing for DendroScan were planed with a razor blade and the rings were counted under a stereo microscope at 50x magnification.

3.3.5 Charcoal Extraction

A wet sieving method (Millspaugh and Whitlock 1995; Whitlock et al. 1997; Whitlock and Millspaugh 1996) was used to extract the charcoal from the sediment as previously described by Laird and Campbell (In Press). Known volumes of sediment (in most cases 2 ml) were soaked in a sodium polyphosphate-based water softening agent (i.e., Calgon) for several days to deflocculate the sediment. Each sample was then very gently washed through nested sieves with mesh openings of 125 μm and 250 μm. The material retained on each screen was washed onto filter paper and examined under a stereo microscope at 25x to 50x magnification. All charcoal particles were tallied. Although separating the sediment into two size fractions facilitated counting, very few charcoal particles > 250 μm were found. Totals from both size fractions were added together and expressed in terms of number of fragments > 125 μm per cc of sediment. The results were then divided by the number of varves in each 1 cm segment of the core to obtain the influx (number of charcoal fragments cm^{-2} yr^{-1}). Although areal estimates are often done to give larger (and presumably more local) particles more weight when counting charcoal on pollen slides (Patterson et al. 1987), areal estimates were deemed unnecessary in this study since only the larger particles were retained.

In a previous study (Laird and Campbell In Press), the charcoal signal obtained by the sieving method was compared to the carbon signal obtained using an acid digestion and ignition method modified from Winkler (1985) and to known fire activity near Christina Lake since 1900. The results showed that the carbon signal was slightly more sensitive than was the sieved charcoal signal for detecting fires in the watershed that did not burn to shore. Neither signal detected fires burning outside the watershed (including a 137 313 ha fire 17 km east of the lakeshore). The carbon curve, however, was highly correlated ($r^2 = .86$) with sediment influx suggesting that this signal is dominated by streamborne charcoal and thus is highly dependent on precipitation. Because some of the charcoal included in the carbon signal may be reworked older material brought in during periods of high stream flow, it is not presented here. The sieved charcoal curve is not correlated with sediment influx ($r^2 = .04$).

3.3.6 Determination of "Significant" Fire Periods

Distinguishing "significant" fire periods from "background" levels of charcoal influx was done using threshold values (Clark 1990; Millspaugh and Whitlock 1995). Two thresholds were chosen by comparing the charcoal curve with known fire activity near the lake (see below). One threshold was low enough to include all peaks corresponding to known fires (> 200 ha) near the lake. A second higher threshold was chosen to include only those peaks corresponding to known fires in which a large proportion of the charcoal catchment was burned. In other studies, large peaks in charcoal influx have been shown to represent fire periods in which large areas were burned (Earle et al. 1996; Millspaugh and Whitlock 1995) although factors other than fire size, such as fire intensity, distance to shore, wind speed and wind direction may also play a role (Earle et al. 1996).

When calculating fire return intervals, fire periods prior to 1940 were dated by assuming the fire occurred in the first (oldest) year of the sample in which the charcoal peak occurred. From 1940 onward, the fire period was dated using the year of the oldest known fire (based on fire tower records and Delisle and Hall, 1987) included in the sample in which the charcoal peak occurred. The assignment of charcoal peaks to the oldest dates rather than the median dates for each sample is to account for possible lags in charcoal transport/deposition in the profundal sediments following a fire (Bradbury 1996; Whitlock et al. 1997; Whitlock and Millspaugh 1996)

3.3.7 Pollen Analyses

A total of 28 samples were chosen for pollen analysis. Samples were chosen from various intervals of the core to ensure that the vegetation from each climatic period was represented. The average time interval between pollen samples was 29 years (maximum 68.5 years). The pollen samples included a small subset of samples chosen from before and after 4 large fire periods to determine if post-fire vegetation changes could be detected in the pollen signal from this large lake.

Samples of known volume were processed using standard techniques as given in Faegri et al. (1989). A *Lycopodium* spike was used and samples were mounted in glycerine or glycerine jelly. A minimum of 300 upland grains were counted per sample on a stereo microscope at 200x magnification.

For pre- and post-fire sample sets, spruce:sprouter ratios were calculated modified after the conifer:sprouter method described by Swain (1973). Sprouter species were considered to be *Populus* spp., *Betula* spp., *Salix* spp., *Alnus* spp., *Corylus cornuta* Marsh., and Gramineae. The post-fire samples were selected to be ~5-15 years after the fire to allow sprouter species to mature enough to produce pollen while ensuring that regenerated spruce would not yet be producing pollen (abundant pollen production in both black and white spruce does not occur until at least 30 years of age (Nienstaedt and Zasada 1990; Viereck and Johnston 1990)). Pine:spruce ratios were also calculated for all pollen samples.

3.4 Results

3.4.1 Basic Geochemical Analyses

The sediment influx curve is shown in Figure 3-2 along with concentrations of organic matter, ash (dominantly non-carbonate clastics), and carbonates. The sediment influx curve shows three broad phases. A long period of generally low influx (with spikes of higher influx) occurred from 1044 to ~1580 AD (especially ~1150 to ~1400). This was followed by a long period of relatively high influx from ~1580 to ~1850 AD (especially ~1700 to ~1850). After ~1850, the influx again dropped to generally low values (although with a few large spikes). The sediment influx is dominated by non-carbonate clastic material ($r^2 = .98$). This makes it useful as an indirect proxy indicator for precipitation since clastic inputs to the lake increase with increased stream discharge and velocity which are in turn dependent on precipitation. Wave action, however, also plays a role in the deposition and resuspension of material in the lake basin (Håkanson and Jansson 1983). Some increase in sediment influx due to erosion after certain fire events is also possible, although most of the area has very low relief with low erosive potential.

During the first phase of generally low sediment influx (and therefore probably relatively dry climate) from 1044 to approximately 1580, diatom blooms were relatively frequent and the varves were regular and distinct (Laird and Campbell In Prep) suggesting very stable thermal stratification, an indication of relatively warm and/or long summers. Relatively high carbonate values over this interval can also suggest warmer and/or longer summers since carbonate precipitation in the water column increases with increasing water temperature and with greater lake productivity (Håkanson and Jansson 1983; Kelts and Hsu 1978). While the amount of carbonates finally buried in the sediment can be affected by other factors, such as pH and decomposition rate (Dean 1998; Håkanson and Jansson 1983), the relatively high values over this interval suggest relatively warm summer temperatures if all other factors remained fairly constant (Håkanson and Jansson 1983; Kelts and Hsu 1978).

The second phase from ~1580 to ~1850 AD (Little Ice Age) showed much higher sediment influx values suggesting this interval was much wetter than the preceding one. This agrees with other regional proxy climate signals (Campbell 1998; Vance et al. 1992) which also indicated that this time period was relatively wet. The decreasing carbonate values suggest this time interval was cooler as well culminating in very low values in the early 1800s coincident with the coldest phase of the Little Ice Age. From ~1700 to ~1850, diatom blooms were infrequent, many of the varves were less distinct and some sections showed evidence of increased turbulence (such as shell hash and disturbed laminations) suggesting less stable meromixis which may be indicative of cooler and/or shorter summers, increased turbulence due to increased stream inflow, or less stable anoxia due to decreased lake productivity (Laird and Campbell In Prep).

The most recent interval from 1850 to 1996 AD appears to be a return to warmer drier conditions as sediment influx decreased while carbonate values increased. A return to drier conditions after 1850 is also shown in the proxy climate signals from Alberta (Campbell 1998; Vance et al. 1992) and a warming trend over this interval has been shown in other studies (eg., Luckman et al. 1997; Overpeck et al. 1997).

Organic influx (not shown) to the lake was highly correlated with sediment influx (r^2 = .81) although not as highly correlated as was ash influx (not shown, r^2 = .98). This suggests that the majority of organic material deposited in the lake is allochthonous (i.e. not produced within the lake itself) which makes it difficult to use organic concentration (Figure 3-2) to gauge changes in lake productivity over time which may be linked to climate. There was, however, a noticeable drop in the concentration of organics in the early to mid-1800s. This drop may be partially due to decreased lake productivity, but increased clastic inputs due to increased erosion over this wet interval would have reduced the proportion of organic matter in the sediment as well. The increase in organic concentration from the late 1800's to 1996 may be due to a combination of several factors: 1) incomplete decomposition of recently deposited organic material; 2) anthropogenic inputs; and 3) decreased clastic inputs due to drier conditions (and resulting in corresponding increases in organic concentration due to universal closure of percentages).

3.4.2 Paleofire Signal and Fire Return Intervals

A map of fires > 200 ha since 1940 is shown in Figure 3-3 along with fire scar results (inset). A comparison of the sieved charcoal curve (Figure 3-4) with the known fire history has been discussed in a previous study (Laird and Campbell In Press). The results showed that large fires reaching the shore (eg. 1949) were represented by high charcoal influx values while smaller shore fires (eg. 1988) were represented by only small increases in charcoal influx. Fires that did not burn to shore were less consistently represented in the charcoal curve. The 1980 fire resulted in only a minor charcoal peak and the 1971 fire did not show at all. Due to the sampling interval, continued influx from the 1930's fires and the close timing of the 1940, 1941 and 1942 fires, it was difficult to determine how the 1940 and 1941 non-shore fires influenced the charcoal curve. The charcoal influx for the 1 cm sample containing the years 1940 and 1941 was very high but this sample also contained part of the sediment influx from the 1942 shore fire. To try to resolve these fires, sediment peels of the varves spanning this interval were examined and they showed that while several charcoal fragments were present in the 1940 varve, they were much more abundant in the 1941 and 1942 varves. This suggests that both the 1941 and 1942 fires resulted in significant charcoal influx to the lake (assuming that the varve count is correct) while the impact if the 1940 fire was less.

The charcoal curve is thus assumed to represent a minimum estimate of the local fire activity (large fires only) for the Christina Lake watershed out to ~4 km from the lake shore (a total area of ~22 000 ha excluding the lake itself) while best representing large fires which burn right to the shore. Fires occurring within a few years of each other are indistinguishable in the charcoal record due to the combination of the sampling interval (avg. ~4.5 years) and the possibility of charcoal from a single fire being deposited over several years (Bradbury 1996; Whitlock et al. 1997; Whitlock and Millspaugh 1996). Since peaks in the charcoal record may represent more than one fire, they will be referred to henceforth as corresponding to fire periods rather than fire events.

The mean charcoal influx was 4.25 particles cm^{-2} yr^{-1} with a standard deviation of 3.25 particles cm^{-2} yr^{-1}. Charcoal maxima above a threshold of 1.5 particles cm^{-2} yr^{-1} were considered to represent fire periods within the charcoal catchment. Based on this criterion, 48 fire periods occurred from 1057 to 1994 (Figure 3-4). The average fire return interval from the first fire period in 1083 to the last fire period in 1988 was ~19 years (min. = 7.5 max. = 44). Charcoal maxima above a threshold of 7 particles cm^{-2} yr^{-1} were considered to represent large fire periods in which a significant proportion of the charcoal catchment was burned. There were

22 large fire periods from the first large fire period in 1083 to the last large fire period in 1949 with an average return interval of ~41 years (min. = 7.5 max. = 130).

The average fire return interval fluctuated somewhat over time and the trends were similar whether all fire periods or only large fire periods were considered. From 1083 to 1490 AD the average return interval for large fire periods was ~68 years (min. = 44 max. = 91.5). The return interval shortened to 29 years (min. = 13 max. = 77) between 1490 and 1723 (which includes the first half of the Little Ice Age). There were no large fire periods between 1723 and 1853 (130 years). From 1853 to the last large fire period in 1949, the return interval averaged ~16 years (min. = 7.5, max. = 50.5) but this was due to pulses of fire events spaced only a few years apart. Some of these fires could have been caused by human activity (for example, the 1941 and 1949 fires were human-caused: Delisle and Hall, 1987). No large fire periods have occurred in the Christina lake area from 1950 to the present.

3.4.3 Pollen

Pollen percentage results (Figure 3-5) indicate that the floristic composition of the surrounding vegetation remained fairly constant over the time period studied. There were, however, some shifts in the relative abundances of several species over certain time intervals. The most significant change occurred in the relative abundance of pine pollen in the 1797 and 1853 samples. In all other samples, the average pine to spruce ratio is 2.18 (standard deviation .52) but in the 1797 sample, the pine:spruce ratio dropped to 0.7 and recovered somewhat to 1.07 by 1853. An anomalously low pine influx over a similar time interval was also noted by Larsen and MacDonald (1998b). *Populus* spp. and *Corylus cornuta* Marsh. pollen were also consistently slightly more abundant prior to 1250 suggesting a higher deciduous component in the mixedwood forest at that time.

Pollen influx is shown in Figure 3-6. Analysis of the 4 pre- and post-fire sets of samples for large fire periods showed that the total pollen influx after the fire was significantly lower than the pre-fire influx (paired t-tests, $p=.04$). This suggests that these fires were of sufficient size to significantly affect the pollen influx into the lake. The pollen dispersal model developed by Sugita et al. (1997) suggests that a fire (or other disturbance) must be at least 8 times larger than the lake and burn to within a few hundred meters of shore before the pollen rain was significantly affected. Applying these findings to Christina Lake (2130 ha) means that only near shore fires > ~17 000 ha will produce any noticeable changes in pollen inputs.

Comparison of the spruce:sprouter ratios before and after the 4 large fire periods showed that while the post-fire ratio was lower for 3 of the 4 cases, the changes were insignificant (paired t-tests, $p=.35$). These results are consistent with the findings of the model developed by Sugita et al. (1997) which showed that changes in post-fire pollen percentages were extremely subtle, especially for large lakes. The largest lake in their model was 400 ha and a 2500 ha fire (8 times larger than the lake) right on the lake shore produced changes in post-fire pollen percentages of only 5-10% from pre-fire levels. Christina Lake is 5 times larger and its pollen inputs should therefore be dominated by regional pollen sources to an even greater extent (Jacobson and Bradshaw 1981), so it is not surprising that no significant changes in post-fire pollen percentages were found.

3.5 Discussion

Comparison of the prehistoric paleofire signal from Christina Lake to the general proxy climate signal inferred from sedimentological analyses of Christina Lake and other regional studies (Campbell 1998; Vance et al. 1992) indicates that generally warm/dry or cool/wet conditions do not always lead to greater or lesser fire activity respectively. The shortest average return interval between large fire periods in the prehistoric period occurred between ~1490 and 1723 (~29 years) which included the moister climate of the early Little Ice Age, while the drier period prior to 1490 experienced longer average fire return intervals (~68 years). It must be borne in mind, however, that the general proxy climate signals for Christina Lake and other Alberta lakes do not yield information on the frequency or seasonal timing of the precipitation. Flannigan and Harrington (1988) analysed the relationship of precipitation to area burned by wildfire in Canada and found that months in which large areas were burned were dependent on the frequency of precipitation rather than the total precipitation amount. It may be, then, that although the total precipitation was higher during the early Little Ice Age, most precipitation could have occurred outside the fire season, or alternatively, the precipitation pattern during the fire season could have been characterized by infrequent high intensity rainfall events with intervening dry spells.

The shorter average fire return intervals in the early part of the Little Ice Age observed in this study have also been found in other regional fire history studies. Larsen and MacDonald's (1998a) 840-year paleofire study in Wood Buffalo National Park showed shorter fire return intervals between ~1550 and 1700 and longer return intervals before and after this time period. Similarly, the average fire return intervals from Fariya Lake just outside Wood Buffalo National Park were shorter between 1552 and 1680 and longer before and afterward (Larsen and MacDonald 1998b). Several studies in the Canadian Rocky Mountains also found shorter fire cycles from ~1500 to the mid-1700s and longer fire cycles afterwards (Johnson et al. 1990; Johnson and Larsen 1991; Johnson and Wowchuk 1993; Masters 1990). The dendrochronological studies from the mountains do not go back further than ~1500 so the fire cycles before the onset of the Little Ice Age are not known.

Johnson and Wowchuk (1993) noted the general synchroneity in the timing of the fire cycle changes in the mountain sites cited above and reasoned that such consistency over such a large region must be due to large-scale climatic factors. They showed that recent large fires in the mountains were related to persistent upper level ridges in the mid-troposphere which were in turn related to mid-tropospheric troughs over the northern Pacific Ocean. They suggest that the shift in the mid-1700's from shorter fire cycles to longer fire cycles may have been due to altered Northern Hemisphere atmospheric circulation patterns during the latter phase of the Little Ice Age which may have reduced the frequency of persistent upper ridges over the mountains. Large fires have often been linked to blocking upper level ridges in the mid-troposphere (50 kPa) (Flannigan and Harrington 1988; Johnson 1992; Newark 1975; Nimchuk 1983). These blocking ridges create high pressure systems at the surface which contain dry subsiding air which dries out forest fuels. When the ridge finally breaks down into a trough, a storm front is created which generates lightning (which may ignite the previously dried fuels), and high winds (which may enhance fire spread).

Lamb (1982) stated that, in Europe, the period from ~1550 to the 1700s was characterized by a "remarkable frequency" of blocking highs in more northerly latitudes resulting in severe storms and extremely variable weather. It seems reasonable to assume that the anomalies in the circulation pattern of the Northern Hemisphere that affected Europe during this time period may have created great variability and extremes in the Canadian climate as well.

It is perhaps not too surprising that the expression of these broad climatic patterns in the early Little Ice Age was similar in both the mountains and Christina Lake due to their reasonable proximity. The specific position of the lake relative to the mountains may also play a role. Mesoscale (100 to 1000 km) convective complexes move eastward from the Rocky Mountains creating bands of high lightning activity at ~100 km and ~200 km east due to leewave cyclogenesis. (Hudson 1997; Nash and Johnson 1996). Christina Lake lies within the second (smaller and weaker) band of high lightning occurrence (Nash and Johnson 1996) and thus some of the storms affecting the mountains may affect Christina Lake as well.

When compared to the average return intervals for large fires between 1853 and 1949 (~16 years) and 1490 to 1723 (~29 years), the average return interval for the period from 1083 to 1490 seems rather long at ~68 years. This may be a false impression, however. It may be that the longer fire return intervals over this period are more "normal" and that the shorter fire cycles during the first half of the Little Ice Age and between 1853 and 1949 were unusually short due to climatic anomalies (as discussed above) and anthropogenic factors respectively. In Wood Buffalo National Park, Larsen (1997) reported average fire cycles of 39 years for aspen stands and jack pine stands, 78 years for black spruce, and 96 years for white spruce stands for the period of 1750 to 1989. Since actual fire size is unknown for the older portion of the Christina Lake record, a true fire cycle cannot be calculated (Romme 1980). However, considering Larsen's data, an average return interval of ~68 years for large fires may not be unreasonably long given the mixture of forest types near the lake.

Even so, considering that the period between 1057 and 1490 appears to be dominated by warm and dry conditions including, perhaps, prolonged periods of severe drought prior to ~1300 (Vance et al. 1992), one may wonder why the average return interval for large fire periods wasn't a little shorter here. It may be that although total precipitation was very low, frequent low-intensity rainfall events occurred during the fire season. Alternatively, if prolonged droughts frequently occurred during this period as suggested by Vance et al.(1992), there may have been very little moisture in the atmosphere and so less convective activity, less lightning and fewer opportunities for ignition (Kerry Anderson, pers. comm.). Another alternative is that warmer and drier conditions may have promoted an increase in the proportion of deciduous species on upland sites which may have reduced the risk of fire spread (Forestry Canada Fire Danger Group 1992). The pollen results from Christina Lake showed small but consistent increases in *Populus* and *Corylus* pollen prior to ~1250 AD. As *Populus* pollen is preserved very poorly in lake sediments (Hadden 1978; Lichti-Federovich 1970), a small increase in pollen could represent a substantial increase in the number of trees on the landscape. Larson and MacDonald (1998a) also noted greater *Populus* pollen abundance between ~1250 and ~1550 and suggested it may have been caused by warmer drier conditions allowing aspen to increase at the expense of white spruce. Drier conditions, however, would have also lead to lower water tables in the peatland areas near Christina Lake and increased the risk of fire ignition and spread in those areas, so it is difficult to predict what the net effect on fire activity would have been.

Sedimentological evidence from Christina Lake and other regional studies (Campbell 1998; Vance et al. 1992) show that the latter phase of the Little Ice Age (~1700 - 1850) was very wet. The charcoal curve showed only "small" charcoal peaks between 1723 and 1853 suggesting that relatively small areas of the charcoal catchment were burned during this time period. Smaller fires would be consistent with the wetter climate as rising water tables would create ample fire breaks in the poorly drained peatland areas near the lake, increase paludification, and limit most fires to well-drained upland areas. Larsen and MacDonald's (1998a) results from Wood Buffalo National Park also indicate no fires between 1700 and 1805.

The decline in pine pollen from 1797 to 1853 in the Christina Lake record may also be due to the cold wet Little Ice Age climate. Larsen and MacDonald (1998a; 1998b) also found an unusual decline in pine pollen between 1790 and 1850 in Rainbow Lakes in Wood Buffalo National Park and between 1816 and 1861 at Fariya Lake (near Wood Buffalo National Park) so a climate-related cause seems most likely. It is not known whether there were actually fewer pine trees on the landscape at that time or whether pollen production per tree merely declined. A recent study on modern pollen rain in the boreal forest (Lee et al. 1996) showed that pine pollen production severely declined during cool humid weather so it may be that the climate at the end of the Little Ice Age was not conducive to pine pollen production. Alternatively, the climate may have been so wet during this time that the mortality of pine (which prefers well-drained sites) increased. Increased paludification may have also reduced the number of sites suitable for jack pine regeneration.

Another alternative is that a decline in fire disturbance may have adversely affected the number of pine regenerating in the landscape. The charcoal curve suggests that no large fire periods occurred between 1723 and 1853 -- a time span of 130 years which is close to the ~150 year maximum lifespan of jack pine (Farrar 1995). Pine has serotinous cones which require fire (or another heat source) to open the cone scales and release the seeds (Farrar 1995). With less fire disturbance, it is possible that the number of jack pine senescing and dying in the landscape was greater than the number of new jack pine regenerating after fire. The possibility of disease can also not be discounted.

If smaller fires and greater tree mortality occurred during the latter phase of the Little Ice Age, this would have lead to increased fuel buildup in the landscape. The frequent and apparently very large fires occurring in the late 1800's may therefore have been a result of the combination of a return to warmer, drier conditions and above average fuel loads which created a high fire hazard similar to the situation surrounding the 1988 fire in Yellowstone National Park (Millspaugh and Whitlock 1995).

Although climate appears to have been the dominant influence on fire activity near Christina Lake prior to 1900, it is possible that fires intentionally set by Aboriginal peoples played a role. Lewis (1982) states that the Cree people of northern Alberta frequently set fires to maintain meadows, enhance berry production and animal habitat, and keep traplines and travel routes open. These fires, however, were small (often <1 ha) and usually set in early spring when there were still snow patches in the forest to minimize the possibility of escape. The charcoal produced by these small fires would probably not be sufficient to significantly impact the charcoal curve for Christina Lake which is only sensitive to very large fires (> 200 ha).

The recent fire history (since 1900) is more difficult to interpret as some of these fires could have been human-caused. The 1941 and 1949 fires are known to have been caused by human activity (Delisle and Hall 1987). It is also possible that some of the fires in the early 1900s were related to railroad building in the area which began ca. 1915. The charcoal curve shows no large fire periods in the charcoal catchment from 1950 to 1994 (44 years) which is only slightly longer than the average for the entire period (~41 years) so it is not yet clear whether or not active fire suppression in the area is having a significant effect.

3.5 Summary and Conclusions

Basic geochemical analysis of the sediment from Christina Lake yielded a general proxy climate signal that was similar to those obtained from other regional sites. Sediment influx suggested wetter conditions between ~1580 to ~1850 AD (especially ~1700 to ~1850) and drier conditions before and after this interval while carbonate concentrations and other sediment characteristics suggested cooler conditions ~1580 to ~1850 AD and warmer conditions before and afterwards. While the pollen record shows the vegetation was relatively stable over the last millennium, declines in *Pinus* pollen and increases in *Populus* and *Corylus* occurred during cool/wet and warm/dry periods respectively. Charcoal evidence showed that fire return intervals varied over time apparently in response to climatic factors as the patterns were similar to those of other regional studies.

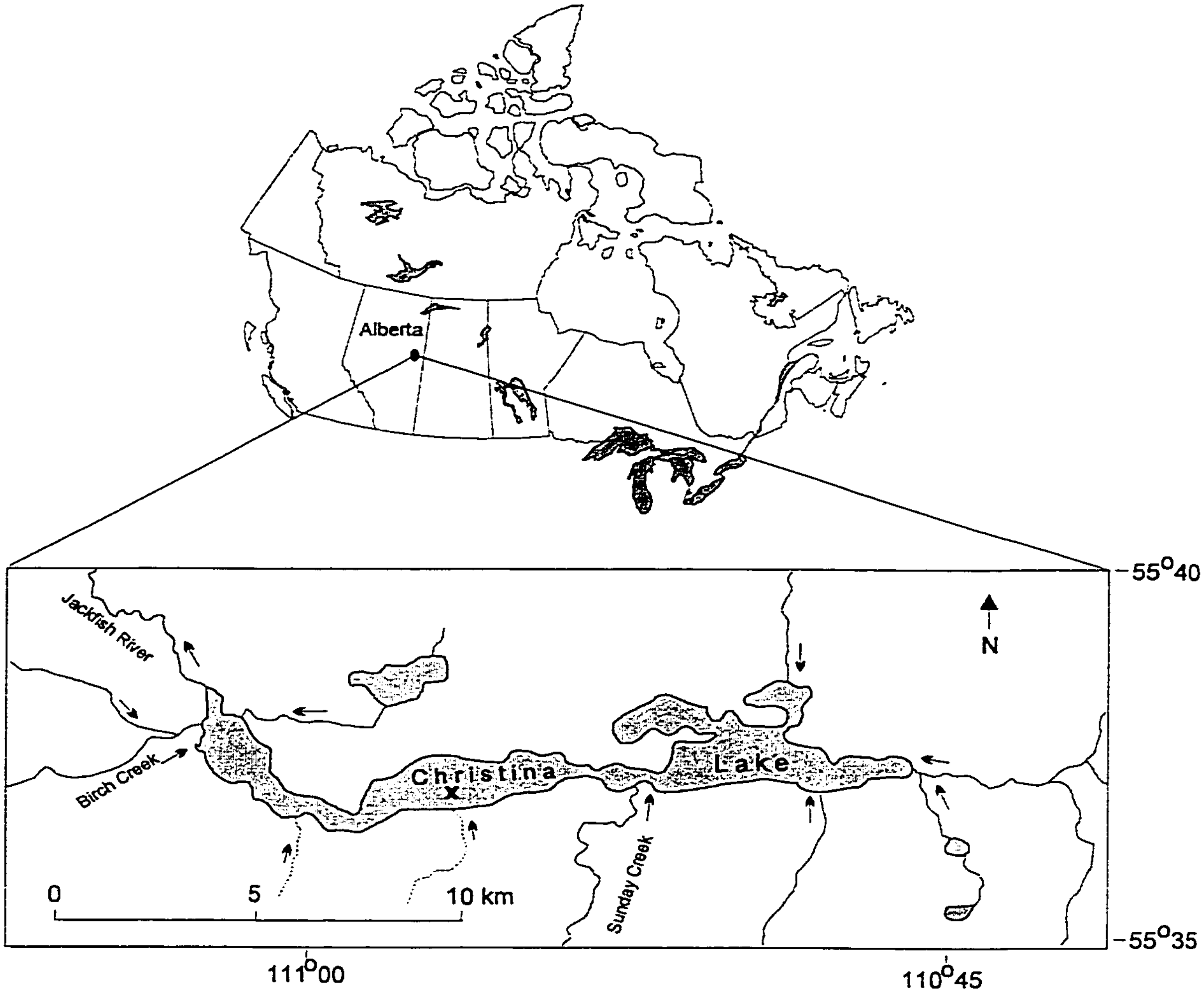


Figure 3-1: Location of Christina Lake. The coring site is marked with an "x".

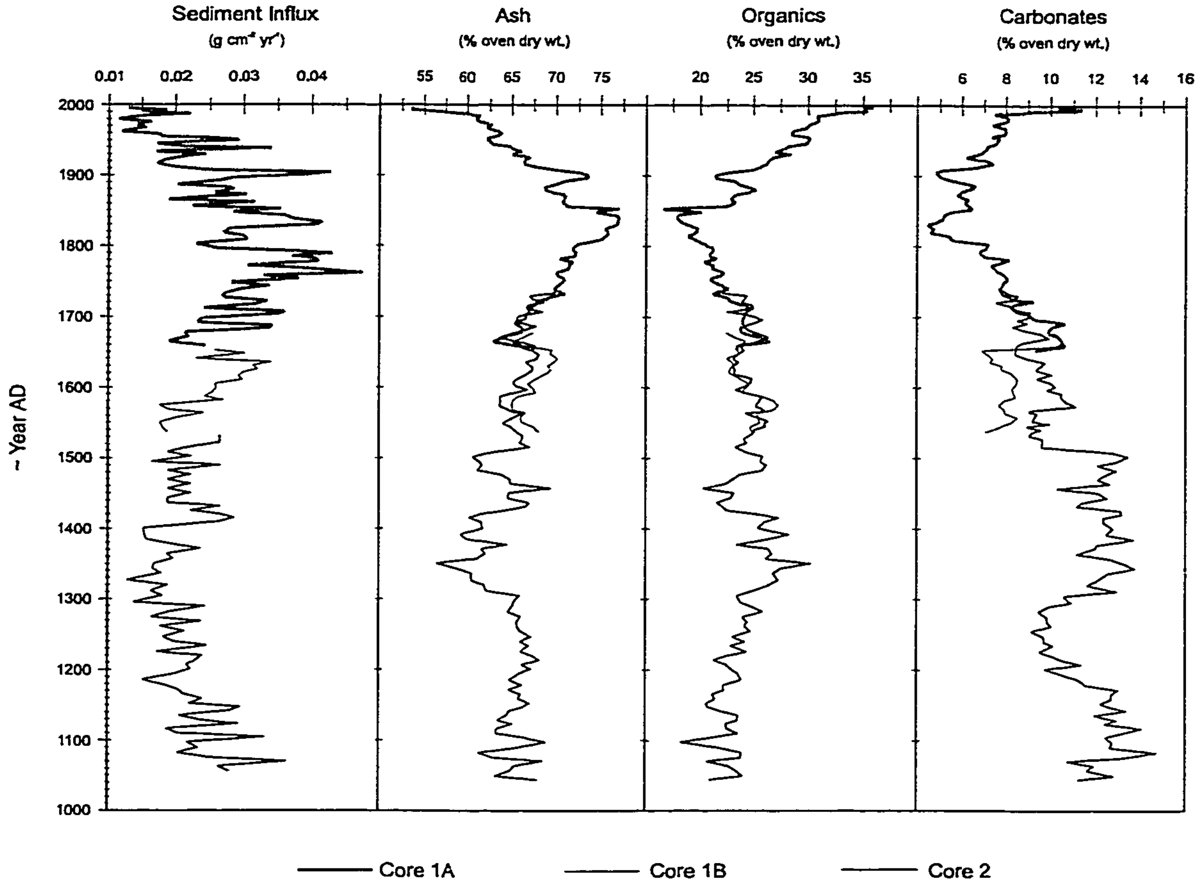
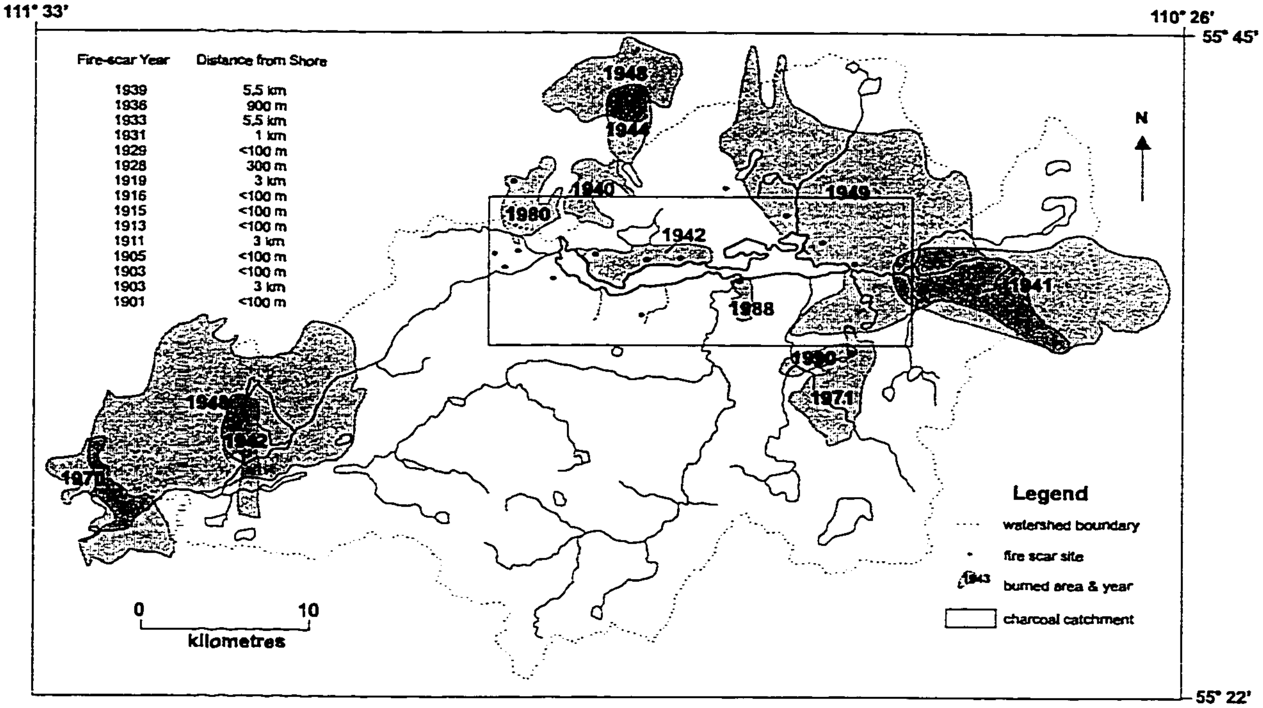


Figure 3-2: Results for sediment influx and concentrations of ash, organics and carbonates.

Figure 3-3: Known fire activity near Christina Lake. Fires (> 200 ha) since 1940 are mapped (Delisle and Hall 1987; Peter Englefield, pers. comm.; Rick Strickland, pers. comm.) and fire-scar results are shown in inset. The estimated charcoal catchment area for the charcoal results is also shown.



Fire-scar Year	Distance from Shore
1939	5.5 km
1936	900 m
1933	5.5 km
1931	1 km
1929	<100 m
1928	300 m
1919	3 km
1916	<100 m
1915	<100 m
1913	<100 m
1911	3 km
1905	<100 m
1903	<100 m
1903	3 km
1901	<100 m

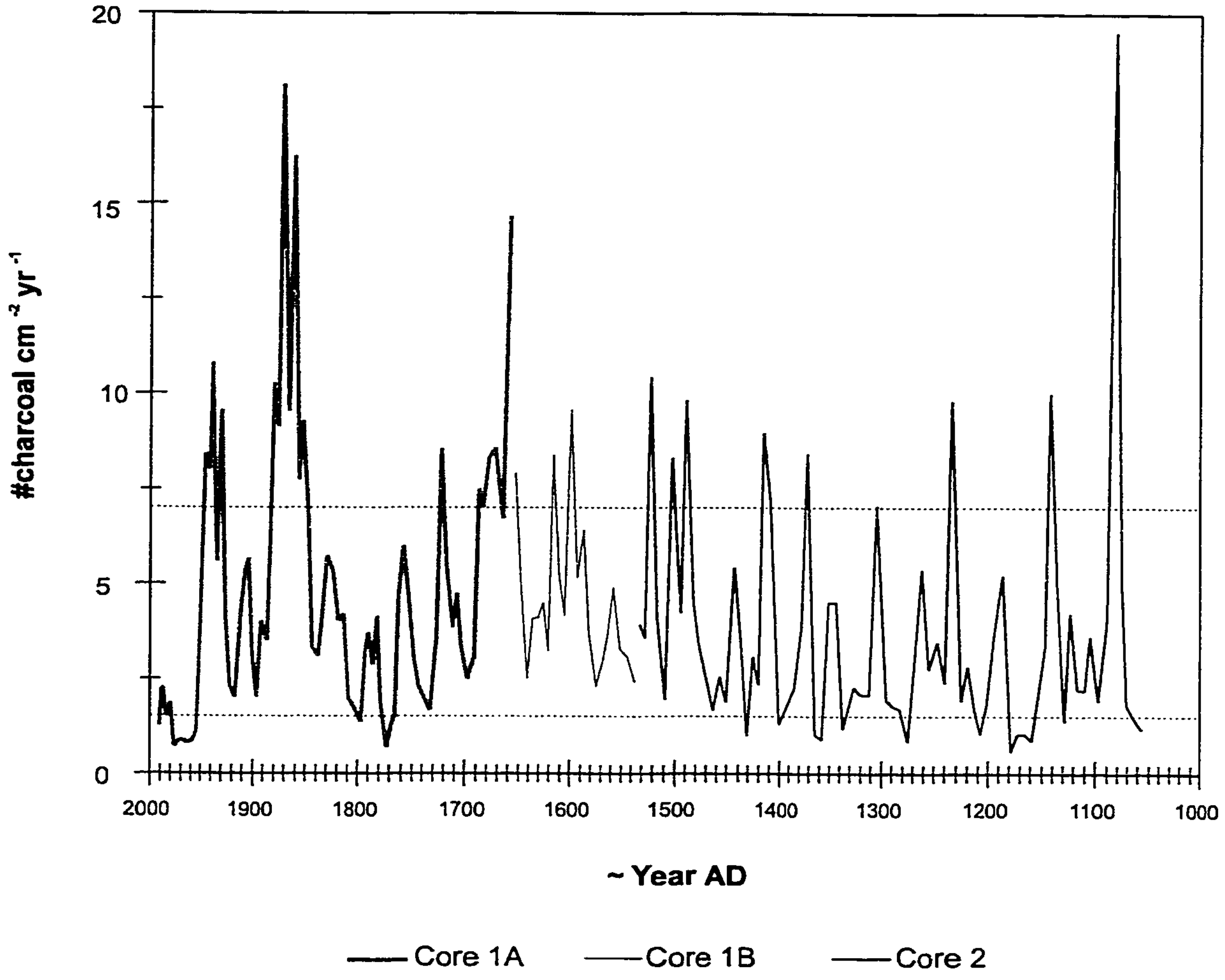


Figure 3-4: Charcoal results for Christina Lake. Results represent all charcoal fragments > 125 μm in diameter. Both thresholds are shown with dotted lines. The lower threshold includes all fire periods within the charcoal catchment while the higher threshold includes only "large" fire periods in which a significant proportion of the charcoal catchment was burned.

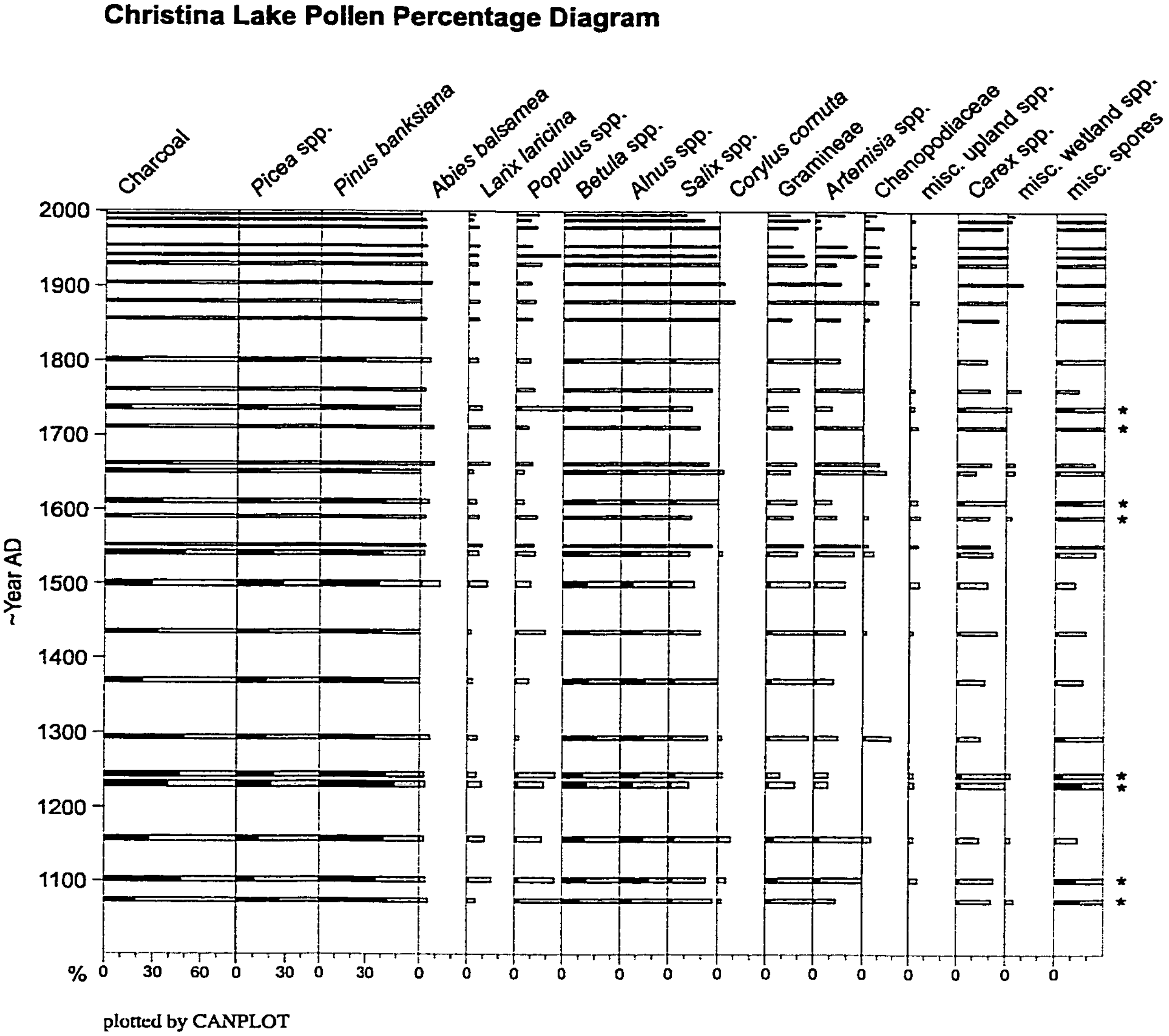


Figure 3-5: Christina Lake pollen percentage diagram. Each taxon is expressed as a percentage of the total upland pollen sum (*Carex*, spores, wetland species and charcoal are not included in the upland pollen sum). Pre- and post-fire sample sets are marked with an *. Black bars show the percentage abundance of each taxon while gray bars represent an 10x exaggeration.

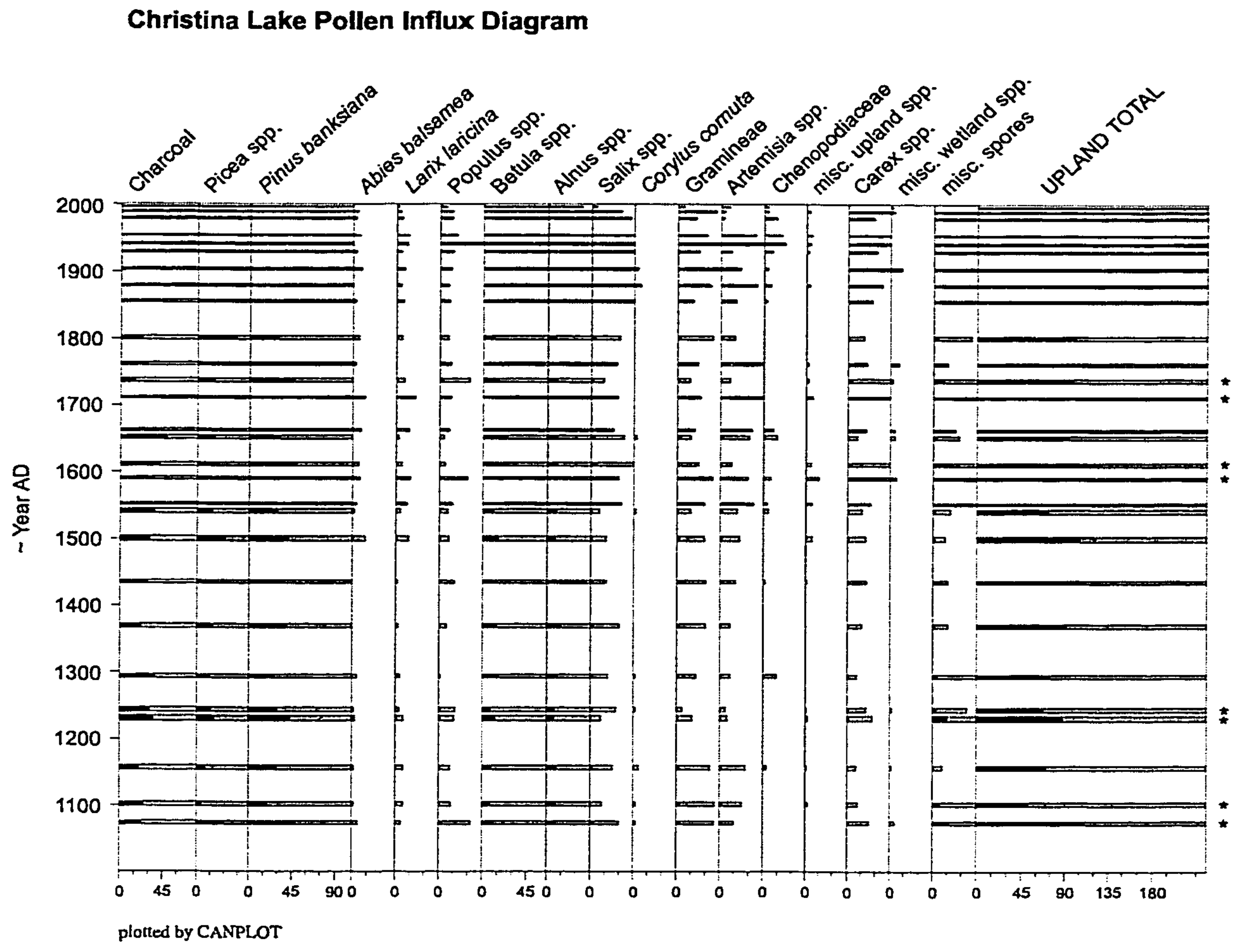


Figure 3-6: Christina Lake pollen influx diagram. Results are represented as the number of grains cm^{-2} yr^{-1} divided by 10000. Pre- and post-fire sample sets are marked with an *. Black bars represent the influx of each taxon while gray bars represent a 10x exaggeration.

3.6 References

Alberta Environmental Protection. 1994. Natural regions and subregions of Alberta: summary. Alberta Environmental Protection, Edmonton.

Arno, S.F., and Sneck, K.M. 1977. A method for determining fire history in coniferous forests of the mountain west. USDA Forest Service General Technical Report INT-42.

Bergeron, Y., and Flannigan, M.D. 1995. Predicting the effects of climate change on fire frequency in the southeastern Canadian boreal forest. Wat. Air Soil Pollut. **82**: 437-444.

Bergeron, Y., Richard, P.J.H., Carcaillet, C., Gauthier, S., Flannigan, M., and Prairie, Y.T. 1998. Variability in fire frequency and forest composition in Canada's southeastern boreal forest: a challenge for sustainable forest management. Conservation Ecology [online] **2**: 6.

Bradbury, J.P. 1996. Charcoal deposition and redeposition in Elk Lake, Minnesota, USA. Holocene **6**: 339- 344.

Bradford, M.E. 1990. Athabasca River Basin: Christina Lake. *In* Atlas of Alberta lakes. *Edited by* P. Mitchell, and E. Prepas. University of Alberta Press, Edmonton. pp. 136-139.

Bradley, R.S., and Jones, P.D. 1992. When was the "Little Ice Age"? *In* Proceedings of the International Symposium on the Little Ice Age Climate (1992). *Edited by* T. Mikami .Metropolitan University, Tokyo. pp. 1-4.

Campbell, C. 1998. Late Holocene lake sedimentology and climate change in southern Alberta, Canada. Quat. Res. **49**: 96-101.

Campbell, I.D., and Campbell, C. In Press. Late Holocene vegetation and fire history at the southern boreal forest margin in Alberta, Canada. Palaeogeogr. Palaeoclim. Palaeoecol.

Campbell, I.D., and Flannigan, M.D. 2000. Long-term perspectives on fire-climate-vegetation relationships in the North American boreal forest. *In* Fire, climate change, and carbon cycling in the boreal forest. *Edited by* E.S. Kasischke and B.J. Stocks. Springer, New York. pp. 151-172.

Campbell, I.D., Last, W.M., Campbell, C., Clare, S., and McAndrews, J.H. In Press. The late-Holocene paleohydrology of Pine lake, Alberta: a multiproxy investigation. J. Paleolim.

Carroll, S.B., and Bliss, L.C. 1982. Jack pine - lichen woodland on sandy soils in northern Saskatchewan and northeastern Alberta. Can. J. Bot. **60**: 2270-2282.

Clark, J.S. 1990. Fire and climate change during the last 750 yr in northwestern Minnesota. Ecol. Monogr. **60**: 135-159.

Clark, J.S., and Robinson, J. 1993. Paleoecology of Fire. *In* Fire in the environment: the ecological, atmospheric, and climatic importance of vegetation fires. *Edited by* P.J. Crutzen, and J.G. Goldammer. John Wiley and Sons, Ltd., New York. pp. 193-214.

Cwynar, L.C. 1978. Recent history of fire and vegetation from laminated sediment of Greenleaf Lake, Algonquin Park, Ontario. Can. J. Bot. **56**: 10-21.

Dean, W.E., Jr. 1974. Determination of carbonate and organic matter in calcareous sediments and sedimentary rocks by loss on ignition: comparison with other methods. J. Sed. Petrol. **44**: 242-248.

Dean, W.E. 1998. The carbon cycle and bigeochemical dynamics in lake sediments. J. Paleolim. **21**: 375-394.

Delisle, G.P., and Hall, R.J. 1987. Forest fire history maps of Alberta, 1931-1983. Canadian Forestry Service, Northern Forestry Centre, Edmonton, Alta.

Earle, C.J., Brubaker, L.B., and Anderson, P.M. 1996. Charcoal in northcentral Alaskan lake sediments: relationships to fire and late-Quaternary vegetation history. Rev. Palaeobot. Palynol. **92**: 83-95.

Faegri, K., Kaland, P.E., and Kryzwinski, K. 1989. Textbook of pollen analysis, by Knut Faegri and Johs. Iverson. John Wiley and Sons, Chichester, U.K.

Farrar, J.L. 1995. Trees in Canada. Fitzhenry & Whiteside Limited and Canadian Forest Service, Natural Resources Canada, Markham, Ontario.

Flannigan, M.D., and Harrington, J.B. 1988. A study of the relation of meteorological variables to monthly provincial area burned by wildfire in Canada. J. Appl. Meteorol. **27**: 441-452.

Forestry Canada Fire Danger Group. 1992. Development and structure of the Canadian Forest Fire Behavior Prediction System. Forestry Canada Information Report ST-X-3.

Hadden, K. 1978. Investigation of the registration of poplar pollen in lake sediments. Master of Science thesis, University of Toronto, Toronto.

Håkanson, L., and Jansson, M. 1983. Principles of Lake Sedimentology. Springer-Verlag, New York.

Hickman, M., Schweger, C.E., and Klarer, D.M. 1990. Baptiste Lake, Alberta - a late Holocene history of changes in a lake and its catchment in the southern boreal forest. J. Paleolim. **4**: 253-267.

Hu, F.S., Brubaker, L.B., and Anderson, P.M. 1993. A 12 000 year record of vegetation change and soil development from Wein Lake, central Alaska. Can. J. Bot. **71**: 1133-1142.

Hu, F.S., Brubaker, L.B., and Anderson, P.M. 1996. Boreal ecosystem development in the northwestern Alaska Range since 11.000 yr B.P. Quat. Res. **45**: 188-201.

Hudson, E. 1997. The climate of the Peace, Athabasca and Slave river basins. Northern River Basins Study Project Report No. 124.

Hughes, M.K., and Diaz, H.F. 1994. Was there a 'Medieval Warm Period', and if so, where and when? Clim. Change **26**: 109-142.

Jacobson, G.L., Jr., and Bradshaw, R.H.W. 1981. The selection of sites for paleovegetational studies. Quat. Res. **16**: 80-96.

Jacoby, G.C., Jr., and D'Arrigo, R. 1989. Reconstructed northern hemisphere annual temperature since 1671 based on high-latitude tree-ring data from North America. Clim. Change **14**: 39-59.

Johnson, E.A. 1992. Fire and vegetation dynamics: studies from the North American boreal forest. Cambridge University Press, Cambridge, UK.

Johnson, E.A., and Fryer, G.I. 1987. Historical vegetation change in the Kananaskis Valley, Canadian Rockies. Can. J. Bot. **65**: 853-858.

Johnson, E.A., Fryer, G.I., and Heathcott, M.J. 1990. The influence of man and climate on frequency of fire in the interior wet belt forest, British Columbia. J. Ecol. **78**: 403-412.

Johnson, E.A., and Larsen, C.P.S. 1991. Climatically induced change in fire frequency in the southern Canadian Rockies. Ecology **72**: 194-201.

Johnson, E.A., and Wowchuk, D.R. 1993. Wildfires in the southern Canadian Rocky Mountains and their relationship to mid-tropospheric anomalies. Can. J. For. Res. **23**: 1213-1222.

Kelts, K., and Hsu, K.J. 1978. Freshwater carbonate sedimentation. *In* Lakes: chemistry, geology, physics. *Edited by* A. Lerman. Springer-Verlag, New York. pp. 295-323.

Kuhry, P. 1994. The role of fire in the development of Sphagnum-dominated peatlands in western boreal Canada. J. Ecol. **82**: 899-910.

Laird, L.D., and Campbell, I.D. In Prep. Vivianite in the laminated sediments of Christina Lake, Alberta, Canada and its potential as a paleoenvironmental indicator.

Laird, L.D., and Campbell, I.D. In Press. High resolution palaeofire signals from Christina Lake, Alberta: a comparison of the charcoal signals extracted by two different methods. Palaeogeogr. Palaeoclim. Palaeoecol.

Lamb, H.H. 1977. Climate, present, past and future. Methuen, London

.

Lamb, H.H. 1982. Climate, history and the modern world. Methuen, London.

Larsen, C.P.S. 1997. Spatial and temporal variations in boreal forest fire frequency in northern Alberta. J. Biogeogr. **24**: 663-673.

Larsen, C.P.S., and MacDonald, G.M. 1998a. An 840-year record of fire and succession in a boreal white spruce forest. Ecology **79**: 106-118.

Larsen, C.P.S., and MacDonald, G.M. 1998b. Fire and vegetation dynamics in a jack pine and black spruce forest reconstructed using fossil pollen and charcoal. J. Ecol. **86**: 815-828.

Lee, E.J., Kenkel, N.C., and Booth, T. 1996. Pollen deposition in the boreal forest of west-central Canada. Can. J. Bot. **74**: 1265-1272.

Lewis, H.T. 1982. A time for burning. Boreal Institute for Northern Studies, University of Alberta, Occasional Publication No. 17.

Lichti-Federovich, S. 1970. The pollen stratigraphy of a dated sectoin of Late Pleistocene lake sediment from central Alberta. Can. J. Earth Sci. **7**: 938-945.

Luckman, B.H. 1994. Evidence for climatic conditions between ca. 900-1300 A.D. in the southern Canadian Rockies. Clim. Change **26**: 171-182.

Luckman, B.H. 1997. Developing a proxy climate record for the last 300 years in the Canadian Rockies -- some problems and opportunities. Clim. Change **36**: 455-476.

Luckman, B.H., Briffa, K.R., Jones, P.D., and Schweingruber, F.H. 1997. Tree-ring based reconstruction of summer temperatures at the Columbia Icefield, Alberta, Canada, AD 1073-1983. Holocene **7**: 375-389.

MacDonald, G.M. 1987. Postglacial development of the subalpine-boreal transition forest of western Canada. J. Ecol. **75**: 303-320.

Masters, A.M. 1990. Changes in forest fire frequency in Kootenay National Park, Canadian Rockies. Can. J. Bot. **68**: 1763-1767.

Millspaugh, S.H., and Whitlock, C. 1995. A 750-year fire history based on lake sediment records in central Yellowstone National Park, USA. Holocene **5**: 283-292.

Nash, C.H., and Johnson, E.A. 1996. Synoptic climatology of lightning-caused forest fires in subalpine and boreal forests. Can. J. For. Res. **26**: 1859-1874.

Newark, M.J. 1975. The relationship between forest fire occurrence and 500 mb longwave ridging. Atmosphere **13**: 26-33.

Nicholson, B.J., and Vitt, D.H. 1990. The paleoecology of a peatland complex in continental western Canada. Can. J. Bot. **68**: 121-138.

Nienstaedt, H., and Zasada, J.C. 1990. White Spruce. *In* Silvics of North America: Vol.1, Conifers. *Edited by* R.M. Burns, and B.H. Honkala. USDA Agriculture Handbook 654. pp. 204-226.

Nimchuk, N. 1983. Wildfire behavior associated with upper ridge breakdown. Alberta Energy and Natural Resources, Forest Service ENR Technical Report T/50.

O'Sullivan, P.E. 1983. Annually-laminated lake sediments and the study of Quaternary environmental changes -- a review. Quat. Sci. Rev. **1**: 245-313.

Overpeck, J., Hughen, K., Hardy, D., Bradley, R., Case, R., Douglas, M., Finney, B., Gajewski, K., Jacoby, G., Jennings, A., Lamoureux, S., Lasca, A., MacDonald, G., Moore, J., Retelle, M., Smith, S., Wolfe, A., and Zielinski, G. 1997. Arctic environmental change of the last four centuries. Science **278**: 1251-1256.

Patterson, W.A., III, Edwards, K.J., and Maguire, D.J. 1987. Microscopic charcoal as a fossil indicator of fire. Quat. Sci. Rev. **6**: 3-23.

Payette, S. 1992. Fire as a controlling process in the North American boreal forest. *In* A systems analysis of the global boreal forest. *Edited by* H. Shugart, R. Leemans, and G.B. Bonan. Cambridge University Press. pp. 144-169.

Petterson, G. 1996. Varved sediments in Sweden: a brief review. *In* Palaeoclimatology and palaeoceanography from laminated sediments. *Edited by* A.E.S. Kemp. The Geological Society, London. pp. 73-77.

Romme, W. 1980. Fire history terminology: report of the ad hoc committee. *In* Proceedings of the fire history workshop, October 20-24, 1980, Tuscon, Arizona. USDA Forest Service, Rocky Mountain Forest and Range Experimental Station, General Technical Report RM-81. pp. 135-137.

Rowe, J.S., and Scotter, G.W. 1973. Fire in the boreal forest. Quat. Res. **3**: 444-464.

Sugita, S., MacDonald, G.M., and Larsen, C.P.S. 1997. Reconstruction of fire disturbance and forest succession from fossil pollen in lake sediments: potential and limitations. *In* Sediment records of biomass burning and global change. *Edited by* J.S. Clark, H. Cachier, J.G. Goldammer, and B.J. Stocks. Springer-Verlag, Berlin. pp. 387-412.

Swain, A.M. 1973. A history of fire and vegetation in northeastern Minnesota as recorded in lake sediments. Quat. Res. **3**: 383-396.

Swain, A.M. 1978. Environmental changes during the past 2000 years in north-central Wisconsin; analysis of pollen, charcoal, and seeds from varved lake sediments. Quat. Res. **10**: 55-68.

Tolonen, K. 1986. Charred particle analysis. *In* Handbook of Holocene palaeoecology and palaeohydrology. *Edited by* B.E. Berglund. John Wiley and Sons, New York. pp. 485-496.

Van Horne 1998. Christina Lake Thermal Project. Application to Alberta Energy and Utilities Board and to Alberta Environmental Protection. Volume 1 - Joint Submission. Report available at Alberta Environmental Protection library, Edmonton, Alberta.

Vance, R.E., Mathewes, R.W., and Clague, J.J. 1992. 7000 year record of lake-level change on the northern Great Plains: a high-resolution proxy of past climate. Geology **20**: 879-882.

Varem-Sanders, T.M.L., and Campbell, I.D. 1996. DendroScan: a tree-ring width and density measurement system. Canadian Forest Service, Northern Forestry Centre.

Viereck, L.A., and Johnston, W.F. 1990. Black Spruce. *In* Silvics of North America: 1, Conifers. Agriculture Handbook 654. *Edited by* R.M. Burns, and B.H. Honkala. United States Department of Agriculture., Washington, D.C.

Walling, D.E., and He, Q. 1993. Towards Improved Interpretation of ^{137}Cs profiles in lake sediments. *In* Geomorphology and sedimentology of lakes and reservoirs. *Edited by* J. McManus, and R.W. Duck. John Wiley & Sons Ltd., Toronto. pp. 31-53.

Weber, M.G., and Flannigan, M.D. 1997. Canadian boreal forest ecosystem structure and function in a changing climate: impact on fire regimes. Environ. Rev. **5**: 145-166.

Wein, R.W., and de Groot, W.J. 1996. Fire - climate change hypotheses for the Tiaga. *In* Fire in ecosystems of boreal Eurasia. *Edited by* J.G. Goldammer, and V.V. Furyaev. Kluwer Academic Press, The Netherlands. pp. 505-512.

Wein, R.W., and MacLean, D.A. (*Eds.*). 1983. The role of fire in northern circumpolar ecosystems. John Wiley and Sons, New York.

Weir, J.M.H., and Johnson, E.A. 1998. Effects of escaped settlement fires and logging on forest composition in the mixedwood boreal forest. Can. J. For. Res. **28**: 459-467.

Whitlock, C., Bradbury, J.P., and Millspaugh, S.H. 1997. Controls on charcoal distribution in lake sediments: case studies from Yellowstone National Park and northwestern Minnesota. *In* Sediment records of biomass burning and global change. *Edited by* J.S. Clark, H. Cachier, J.G. Goldammer, and B.J. Stocks. Springer-Verlag, Berlin. pp. 367-386.

Whitlock, C., and Millspaugh, S.H. 1996. Testing the assumptions of fire-history studies: an examination of modern charcoal accumulation in Yellowstone National Park, USA. Holocene **6**: 7-15.

Winkler, M.G. 1985. Charcoal analysis for paleoenvironmental interpretation: a chemical assay. Quat. Res. **23**: 313-326.

Wotton, B.M., and Flannigan, M.D. 1993. Length of the fire season in a changing climate. For. Chron. **69**: 187-192.

CHAPTER 4

Vivianite in the Laminated Sediments of Christina Lake, Alberta, Canada and its Potential as a Paleoenvironmental Indicator[2]

4.1 Introduction

Vivianite, $Fe_3(PO_4)_2 \cdot 8H_2O$, is a fairly common authigenic mineral in anoxic soils and sediments and its peculiar characteristic of turning bright blue upon exposure to oxygen makes it easily recognized. Nriagu (1972) describes vivianite as the most stable solid phase ferrous orthophosphate found in sedimentary environments. In order to precipitate and remain stable, vivianite requires that a particular set of geochemical conditions be met and maintained. While vivianite formation is often related to microsite conditions within the soil or sediment, these microsite conditions can be related to the general geochemistry within the sediment or soil, and sometimes to larger scale environmental factors as well. Thus, in certain situations, the presence of vivianite may provide important clues to paleoenvironmental conditions. This is especially so because vivianite is a phosphate mineral and phosphorus is a limiting nutrient in many ecosystems.

Bright blue vivianite concretions were found to be especially abundant in certain sections of the annually-laminated sediment retrieved from Christina Lake, Alberta. Because its presence or absence might be linked in some way to the paleoenvironment in and around the lake, an effort was made to quantify the amount of vivianite in the Christina Lake core and to relate the changes in its abundance to other geochemical and physical analyses to determine its potential value as a paleoenvironmental indicator for this site. Before the Christina Lake vivianite results are presented and discussed below, some background information is given including a summary of the basic geochemistry involved in vivianite precipitation followed by a brief literature review of its occurrence in a variety of sedimentary environments. This review will focus on those studies in which the presence of vivianite was shown to reflect and/or influence larger-scale environmental parameters (especially in freshwater lakes).

4.2 Study Site

Christina Lake (55° 37' N, 110° 56' W) is located in the Central Mixedwood subregion of the Boreal Forest Natural Region in northern Alberta, Canada (Figure 4-1)(Alberta Environmental Protection, 1994). The lake is large (2130 ha) with six permanent inflowing streams and a drainage basin of 1250 km^2 (Bradford, 1990). The morphology of the lake is long and narrow reaching a maximum length and width of approximately 13 km and 2 km

---

[2] A version of this chapter will be submitted to *Journal of Paleolimnology*.

respectively. The deepest basin reaches a maximum depth of 33 m and here the sediments are laminated. This portion of the lake is presumed to be meromictic, or at least to be sufficiently depleted in oxygen that bottom fauna are excluded. Most of the lake basin has steeply sloping sides and there are only isolated pockets of littoral areas. The trophic status of the lake is not known but based on the limited data available (see Table 4-1), the lake is considered to be quite unproductive (Bradford, 1990).

The surrounding landscape is level to gently rolling terrain largely dominated by peatlands. Vegetation on upland areas is a mixed forest of trembling aspen (*Populus tremuloides* Michx.), white spruce (*Picea glauca* (Moench) Voss), jack pine (*Pinus banksiana* Lamb.), and birch (*Betula papyrifera* Marsh). Black spruce (*Picea mariana* (Mill.) BSP) and larch (*Larix laricina* (Du Roi) Koch) are the dominant trees in low lying areas. The underlying substrate consists of a thick (up to 150 m) mantle of glacial till, glaciofluvial, and glaciolacustrine materials (Van Horne, 1998).

Human impact on the area was minimal until oil and gas exploration began in the region in the mid 1980s. The lake has been accessible by an all weather road only since 1986. The hamlet of Conklin (population 205 in 1995) is located immediately west of the lake but other than a recreational lodge and campground on the north shore at the western end of the lake, there is no other shoreline development (Bradford, 1990). The nearest large population centre is Fort McMurray 125 km to the north.

4.3 Methodology

4.3.1 Core Retrieval and Sampling

Two cores of laminated sediment were retrieved using a box type freeze-corer (Swain, 1973) at a water depth of approximately 30 m. One core included the water/sediment interface and penetrated to a depth of ~100 cm while the other was buried below the sediment-water interface and retrieved material from approximately 57 cm to 174 cm depth. The best faces (i.e. those faces which showed the least disturbance in the laminations) of each core were selected for sampling and correlated by means of several white diatomaceous marker horizons. These faces were cleaned using a plane and left uncovered in a freezer for several days to allow the outermost surface to freeze dry to a depth of approximately 1 mm. Sediment peels were then taken by spreading a very thin even film of Histoprep (an embedding medium suitable for frozen material) over a microscope slide using a razor blade and then gently pressing the slide onto the core for approximately 30 seconds before removing it. Bulk sediment samples were retrieved by cutting the core face into contiguous 1 cm strips parallel to the plane of deposition using a scalpel. These samples were then stored in a cold room (2°C) until analysed.

4.3.2 Geochronology

The laminations were examined under a stereoscope at 50x magnification and were found to be similar to those described from other varved lakes (O'Sullivan, 1983; Petterson, 1996) and consistent with the successional deposition of material over one year. Typically, a thicker (1-1.5 mm) light-coloured layer consisting of a mixture of silt, diatoms, and organic material (representing spring to autumn) alternated with a thinner (< 1 mm) dark layer consisting of very fine organic material (deposited while the lake was frozen over in winter). The light layer sometimes included a white band of pure diatoms representing an algae "bloom" in the spring or autumn. Each couplet of a light layer (with or without a diatom bloom) and a dark layer was assumed to be a true varve (i.e. to represent one year of deposition) and the cores were dated by varve counting.

Independent confirmation of the annual nature of the laminations was given by ^{137}Cs analysis of the upper 20 cm of core 1 (see Appendix 1). The greatest cesium activity occurred in the 1 cm sample containing sediment deposited in the years 1963 to 1967 as determined by the varve count (Laird and Campbell, In Press). This is consistent with the peak in ^{137}Cs fallout in the northern hemisphere (due to the atmospheric testing of nuclear weapons) in 1963 (Walling & He, 1993).

4.3.3 Vivianite Quantification via Image Analysis

The sediment peels were photographed at identical resolution in natural daylight using Fuji Reala film and a Pentax MZ-10 camera with a 50 mm macro lens. Photographs were then scanned into Adobe Photoshop 4.0 using a AGFA Duoscan scanner at 400 dpi optical resolution. In Photoshop, the images were joined and cropped to form a contiguous image of a longitudinal strip of sediment of equal width (equivalent to .9 cm of sediment) and colour adjusted by enhancing the blue content by 50 units in RGB to allow the vivianite to stand out more sharply. A specially written computer program was then used to quantify the proportion of "blue" pixels in each interval (equivalent to 1 cm of sediment depth) of the image where "blue" was defined using the formula: (blue) > (green) > (red+20) in RGB (Thierry Varem-Sanders, pers. comm.). The results were compared with the photographs to ensure that no significant vivianite concretions were missed and nothing other than vivianite was included. While the image analysis program somewhat underestimated the amount of visible vivianite, the relative abundances from one interval to another were fairly represented. X-ray diffraction analysis of several samples confirmed that the blue material was vivianite.

4.3.4 Geochemical Analyses

Organic matter, carbonate, and ash content were determined by loss on ignition following Dean (1974). The geochemistry of the authigenic fraction of the sediment was determined by leaching with .25 N HCl and analysing the leachate with ICP-AES using the method described by Malo (1977). Two aspects of our methodology differed from that described by Malo: 1) organic matter was not removed from the sediment prior to leaching with HCl because we were interested in all components of the sediment, including the organic fraction; 2) the sediment was soaked in HCl for 90 minutes at 90°C rather than the minimum 30 minutes suggested by Malo.

4.4 Basic Geochemistry of Vivianite Precipitation

In order to precipitate and remain stable, vivianite typically requires reducing conditions ($Eh<0$), high ferrous (rather than ferric) iron concentrations, low sulfide activity, moderate to high phosphorus concentrations, and near neutral pH (Nriagu, 1972; Nriagu & Dell, 1974; Virtanen, 1994). All of these factors are interrelated in complex ways.

Reducing conditions are necessary to transform iron from the ferric form (Fe^{3+}), which is the most common phase found in surface environments, into the ferrous form (Fe^{2+}). Iron reduction begins at a redox potential (Eh) < 200 mV at neutral pH (Håkanson & Jansson, 1983) and reduction is usually facilitated by microbial organisms during the decomposition of organic matter. Reducing conditions must be persistent, rather than merely seasonal, in order for vivianite to remain stable (Virtanen, 1994). Such conditions can occur in a variety of aqueous and water-logged environments including groundwater, the hypolimnion of lakes, gleyed and pseudo gleyed soils, lake and swamp sediments, and peatlands. As soon as oxygen is introduced, ferrous iron immediately reoxidizes to the ferric form and vivianite begins to break down. Because decomposing organic matter consumes oxygen and thereby promotes reducing conditions, vivianite is often found associated with organic material such as bone, wood, roots, diatoms, etc. (Henderson et al., 1983).

Sources of iron which may potentially undergo reduction include a variety of iron oxides which are ubiquitous in surface environments. These oxides form as the weathering products of primary silicate and sulfide minerals and may be especially abundant in temperate glaciated landscapes which contain an abundance of mechanically ground material available for weathering (Jones & Bowser, 1978; Schwertmann & Fitzpatrick, 1992). Sources of phosphorus which may potentially bond with reduced iron include weathered phosphate minerals (mainly apatite), naturally occurring organic matter, drainage water from agricultural land, and municipal and industrial waste (Håkanson & Jansson, 1983).

Once reduced, Fe^{2+} can combine with a variety of anions including hydroxyl, carbonate, phosphate, and sulfide ions. It combines with sulfides preferentially, however, and high concentrations of these ions may use up all the available Fe^{2+} in the formation of iron monosulfides and preclude the formation of other ferrous iron minerals. These iron monosulfides may be subsequently transformed into pyrite (FeS_2) if sufficient sulfur is available

(Berner, 1981). Low concentrations of sulfide ions are therefore usually necessary to ensure sufficiently high concentrations of Fe^{2+} are available to combine with phosphate ions to form vivianite.

Sulfide ion concentration is related to both redox potential and type of environment, and was used by Berner (1981) in his geochemical classification of sediments. Iron reduction occurs before the reduction of sulfate which begins at an Eh < 100 mV (Håkanson & Jansson, 1983). Thus, under mildly reducing conditions, iron will be reduced to the necessary Fe^{2+} but sulfate will not be reduced. Such conditions are termed "anoxic non-sulfidic post oxic" by Berner and they occur where the amount of available organic matter is very low, such as in oligotrophic lake sediments. The paucity of organic matter means that decomposition can be completed before anaerobic microbes begin to utilize lower-yielding forms of energy such as sulfates. It also means, however, that the amount of phosphorus released from organic matter will also be low and consequently, only a small amount of vivianite (if any) will be precipitated if organic matter is the main phosphorus source.

Strongly reducing conditions and very high concentrations of ferrous iron can also produce the requisite low levels of sulfides. In this scenario, called "anoxic non-sulfidic methanic" by Berner, there is an abundance of organic matter to be decomposed and all sulfates are eventually reduced to sulfides. The sulfides immediately bond with ferrous iron to form iron monosulfides but ferrous iron concentrations are sufficiently high (or initial sulfate concentrations were sufficiently low) that even after all available sulfides have satisfied their ferrous iron needs, there is still enough Fe^{2+} left over to form vivianite. Such situations are common in freshwater environments which are usually low in sulfates to begin with, resulting in minimal ferrous iron loss to sulfide scavenging. In contrast, marine and brackish water usually contains high sulfate concentrations and so extremely high levels of ferrous iron would have to be present in order to have enough leftover for vivianite precipitation once sulfate reduction is completed (or, alternatively, these sediments would have to be so poor in organic matter that the available sulfate is never reduced to sulfide).

Even in the absence of sulfide ions, other ions such as Ca^{+} and CO_3^{2-} compete for phosphate and ferrous iron ions. High concentrations of Ca^{+} (i.e. a Ca/Fe ratio greater than 10) will lead to the precipitation of hydroxyl apatite, while high concentrations of CO_3^{2-} will facilitate siderite precipitation (Rosenquist, 1970; Jakobsen, 1988). Siderite has almost the same geochemical requirements as vivianite in terms of pH, redox potential, ferrous iron requirements and sulfide intolerance and is often found in association with vivianite (Jakobsen, 1988).

Phosphate ions not only bond with ferrous iron but are also readily adsorbed by ferric oxides. A common method of vivianite formation often involves both forms of iron as follows. Ferric oxides precipitate under aerobic conditions and adsorb phosphate ions. Subsequent burial in anoxic conditions causes reduction whereby phosphate is released and ferric iron transformed into the ferrous form. Phosphate and ferrous iron ions are then free to bond to form vivianite. In mildly reducing conditions, it may take some time to reduce ferric oxides to ferrous iron however, and so even after burial, ferric oxides may compete with ferrous iron for phosphate ions.

Another important variable in vivianite formation is pH. At low pH, higher concentrations of both phosphate and ferrous iron are required for vivianite to precipitate (Nriagu & Dell, 1974). At high pH, the sensitivity of ferrous iron to sulfide ions goes up (Kjensmo, 1967). Thus, the "ideal" pH for vivianite precipitation given average conditions is around 7.

Under anoxic conditions, fresh vivianite is colourless or white and occurs as spherical nodules or concretions. On exposure to oxygen, some of the ferrous iron is oxidized to the ferric form triggering a colour change to bright blue (McCammon & Burns, 1980). This partially oxidized form of vivianite is sometimes referred to as kertschenite (Nriagu, 1972). With continued exposure to oxidizing conditions, more and more ferrous iron is oxidized and vivianite eventually breaks down into a buff or yellowish friable mass which may be composed of several minerals including lipscombite, rockbridgite and strengite (Nriagu, 1972). Because of this intolerance to oxygen, vivianite is not preserved well in the geologic record and most known occurrences are Quaternary in age (Nriagu, 1972; Henderson et al., 1984). In this paper, vivianite and its oxidation products will be collectively referred to as vivianite.

4.5 Vivianite as a Paleoenvironmental Indicator

In several studies, the presence of vivianite was shown to be linked to, and therefore a potentially useful indicator of, a variety of paleoenvironmental factors including ground water source and ground water levels. It has also been shown to both reflect and influence productivity in certain freshwater lakes, and has been linked to stable meromixis and slow sedimentation rates in others.

4.5.1 *Groundwater Source*

Several studies have shown that vivianite may be useful as an indicator of fresh, sulfate poor groundwater conditions. Rosenqvist (1970), for example, found evidence of three different facies in the bottom sediments of Lake Asrum, (Norway) ranging from marine at the base through lagunal in the middle and freshwater lacustrine in the upper four metres. Vivianite was abundant in the lacustrine sediments but totally absent in the underlying lagunal and marine sediments.

Jakobsen (1988) studied a lowland moor in Denmark that was influenced by two different sources of groundwater. One source was rich in iron and sulfur while the other was low in sulfur and rich in carbonate. Pyrite was formed in the sediments influenced by the sulfur-rich groundwater while siderite and vivianite precipitated in the sediments influenced by low sulfur groundwater inflow. In the latter case, vivianite was more common in the upper more peaty part of the sediment whereas siderite was more abundant in the lower gyttja. Jakobsen explained this by the high amounts of CO_3^{2-} in the groundwater which out-competed phosphate ions for available ferrous ions in the lower part of the sediment column. As groundwater percolated up through the mineral soil and gyttja, CO_3^{2-} and any sulfide ions combined with ferrous ions to form siderite and iron monosulfides, respectively. By the time the groundwater reached the upper peaty part of the sediment, phosphate ions could bond with ferrous iron to form vivianite with relatively little competition.

Similarly, Postma (1982) studied a deltaic swamp near the coast of Denmark which was subject to both brackish and freshwater inflows. Sediments influenced by brackish water contained pyrite while sediments with freshwater inflow contained siderite and vivianite. He cautioned against using siderite/vivianite occurrence as an indicator of freshwater conditions however, because providing sufficiently high levels of ferrous iron were present, it would be theoretically possible for vivianite and siderite to form in brackish water sediments after the complete reduction of the sulfate and precipitation of iron sulfides.

4.5.2 Groundwater Level

Because of vivianite's sensitivity to oxygen and the dramatic colour changes it goes through with continued exposure to oxidizing conditions, vivianite can be a useful indicator of changing water table levels. Landuydt (1990) examined bogs along small rivers in the Belgian Campine area, which were rich in organic matter with very high iron and high phosphorus contents. The water table was near the surface in the winter but dropped 1 to 1.5 metres in the summer. Vivianite was found in the permanently reduced sediment below the level of seasonal fluctuation. An artificially low water table level due to pumping of groundwater was marked by a thick 10 cm layer of vivianite which had oxidized to a yellowish isotropic material. Similarly, Leavens (1972) found vivianite nodules below the current water table in a stream bed in New Jersey. Above the current water table level, a layer of dull brown partly oxidized vivianite was found indicating that former groundwater levels were higher.

4.5.3 Lake Productivity, Stratification, and Sedimentation

Sedimentary vivianite is more often associated with low to moderately productive lakes since eutrophic conditions often result in sulfate reduction and precipitation of iron sulfides rather than vivianite unless iron levels are very high and sufficient to precipitate both minerals. Also, vivianite itself can limit lake productivity by sequestering phosphorus and thus limiting its availability in the water column (see below). Vivianite has been found in the sediments of ultra-oligotrophic to eutrophic lakes, however, and so associating vivianite with any particular level of lake productivity should be done with caution.

The sudden appearance or disappearance of vivianite can, however, sometimes be associated with changes in lake productivity. In Baptiste Lake, Alberta, for example, Manning et al. (1999) found that the sudden absence of vivianite in the upper 25 cm of sediment coincided with the period of land clearance in this area. This alteration of the watershed increased nutrient runoff into the lake and may have altered groundwater flow patterns resulting in eutrophication of the formerly mesotrophic lake. The upper 25 cm of sediment were high in pyrite whereas below this level, vivianite was present and pyrite was absent. Since redox potentials within the vivianite rich sediments were not low enough to generate sulfide ions, organic matter deposition must have been much less than at present, and perhaps the bottom waters were better oxygenated as well. Prior to the land clearance, high concentrations of Fe^{2+} and phosphate ions in the groundwater percolated upward through the sediment and were precipitated at the sediment-water interface (similar to Narrow Lake, below). Now the lake water is depleted in iron due to precipitation of iron sulfides, there is not enough iron left over to bind with increased levels of phosphates, and the lake has become eutrophic.

As long as it remains stable, vivianite can act as a phosphate sink in freshwater systems and thus has the potential to not only reflect lake productivity as above, but to influence it as well. In the case of Narrow Lake, Alberta, Manning et al. (1991) suggest that the precipitation of vivianite in the sediments is the only reason this lake has remained mesotrophic while other prairie lakes in similar settings have become eutrophic due to nutrient rich runoff from surrounding agricultural land. In this lake, groundwater rich in ferrous iron percolates up through the bottom sediments and then oxidizes to ferric oxides at the mud water interface. The ferric oxides adsorb phosphate ions from the bottom waters. Upon burial, the ferric iron is reduced to ferrous iron which recombines with the released phosphate ions to form vivianite. During summer stratification, the bottom waters are anoxic and upwelling Fe^{2+} can bond directly with phosphate ions and form vivianite at the sediment surface. Thus, both ferric oxides and vivianite effectively remove phosphate ions from the overlying water before they can stimulate algal growth and eutrophication is prevented.

Similarly, Cornwall (1987) implicated ferric oxides and vivianite in the suppression of the productivity in ultraoligotrophic Toolik Lake, Alaska. This lake is oxic year round and the top 8 cm of sediment are oxidized and contain an abundance of ferric oxides. Below 8 cm, reducing conditions release Fe^{2+} and phosphate ions and some of these bond to form vivianite. The rest of the ions diffuse upward to the oxidizing zone again (due to the redox gradient) where ferrous iron is reoxidized and phosphate is adsorbed to ferric oxides again. The retention of most of this upward flux of phosphate via adsorption limits the recycling of phosphorus, thus limiting lake productivity. Phosphate inputs are low to begin with, and most of it is lost to the sediment. Cornwall concluded that as long as the ferric oxide "trap" remained intact, an increase in lake productivity would be unlikely.

While vivianite is usually associated with moderate or low lake productivity, it has occasionally been found in eutrophic lakes with very high levels of iron. Lake Greifensee, Switzerland (Emerson, 1976), for example, is eutrophic and the abundance of organic debris deposited results in the production of sulfides and dissolved phosphates among other ions. This lake is sufficiently iron rich, however, that all ferrous iron is not used up in the formation of iron monosulfides. Below the level of sulfate reduction, Fe^{2+} builds up resulting in a diffusion gradient which causes Fe^{2+} to move up towards the surface again. With all sulfides now otherwise bonded, Fe^{2+} is free to bond with phosphate ions to form vivianite and pore waters in the top 15 cm become supersaturated with this mineral. The kinetics of vivianite precipitation are so slow however, that only about 15% of the available phosphate is tied up and the rest is lost to the overlying water. This reinforces the eutrophy of the lake when phosphorus is mixed into the epilimnion during the next overturn period. Although vivianite precipitation in the sediments of this lake is not sufficient to prevent eutrophy, the lake is not as eutrophic as it would have been without the influence of vivianite.

In addition to its association with and influence on different levels of lake productivity, vivianite has been associated with lake stratification and sedimentation as well. In iron rich Lake of the Clouds, for example, Anthony (1977) reported that vivianite nodules were especially large where the annual laminations were particularly wide and distinct. The most distinct laminations were formed during periods of very stable meromixis and also contained very high amounts of iron in the light (summer) layers. Nembrini et al. (1983) found a high concentration of large vivianite nodules between 7-8 cm of the sediment of Lago Maggiore in Italy. During this interval, the sedimentation rate was very slow (as indicated by Pb^{210} dating) and thus the large size was attributed to a long period of diffusion wherein Fe^{2+} and phosphate ions continued to move up to and precipitate at the surface before this horizon was finally buried.

4.6 Christina Lake Vivianite - Results and Discussion

The Christina Lake vivianite curve based on image analysis is shown in Figure 4-2 along with sediment influx, organic matter concentration (based on loss on ignition), and the phosphorus, iron and sulfur results (from ICP-AES analysis of the .25N HCl leachate). Pearson correlation results for vivianite, number of varves per cm depth,sediment influx, organic matter, ash, and carbonate concentrations, and the concentrations of the 15 elements analysed by ICP-AES are given in Table 4-2. Vivianite abundance showed no strong correlation with any of the other elements analysed including iron and phosphorus. Such weak correlations emphasize the importance of microsite conditions (rather than average conditions) for the formation of diagenetic minerals such as vivianite. They may also reflect the difference in sensitivity of the analytical methods used since ICP-AES analysis can detect minute fluctuations measured in ppm while vivianite quantification based on image analysis was measured in ppt and is limited to only those nodules that were large enough to be visually detected.

Despite the poor correlation results, however, the trends in the graphed results (Figure 4-2) indicate some general associations. Below ~25 cm, vivianite was most abundant where both phosphorus and organic matter concentrations were relatively high and sediment influx was relatively low. The highest concentrations of vivianite occurred between ~80 and 148 cm and the varves over this interval were very regular and distinct suggesting stable thermal stratification (and therefore probably stable anoxia). The frequency of diatomaceous bands was also greater here (Laird, personal observation) indicating greater lake productivity. Greater diatom abundance combined with low sediment influx values, suggest that a greater proportion of the organic inputs to the sediment over this interval were authigenic rather than partially decomposed allogenic materials from which phosphorus may have already been stripped. A greater proportion of authigenic organic matter would mean that more phosphorus would be available in the sediment. Some of the dissolved phosphorus in the sediment porewaters would have moved up into the overlying water until equilibrium between the sediment porewater and the water immediately overlying the sediment was reached. After equilibrium was attained, however, stable thermal stratification would minimize further loss of dissolved phosphorus; with no current activity to dilute the phosphorus concentrations at the sediment/water interface, equilibrium could be maintained with minimal diffusion from the sediment.

The concentrations of organic matter and phosphorus were lowest, and sediment influx was highest between ~25 cm and 63 cm and vivianite values are low here as well. This interval coincides with the end phase of the Little Ice Age (~1750 to 1850) when conditions in Alberta were possibly colder and wetter than at any other time in the Holocene (Vance et al., 1992; Campbell, 1998). This interval of the sediment column contained fewer diatomaceous bands (Laird, personal observation) indicating lower lake productivity. Many of the varves were also less distinct and some sections showed evidence of greater turbulence in the overlying water (including shell hash and irregular laminations) suggesting less stable thermal stratification during this period and possibly less stable anoxia. With lower lake productivity and higher sediment influx, the proportion of authigenic organic matter in the sediment would be low and so less phosphorus would be available in the sediments for vivianite precipitation. In addition, with greater turbulence in the overlying water, the phosphorus concentrations near the sediment/water interface may have been frequently diluted creating a diffusion gradient along which more dissolved phosphorus moved out of the sediment and into the overlying water (Håkanson & Jansson, 1983).

Above ~25 cm, phosphorus and organic concentrations increase while vivianite abundance remains low and the image analysis results suggest there is no vivianite at all in the upper 10 cm of the core. X-ray diffraction results also showed no vivianite in samples from the upper 10 cm. Careful examination of the sediment peels, however, revealed that a few small vivianite nodules were indeed present. Apparently, the crystals were not yet large enough to be detected using the image analysis technique (which tended to underestimate vivianite abundance), or by x-ray diffraction. The scarcity and small size of the vivianite nodules in the upper sediments might be due to the very slow kinetics of vivianite precipitation and crystal growth (Mackereth, 1965; Emerson, 1976). Unlike Baptiste Lake, Alberta (Manning et al., 1999), Christina Lake has not become eutrophic (Bradford, 1990) and no pyrite was observed in the sediments nor is any evident in the x-ray diffraction results (Diane Caird, pers. comm.). It is therefore unlikely that the low amount of vivianite in recent sediments is due to sulfate reduction and the scavenging of ferrous iron by sulfide ions.

Anomalously low iron levels occur between 5-10 cm depth suggesting that low iron levels might be at least partially responsible for the scarcity of vivianite over that interval. Stereoscopic examination of the sediment peels, however, showed that small vivianite concretions occurred with the same frequency as they did immediately above and below this interval where iron concentrations were much higher. It is unlikely, then, that the scarcity of vivianite is entirely due to low iron abundance. Why these low levels of iron occurred here and in two other samples further down core is unknown. Perhaps the iron was bound in minerals which were not leachable by dilute HCl, or, perhaps much of the iron from this interval diffused upward or downward a few centimeters (the iron levels for samples on either side of the anomalous trough are quite high). Alternatively, recent road building activity and oil and gas exploration may have interfered with one of the iron sources to the lake.

Deleting the upper 25 cm (which may not have had time to equilibrate and precipitate vivianite nodules of sufficient size) does not significantly improve the Pearson correlation results (Table 4-2) which remain very weak. It is interesting to note, however, that the only significant ($p = .05$) positive correlations occur between vivianite and the number of varves per cm depth (indicating a slow sedimentation rate), and organic matter and phosphorus concentrations (which may be indicative of greater lake productivity).

4.7 Conclusion

In Christina Lake, vivianite abundance in the sedimentary column (excluding the upper 25 cm) appears to be associated with stable thermal stratification (and therefore, probably stable anoxia and minimal dilution of Fe and P in the bottom waters of the hypolimnion), relatively slow sedimentation rate, and somewhat greater lake productivity (as indicated by organic matter and phosphorus concentrations, and the frequency of diatom blooms). Changes in vivianite abundance did not provide any paleoenvironmental information for Christina Lake that could not be provided by other physical or chemical analyses of the laminations and thus its value as a paleoenvironmental indicator at this site is limited. Nevertheless, knowing how vivianite abundance changed in response to various paleoenvironmental factors in Christina Lake might prove useful for studying massive sediments of other lakes in which bright blue concretions of vivianite might be easily seen while changes in lake stratification, sedimentation rate, and productivity are not as readily discernable as they are in laminated lake sediments.

Table 4-1: Characteristics of Christina Lake. Water chemistry is based on a composite sample collected from the euphotic zone August 29, 1983 (modified from Bradford, 1990).

elevation	~554 m
surface area	21.3 km^2
volume	369 x 10^6
maximum depth	32.9 m
mean depth	17.9 m
pH	8.2
total alkalinity ($CaCO_3$)	115 mg L^{-1}
total dissolved solids (calculated)	117 mg L^{-1}
specific conductivity	220 μS cm^{-1}
total hardness ($CaCO_3$)	98 mg L^{-1}
HCO_3	140 mg L^{-1}
CO_3	0 mg L^{-1}
Mg	8 mg L^{-1}
Na	7 mg L^{-1}
K	1 mg L^{-1}
Cl	< 1 mg L^{-1}
SO_4	< 5 mg L^{-1}
Ca	26 mg L^{-1}
total phosphorus	16 μg L^{-1}
total Kjeldahl nitrogen	540 μg L^{-1}
NH_4 - nitrogen	18 μg L^{-1}
iron	< 20 μg L^{-1}
Secchi depth	5.0 m

Table 4-2: Pearson correlation results (two-tailed) between vivianite and other physical and chemical factors. Column A shows correlation results for the entire sediment column (n = 167-168). Column B shows results with the top 25 cm excluded from the correlation analysis (n = 141-143).

	A	B
varves (# cm^{-1})	.288**	.241**
sediment influx (g cm^{-2} yr^{-1})	-0.115	-.219**
organic matter	-0.031	.198*
carbonates	.153*	0.134
ash	-0.064	-.195*
Fe	0.117	0.129
P	0.128	.208*
S	-.186*	-0.107
Al	-0.012	-0.072
As	-0.123	0.041
Ca	-.217**	-.192*
Cu	-.242**	-.273**
K	-.162*	-0.097
Mg	-.266**	-.236**
Mn	-.181*	-0.102
Na	-0.152	-0.052
Ni	-.171*	-0.087
Pb	-.177*	0.006
Ti	-0.064	0.151
Zn	-0.042	0.114

* Correlation is significant at the 0.05 level

** Correlation is significant at the 0.01 level

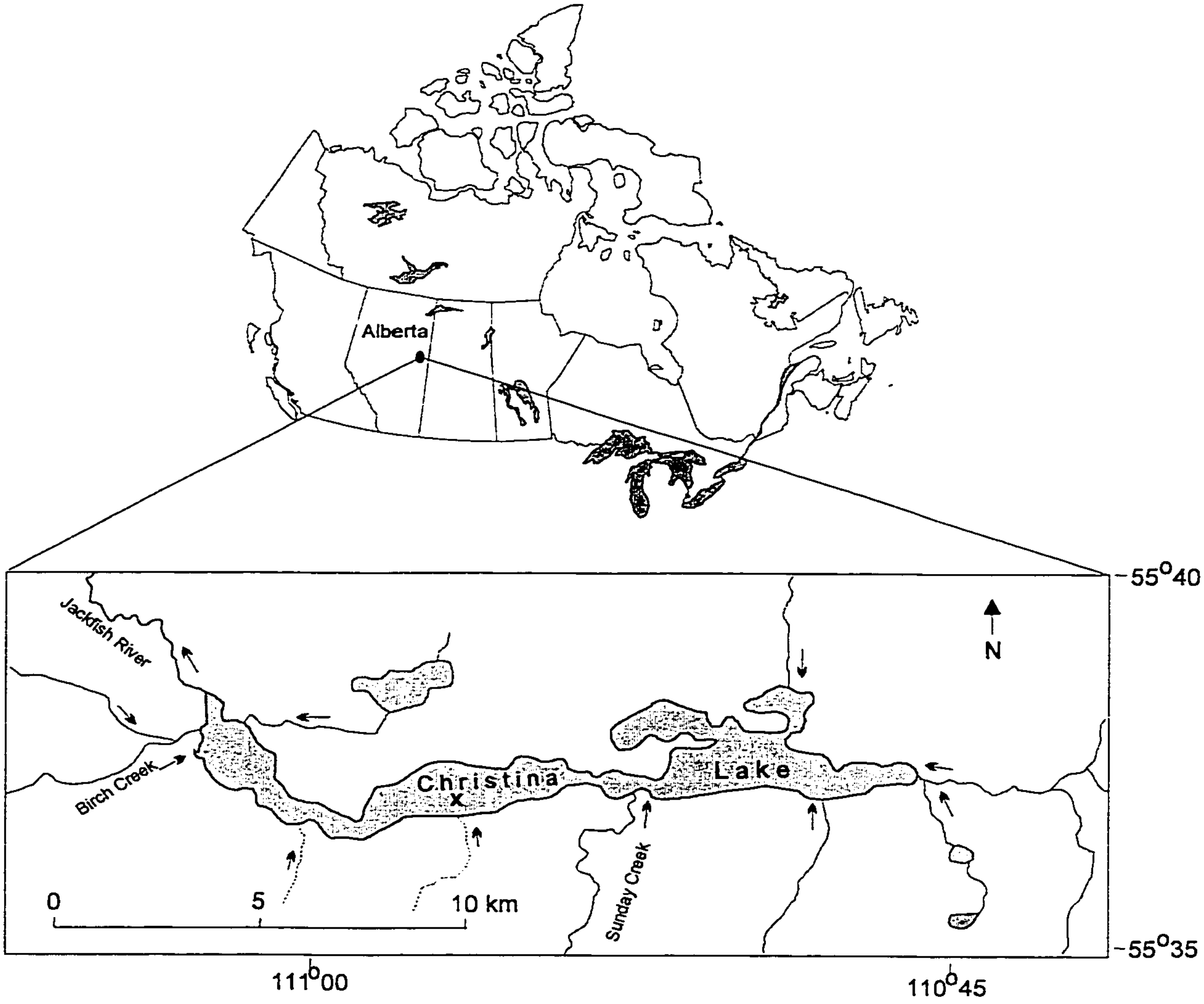
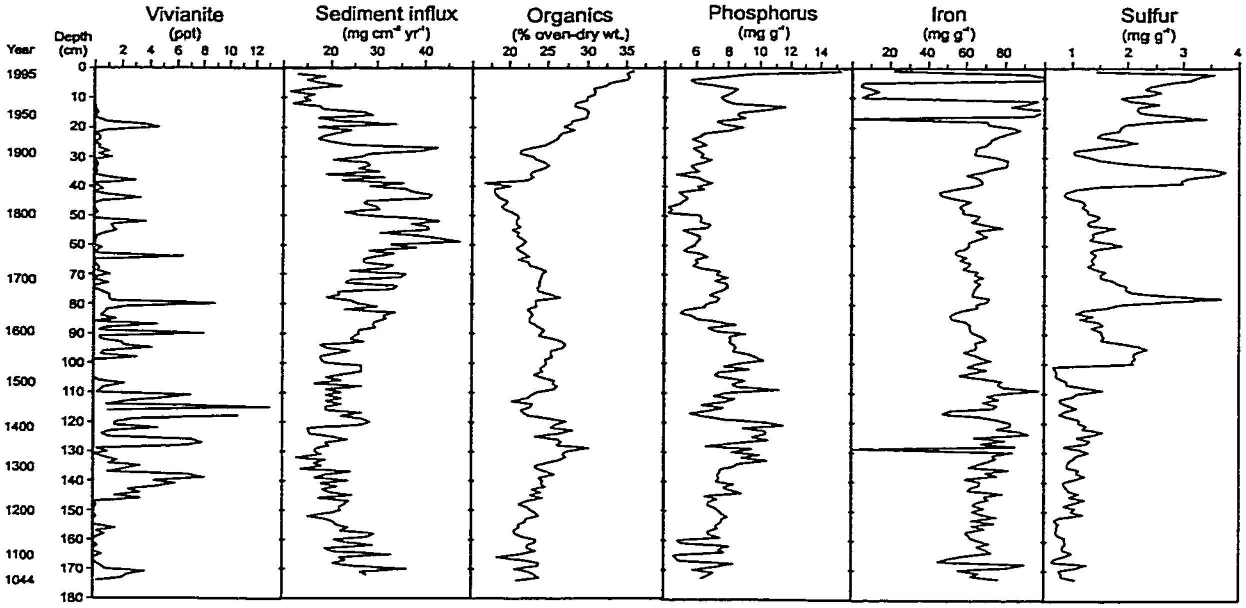


Figure 4-1: Location of Christina Lake. The coring site is marked with an “x”

Figure 4-2: Vivianite abundance in Christina Lake (based on image analysis) shown with sediment influx, organic matter concentration (loss on ignition), and phosphorus, iron, and sulfur concentrations.



4.8 References

Alberta Environmental Protection, 1994. Natural regions and subregions of Alberta: summary. Alberta Environmental Protection, Edmonton.

Anthony, R.S., 1977. Iron-rich rhythmically laminated sediments in Lake of the Clouds, northeastern Minnesota. Limnol. Oceanogr. 22: 45-54.

Berner, R.A., 1981. A new geochemical classification of sedimentary environments. J. Sed. Petrol. 51: 359-365.

Bradford, M.E., 1990. Athabasca River Basin: Christina Lake. *In* P. Mitchell & E. Prepas (eds.), Atlas of Alberta lakes. University of Alberta Press, Edmonton: 136-139.

Campbell, C., 1998. Late Holocene lake sedimentology and climate change in southern Alberta, Canada. Quat. Res. 49: 96-101.

Cornwell, J.A., 1987. Phosphorus cycling in arctic lake sediment: adsorption and authigenic minerals. Arch. Hydrobiol. 109: 161-179.

Dean, W.E., Jr., 1974. Determination of carbonate and organic matter in calcareous sediments and sedimentary rocks by loss on ignition: comparison with other methods. J. Sed. Petrol. 44: 242-248.

Emerson, S., 1976. Early diagenesis in anaerobic lake sediments: chemical equilibria in interstitial waters. Geoch. Cosmosch. Acta. 40: 925-934.

Håkanson, L. & M. Jansson, 1983. Principles of Lake Sedimentology. Springer-Verlag, New York, 316 pp.

Henderson, G., K. Rodgers & V. Cassie, 1983. Diatoms accompanying vivianite from Auckland Province. N. Z. J. Geol. Geophys. 26: 309-310.

Henderson, G.S., P.M. Black, K.A. Rodgers & P.C. Rankin, 1984. New data on New Zealand vivianite and metavivianite. N. Z. J. Geol. Geophys. 27: 367-378.

Jakobsen, B.H., 1988. Accumulation of pyrite and Fe-rich carbonate and phosphate minerals in a lowland moor area. J. Soil Sci. 39: 447-455.

Jones, B.F. & C.J. Bowser, 1978. The Mineralogy and Related Chemistry of Lake Sediments. *In* A. Lerman (ed.), Lakes: Chemistry, Geology, Physics. Springer-Verlag, New York: 179-235.

Kjensmo, J., 1967. The development and some main features of "iron-meromictic" soft-water lakes. Arch. Hydrobiol. Suppl. 32: 137-312.

Laird, L.D. & I.D. Campbell, In Press. High resolution palaeofire signals from Christina Lake, Alberta: a comparison of the charcoal signals extracted by two different methods. Palaeogeogr. Palaeoclim. Palaeoecol.

Landuydt, C.J., 1990. Micromorphology of iron minerals from bog ores of the Belgian Campine area. Dev. Soil Sci. 19: 289-294.

Leavens, P.B., 1972. Oxidation of vivianite in New Jersey Cretaceous greensands. Abstracts, 24th International Geological Congress, Montreal, 423.

Mackereth, F.J.H., 1965. Some chemical observations on post-glacial lake sediments. Phil. Trans. Roy. Soc. London 250: 165-213.

Malo, B.A., 1977. Partial extraction of metals from aquatic sediments. Env. Sci. Technol. 11: 277-282.

Manning, P.G., T.P. Murphy & E.E. Prepas, 1991. Intensive formation of vivianite in the bottom sediments of mesotrophic Narrow Lake, Alberta. Can. Mineral. 29: 77-85.

Manning, P.G., E.E. Prepas & M.S. Serediak, 1999. Pyrite and vivianite intervals in the bottom sediments of eutrophic Baptiste Lake, Alberta. Can. Mineral. 37: 593-601.

McCammon, C.A. & R.G. Burns, 1980. The oxidation mechanism of vivianite as studied by Mossbauer spectroscopy. Am. Mineral. 65: 361-366.

Nembrini, G.P., J.A. Capobianco, M. Viel & A.F. Williams, 1983. A Mossbauer and chemical study of the formation of vivianite in sediments of Lago Maggiore (Italy). Geoch. Cosmosch. Acta. 47: 1459-1464.

Nriagu, J.O., 1972. Stability of vivianite and ion-pair formation in the system $Fe_3(PO_4)_2$ - H_3PO_4 - H_20. Geoch. Cosmosch. Acta. 36: 459-470.

Nriagu, J.O. & C.I. Dell, 1974. Diagenetic formation of iron phosphates in recent lake sediments. Am. Mineral. 59: 934-946.

O'Sullivan, P.E., 1983. Annually-laminated lake sediments and the study of Quaternary environmental changes -- a review. Quat. Sci. Rev. 1: 245-313.

Petterson, G., 1996. Varved sediments in Sweden: a brief review. *In* A.E.S. Kemp (ed.), Palaeoclimatology and palaeoceanography from laminated sediments. Geological Society Special Publication No. 116. The Geological Society, London: 73-77.

Postma, D., 1982. Pyrite and siderite formation in brackish and freshwater swamp sediments. Am. J. Sci. 282: 1151-1183.

Rosenquist, I.T., 1970. Formation of vivianite in Holocene clay sediment. Lithos 3: 327-334.

Schwertmann, U. & R.W. Fitzpatrick, 1992. Iron minerals in surface environments. Catena Suppl. 21: 7-30.

Swain, A.M., 1973. A history of fire and vegetation in northeastern Minnesota as recorded in lake sediments. Quat. Res. 3: 383-396.

Van Horne, 1998. Christina Lake Thermal Project. Application to Alberta Energy and Utilities Board and to Alberta Environmental Protection. Volume 1 - Joint Submission. Report available at Alberta Environmental Protection library, Edmonton, Alta.

Vance, R.E., R.W. Mathewes & J.J. Clague, 1992. 7000 year record of lake-level change on the northern Great Plains: a high-resolution proxy of past climate. Geology 20: 879-882.

Virtanen, K., 1994. Geological control of iron and phosphorus precipitates in mires of the Ruukki-Vihanti area, central Finland. Geological Survey of Finland, Bulletin 375, 69 pp.

Walling, D.E. & Q. He, 1993. Towards Improved Interpretation of ^{137}Cs profiles in lake sediments. *In* J. McManus & R.W. Duck (eds.), Geomorphology and sedimentology of lakes and reservoirs. John Wiley & Sons Ltd., Toronto: 31-53.

CHAPTER 5

Summary, Discussion, Conclusion, and Suggestions for Further Research

5.1 Summary

The boreal forest of Canada is a fire-dependent biome (Johnson 1992; Rowe and Scotter 1973; Wein and MacLean 1983). Climate change models suggest that the fire regime of the boreal forest will be altered in a 2X CO_2 world (Bergeron and Flannigan 1995; Weber and Flannigan 1997; Wotton and Flannigan 1993) and the changed fire regime may impact the forest to a greater extent than will the direct effects of the climate change itself (Bergeron and Flannigan 1995; Weber and Flannigan 1997; Wein and de Groot 1996). While the rate of change in the future is likely to be greater than at any time in the past, studying the responses of fire and vegetation to past climate changes may yield information that will be useful in predicting and preparing for changes in the future (Weber and Flannigan 1997). Concern over future climate change along with the need of park managers and forest managers to understand the "natural" fire regime of the forest in order to develop appropriate fire management or harvesting policies, has prompted an increased demand for high-resolution paleofire research.

At the time this project was initiated, there were no long-term high-resolution paleofire studies completed for the western boreal forest. The objective of this study was, therefore, to begin to fill in some of the knowledge gaps concerning the response of the fire regime and vegetation of the western boreal to climatic fluctuations over the last millennium. To this end, charcoal, pollen, and sedimentological characteristics of the annually-laminated sediments deposited over the last ~940 years in Christina Lake, Alberta were studied. Christina Lake is large and open (which is generally thought to be a disadvantage for extracting a local fire history) and located in the mid-boreal (far from any ecotones which are assumed to be more sensitive to climatic fluctuations). It was thought, however, that by choosing a method of charcoal analysis which focussed on large charcoal fragments, a local paleofire signal could be extracted, and that if pollen analysis was done at sufficiently high resolution, subtle vegetational changes in response to climate might be detected.

This study thus attempted to disprove the following null hypothesis:

> *The mid-boreal forest is sufficiently stable in the face of minor climate changes that none of the known climate changes over the last 1000 years will be detectable in the pollen, charcoal, or sedimentological records of a moderately large lake in the mid boreal forest.*

The results of this study suggest that the pollen, charcoal, and sedimentological records of Christina Lake were indeed impacted by climatic fluctuations over the last millennium, as indicated in the summary and discussion below, and, therefore, the null hypothesis can be rejected.

5.1.1 Pollen

While the pollen results showed that the overall vegetation remained relatively stable over the past ~900 years, there was some evidence to suggest that the relative proportion of several species changed over time in response to climate. Consistent small increases in the concentrations of *Populus* and *Corylus* pollen prior to ~1250 AD suggested a greater deciduous component in the mixedwood forest surrounding Christina Lake, perhaps caused by the generally warmer climate of the Medieval Warm Period ca. 900-1300 AD (Hughes and Diaz 1994). As poplar pollen preserves extremely poorly in lake sediments (Hadden 1978; Lichti-Federovich 1970), the small increases in poplar pollen abundance could represent a much greater increase in the number of trees in the landscape. Other evidence for climate-induced vegetation change came from a strong decline in pine pollen in the samples from 1797 and 1853. A similar decline over a similar time frame was noted in other studies from the Wood Buffalo National Park area (Larsen and MacDonald 1998a; 1998b) and could be directly related to the cold, wet Little Ice Age climate or to climate-induced changes in fire disturbance.

The changes in vegetation observed in the Christina Lake data were not as dramatic as those observed in some ecotonal sites. For example, a mass die-off of white spruce between 1800 and 1860 was noted at an alpine treeline site in the Northwest Territories (Szeicz and MacDonald 1995); fire and climate-induced deforestation occurred in many forest-tundra sites in Quebec during the Little Ice Age (Arseneault and Payette 1992); and evidence for higher treelines ~1000 AD was found in the southern Canadian Rocky Mountains (Luckman 1994). The results do suggest, however, that climate fluctuations over the last 1000 years were sufficient to cause vegetational changes even in a non-ecotonal site. As Gajewski (1993) points out, while changes away from the ecotone may be less noticeable, they may still be significant as the sum of a small change in abundance over the entire range of a species is likely to be much greater than the sum of the larger change along a small ecotone.

The evidence for climate-induced vegetation change at Christina Lake suggests that the resolution of the study may be more important than its location for detecting changes over shorter time-scales. A further illustration comes from Vance et al. (1983) and Mott (1973) who did palynological studies in the ecotone between the boreal forest and the Aspen Parkland. Due to the coarse resolution of their studies (5 to 10 samples per 1000 years), they concluded that little vegetational change had occurred over the last 3000 years. By contrast, Campbell and Campbell (In Press) noted changes in both vegetation and fire in their high-resolution study spanning the last ~1400 years in the same ecotone (as reviewed in Chapter 1).

While climate-induced changes in vegetation were noted in Christina Lake, fire-induced changes in vegetation were difficult to detect as the pollen signal in large open lakes is dominated by regional rather than local pollen rain (Jacobson and Bradshaw 1981; Sugita et al. 1997) and thus the pollen catchment was much larger than the charcoal catchment for this site.

Small lakes, such as those studied by Larsen and MacDonald (1998a; 1998b) in the Wood Buffalo National Park area, would, therefore, be a better study site choice for determining vegetation responses to fire activity.

5.1.2 Charcoal

By choosing a method of charcoal extraction which focussed on large charcoal fragments (> 125 μm), a local fire signal (which emphasized large fires burning right to shore) was obtained despite the large size of the lake and its many inflowing streams. The paleofire signal obtained by the nitric acid digestion - Total Carbon Analyser ignition method proved to be too correlated with sediment influx (and thus variable stream inflow and erosion), to be useful in this study. The results from this method were important, however, in that they showed that even in a large, open lake, the "total" charcoal influx is relatively local (i.e. confined to the watershed) and that aerial transport of charcoal from fires (even very large fires) outside the watershed is relatively unimportant at this site.

General patterns in fire activity for the prehistoric portion of the Christina Lake charcoal curve (extracted by the sieving method) were similar to those found in the Wood Buffalo National Park area and several mountain sites in Alberta and British Columbia with greater fire activity from the 16th century to the early-to-middle 18th century and less fire activity before and after this interval (Johnson et al. 1990; Johnson and Larsen 1991; Johnson and Wowchuk 1993; Larsen and MacDonald 1998a, 1998b; Masters 1990). The consistency in fire activity patterns over a broad geographic area suggests that the shifts in the fire regimes were related to large-scale climatic factors (Johnson and Wowchuk 1993). The specific nature of the climatic variables to which fire activity near Christina Lake was responding was not always clear, however, as only general climate trends could be inferred from the sedimentological data (see below) whereas fires often occur during short-term extremes in weather (Flannigan and Harrington 1988). This problem was most evident in the short average fire return intervals for large fires during the first part of the Little Ice Age despite the general moistening trend indicated by the proxy climate data.

The very long return interval for large fires during the latter half of the Little Ice Age was, however, consistent with the cold, wet conditions inferred from the sedimentological data. The situation near Christina Lake during this time interval may have been similar to that described by Foster (1983) in southeastern Labrador wherein the preponderance of wetlands and paludified sites in the landscape prevented the spread of large fires and resulted in the exclusion of fire-dependent species. Less fire activity near Christina Lake may have lead to greater mortality of fire-dependent jack pine and greater fuel buildup in the landscape. These factors may have contributed to the frequent large fires of the mid- to late-1800s. Current research suggests, however, that coarse woody debris decomposes within 20-40 years (R. Wein, pers. comm.) so any increase in fuel buildup would have been limited to trees dying after ~1825.

5.1.3 Sedimentology

Sediment influx (g cm^{-2} yr^{-1}) and carbonate concentration results yielded proxy climate information concerning general trends in precipitation and temperature respectively. The results showed a cooler wetter Little Ice Age interval preceded and followed by warmer, drier conditions which is consistent with other regional proxy climate information (Campbell 1998; Vance et al. 1992). Visible physical features of the sediment core such as varve regularity and distinctiveness, diatom blooms, sedimentation rate (varves cm^{-1}), and vivianite abundance also helped to give a general picture of lake productivity and thermal stratification that was consistent with the proxy climate information.

The presence of inflowing streams in Christina Lake was both an advantage and a disadvantage for extracting sedimentological information which may be related to climate. Variations in sediment influx (which was dominantly stream-borne clastic material) allowed a general precipitation trend to be inferred (although with no information on the seasonality or frequency of precipitation). The organic concentration of the sediment was also dominated by allochthonous (i.e. stream-borne) material, however, which precluded its use as an indicator of lake productivity (from which summer climate may have been inferred).

The changes in sedimentology in response to climate were not as pronounced in Christina Lake as they were in Chappice Lake near Medicine Hat, Alberta (Vance et al. 1992). The sediments of Chappice Lake fluctuated between annually-laminated sequences during dry periods and massive sediments during wet periods. By contrast, the sediments of Christina Lake remained varved throughout, although the laminations were generally much less distinct during the latter phase of the Little Ice Age.

5.2 Discussion - Potential Impact of Future Climate Change on Christina Lake

The sensitivity of the fire regime of the Christina Lake area to the climatic fluctuations over the last millennium suggests that the fire regime will be very sensitive to climate change of the future which is expected to be of greater magnitude. The exact nature of the change in fire regime is, however, difficult to predict. Flannigan et al. (1998) modelled changes in the Fire Weather Index (FWI) (a measure of fire danger) for Canada under 2 X CO_2 conditions. Their results show that the average FWI will be slightly lower in the Christina Lake region while extreme FWI values will remain about the same as it is now because increases in precipitation will offset temperature increases. The resolution of the GCM is coarse, however, aerosols are not incorporated, and land surface paramaterization in the model needs improvement (Flannigan et al. 1998).

Other modelling research suggests the fire season will lengthen by ~24 days in Alberta (Wotton and Flannigan 1993), and lightning frequency will increase by 30-40% between latitudes 50° N and 70° N (Fosberg et al. 1996; Price and Rind 1994). The impact of the latter on the Christina Lake area may be especially profound since it is located within a zone of higher-than-average lightning activity due to its position relative to the mountains (Nash and Johnson 1996). The climate of a 2 X CO_2 world is also expected to be much more variable with more extreme events (Flannigan et al. 1998). A period of greater climatic variability occurred from ~1550 -1700 in Europe (Lamb 1982) and perhaps in western Canada as well (Johnson and Wowchuk 1993). This period was characterized by a much greater frequency in the occurrence of blocking highs in high latitudes. Large fires have been shown to be related to blocking high pressure systems (Flannigan and Harrington 1988; Johnson and Wowchuk 1993; Newark 1975; Nimchuk 1983) so if the greater climate variability in a 2 X CO_2 environment is also characterized by a greater frequency of blocking highs, an increase in fire activity seems likely, especially when combined with longer fire seasons and greater lightning frequency.

The impact on the vegetation of the Christina Lake area of an increase in fire activity coupled with the stresses induced by the climate change itself is difficult to predict, but the following brief speculations are offered (a much more comprehensive review of this topic is given by Weber and Flannigan, 1997). If fire activity increases, species that can adapt to very short fire cycles (such as jack pine, black spruce, and aspen) will be favoured over species that cannot (such as white spruce and balsam fir). An increase in fire activity may also accelerate the eventual climate-induced vegetational change from the present mixedwood forest to the predicted aspen/grassland mosaic (Flannigan et al. 1998) as fire removes species poorly adapted to the new climate and provides an opportunity for better-adapted species to move in (Wein and de Groot 1996). During the transition to the new vegetation type, tree mortality due to climate stress and disease is likely to be very high and this may lead to larger or more severe fires due to an excess of dead and downed fuels (Weber and Flannigan 1997).

5.3 Conclusion

The completion of this project and recent work by Larsen and MacDonald in the Wood Buffalo National Park are important steps towards a greater understanding of the relationships among fire, vegetation, and climate in the western boreal forest. The results of this study are valuable in that they showed that both the fire regime and the vegetation of the mid-boreal forest were sensitive to climate changes over the last 1000 years, despite the relatively small magnitude of the climatic fluctuations and the location of the study site far from an ecotone. The similarity of the pollen and fire results from Christina Lake to those of other studies in western Canada highlighted the great influence large-scale climatic patterns have on vegetation and fire regimes. It is hoped that some of the results of this study will be useful in determining the potential sensitivity of the fire regime and vegetation of the mid-boreal forest to climate changes in the future.

5.4 Suggestions for Further Research

1. Testing the nitric acid digestion-Total Carbon Analyser ignition method of carbon quantification on sediments from a closed varved lake would help to determine the utility of this method for paleofire studies in lakes which are not confounded by variable stream inflow.
2. High-resolution pollen studies from elsewhere in the western boreal forest would be useful in determining the spatial extent of the decline in pine pollen during the early to mid-1800s.
3. The analysis of additional pollen samples from Christina Lake spanning ~1750 to ~1875 would be useful in determining the consistency and temporal limits of the decline in pine pollen at this site.
4. High-resolution charcoal studies from elsewhere in the western boreal forest would be useful in determining the spatial limits to the apparent general synchronicity in the paleofire patterns found in Christina Lake, Wood Buffalo National Park, and several sites in the Rocky Mountains.
5. High-resolution charcoal-based studies in the mountains would extend the paleofire record back beyond the limits of the current dendrochronological studies. It would be interesting to determine if fire cycles lengthen again prior to 1500 as they do in the Christina Lake record and the records from the Wood Buffalo National Park area.
6. A high-resolution study from Christina Lake spanning several thousands of years (ideally right through the Hypsithermal) would help to place this study in a broader temporal context.
7. A detailed multi-proxy varve by varve analysis of lake sediments (from Christina Lake or elsewhere) might yield more specific paleoenvironmental information. Coupling such a study with a detailed analysis of a long dendrochronological record from the same site might be especially useful.

5.5 References

Arseneault, D., and Payette, S. 1992. A postfire shift from lichen-spruce to lichen-tundra vegetation at tree line. Ecology **73**: 1067-1081.

Bergeron, Y., and Flannigan, M.D. 1995. Predicting the effects of climate change on fire frequency in the southeastern Canadian boreal forest. Wat. Air Soil Pollut. **82**: 437-444.

Campbell, C. 1998. Late Holocene lake sedimentology and climate change in southern Alberta, Canada. Quat. Res. **49**: 96-101.

Campbell, I.D., and Campbell, C. In Press. Late Holocene vegetation and fire history at the southern boreal forest margin in Alberta, Canada. Palaeogeogr. Palaeoclim. Palaeoecol.

Flannigan, M.D., Bergeron, Y., Engelmark, O., and Wotton, B.M. 1998. Future wildfire in circumboreal forests in relation to global warming. J. Veg. Sci. **9**: 469-476.

Flannigan, M.D., and Harrington, J.B. 1988. A study of the relation of meteorological variables to monthly provincial area burned by wildfire in Canada. J. Appl. Meteorol. **27**: 441-452.

Fosberg, M.A., Stocks, B.J., and Lynham, T.J. 1996. Risk analysis in strategic planning: fire and climate change in the Boreal forest. *In* Fire in Ecosystems of Boreal Eurasia. *Edited by* J.G. Goldammer, and V.V. Furyaev. Kluwer Academic Publishers, The Netherlands. pp. 495-505.

Foster, D.R. 1983. The history and pattern of fire in the boreal forest of southeastern Labrador. Can. J. Bot. **61**: 2459-2471.

Gajewski, K. 1993. The role of paleoecology in the study of global climatic change. Rev. Palaeobot. Palynol. **79**: 141-151.

Hadden, K. 1978. Investigation of the registration of poplar pollen in lake sediments. Master of Science, University of Toronto, Toronto.

Hughes, M.K., and Diaz, H.F. 1994. Was there a 'Medieval Warm Period', and if so, where and when? Clim. Change **26**: 109-142.

Jacobson, G.L., Jr., and Bradshaw, R.H.W. 1981. The selection of sites for paleovegetational studies. Quat. Res. **16**: 80-96.

Johnson, E.A. 1992. Fire and vegetation dynamics: studies from the North American boreal forest. Cambridge University Press, Cambridge, UK.

Johnson, E.A., Fryer, G.I., and Heathcott, M.J. 1990. The influence of man and climate on frequency of fire in the interior wet belt forest, British Columbia. J. Ecol. **78**: 403-412.

Johnson, E.A., and Larsen, C.P.S. 1991. Climatically induced change in fire frequency in the southern Canadian Rockies. Ecology **72**: 194-201.

Johnson, E.A., and Wowchuk, D.R. 1993. Wildfires in the southern Canadian Rocky Mountains and their relationship to mid-tropospheric anomalies. Can. J. For. Res. **23**: 1213-1222.

Lamb, H.H. 1982. Climate, history and the modern world. Methuen, London.

Larsen, C.P.S., and MacDonald, G.M. 1998a. An 840-year record of fire and succession in a boreal white spruce forest. Ecology **79**: 106-118.

Larsen, C.P.S., and MacDonald, G.M. 1998b. Fire and vegetation dynamics in a jack pine and black spruce forest reconstructed using fossil pollen and charcoal. J. Ecol. **86**: 815-828.

Lichti-Federovich, S. 1970. The pollen stratigraphy of a dated section of Late Pleistocene lake sediment from central Alberta. Can. J. Earth Sci. **7**: 938-945.

Luckman, B.H. 1994. Evidence for climatic conditions between ca. 900-1300 A.D. in the southern Canadian Rockies. Clim. Change **26**: 171-182.

Masters, A.M. 1990. Changes in forest fire frequency in Kootenay National Park, Canadian Rockies. Can. J. Bot. **68**: 1763-1767.

Mott, R.J. 1973. Palynological studies in central Saskatchewan: pollen stratigraphy from lake sediment sequences. Geological Survey of Canada Paper 72-49.

Nash, C.H., and Johnson, E.A. 1996. Synoptic climatology of lightning-caused forest fires in subalpine and boreal forests. Can. J. For. Res. **26**: 1859-1874.

Newark, M.J. 1975. The relationship between forest fire occurrence and 500 mb longwave ridging. Atmosphere **13**: 26-33.

Nimchuk, N. 1983. Wildfire behavior associated with upper ridge breakdown. Alberta Energy and Natural Resources, Forest Service ENR Technical Report T/50.

Price, C., and Rind, D. 1994. The impact of a 2 X CO2 climate on lightning-caused fires. J. of Climate **7**: 1484-1494.

Rowe, J.S., and Scotter, G.W. 1973. Fire in the boreal forest. Quat. Res. **3**: 444-464.

Sugita, S., MacDonald, G.M., and Larsen, C.P.S. 1997. Reconstruction of fire disturbance and forest succession from fossil pollen in lake sediments: potential and limitations. *In* Sediment records of biomass burning and global change. *Edited by* J.S. Clark, H. Cachier, J.G. Goldammer, and B.J. Stocks. Springer-Verlag, Berlin. pp. 387-412.

Szeicz, J.M., and MacDonald, G.M. 1995. Recent white spruce dynamics at the subarctic alpine treeline of north-western Canada. J. Ecol. **83**: 873-885.

Vance, R.E., Emerson, D., and Habgood, T. 1983. A mid-Holocene record of vegetative change in central Alberta. Can. J. Earth Sci. **20**: 364-376.

Vance, R.E., Mathewes, R.W., and Clague, J.J. 1992. 7000 year record of lake-level change on the northern Great Plains: a high-resolution proxy of past climate. Geology **20**: 879-882.

Weber, M.G., and Flannigan, M.D. 1997. Canadian boreal forest ecosystem structure and function in a changing climate: impact on fire regimes. Environ. Rev. **5**: 145-166.

Wein, R.W., and de Groot, W.J. 1996. Fire - climate change hypotheses for the Tiaga. *In* Fire in ecosystems of boreal Eurasia. *Edited by* J.G. Goldammer, and V.V. Furyaev. Kluwer Academic Press, The Netherlands. pp. 505-512.

Wein, R.W., and MacLean, D.A. (*Eds.*). 1983. The role of fire in northern circumpolar ecosystems. John Wiley and Sons, New York.

Wotton, B.M., and Flannigan, M.D. 1993. Length of the fire season in a changing climate. For. Chron. **69**: 187-192.

Appendix 1: Description of ^{137}Cs determination

Samples of the dried Christina Lake sediment, weighing *ca.* 0.5-0.6 g each, were weighed into polyethylene counting vials. Each sample was counted at the University of Alberta SLOWPOKE Facility using a 22% hyperpure Ge detector housed in a 10 cm Pb cave. Sample counting times varied, but were never less than 80,000 s (*ca.* 22 hrs). The counting system was efficiency calibrated using certified CANMET radioactive reference standards DL-1a (116 ug/g U) and DH-1 (2673 ug/g U). The results of the analyses are listed in Table A-1 below. For sample LL 18-19 the ^{137}Cs activity was below the detection limit of the system. (M.J.M. Duke, pers. comm.)

ID	Varve Date	^{137}Cs Bq/g
LL 7-9	1976.5-1983	0.177
LL 9-10	1974-1976.5	0.232
LL 10-11	1970-1974	0.134
LL 11-12	1967-1970	0.259
LL 12-13	1963-1967	0.304
LL 13-14	1960.5-1963	0.265
LL 14-15	1958-1960.5	0.209
LL 16-17	1952.5-1955	0.106
LL 17-18	1949-1952.5	0.031
LL 18-19	1945-1949	<0.01

Table A-1. ^{137}Cs gamma-ray spectrometry results.

Appendix 2 - Basic pollen preparation procedure

1) dry and weigh sample
2) add *Lycopodium* spike
3) soak in 10% KOH in a hot water bath - centrifuge and decant (C+D)(removes humics and disaggregates sample)
4) rinse with distilled water - C+D
5) add 5% HCl - C+D (removes carbonates and acidifies for HF)
6) add HF in hot water bath (removes fine silicates)
7) add 5% HCl - C+D (removes HF in acid medium to prevent formation of hydrofluorosilicates)
8) add Glacial Acetic Acid - C+D (dehydrates sample to prepare for acetolysis)
9) add Acetolysis mixture in hot water bath - C+D (removes fine cellulose)
10) add Glacial Acetic Acid - C+D (removes acetolytic solution in acid dehydrated medium)
11) add distilled water - C+D
12) add 50% glycol - C+D
13) mount in glycerine or glycerine jelly

Appendix 3 - Full pollen diagrams

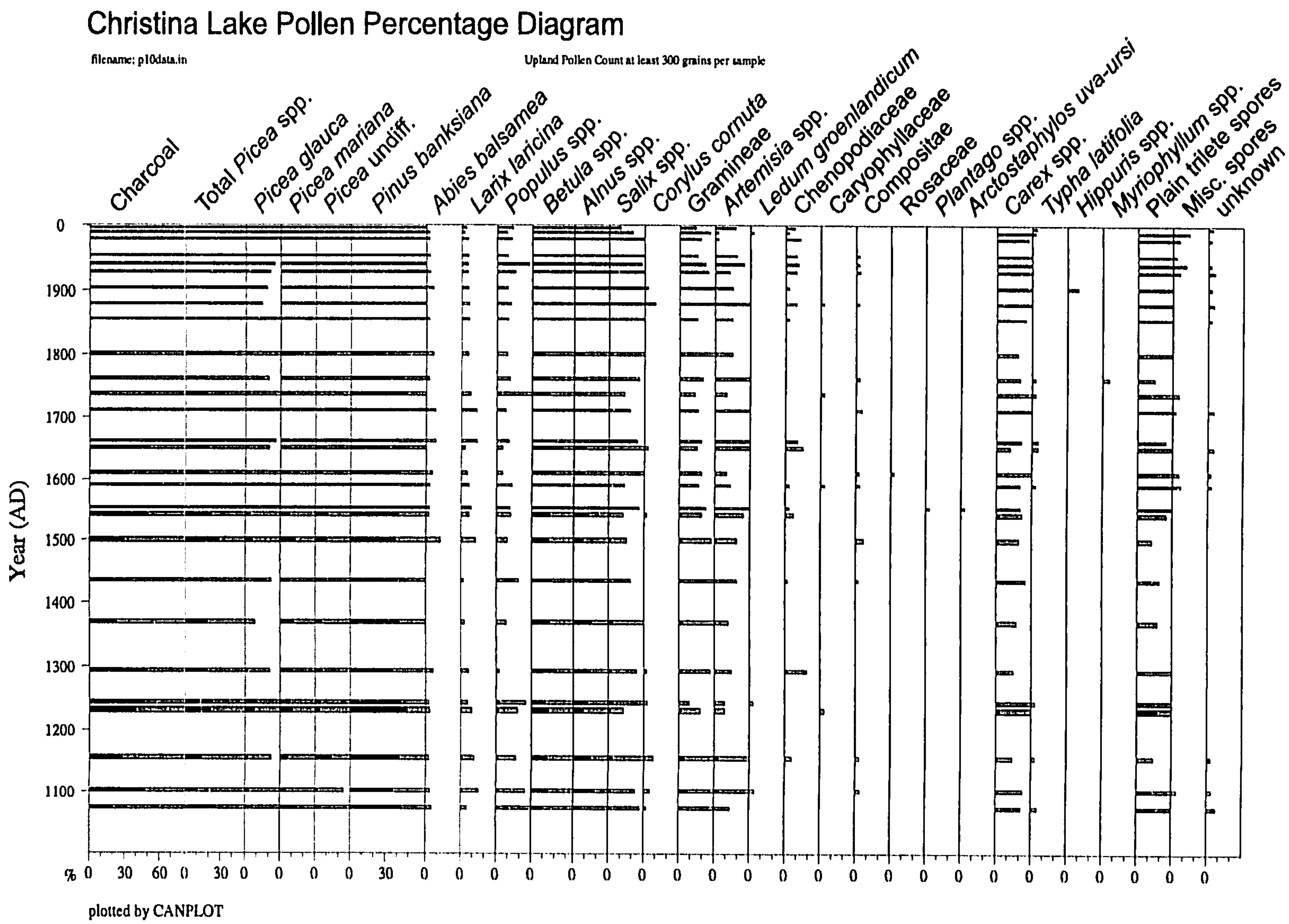


Figure A-1: Full pollen percentage diagram for Christina Lake.

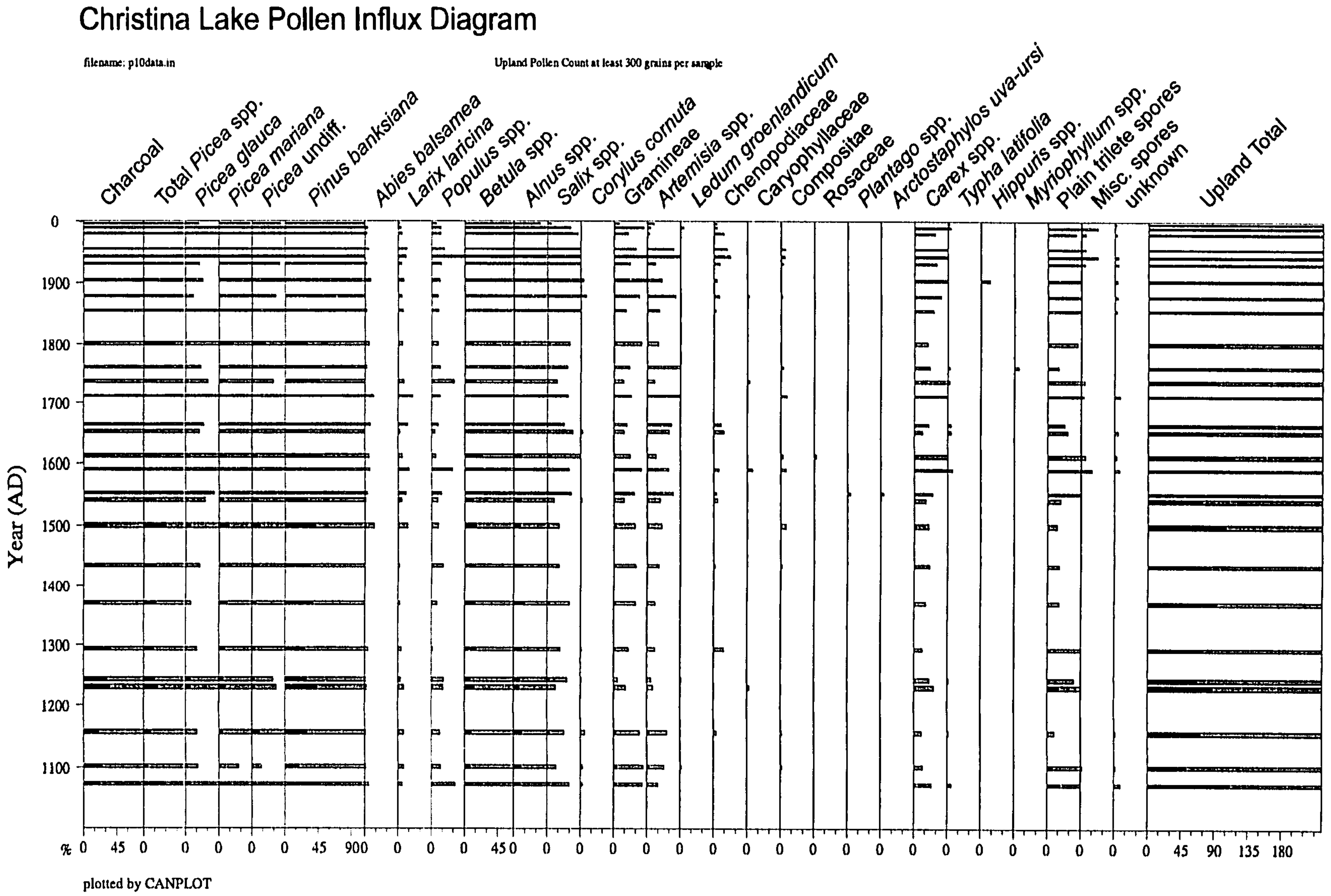


Figure A-2: Full pollen influx diagram for Christina Lake. Expressed in terms of number of grains divided by 10000.

Appendix 4: Results from geochemical analyses. (ICP-AES analysis of .25N HCl leachate).

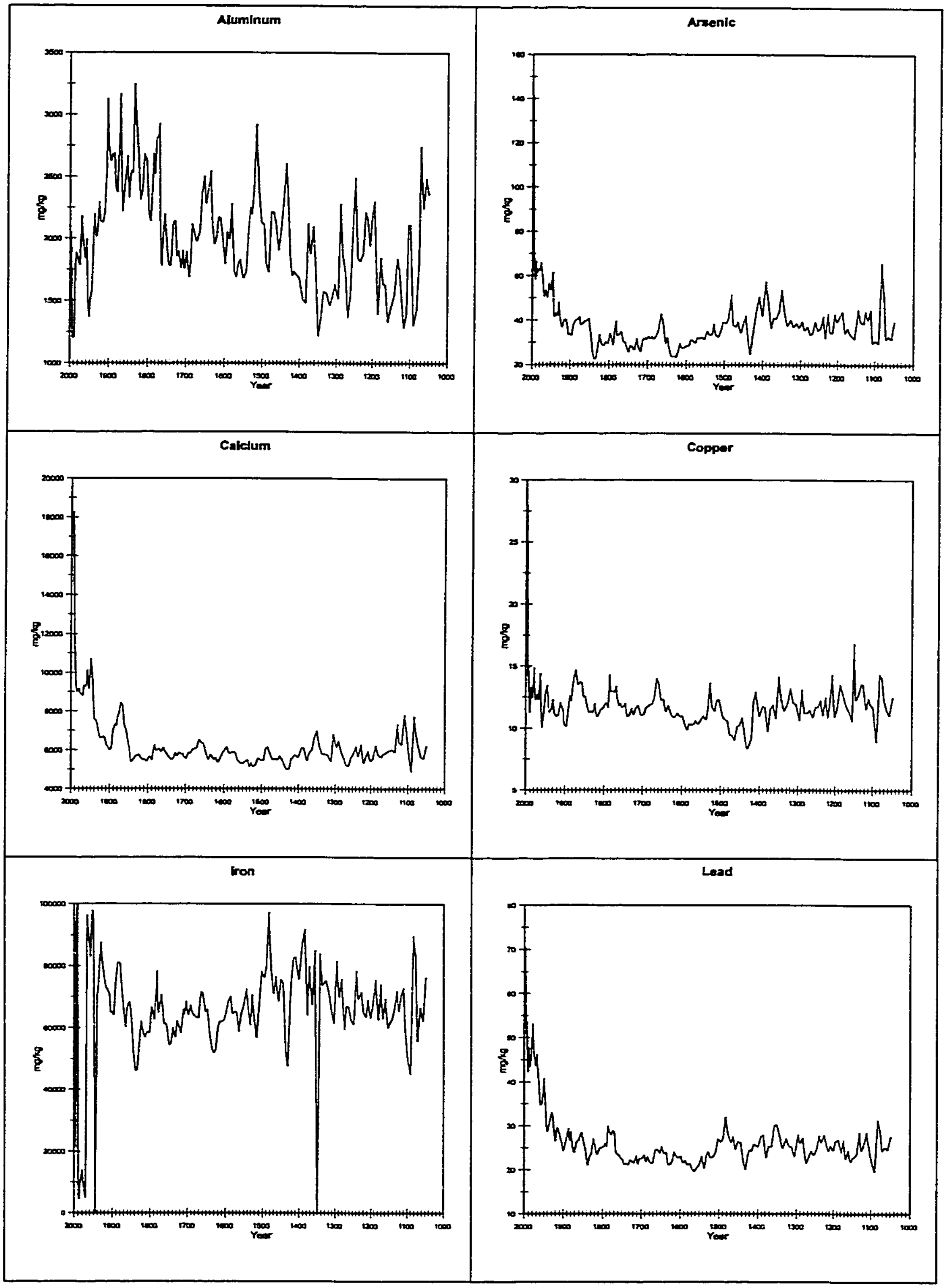


Figure A-3: Concentrations of aluminum, arsenic, calcium, copper, iron, and lead.

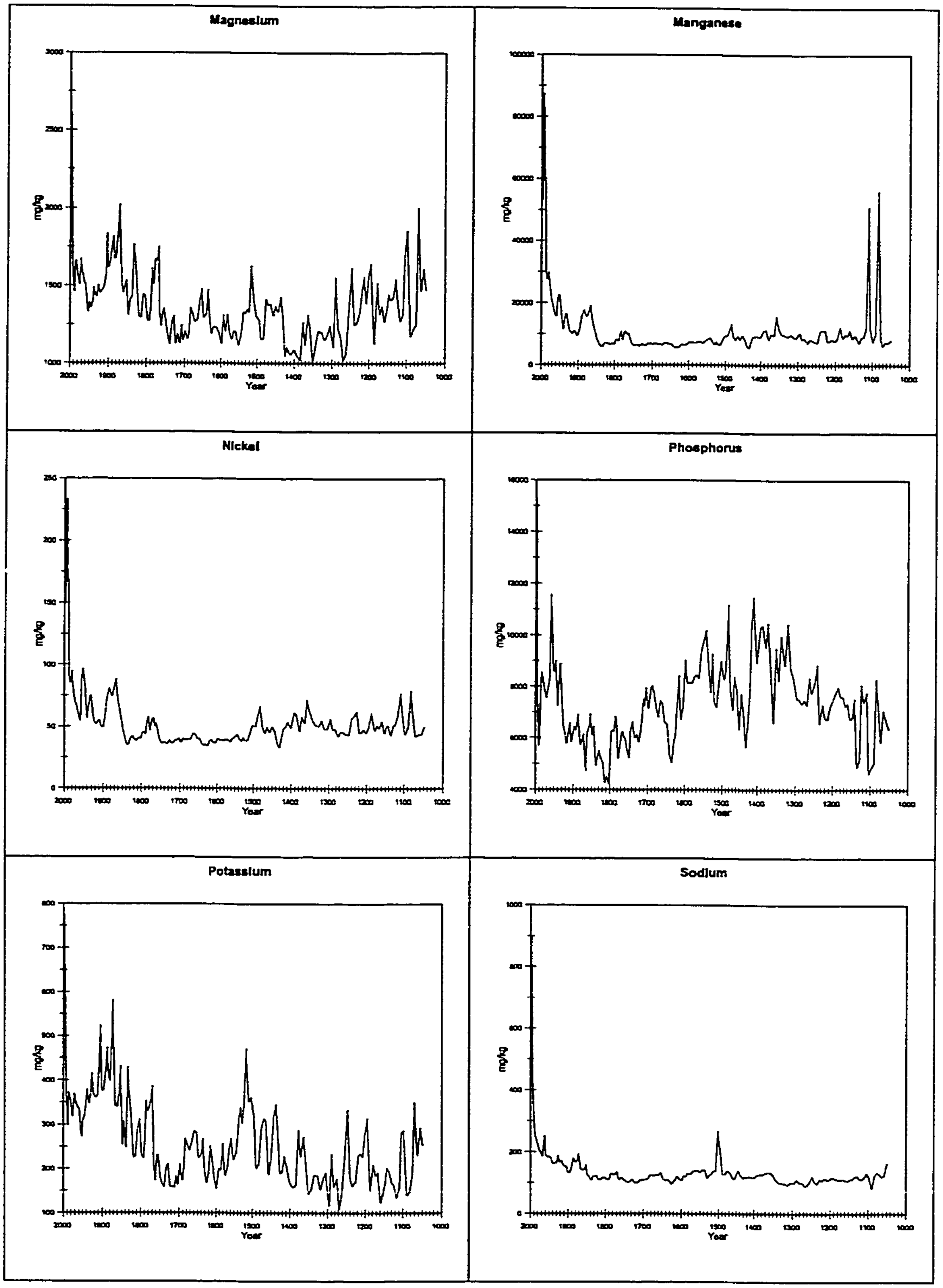


Figure A-4: Concentrations of magnesium, manganese, nickel, phosphorus, potassium and sodium.

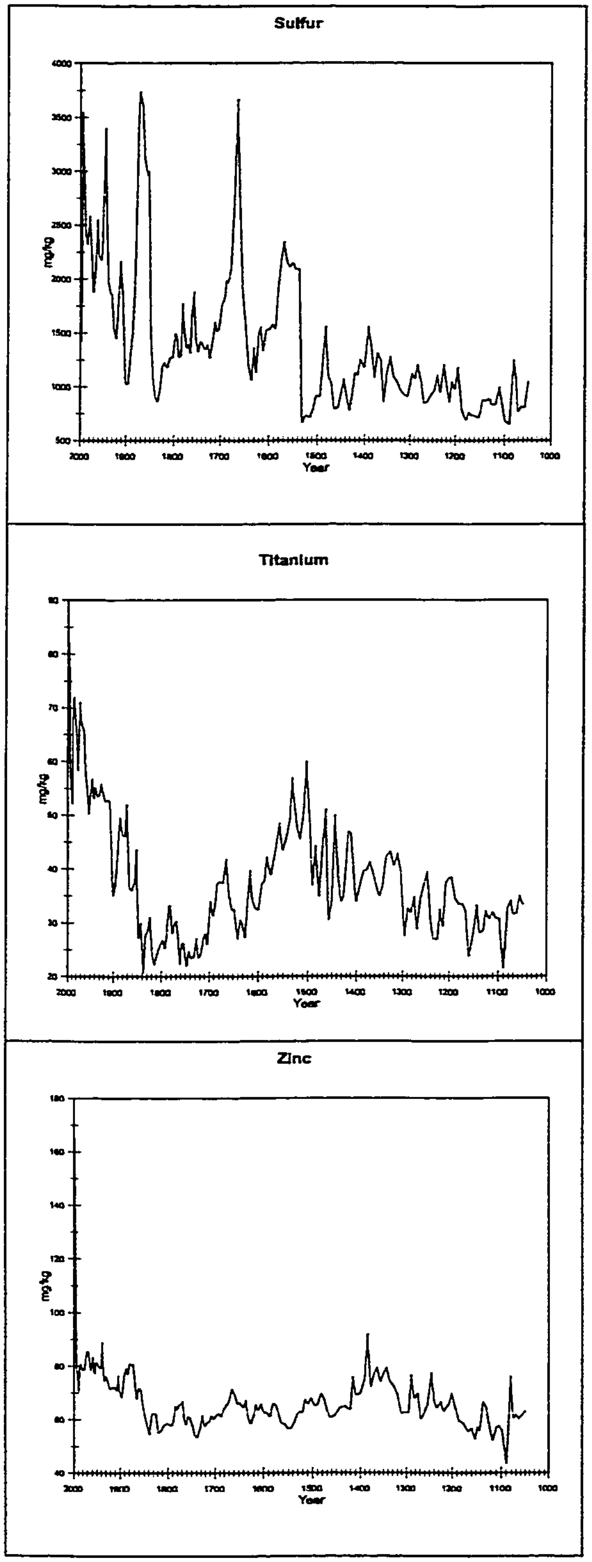


Figure A-5: Concentrations of sulfur, titanium, and zinc.

Appendix 5: Digestion-TCA ignition results compared to sieved charcoal and sediment influx.

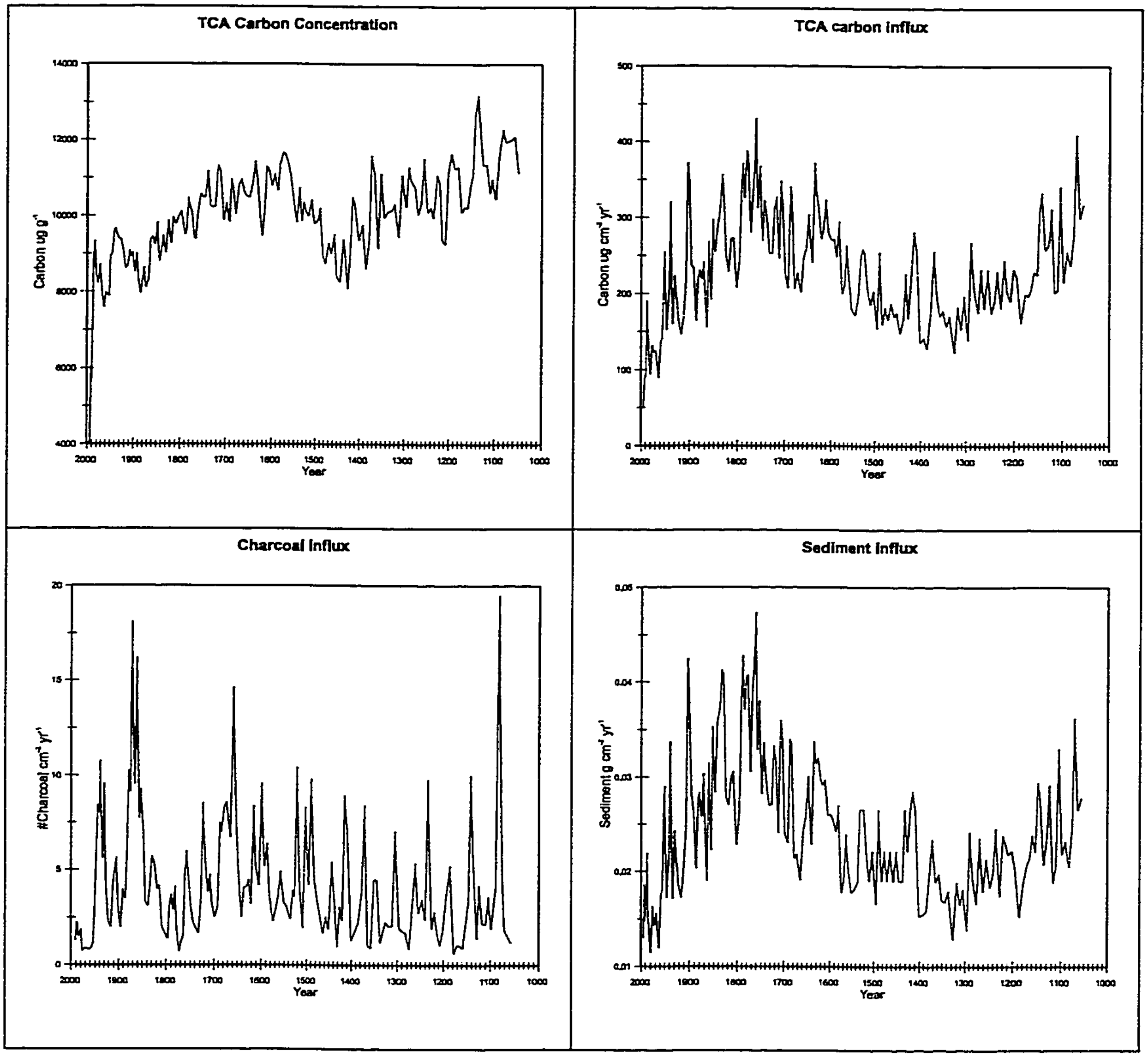


Figure A-6: TCA carbon concentration, TCA carbon influx, sieved charcoal influx, and sediment influx.

Appendix 6: Pearson correlation results for sedimentological characteristics, sieved charcoal, TCA carbon, vivianite, and geochemistry results.

Correlations

		SEDinflux	ASHcon	ASHinflux	ORGcon	ORGinflux	CARBcon	CARBinflux	CHAR/g	CHARinflux	ODWT/cc	VARVES/cm
Pearson Correlation	SEDinflux	1.000	.659**	.989**	-.563**	.898**	-.417**	.510**	-.101	.198**	.486**	-.504*
	ASHcon	.659**	1.000	.756**	-.825**	.354**	-.667**	-.049	-.107	.088	.509**	-.112
	ASHinflux	.989**	.756**	1.000	-.631**	.839**	-.496**	.415**	-.116	.177*	.502**	-.476*
	ORGcon	-.563**	-.825**	-.631**	1.000	-.171*	.129	-.356**	.119	-.031	-.799**	-.258*
	ORGinflux	.898**	.354**	.839**	-.171*	1.000	-.392**	.470**	-.025	.258**	.207**	-.669*
	CARBcon	-.417**	-.667**	-.496**	.129	-.392**	1.000	.539**	.034	-.107	.144	.537*
	CARBinflux	.510**	-.049	.415**	-.356**	.470**	.539**	1.000	-.051	.091	.551**	.010
	CHAR/g	-.101	-.107	-.116	.119	-.025	.034	-.051	1.000	.931**	-.090	.025
	CHARinflux	.198**	.088	.177*	-.031	.258**	-.107	.091	.931**	1.000	.017	-.183*
	ODWT/cc	.486**	.509**	.502**	-.799**	.207**	.144	.551**	-.090	.017	1.000	.466*
	VARVES/cm	-.504**	-.112	-.476**	-.258**	-.669**	.537**	.010	.025	-.183*	.466**	1.000
	VIVIANITE	-.115	-.064	-.119	-.031	-.124	.153*	.023	.043	.005	.152	.288*
	TCAcon	.155*	.154*	.137	-.407**	.045	.254**	.417**	.084	.085	.694**	.514*
	TCAinflux	.928**	.598**	.904**	-.594**	.823**	-.272**	.610**	-.061	.211**	.647**	-.295*
	ALcon	.499**	.682**	.567**	-.484**	.319**	-.561**	-.100	-.017	.143	.278**	-.227*
	ALinflux	.898**	.765**	.928**	-.597**	.738**	-.554**	.262**	-.086	.183*	.438**	-.450*
	AScon	-.522**	-.655**	-.563**	.728**	-.279**	.193*	-.266**	.210**	.051	-.755**	-.281*
	ASinflux	.635**	.119	.576**	.004	.751**	-.210**	.385**	.125	.322**	-.096	-.677*
	CAcon	-.277**	-.503**	-.305**	.717**	-.040	-.061	-.320**	.120	.060	-.772**	-.544*
	CAinflux	.750**	.302**	.716**	-.057	.835**	-.447**	.266**	.012	.274**	-.075	-.810*
	CUcon	.005	-.231**	-.007	.308**	.063	.000	-.016	.280**	.272**	-.213**	-.288*
	CUinflux	.941**	.587**	.926**	-.484**	.860**	-.392**	.486**	-.005	.272**	.397**	-.527*
	FEcon	-.068	-.102	-.094	-.005	-.014	.185*	.097	.100	.103	-.008	.145
	FEinflux	.791**	.429**	.757**	-.398**	.768**	-.230**	.496**	.004	.253**	.356**	-.393*
	Kcon	.091	.066	.125	.238**	.141	-.430**	-.371**	.121	.189*	-.450**	-.564*
	Kinflux	.685**	.554**	.709**	-.291**	.634**	-.583**	.042	.033	.260**	.035	-.613*
	MGcon	.179*	.126	.213**	.070	.137	-.313**	-.169*	-.078	.011	-.250**	-.490*
	MGinflux	.904**	.660**	.912**	-.510**	.789**	-.484**	.351**	-.109	.165*	.332**	-.561*
	MNcon	-.296**	-.521**	-.325**	.636**	-.103	.077	-.216**	.185*	.086	-.649**	-.413*
	MNinflux	.051	-.279**	.011	.423**	.231**	-.060	-.028	.205**	.239**	-.507**	-.555*
	NAcon	-.286**	-.450**	-.306**	.632**	-.066	-.041	-.349**	.081	.027	-.781**	-.496*
	NAinflux	.594**	.193*	.567**	.087	.708**	-.445**	.118	.024	.260**	-.260**	-.844*
	NIcon	-.299**	-.531**	-.330**	.683**	-.081	.032	-.260**	.143	.062	-.727**	-.463*
	NIinflux	.418**	-.009	.376**	.217**	.572**	-.263**	.123	.095	.271**	-.360**	-.746*
	PBcon	-.360**	-.522**	-.378**	.720**	-.144	-.031	-.374**	-.034	-.127	-.801**	-.472*
	PBinflux	.791**	.365**	.765**	-.142	.833**	-.449**	.290**	-.101	.146	-.008	-.769*
	Pcon	-.475**	-.646**	-.529**	.577**	-.272**	.374**	-.062	.142	.006	-.298**	.124
	Pinflux	.730**	.226**	.666**	-.204**	.796**	-.129	.552**	.034	.263**	.305**	-.387*
	Scon	-.119	-.125	-.118	.481**	.082	-.414**	-.450**	.383**	.380**	-.616**	-.467*
	Sinflux	.490**	.294**	.482**	.050	.598**	-.570**	-.062	.310**	.498**	-.208**	-.649*
	TIcon	-.479**	-.546**	-.503**	.763**	-.215**	-.045	-.453**	.155*	.049	-.824**	-.363*
	TIinflux	.502**	.141	.460**	.128	.672**	-.405**	.099	.130	.328**	-.261**	-.722*
	ZNcon	-.337**	-.469**	-.362**	.665**	-.071	-.052	-.411**	.229**	.160*	-.691**	-.352*
	ZNinflux	.907**	.511**	.883**	-.316**	.921**	-.477**	.362**	.021	.308**	.228**	-.633*

Correlations

		VIVIANITE	TCAcon	TCAinflux	ALcon	ALinflux	AScon	ASinflux	CAcon	CAinflux	CUcon	CUinflux
Pearson Correlation	SEDinflux	-.115	.155*	.928**	.499**	.898**	-.522**	.635**	-.277**	.750**	.005	.941*
	ASHcon	-.064	.154*	.598**	.682**	.765**	-.655**	.119	-.503**	.302**	-.231**	.587*
	ASHinflux	-.119	.137	.904**	.567**	.928**	-.563**	.576**	-.305**	.716**	-.007	.926*
	ORGcon	-.031	-.407**	-.594**	-.484**	-.597**	.728**	.004	.717**	-.057	.308**	-.484*
	ORGinflux	-.124	.045	.823**	.319**	.738**	-.279**	.751**	-.040	.835**	.063	.860*
	CARBcon	.153*	.254**	-.272**	-.561**	-.554**	.193*	-.210**	-.061	-.447**	.000	-.392*
	CARBinflux	.023	.417**	.610**	-.100	.262**	-.266**	.385**	-.320**	.266**	-.016	.486*
	CHAR/g	.043	.084	-.061	-.017	-.086	.210**	.125	.120	.012	.280**	-.005
	CHARinflux	.005	.085	.211**	.143	.183*	.051	.322**	.060	.274**	.272**	.272*
	ODWT/cc	.152	.694**	.647**	.278**	.438**	-.755**	-.096	-.772**	-.075	-.213**	.397*
	VARVES/cm	.288**	.514**	-.295**	-.227**	-.450**	-.281**	-.677**	-.544**	-.810**	-.288**	-.527*
	VIVIANITE	1.000	.091	-.073	-.012	-.088	-.123	-.200**	-.217**	-.252**	-.242**	-.190*
	TCAcon	.091	1.000	.491**	-.040	.049	-.463**	-.158*	-.665**	-.277**	-.063	.136
	TCAinflux	-.073	.491**	1.000	.409**	.794**	-.602**	.510**	-.434**	.583**	-.006	.872*
	ALcon	-.012	-.040	.409**	1.000	.807**	-.323**	.173*	-.225**	.296**	-.012	.467*
	ALinflux	-.088	.049	.794**	.807**	1.000	-.514**	.515**	-.270**	.655**	.012	.849*
	AScon	-.123	-.463**	-.602**	-.323**	-.514**	1.000	.286**	.783**	.011	.675**	-.358*
	ASinflux	-.200**	-.158*	.510**	.173*	.515**	.286**	1.000	.254**	.812**	.371**	.723*
	CAcon	-.217**	-.665**	-.434**	-.225**	-.270**	.783**	.254**	1.000	.401**	.571**	-.144
	CAinflux	-.252**	-.277**	.583**	.296**	.655**	.011	.812**	.401**	1.000	.301**	.797*
	CUcon	-.242**	-.063	-.006	-.012	.012	.675**	.371**	.571**	.301**	1.000	.333*
	CUinflux	-.190*	.136	.872**	.467**	.849**	-.358**	.723**	-.144	.797**	.333**	1.000
	FEcon	.117	-.111	-.099	-.085	-.093	-.098	.058	-.017	.025	-.159*	-.056
	FEinflux	-.035	.058	.711**	.352**	.682**	-.354**	.636**	-.166*	.663**	.019	.763*
	Kcon	-.162*	-.552**	-.102	.604**	.392**	.411**	.289**	.520**	.377**	.404**	.153*
	Kinflux	-.151	-.248**	.511**	.801**	.871**	-.178*	.597**	.058	.702**	.141	.693*
	MGcon	-.266**	-.349**	.058	.557**	.434**	.369**	.295**	.519**	.452**	.508**	.278*
	MGinflux	-.185*	.007	.799**	.687**	.948**	-.383**	.644**	-.098	.792**	.137	.897*
	MNcon	-.181*	-.600**	-.438**	-.312**	-.310**	.695**	.219**	.884**	.289**	.418**	-.184*
	MNinflux	-.220**	-.540**	-.122	-.169*	-.011	.570**	.519**	.791**	.588**	.373**	.159*
	NAcon	-.152	-.711**	-.463**	-.057	-.203**	.810**	.182*	.864**	.299**	.660**	-.185*
	NAinflux	-.231**	-.454**	.385**	.388**	.604**	.120	.729**	.478**	.887**	.265**	.638*
	NIcon	-.171*	-.693**	-.475**	-.282**	-.297**	.719**	.260**	.922**	.331**	.441**	-.172*
	NIinflux	-.228**	-.520**	.203**	.082	.346**	.355**	.767**	.644**	.857**	.381**	.516*
	PBcon	-.177*	-.641**	-.516**	-.188*	-.304**	.871**	.259**	.867**	.213**	.572**	-.228*
	PBinflux	-.210**	-.233**	.619**	.383**	.729**	.012	.862**	.226**	.913**	.256**	.825*
	Pcon	.128	-.036	-.423**	-.447**	-.539**	.569**	-.079	.272**	-.353**	.252**	-.446*
	Pinflux	.009	.177*	.705**	.158*	.546**	-.230**	.654**	-.226**	.547**	-.012	.687*
	Scon	-.186*	-.460**	-.244**	-.005	-.073	.326**	.220**	.563**	.337**	.254**	.001
	Sinflux	-.200*	-.243**	.350**	.295**	.462**	.024	.574**	.299**	.708**	.299**	.562*
	TIcon	-.064	-.532**	-.574**	-.065	-.340**	.685**	.062	.626**	-.049	.317**	-.398*
	TIinflux	-.117	-.275**	.368**	.438**	.545**	.107	.692**	.197**	.646**	.140	.518*
	ZNcon	-.042	-.495**	-.447**	.020	-.188*	.811**	.216**	.681**	.114	.622**	-.223*
	ZNinflux	-.110	-.024	.792**	.554**	.874**	-.279**	.767**	-.073	.832**	.120	.891*

Correlations

		FEcon	FEinflux	Kcon	Kinflux	MGcon	MGinflux	MNcon	MNinflux	NAcon	NAinflux	NIcon
Pearson Correlation	SEDinflux	-.068	.791**	.091	.685**	.179*	.904**	-.296**	.051	-.286**	.594**	-.299*
	ASHcon	-.102	.429**	.066	.554**	.126	.660**	-.521**	-.279**	-.450**	.193*	-.531*
	ASHinflux	-.094	.757**	.125	.709**	.213**	.912**	-.325**	.011	-.306**	.567**	-.330*
	ORGcon	-.005	-.398**	.238**	-.291**	.070	-.510**	.636**	.423**	.632**	.087	.683*
	ORGinflux	-.014	.768**	.141	.634**	.137	.789**	-.103	.231**	-.066	.708**	-.081
	CARBcon	.185*	-.230**	-.430**	-.583**	-.313**	-.484**	.077	-.060	-.041	-.445**	.032
	CARBinflux	.097	.496**	-.371**	.042	-.169*	.351**	-.216**	-.028	-.349**	.118	-.260*
	CHAR/g	.100	.004	.121	.033	-.078	-.109	.185*	.205**	.081	.024	.143
	CHARinflux	.103	.253**	.189*	.260**	.011	.165*	.086	.239**	.027	.260**	.062
	ODWT/cc	-.008	.356**	-.450**	.035	-.250**	.332**	-.649**	-.507**	-.781**	-.260**	-.727*
	VARVES/cm	.145	-.393**	-.564**	-.613**	-.490**	-.561**	-.413**	-.555**	-.496**	-.844**	-.463*
	VIVIANITE	.117	-.035	-.162*	-.151	-.266**	-.185*	-.181*	-.220**	-.152	-.231**	-.171*
	TCAcon	-.111	.058	-.552**	-.248**	-.349**	.007	-.600**	-.540**	-.711**	-.454**	-.693*
	TCAinflux	-.099	.711**	-.102	.511**	.058	.799**	-.438**	-.122	-.463**	.385**	-.475*
	ALcon	-.085	.352**	.604**	.801**	.557**	.687**	-.312**	-.169*	-.057	.388**	-.282*
	ALinflux	-.093	.682**	.392**	.871**	.434**	.948**	-.310**	-.011	-.203**	.604**	-.297*
	AScon	-.098	-.354**	.411**	-.178*	.369**	-.383**	.695**	.570**	.810**	.120	.719*
	ASinflux	.058	.636**	.289**	.597**	.295**	.644**	.219**	.519**	.182*	.729**	.260*
	CAcon	-.017	-.166*	.520**	.058	.519**	-.098	.884**	.791**	.864**	.478**	.922*
	CAinflux	.025	.663**	.377**	.702**	.452**	.792**	.289**	.588**	.299**	.887**	.331*
	CUcon	-.159*	.019	.404**	.141	.508**	.137	.418**	.373**	.660**	.265**	.441*
	CUinflux	-.056	.763**	.153*	.693**	.278**	.897**	-.184*	.159*	-.185*	.638**	-.172*
	FEcon	1.000	.532**	-.079	-.028	-.165*	-.086	.026	.109	-.104	.028	.063
	FEinflux	.532**	1.000	.092	.566**	.096	.700**	-.185*	.135	-.191*	.533**	-.153*
	Kcon	-.079	.092	1.000	.752**	.841**	.410**	.371**	.342**	.652**	.629**	.450*
	Kinflux	-.028	.566**	.752**	1.000	.679**	.876**	-.026	.234**	.167*	.781**	.038
	MGcon	-.165*	.096	.841**	.679**	1.000	.561**	.370**	.365**	.589**	.564**	.423*
	MGinflux	-.086	.700**	.410**	.876**	.561**	1.000	-.156*	.167*	-.084	.711**	-.130
	MNcon	.026	-.185*	.371**	-.026	.370**	-.156*	1.000	.912**	.725**	.391**	.939*
	MNinflux	.109	.135	.342**	.234**	.365**	.167*	.912**	1.000	.698**	.619**	.842*
	NAcon	-.104	-.191*	.652**	.167*	.589**	-.084	.725**	.698**	1.000	.569**	.758*
	NAinflux	.028	.533**	.629**	.781**	.564**	.711**	.391**	.619**	.569**	1.000	.450*
	NIcon	.063	-.153*	.450**	.038	.423**	-.130	.939**	.842**	.758**	.450**	1.000
	NIinflux	.127	.468**	.451**	.551**	.473**	.526**	.621**	.834**	.566**	.845**	.703*
	PBcon	-.137	-.284**	.504**	.009	.486**	-.178*	.773**	.649**	.816**	.340**	.810*
	PBinflux	-.036	.677**	.357**	.732**	.412**	.819**	.158*	.472**	.182*	.831**	.198*
	Pcon	.151*	-.209**	.005	-.402**	-.178*	-.551**	.215**	-.023	.364**	-.272**	.222*
	Pinflux	.137	.729**	-.042	.423**	-.131	.549**	-.239**	.036	-.228**	.437**	-.235*
	Scon	-.004	-.067	.406**	.192*	.219**	-.023	.434**	.429**	.381**	.402**	.505*
	Sinflux	.006	.452**	.402**	.565**	.268**	.499**	.137	.352**	.245**	.657**	.208*
	TIcon	-.037	-.343**	.639**	.086	.390**	-.287**	.513**	.321**	.665**	.233**	.565*
	TIinflux	.035	.493**	.654**	.776**	.439**	.597**	.084	.310**	.312**	.765**	.150
	ZNcon	-.028	-.147	.605**	.154*	.494**	-.143	.487**	.364**	.770**	.239**	.550*
	ZNinflux	.016	.791**	.326**	.811**	.330**	.898**	-.151*	.198**	-.089	.726**	-.112

Correlations

		NIinflux	PBcon	PBinflux	Pcon	Pinflux	Scon	Sinflux	TIcon	TIinflux	ZNcon	ZNinflux
Pearson Correlation	SEDinflux	.418**	-.360**	.791**	-.475**	.730**	-.119	.490**	-.479**	.502**	-.337**	.907**
	ASHcon	-.009	-.522**	.365**	-.646**	.226**	-.125	.294**	-.546**	.141	-.469**	.511**
	ASHinflux	.376**	-.378**	.765**	-.529**	.666**	-.118	.482**	-.503**	.460**	-.362**	.883**
	ORGcon	.217**	.720**	-.142	.577**	-.204**	.481**	.050	.763**	.128	.665**	-.316**
	ORGinflux	.572**	-.144	.833**	-.272**	.796**	.082	.598**	-.215**	.672**	-.071	.921**
	CARBcon	-.263**	-.031	-.449**	.374**	-.129	-.414**	-.570**	-.045	-.405**	-.052	-.477**
	CARBinflux	.123	-.374**	.290**	-.062	.552**	-.450**	-.062	-.453**	.099	-.411**	.362**
	CHAR/g	.095	-.034	-.101	.142	.034	.383**	.310**	.155*	.130	.229**	.021
	CHARinflux	.271**	-.127	.146	.006	.263**	.380**	.498**	.049	.328**	.160*	.308**
	ODWT/cc	-.360**	-.801**	-.008	-.298**	.305**	-.616**	-.208**	-.824**	-.261**	-.691**	.228**
	VARVES/cm	-.746**	-.472**	-.769**	.124	-.387**	-.467**	-.649**	-.363**	-.722**	-.352**	-.633**
	VIVIANITE	-.228**	-.177*	-.210**	.128	.009	-.186*	-.200*	-.064	-.117	-.042	-.110
	TCAcon	-.520**	-.641**	-.233**	-.036	.177*	-.460**	-.243**	-.532**	-.275**	-.495**	-.024
	TCAinflux	.203**	-.516**	.619**	-.423**	.705**	-.244**	.350**	-.574**	.368**	-.447**	.792**
	ALcon	.082	-.188*	.383**	-.447**	.158*	-.005	.295**	-.065	.438**	.020	.554**
	ALinflux	.346**	-.304**	.729**	-.539**	.546**	-.073	.462**	-.340**	.545**	-.188*	.874**
	AScon	.355**	.871**	.012	.569**	-.230**	.326**	.024	.685**	.107	.811**	-.279**
	ASinflux	.767**	.259**	.862**	-.079	.654**	.220**	.574**	.062	.692**	.216**	.767**
	CAcon	.644**	.867**	.226**	.272**	-.226**	.563**	.299**	.626**	.197**	.681**	-.073
	CAinflux	.857**	.213**	.913**	-.353**	.547**	.337**	.708**	-.049	.646**	.114	.832**
	CUcon	.381**	.572**	.256**	.252**	-.012	.254**	.299**	.317**	.140	.622**	.120
	CUinflux	.516**	-.228**	.825**	-.446**	.687**	.001	.562**	-.398**	.518**	-.223**	.891**
	FEcon	.127	-.137	-.036	.151*	.137	-.004	.006	-.037	.035	-.028	.016
	FEinflux	.468**	-.284**	.677**	-.209**	.729**	-.067	.452**	-.343**	.493**	-.147	.791**
	Kcon	.451**	.504**	.357**	.005	-.042	.406**	.402**	.639**	.654**	.605**	.326**
	Kinflux	.551**	.009	.732**	-.402**	.423**	.192*	.565**	.086	.776**	.154*	.811**
	MGcon	.473**	.486**	.412**	-.178*	-.131	.219**	.268**	.390**	.439**	.494**	.330**
	MGinflux	.526**	-.178*	.819**	-.551**	.549**	-.023	.499**	-.287**	.597**	-.143	.898**
	MNcon	.621**	.773**	.158*	.215**	-.239**	.434**	.137	.513**	.084	.487**	-.151*
	MNinflux	.834**	.649**	.472**	-.023	.036	.429**	.352**	.321**	.310**	.364**	.198**
	NAcon	.566**	.816**	.182*	.364**	-.228**	.381**	.245**	.665**	.312**	.770**	-.089
	NAinflux	.845**	.340**	.831**	-.272**	.437**	.402**	.657**	.233**	.765**	.239**	.726**
	NIcon	.703**	.810**	.198**	.222**	-.235**	.505**	.208**	.565**	.150	.550**	-.112
	NIinflux	1.000	.493**	.770**	-.184*	.319**	.427**	.591**	.181*	.557**	.308**	.572**
	PBcon	.493**	1.000	.257**	.333**	-.275**	.400**	.110	.700**	.182*	.732**	-.142
	PBinflux	.770**	.257**	1.000	-.348**	.591**	.163*	.585**	-.063	.665**	.086	.861**
	Pcon	-.184*	.333**	-.348**	1.000	.229**	.073	-.194*	.518**	.016	.501**	-.345**
	Pinflux	.319**	-.275**	.591**	.229**	1.000	-.068	.400**	-.172*	.589**	-.115	.729**
	Scon	.427**	.400**	.163*	.073	-.068	1.000	.775**	.462**	.305**	.357**	.076
	Sinflux	.591**	.110	.585**	-.194*	.400**	.775**	1.000	.095	.566**	.215**	.615**
	TIcon	.181*	.700**	-.063	.518**	-.172*	.462**	.095	1.000	.468**	.689**	-.205**
	TIinflux	.557**	.182*	.665**	.016	.589**	.305**	.566**	.468**	1.000	.354**	.711**
	ZNcon	.308**	.732**	.086	.501**	-.115	.357**	.215**	.689**	.354**	1.000	.071
	ZNinflux	.572**	-.142	.861**	-.345**	.729**	.076	.615**	-.205**	.711**	.071	1.000

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

Appendix 7: Data spreadsheet

Depth	Year	Sample #	varves/cm	%water	sed. influx	ODwt/cc	vivianite	charinflux	chargram	TCA con	TCAinflux	%Org	%Carb
1	1997	WC2B 1/WC2D top	1				0					35.95	10.33
2	1995	WC2B 2	2	97.42	0.0130	0.0259	0		0.007504334	4025	51	35.00	11.36
3	1993.5	WC2B 3	1.5	97.22	0.0187	0.0280	0			4161	76	35.41	11.18
4	1991.5	WC2B 4	2	97.06	0.0149	0.0297	0	1.25	84.17	6043	87	35.13	9.01
5	1989.5	WC2B 5	2	96.59	0.0171	0.0342	0	2.25	131.58	5711	96	32.99	8.79
6	1987.5	WC2B 6	2	95.71	0.0220	0.0439	0	2.25	102.51	8869	191	32.46	7.43
7	1984.5	WC2B 7	3	95.46	0.0155	0.0464	0	1.50	96.98	9346	142	30.68	7.98
8	1980	WC2B 8	4.5	94.96	0.0114	0.0514	0	1.89	165.37	8381	94	31.01	8.12
9	1976.5	WC2B 9	3.5	94.44	0.0163	0.0572	0	0.71	43.71	8234	132	30.79	7.94
10	1972	WC2B 10	4.5	93.76	0.0143	0.0643	0	0.89	62.21	8724	122	29.96	7.35
11	1968	WC2B 11	4		0.0157	0.0626	0	0.88	55.91	8085	124	29.93	7.95
12	1963	WC2B 12	5	94.26	0.0119	0.0585	0	0.80	67.23	7580	89	28.51	7.97
13	1959	WC2B 13	4	93.21	0.0176	0.0704	0.1	0.88	49.72	7997	138	28.41	7.89
14	1955	WC2B 14	4	93.02	0.0182	0.0727	0.1	1.13	61.90	7930	142	29.76	7.31
15	1952.5	WC2B 15	2.5	93.39	0.0272	0.0679	0.3	2.60	95.73	7882	210	30.16	7.71
16	1950	WC2B 16	2.5	93.03	0.0291	0.0727	0.1	4.60	158.18	8935	255	29.98	7.63
17	1945.5	WC2B 17	4.5	92.56	0.0172	0.0776	0.2	8.44	489.69	9000	152	29.83	7.50
18	1941.5	WC2B 18	4	91.80	0.0215	0.0860	0.9	8.00	372.09	9590	202	28.00	7.07
19	1939	WC2B 19	2.5	91.85	0.0338	0.0845	3.6	10.80	319.53	9674	321	27.97	7.12
20	1934	WC2B 20	5	91.69	0.0172	0.0858	4.6	5.60	326.34	9496	160	27.00	6.94
21	1930.5	WC2B 21	3.5	91.96	0.0243	0.0850	0.8	9.57	394.12	9396	224	28.35	6.68
22	1926.5	WC2B 22	4	91.92	0.0211	0.0845	0	4.13	195.27	9393	195	26.86	6.19
23	1922	WC2B 23	4.5	92.08	0.0186	0.0836	0.4	2.33	125.60	9087	166	26.44	7.07
24	1917	WC2B 24	5	91.89	0.0172	0.0862	0.4	2.00	116.01	8624	146	26.22	7.38
25	1912	WC2B 25	5	90.99	0.0200	0.0999	0.1	4.30	215.22	8722	171	25.53	6.60
26	1907.5	WC2B 26	4.5	90.10	0.0243	0.1094	0.4	5.33	219.38	9086	217	24.77	5.19
27	1904.5	WC2B 27	3	88.32	0.0425	0.1276	0.3	5.67	133.23	8923	373	22.88	4.81
28	1901	WC2B 28	3.5	87.34	0.0392	0.1372	1	3.14	80.17	9042	348	21.50	4.97
29	1896.5	WC2B 29	4.5	88.25	0.0284	0.1276	0.3	2.00	70.53	8529	237	21.39	5.17
30	1892	WC2B 30	4.5	89.40	0.0263	0.1184	1.2	4.00	152.03	9012	233	23.23	5.76
31	1887	WC2B 31	5	90.51	0.0203	0.1016	0	3.50	172.24	8217	164	23.62	6.49
32	1883.5	WC2B 32	3.5	91.01	0.0277	0.0971	0.2	6.14	221.42	7960	217	24.61	6.55
33	1880	WC2B 33	3.5	90.66	0.0284	0.0993	0.2	10.29	362.54	8302	231	25.18	6.18
34	1876	WC2B 34	4	90.41	0.0258	0.1033	0.1	9.13	353.34	8652	219	24.49	5.94
35	1872.5	WC2B 35	3.5	89.97	0.0304	0.1064	0.2	18.14	596.80	8110	242	23.21	5.77
36	1866	WC2B 36	6.5	88.87	0.0190	0.1232	0	9.54	503.25	8348	155	22.81	6.27
37	1862	WC2B 37	4	88.63	0.0315	0.1261	1	16.25	515.46	9361	269	23.24	6.13
38	1856.5	WC2B 38	5.5	88.78	0.0222	0.1223	3	7.73	347.51	9454	192	22.40	6.32
39	1853	WC2B 39	3.5	88.61	0.0353	0.1237	0.1	9.29	262.73	9234	298	16.57	6.43
40	1848	WC2B 40	5	87.42	0.0283	0.1417	0.3	7.00	247.00	9831	254	20.11	5.45
41	1843.5	WC2B 41	4.5	85.53	0.0359	0.1617	0.6	3.33	92.76	8802	289	17.93	5.20
42	1838.5	WC2B 42	5	83.71	0.0373	0.1867	0	3.10	83.02	9108	310	17.94	5.11
43	1834	WC2B 43	4.5	83.42	0.0414	0.1861	1	4.22	102.10	9480	358	18.22	4.89
44	1830	WC2B 44	4	85.30	0.0408	0.1634	3.3	5.75	140.76	9021	336	18.79	4.45
45	1824.5	WC2B 45	5.5	86.16	0.0279	0.1535	0.5	5.36	192.18	9878	252	19.74	4.74
46	1819	WC2B 46	5.5	86.63	0.0270	0.1485	0	4.00	148.15	9269	228	19.60	4.59
47	1814	WC2B 47	5	86.15	0.0300	0.1498	0	4.20	140.19	9970	273	18.89	5.46
48	1809	WC2B 48	5	86.40	0.0306	0.1530	0.1	2.00	65.36	9775	273	19.48	5.50
49	1802.5	WC2B 49	6.5	86.34	0.0228	0.1483	0.2	1.69	74.17	9983	208	20.36	7.20
50	1797	WC2B 50	5.5	86.72	0.0264	0.1451	0	1.36	51.69	10116	244	21.16	7.05
51	1793	WC2B 51	4	86.36	0.0378	0.1511	0.1	3.25	86.04	9869	340	21.18	6.77
52	1789.5	WC2B 52	3.5	86.36	0.0429	0.1501	3.7	3.71	86.61	9502	372	20.92	6.81
53	1785.5	WC2B 53	4	86.57	0.0371	0.1483	1.2	2.88	77.55	9625	326	20.97	7.05
54	1782	WC2B 54	3.5	86.95	0.0407	0.1424	1.4	4.14	101.83	10475	389	21.49	8.14
55	1778	WC2B 55	4	85.03	0.0408	0.1630	1.6	1.88	46.01	10264	382	20.37	7.81
56	1773	WC2B 56	5	85.98	0.0306	0.1528	0.8	0.70	22.91	10031	280	21.27	7.29
57	1769	WC2B 57	4	85.97	0.0386	0.1544	0.2	1.25	32.38	9416	332	21.05	7.51
58	1765.5	WC2B 58	3.5	86.15	0.0431	0.1507	0.1	1.57	36.50	9400	369	21.70	7.54
59	1762.5	WC2B 59	3	86.93	0.0474	0.1423	0.1	4.67	98.38	9965	431	22.21	7.83
60	1758	WC2B 60	4.5	86.53	0.0328	0.1478	0	6.00	182.68	10422	312	21.79	8.00
61	1754	WC2B 61	4	86.06	0.0381	0.1522	0.5	4.75	124.84	10594	368	20.96	8.06
62	1748.5	WC2B 62	5.5	86.07	0.0282	0.1551	0.2	3.09	109.61	10469	269	21.41	7.91
63	1744	WC2B 63	4.5	86.39	0.0336	0.1514	0.2	2.33	69.35	10508	323	22.06	7.81
64	1739	WC2B 64	5	86.62	0.0296	0.1480	6.4	2.00	67.57	11179	302	22.64	7.68
65	1733	WC2B 65	6	85.38	0.0270	0.1619	0	1.67	61.77	10250	252	21.19	7.86
66	1727.5	WC2B 66	5.5	86.11	0.0271	0.1492	0	3.55	130.70	10219	253	22.59	8.23
67	1723	WC2B 67	4.5	86.21	0.0333	0.1499	0.2	8.56	256.84	10248	312	22.75	9.25
68	1718	WC2B 68	5	85.64	0.0317	0.1585	0.4	5.50	173.50	11336	328	23.91	8.32
69	1712	WC2B 69	6	86.64	0.0240	0.1442	0.2	3.83	159.50	11219	246	24.83	8.35
70	1708	WC2B 70	4	86.69	0.0360	0.1441	1.1	4.75	131.85	10594	348	24.36	8.52
71	1704	WC2B 71	4	86.92	0.0351	0.1403	0.1	3.38	96.22	9878	316	24.23	9.07
72	1698	WC2B 72	6	86.75	0.0240	0.1439	0.2	2.50	104.24	10332	226	24.04	9.32
73	1692	WC2B 73	6	87.39	0.0231	0.1384	1	3.08	133.67	9830	207	23.99	10.67
74	1688	WC2B 74	4	87.44	0.0340	0.1361	0	7.50	220.43	10977	341	24.03	10.19
75	1684	WC2B 75	4	87.60	0.0335	0.1341	0.1	7.00	208.80	10767	329	23.71	10.00
76	1678	WC2B 76	6	87.94	0.0214	0.1282	0.6	8.33	390.02	10031	206	23.95	9.93
77	1672	WC2B 77	6	87.79	0.0219	0.1313	1.1	8.58	392.23	10799	228	25.51	10.39
78	1665	WC2B 78	7	87.47	0.0191	0.1337	1.1	6.71	351.53	10973	202	26.55	10.54
79	1659	WC2B 79	6	86.55	0.0242	0.1453	1.3	14.67	605.64	10611	247	23.54	10.64
80	1653	WC2D 80	6	85.84	0.0258	0.1550	8.8	7.92	306.45	10494	261	23.55	6.89
81	1648	WC2D 81	5	86.01	0.0301	0.1505	2.4	5.00	166.11	10498	304	23.59	7.10
82	1641	WC2D 82	7	85.07	0.0228	0.1599	0.9	2.50	109.44	10922	240	22.45	7.39
83	1636	WC2D 83	5	84.63	0.0338	0.1690	0.8	4.10	121.30	11444	373	23.02	7.26
84	1631	WC2D 84	5	85.80	0.0314	0.1570	0.5	4.10	130.57	10078	332	23.12	7.82
85	1626	WC2D 85	5	85.53	0.0320	0.1602	1.6	4.50	140.45	10078	311	22.78	7.80
86	1621	WC2D 86	5	86.40	0.0298	0.1491	0	3.20	107.31	9468	272	22.74	8.23
87	1616	WC2D 87	5	86.54	0.0292	0.1458	4.5	8.40	288.07	10149	285	23.32	8.42
88	1611	WC2D 88	5	86.24	0.0298	0.1488	0.8	5.20	174.73	11297	324	23.92	8.55

Depth	Year	Sample #	varves/cm	%water	sed. influx	ODwt/cc	vivianite	charinflux	chargram	TCA con	TCAinflux	%Org	%Carb
89	1605	WC2D 89	6	85.55	0.0259	0.1556	0.4	4.17	160.67	11180	279	24.61	8.47
90	1599	WC2D 90	6	85.71	0.0260	0.1562	8	9.58	368.12	10789	271	24.26	8.29
91	1593	WC2D 91	6	85.97	0.0254	0.1525	0.4	5.17	203.28	11105	272	23.93	8.35
92	1587	WC2D 92	6	86.66	0.0242	0.1453	0.5	6.42	264.97	10657	249	25.88	8.45
93	1582	WC2D 93	5	87.55	0.0270	0.1349	2	3.70	137.14	11370	295	26.91	7.92
94	1575	WC2D 94	7	88.46	0.0178	0.1244	2.2	2.29	128.62	11674	200	27.33	7.67
95	1569	WC2D 95	6	89.11	0.0191	0.1145	4.1	2.92	152.84	11589	213	26.90	7.94
96	1564	WC2D 96	5	88.77	0.0240	0.1199	0.7	3.60	150.13	11426	264	25.44	7.96
97	1558	WC2D 97	6	88.38	0.0204	0.1226	0.5	4.92	240.62	11157	220	25.45	8.53
98	1551	WC2D 98	7	88.27	0.0178	0.1245	3.1	3.29	184.74	10499	180	25.62	8.21
99	1544	WC2D 99	7	88.03	0.0181	0.1270	0	3.07	169.29	9822	172	24.72	7.70
100	1537	WC2D 100	7	87.51	0.0189	0.1323		2.43	128.50	10742	196	24.94	7.04
101	1532	WC1B 47	5		0.0266	0.1329		3.93	147.75	9859	247	24.68	9.07
102	1527	WC1B 48	5		0.0266	0.1329		3.58	134.79	10359	259	24.13	9.65
103	1522	WC1B 49	5		0.0266	0.1329		10.44	392.68	10124	253	24.40	9.56
104	1516	WC1B 50	6		0.0222	0.1329		4.12	185.95	9986	208	23.32	9.64
105	1509	WC1B 51	7		0.0190	0.1329	0	1.94	102.36	10419	186	24.33	12.72
106	1503	WC1B 52	6		0.0222	0.1329	0.4	8.31	375.21	9792	204	25.86	13.45
107	1495	WC1B 53	8		0.0166	0.1329	2.2	4.22	254.01	9871	154	25.69	12.91
108	1490	WC1B 54	5		0.0266	0.1329	0.8	9.82	369.31	10192	255	26.26	12.09
109	1483	WC1B 55	7		0.0190	0.1329	0.6	4.49	236.64	8943	160	25.84	12.93
110	1477	WC1B 56	6		0.0222	0.1329	0.2	3.42	154.35	8748	182	23.73	12.45
111	1470	WC1B 57	7		0.0190	0.1329	7	2.41	127.06	9286	166	23.05	12.13
112	1464	WC1B 58	6		0.0222	0.1329	4.9	1.67	75.53	9014	188	22.48	12.62
113	1457	WC1B 59	7		0.0190	0.1329	2.5	2.56	135.08	9521	170	20.33	10.31
114	1451	WC1B 60	6		0.0222	0.1329	0.9	1.89	85.13	8402	175	23.13	12.15
115	1444	WC1B 61	7		0.0190	0.1329	13	5.44	286.42	8262	148	22.91	12.52
116	1437	WC1B 62	7		0.0190	0.1329	1	3.20	168.40	9384	168	21.60	11.41
117	1432	WC1B 63	5		0.0266	0.1329		0.99	37.06	9064	227	22.09	11.17
118	1426	WC1B 64	6		0.0222	0.1329	10.6	3.08	139.16	8082	168	22.61	13.12
119	1421	WC1B 65	5		0.0266	0.1329	3	2.35	88.45	9027	226	25.41	13.15
120	1416	WC1B 66	5	86.97	0.0285	0.1427	1.5	8.98	314.51	10493	282	27.35	12.36
121	1410	WC1B 67	6	84.98	0.0265	0.1589	1.5	7.19	271.30	10313	257	26.11	12.36
122	1401	WC1B 68	9	87.34	0.0153	0.1380	4.6	1.30	84.56	9352	135	25.47	12.78
123	1392	WC1B 69	9	87.15	0.0155	0.1394	1.2	1.81	116.97	9759	142	28.24	12.50
124	1385	WC1B 70	7	89.30	0.0158	0.1107	0.6	2.25	141.98	8609	128	26.29	13.72
125	1378	WC1B 71	7	86.66	0.0200	0.1397	1.1	3.87	193.73	9362	176	23.44	12.07
126	1372	WC1B 72	6	86.49	0.0235	0.1410	7.1	8.43	358.80	11589	256	26.43	11.95
127	1364.5	WC1B 73	7.5	86.25	0.0189	0.1419	7.9	1.05	55.28	11079	197	26.80	11.14
128	1358	WC1B 74	6.5	87.46	0.0198	0.1284	6.7	0.91	45.86	9137	170	26.21	12.67
129	1351	WC1B 75	7	88.55	0.0170	0.1191	0.2	4.50	264.12	11124	178	30.26	13.29
130	1344	WC1B 76	7	88.70	0.0168	0.1176	1	4.50	267.77	9946	157	27.57	13.77
131	1337	WC1B 77	7	88.14	0.0180	0.1260	0.1	1.18	65.72	10108	171	26.93	12.55
132	1327	WC1B 78	10	87.96	0.0129	0.1288	0.8	2.27	176.05	10143	123	27.36	12.09
133	1320	WC1B 79	7	87.57	0.0189	0.1324	1.7	2.08	109.97	10313	184	26.44	11.64
134	1312	WC1B 80	8	87.61	0.0165	0.1323	1.1	2.08	125.52	9434	153	24.89	12.93
135	1305	WC1B 81	7	87.85	0.0182	0.1272	3.4	7.08	389.47	11071	198	23.46	10.63
136	1296	WC1B 82	9		0.0138	0.1245	2.2	1.95	141.22	10229	139	23.82	10.92
137	1290	WC1B 83	6	86.06	0.0242	0.1455	1	1.78	73.28	11285	269	24.87	9.98
138	1283	WC1B 84	7	86.91	0.0194	0.1355	6.8	1.70	88.00	10911	207	25.90	9.48
139	1275	WC1B 85	8	87.24	0.0166	0.1328	8.1	0.84	50.36	10745	175	24.03	9.87
140	1269	WC1B 86	6	86.95	0.0236	0.1417	4.3	2.85	120.86	10034	233	24.46	9.87
141	1262	WC1B 87	7	88.12	0.0179	0.1252	5.9	5.37	300.32	10338	182	24.25	10.06
142	1255	WC1B 88	7	85.86	0.0214	0.1496	4.4	2.75	128.71	11527	232	24.76	9.17
143	1247	WC1B 89	8	85.81	0.0183	0.1467	2.5	3.47	189.36	10091	174	23.06	9.72
144	1240	WC1B 90	7	86.48	0.0199	0.1393	3.4	2.39	119.88	10222	192	24.22	9.74
145	1234.5	WC1B 91	5.5	86.97	0.0246	0.1352	1.5	9.80	398.67	9934	230	22.86	10.12
146	1226	WC1B 92	8.5	85.92	0.0174	0.1478	3.4	1.91	110.06	11075	182	24.39	9.53
147	1220	WC1B 93	6	86.25	0.0239	0.1433	0	2.82	117.96	10864	245	22.47	10.09
148	1214	WC1B 94	6	86.77	0.0230	0.1382	0.2	1.69	73.43	9351	203	21.27	10.55
149	1208	WC1B 95	6	87.53	0.0218	0.1307	0.1	1.05	48.22	9261	190	22.45	11.36
150	1201.5	WC1B 96	6.5	86.34	0.0222	0.1443	0.1	1.81	81.41	11129	233	22.97	9.79
151	1195	WC1B 97	6.5	87.60	0.0202	0.1313	0	3.56	176.35	11645	222	23.58	10.42
152	1186.5	WC1B 98	8.5	87.42	0.0152	0.1295	0.2	5.22	342.86	11235	161	23.92	11.26
153	1178.5	WC1B 99	8	85.76	0.0188	0.1501	0	0.59	31.62	11292	200	22.18	11.58
154	1172	WC1B 100	6.5	87.00	0.0207	0.1345	0	1.05	50.62	10089	197	22.29	13.01
155	1166	WC1B 101	6	87.47	0.0214	0.1284	0	1.05	48.99	10236	206	21.20	12.72
156	1159.5	WC1B 102	6.5	85.49	0.0238	0.1550	1.6	0.87	36.50	10207	229	21.42	12.70
157	1153	WC1B 103	6.5	86.61	0.0221	0.1436	0.2	2.17	98.20	10798	225	20.66	12.23
158	1148	WC1B 104	5	86.21	0.0295	0.1474	0.8	3.34	113.40	11093	308	20.88	12.71
159	1143	WC1B 105	5	86.61	0.0281	0.1403	0.3	10.01	356.69	12620	334	21.76	13.37
160	1136	WC1B 106	7	86.64	0.0207	0.1450	0	5.06	244.08	13196	258	23.58	11.95
161	1129	WC1B 107	7	84.56	0.0236	0.1650	0	1.38	58.63	11976	266	23.53	12.94
162	1124	WC1B 108	5	86.22	0.0292	0.1460	0.3	4.23	144.78	11350	312	22.47	12.41
163	1117	WC1B 109	7	87.62	0.0188	0.1318	0	2.20	117.11	11364	202	22.53	14.08
164	1110	WC1B 110	7	86.57	0.0205	0.1436	0	2.19	106.64	10603	205	23.52	13.14
165	1105	WC1B 111	5	84.75	0.0331	0.1653	0.6	3.63	109.71	10974	342	21.44	12.47
166	1098	WC1B 112	7	85.62	0.0218	0.1529	0	1.92	87.88	10435	215	18.32	12.78
167	1090	WC1B 113	8	83.01	0.0233	0.1860	0	4.06	174.57	11659	256	21.74	12.68
168	1082.5	WC1B 114	7.5	85.33	0.0205	0.1535	0.2	19.54	954.59	12289	237	23.93	14.74
169	1076	WC1B 115	6.5	85.22	0.0246	0.1598	0.6	5.00	203.32	11954	277	23.85	13.24
170	1071	WC1B 116	5	83.42	0.0363	0.1816	0.9	1.84	50.74	11981	410	20.73	10.77
171	1064	WC1B 117	7	82.98	0.0265	0.1852	3.7	1.49	56.28	12010	300	22.72	11.93
172	1057	WC1B 118	7	82.02	0.0279	0.1952	2.4	1.17	42.01	12098	317	23.47	11.64
173	1049.5	WC1B 119	7.5				2.1			11123		24.05	12.81
174	1044	WC1B 120	5.5				0.2					20.95	11.23

Depth	%Ash	OrgInflux	CarbInflux	AshInflux	Al con	As con	Ca con	Cu con	Fe con	K con	Mg con	Mn con	Na con
1	53.72				2053	141.4	18054	28.02	21361	775.1	2613	53168	897.9
2	53.64	0.45	0.15	0.69	1680	71.92	18307	14.28	92103	569.9	1962	87429	496.7
3	53.41	0.66	0.21	1.00	1216	60.75	16866	14.98	99573	417.7	1694	79873	442.1
4	55.86	0.52	0.13	0.83	1201	58.29	14034	11.26	99618	352.6	1557	59253	343.7
5	58.22	0.56	0.15	1.00	1225	66.68	11489	11.99	6359	298.2	1462	59332	285.2
6	60.11	0.71	0.16	1.32	1739	60.97	9446	13.33	4552	373.1	1647	30131	260.6
7	61.33	0.47	0.12	0.95	1892	63.05	9018	12.43	10322	366.9	1662	27400	240.1
8	60.88	0.35	0.09	0.70	1850	62.36	9185	14.92	14064	348.9	1567	29892	225.6
9	61.27	0.50	0.13	1.00	1787	65.9	8920	12.26	8433	318	1507	25527	206
10	62.69	0.43	0.11	0.90	2184	59.74	8804	12.73	5044	369.8	1673	20876	199.1
11	62.12	0.47	0.12	0.97	2012	50.55	9327	12.28	96517	351.8	1597	19366	185.3
12	63.52	0.34	0.09	0.76	1840	53.9	9296	14.43	91513	337.4	1526	16462	252.9
13	63.71	0.50	0.14	1.12	1994	50.21	10140	10.07	83042	335.3	1502	15683	187.9
14	62.93	0.54	0.13	1.14	1458	56.76	9165	11.16	98006	280	1351	21725	181.1
15	62.13	0.82	0.21	1.69	1369	55.11	9959	11.8	97886	272.4	1330	22647	186.4
16	62.39	0.87	0.22	1.81	1522	53.41	10730	12.79	94845	308.2	1394	22144	183.8
17	62.67	0.51	0.13	1.08	1586	61.62	9956	13.46	324.8	322.1	1356	17883	181.1
18	64.92	0.60	0.15	1.40	2060	41.4	7578	12.51	70965	358.2	1411	11485	163.5
19	64.91	0.95	0.24	2.19	2202	43.25	7588	11.28	71815	379.6	1491	13178	162.6
20	66.07	0.46	0.12	1.13	2015	42.01	7421	11.51	83002	347.7	1443	16493	164.9
21	64.96	0.69	0.16	1.58	2054	48.21	7066	12.33	87736	366.5	1429	16540	165.3
22	66.95	0.57	0.13	1.41	2297	40.75	6660	11.19	81313	416.4	1504	12642	189.8
23	66.50	0.49	0.13	1.24	2135	36.73	6617	10.93	76660	368.5	1452	10823	166.1
24	66.40	0.45	0.13	1.14	2128	39.85	6718	11.1	73013	360.3	1473	10127	172.8
25	67.88	0.51	0.13	1.36	2198	40.55	6611	12.07	72308	365	1494	11080	156.9
26	70.03	0.60	0.13	1.70	2587	38.39	6211	11.69	70873	447.2	1575	10672	152.8
27	72.31	0.97	0.20	3.08	3131	33.4	6189	11.43	64817	524.5	1836	9431	154.2
28	73.53	0.84	0.19	2.88	2747	34.15	5984	10.26	65366	375.4	1616	9927	134.2
29	73.44	0.61	0.15	2.08	2624	32.99	6091	10.12	64126	377.3	1649	11385	132.6
30	71.02	0.61	0.15	1.87	2682	38.2	6962	11.13	75246	419.9	1745	15165	147.9
31	69.89	0.48	0.13	1.42	2688	39.9	7364	12.63	81323	474.6	1818	17102	180.1
32	68.83	0.68	0.18	1.91	2417	40	7255	12.18	81257	415.6	1670	17786	174.4
33	68.64	0.71	0.18	1.95	2373	40.76	7714	13.28	80847	398.2	1699	16283	166.1
34	69.57	0.63	0.15	1.80	2691	41.58	7938	14.25	73570	477.1	1845	15452	171.6
35	71.02	0.71	0.18	2.16	3168	37.91	8467	14.72	69107	582.4	2023	16349	194.2
36	70.92	0.43	0.12	1.34	2217	38.9	8301	13.47	60252	342.3	1532	19249	144.3
37	70.64	0.73	0.19	2.23	2367	39.73	7298	13.73	66036	340.1	1455	14922	141
38	71.28	0.50	0.14	1.58	2541	40.03	6999	13.62	68271	372.9	1516	12117	145.6
39	77.00	0.59	0.23	2.72	2669	41.1	6549	12.51	68369	432.9	1534	10502	158.7
40	74.43	0.57	0.15	2.11	2331	33.86	6103	12.6	62830	253.9	1308	8361	124.8
41	76.87	0.64	0.19	2.76	2550	25.72	5401	11.66	52701	307.6	1411	6935	119.5
42	76.94	0.67	0.19	2.87	2531	22.45	5503	11.24	46038	247.6	1433	6064	108.4
43	76.90	0.75	0.20	3.18	3251	23.01	5626	11.39	46757	429.6	1765	6048	120.3
44	76.76	0.77	0.18	3.14	3013	27.28	5724	11.22	54113	374.5	1669	6948	122.1
45	75.52	0.55	0.13	2.11	2672	33.61	5780	11.99	62218	319.5	1467	7334	123.4
46	75.81	0.53	0.12	2.05	2312	29.37	5616	10.9	58908	224.9	1300	6984	111.4
47	75.65	0.57	0.16	2.27	2399	28.51	5502	11.14	56868	229.2	1296	6533	110.1
48	75.03	0.60	0.17	2.30	2684	30.56	5537	11.51	58888	290.2	1447	6800	116.4
49	72.43	0.46	0.16	1.65	2629	29.5	5423	11.62	58354	311.9	1429	6749	116.9
50	71.79	0.56	0.19	1.89	2198	34.26	5670	12	66832	231.6	1276	8196	113.4
51	72.05	0.80	0.26	2.72	2138	32.45	5664	12.02	65648	223.5	1271	8245	111
52	72.27	0.90	0.29	3.10	2340	28.89	5476	11.64	62725	264.7	1361	7736	113.6
53	71.98	0.78	0.26	2.67	2688	35.64	6089	14.32	69296	354.5	1611	10217	131
54	70.37	0.87	0.33	2.86	2522	39.79	6277	12.96	78470	329.9	1510	10962	130.7
55	71.82	0.83	0.32	2.93	2809	32.89	5959	12.99	64930	338.6	1673	8052	124.7
56	71.44	0.65	0.22	2.18	2819	33.7	6046	12.89	67958	360.6	1655	10800	129.2
57	71.44	0.81	0.29	2.76	2930	34.92	6104	13.42	70830	388.1	1751	10873	137
58	70.76	0.93	0.32	3.05	2058	33.35	5893	12.37	66244	212.7	1346	9723	114.2
59	69.97	1.05	0.37	3.32	1782	30.38	5988	11.77	61348	173.1	1242	10382	109.9
60	70.22	0.72	0.26	2.31	2118	30.26	6127	12.04	61513	232.4	1334	8796	118.3
61	70.98	0.80	0.31	2.70	2200	28.43	5933	11.63	60112	229.8	1355	7136	114.2
62	70.68	0.60	0.22	1.99	1920	25.53	5781	11.77	54396	180.4	1262	6314	107.7
63	70.13	0.74	0.26	2.36	1785	28.62	5643	12.04	55373	167	1200	6475	103.3
64	69.69	0.67	0.23	2.06	1787	28.42	5532	10.96	60154	158.9	1122	6629	102.5
65	70.95	0.57	0.21	1.91	2130	26.54	5571	11.06	56910	202.5	1272	6234	106.1
66	69.19	0.61	0.22	1.88	2143	31.77	5868	11.62	62303	211.9	1309	6813	112.2
67	68.00	0.76	0.31	2.27	1854	28.42	5685	11.06	61084	159.3	1127	6466	102.4
68	67.77	0.76	0.26	2.15	1902	25.71	5885	11.57	58320	160.9	1191	6284	99.74
69	66.82	0.60	0.20	1.61	1761	30.98	5793	11.86	66186	157.3	1128	7017	104
70	67.13	0.88	0.31	2.42	1905	32.08	5826	11.52	64316	184	1247	6849	110
71	66.69	0.85	0.32	2.34	1757	31.33	5656	11.03	68609	163.5	1148	7257	109.3
72	66.64	0.58	0.22	1.60	1895	32.65	5576	11.11	64161	210.9	1206	6560	110.5
73	65.34	0.55	0.25	1.51	1688	31.69	5896	11.65	67381	173	1157	7141	112.3
74	65.79	0.82	0.35	2.24	1818	32.6	5829	11.74	65302	202.2	1197	6910	114.4
75	66.29	0.79	0.34	2.22	2118	31.52	5974	11.9	64194	269	1361	6783	124.4
76	66.13	0.51	0.21	1.41	2064	32.96	6076	11.93	63621	255.6	1331	6841	126
77	64.10	0.56	0.23	1.40	1973	35.53	6094	12.4	63184	241.3	1269	6635	123.8
78	62.91	0.51	0.20	1.20	2056	42.89	6542	14.03	71783	264.8	1284	7224	126.4
79	65.83	0.57	0.26	1.59	2364	38.89	6364	13.61	70989	286.4	1401	7187	125.2
80	69.56	0.61	0.18	1.80	2507	29.41	6352	12.25	65145	281.4	1481	6772	134.1
81	69.31	0.71	0.21	2.09	2281	32.12	5868	12.37	66193	224.2	1295	6758	113.6
82	70.16	0.51	0.17	1.60	2434	25.25	5515	11.3	57708	231.9	1319	5890	108.9
83	69.72	0.78	0.25	2.36	2549	23.35	5787	11.86	53589	268.1	1476	5595	111.2
84	69.06	0.73	0.25	2.17	2115	23.9	5683	11.47	51716	196	1272	5876	105.3
85	69.41	0.73	0.25	2.22	1954	23.38	5524	11.03	53177	167.9	1190	6017	96.52
86	69.03	0.68	0.25	2.06	2012	25.92	5640	10.81	60295	191.3	1235	6738	105.3
87	68.26	0.68	0.25	1.99	2177	29.79	5356	10.99	62133	253	1236	6694	111
88	67.52	0.71	0.25	2.01	2163	27.56	5582	11.22	62009	231.1	1226	6468	122

Depth	%Ash	OrgInflux	CarbInflux	AshInflux	Al con	As con	Ca con	Cu con	Fe con	K con	Mg con	Mn con	Na con
89	66.91	0.64	0.22	1.74	2005	27.59	5845	10.93	62515	182.7	1196	6780	112.7
90	67.44	0.63	0.22	1.76	1796	28.5	6003	11.02	65226	155.4	1126	7518	108.2
91	67.72	0.61	0.21	1.72	2052	28.6	6188	10.38	68659	200.3	1312	7376	122.5
92	65.68	0.63	0.20	1.59	1994	31.29	5832	9.841	70228	196.9	1208	7386	120.8
93	65.17	0.73	0.21	1.76	2285	30.82	5878	10.34	64527	257.6	1317	7216	131
94	65.00	0.49	0.14	1.16	1738	29.66	5903	10.3	65321	184.6	1194	7731	127.5
95	65.16	0.51	0.15	1.24	1688	32.13	5818	10.33	64704	200.9	1154	7606	138.4
96	66.60	0.61	0.19	1.60	1800	31.71	5511	10.66	58800	244.3	1211	7002	139.6
97	66.02	0.52	0.17	1.35	1831	32.46	5377	10.31	64380	269.3	1206	7702	140.3
98	66.16	0.46	0.15	1.18	1678	31.32	5314	10.66	67774	220.9	1117	8235	132.5
99	67.58	0.45	0.14	1.23	1735	35.26	5433	11.01	72684	236.6	1181	8915	141.7
100	68.01	0.47	0.13	1.29	2089	33.26	5500	10.63	65033	311.9	1334	7582	142
101	66.24	0.66	0.24	1.76	2250	33.55	5144	11.58	60817	339.8	1322	6603	115.1
102	66.22	0.64	0.26	1.76	2197	38.51	5352	13.65	70744	303.7	1353	7671	125
103	65.94	0.65	0.26	1.75	2385	33.46	5154	11.73	64435	349.3	1332	6756	128.3
104	67.04	0.52	0.21	1.48	2926	32.27	5231	11.35	56665	472.8	1631	6454	137.9
105	62.95	0.46	0.24	1.20	2386	35.11	5582	12.29	68530	351.5	1414	8109	140.2
106	60.69	0.57	0.30	1.34	2131	39.14	5483	12.3	78398	352	1302	9585	267.7
107	61.40	0.43	0.21	1.02	2108	38.77	5506	11.02	76238	318.5	1275	9483	188.9
108	61.65	0.70	0.32	1.64	1796	40.94	6062	10.7	79621	200.3	1156	10660	127.2
109	61.23	0.49	0.25	1.16	1730	51.62	6169	10.59	97366	212.4	1163	13340	127.2
110	63.82	0.53	0.28	1.41	2219	37.93	5829	9.466	79157	290.1	1417	9432	139.7
111	64.82	0.44	0.23	1.23	2212	37.01	5513	9.402	70966	313.6	1375	8091	133.3
112	64.90	0.50	0.28	1.44	2123	39.37	5567	9.024	76660	309.2	1384	9602	123.9
113	69.35	0.39	0.20	1.32	1905	34.27	5510	10.18	68603	187.3	1307	8356	110.9
114	64.72	0.51	0.27	1.43	2037	38.02	5704	10.23	75638	222	1369	9846	124.3
115	64.58	0.43	0.24	1.23	2279	42.14	5469	10.87	74338	320.4	1331	8230	141.1
116	66.99	0.41	0.22	1.27	2609	30.65	5147	9.329	51765	346	1430	6049	124.7
117	66.74	0.59	0.30	1.77	2374	24.68	4999	8.315	47516	277.4	1312	5631	115.7
118	64.27	0.50	0.29	1.42	1863	33.23	5061	8.655	67319	189.9	1048	7623	121
119	61.44	0.68	0.35	1.63	1698	40.14	5538	9.205	76980	193.3	1106	9219	118.2
120	60.29	0.78	0.35	1.72	1741	46.1	5636	12.12	82685	229	1076	9267	120.6
121	61.53	0.69	0.33	1.63	1710	50.79	5768	12.97	83025	210	1057	9524	119.1
122	61.75	0.39	0.20	0.95	1681	41.81	5629	10.97	75615	169.9	1092	9013	116.4
123	59.26	0.44	0.19	0.92	1516	57.43	6131	11.77	87376	158.2	1044	11240	126
124	59.99	0.42	0.22	0.95	1481	49.45	6103	11.66	92038	163.4	1023	11337	128.1
125	64.49	0.47	0.24	1.29	2124	36.47	5450	9.727	64104	288	1268	8262	127.4
126	61.61	0.62	0.28	1.45	1877	41.19	5833	11.53	79999	227.5	1117	10175	131.3
127	62.06	0.51	0.21	1.17	2098	40.81	6014	11.9	67519	273	1315	9633	135.1
128	61.12	0.52	0.25	1.21	1751	43.95	6667	10.75	85230	211.4	1228	15812	134.5
129	56.45	0.52	0.23	0.96	1214	53.74	7016	14.17	669.2	143.4	1009	11690	126
130	58.66	0.46	0.23	0.99	1372	44	6208	12.26	83977	152.6	1120	10091	110.5
131	60.52	0.48	0.23	1.09	1575	37.51	5804	11.4	73781	185.6	1212	9711	101.4
132	60.56	0.35	0.16	0.78	1557	40.09	5792	12.11	75317	185.3	1199	9178	99.69
133	61.93	0.50	0.22	1.17	1464	36.83	5703	13.26	72006	153.4	1150	9890	98.77
134	62.18	0.41	0.21	1.03	1537	38.71	5427	12	66082	179.8	1185	9061	93.51
135	65.91	0.43	0.19	1.20	1638	36.64	6837	11.98	61448	192.2	1248	8886	101.9
136	65.26	0.33	0.15	0.90	1518	39.68	6138	10.62	81719	116.6	1107	10588	100.9
137	65.15	0.60	0.24	1.58	2285	35.35	6508	13.14	69939	234.5	1555	8337	111.7
138	64.62	0.50	0.18	1.25	1856	37.38	5923	11.2	75938	159.2	1233	8586	101.6
139	66.11	0.40	0.16	1.10	1722	33.25	5555	11.22	59444	177.4	1162	7259	100.8
140	65.67	0.58	0.23	1.55	1367	34.49	5246	11.5	67245	107.9	1018	8196	91.12
141	65.69	0.43	0.18	1.17	1540	39.69	5219	10.84	66981	142.3	1067	8117	91.38
142	66.08	0.53	0.20	1.41	2040	35.45	5640	11.73	62720	225.3	1345	7591	102.4
143	67.22	0.42	0.18	1.23	2498	36.71	5850	11.74	61242	334.6	1619	7423	121.8
144	66.04	0.48	0.19	1.31	1842	42.1	6222	12.28	78688	180.7	1248	10908	102.2
145	67.03	0.56	0.25	1.65	1819	31.99	5690	11.03	69360	161.3	1264	11438	98.32
146	66.08	0.42	0.17	1.15	1881	43.16	6309	12.52	71771	171.7	1333	11405	112.9
147	67.44	0.54	0.24	1.61	2221	34.46	5331	10.87	65305	228.5	1466	7728	109.1
148	68.18	0.49	0.24	1.57	2159	34.34	5675	12.19	63613	235.8	1564	7959	115.7
149	66.19	0.49	0.25	1.44	1940	42.88	5963	14.34	69245	226.5	1389	8495	110
150	67.24	0.51	0.22	1.49	2193	39.27	5431	10.93	63163	277.5	1569	7790	113.3
151	66.00	0.48	0.21	1.33	2309	41.68	5572	11.63	67475	315.5	1643	8487	118.2
152	64.82	0.36	0.17	0.99	1392	44.1	6263	13.56	75627	149.8	1127	12533	112.6
153	66.24	0.42	0.22	1.24	1853	34.26	5771	12.87	62648	210.2	1521	8791	110
154	64.70	0.46	0.27	1.34	1643	36.64	5648	12.08	74212	184.2	1318	10055	111.8
155	66.08	0.45	0.27	1.41	1632	34.5	5832	11.59	63017	192.3	1373	9535	113.4
156	65.87	0.51	0.30	1.57	1330	32.79	5860	11.25	69570	123.5	1269	11344	108.8
157	67.10	0.46	0.27	1.48	1445	31.68	5955	10.59	60011	148.8	1359	8631	106.5
158	66.41	0.62	0.37	1.96	1499	37.8	6002	16.86	61751	168.8	1450	9695	111.8
159	64.87	0.61	0.38	1.82	1556	45.12	6044	12.25	62732	203.7	1407	9167	112.1
160	64.47	0.49	0.25	1.34	1842	39.21	5899	12.71	66757	191.2	1425	7217	119.6
161	63.53	0.55	0.31	1.50	1757	38.63	7382	13.6	72190	166.2	1546	9205	124
162	65.11	0.66	0.36	1.90	1555	44.31	6424	13.57	65465	164.7	1418	9070	114.4
163	63.39	0.42	0.27	1.19	1285	40.2	6304	11.57	70604	135.4	1271	12006	111
164	63.34	0.48	0.27	1.30	1399	44.75	7841	12.45	73130	158.6	1316	51078	120
165	66.08	0.71	0.41	2.19	2116	29.71	7251	11.95	59400	282	1713	12434	132.2
166	68.90	0.40	0.28	1.51	2111	31.1	5943	11.63	50250	287.7	1860	7609	119.9
167	65.57	0.51	0.29	1.52	1307	29.56	4905	8.909	45073	140	1173	10020	81.06
168	61.33	0.49	0.30	1.26	1427	65.87	7770	14.38	89876	149.4	1226	56224	124
169	62.91	0.59	0.33	1.55	1807	50.84	6770	13.98	82905	188	1254	9152	132.9
170	68.50	0.75	0.39	2.49	2747	31.53	6269	12.35	55717	351.7	2005	6305	131
171	65.35	0.60	0.32	1.73	2245	32.91	5638	11.52	66753	230.4	1466	7572	119.9
172	64.89	0.65	0.32	1.81	2492	31.56	5591	11.02	62302	294.2	1610	7317	124.4
173	63.14				2356	39.49	6246	12.53	76485	253.1	1473	8286	165.6
174	67.82												

Depth	Ni con	P con	Pb con	S con	Ti con	Zn con	Al influx	As influx	Ca influx	Cu influx	Fe influx	K influx	Mg influx
1	149.3	15307	70.58	1425	82.22	165.1							
2	233.7	9586	50.91	3552	76.89	86.31	21.76	0.93	237.08	0.18	1192.73	7.38	25.41
3	215.2	7735	53.67	3244	57.39	79.49	22.70	1.13	314.83	0.28	1858.70	7.80	31.62
4	166.9	5690	42.26	3129	54.43	76.15	17.84	0.87	208.43	0.17	1479.48	5.24	23.12
5	168.9	5992	47.85	2694	52.11	70.72	20.95	1.14	196.46	0.21	108.74	5.10	25.00
6	91.79	7327	43.31	2420	71.27	80.27	38.17	1.34	207.34	0.29	99.92	8.19	36.15
7	84.85	8566	45.16	2319	72.04	80.83	29.26	0.98	139.48	0.19	159.65	5.67	25.71
8	95.11	8311	53.23	2588	66.54	78.45	21.13	0.71	104.91	0.17	160.64	3.99	17.90
9	81.85	7975	46.46	2363	58.36	78.97	29.20	1.08	145.78	0.20	137.82	5.20	24.63
10	70.11	7563	43.61	1876	71.17	85.74	31.21	0.85	125.80	0.18	72.07	5.28	23.91
11	66.28	7882	46.18	2034	67.31	85.12	31.49	0.79	145.97	0.19	1510.49	5.51	24.99
12	58.84	8343	39.02	2552	65.75	78.51	21.90	0.64	110.62	0.17	1089.00	4.02	18.16
13	54.4	11580	34.66	2213	57.66	83.39	35.09	0.88	178.46	0.18	1461.54	5.90	26.44
14	91.02	10485	35.17	2174	54.07	77.27	26.50	1.03	166.57	0.20	1781.26	5.09	24.55
15	97.07	8693	37.63	2245	50.22	81.22	37.18	1.50	270.49	0.32	2658.58	7.40	36.12
16	95.85	8579	40.86	2728	53.25	81.38	44.26	1.55	312.03	0.37	2758.09	8.96	40.54
17	81.23	9018	33.95	3409	56.9	79.58	27.35	1.06	171.69	0.23	5.60	5.55	23.38
18	56.61	7250	28.66	2456	53.07	79.42	44.29	0.89	162.93	0.27	1525.75	7.70	30.34
19	62.63	7837	28.84	1970	55.26	89.02	74.43	1.46	256.47	0.38	2427.35	12.83	50.40
20	74.51	8892	31.36	1869	53.47	74.46	34.58	0.72	127.34	0.20	1424.31	5.97	24.76
21	75.16	8030	33.04	1859	53.83	76.36	49.88	1.17	171.60	0.30	2130.73	8.90	34.70
22	59.68	6482	32.41	1536	55.91	74.68	48.52	0.86	140.69	0.24	1717.74	8.80	31.77
23	53.29	6264	26.53	1448	54.14	71.44	39.66	0.68	122.93	0.20	1424.17	6.85	26.97
24	51.72	5772	29.61	1779	52.52	72.03	36.69	0.69	115.82	0.19	1258.74	6.21	25.39
25	55.34	6322	28.92	2166	52.94	72.38	43.92	0.81	132.09	0.24	1444.71	7.29	29.85
26	54	6599	26.93	1849	52.39	70.86	62.89	0.93	151.00	0.28	1723.00	10.87	38.29
27	49.59	5848	26.05	1414	45.12	76.44	133.17	1.42	263.24	0.49	2756.88	22.31	78.09
28	49.54	6165	24.21	1029	35.04	70.65	107.68	1.34	234.57	0.40	2562.35	14.72	63.35
29	54.79	6454	25.5	1035	36.73	68.3	74.40	0.94	172.71	0.29	1818.33	10.70	46.76
30	70.92	6290	26.93	1299	41.97	76.68	70.57	1.01	183.18	0.29	1979.81	11.05	45.91
31	78.15	6925	29.4	1501	49.61	79.44	54.62	0.81	149.64	0.26	1652.48	9.64	36.94
32	81.28	6377	26.63	1925	48.43	76.89	67.05	1.11	201.27	0.34	2254.30	11.53	46.33
33	78.05	5724	28.73	2558	46.28	80.95	67.33	1.16	218.86	0.38	2293.74	11.30	48.20
34	74.32	5933	25.4	3491	46	80.51	69.50	1.07	205.00	0.37	1899.95	12.32	47.65
35	80	6165	23.91	3744	52.14	80.73	96.31	1.15	257.40	0.45	2100.85	17.70	61.50
36	88.86	4727	26.44	3612	36.45	67.64	42.02	0.74	157.34	0.26	1142.01	6.49	29.04
37	72.15	6176	26.68	3115	36.02	72.06	74.62	1.25	230.07	0.43	2081.78	10.72	45.87
38	61.75	6479	28.14	2965	37.49	70.76	56.50	0.89	155.63	0.30	1518.10	8.29	33.71
39	55.97	6941	28.51	3003	43.65	65.89	94.33	1.45	231.46	0.44	2416.36	15.30	54.22
40	45.82	6107	26.14	1489	27.09	60.78	66.06	0.96	172.96	0.36	1780.60	7.20	37.07
41	40.47	6470	24.28	1063	29.96	57.94	91.63	0.92	194.08	0.42	1893.72	11.05	50.70
42	34.88	4924	21.09	904.7	20.72	54.49	94.51	0.84	205.48	0.42	1719.06	9.25	53.51
43	35.85	5221	23.11	861.1	27.82	62.54	134.45	0.95	232.67	0.47	1933.66	17.77	72.99
44	39.97	5517	23.81	957.4	28.35	62.32	123.08	1.11	233.83	0.46	2210.52	15.30	68.18
45	42.08	5209	27.12	1191	31.1	62.38	74.57	0.94	161.31	0.33	1736.45	8.92	40.94
46	39.61	5026	25.55	1230	24.07	55.16	62.42	0.79	151.63	0.29	1590.52	6.07	35.10
47	38.4	4244	23.48	1179	22.16	55.95	71.87	0.85	164.84	0.33	1703.77	6.87	38.83
48	40.7	4518	24.83	1276	24.37	57.88	82.13	0.94	169.43	0.35	1801.97	8.88	44.28
49	40.24	4219	25.15	1272	25.84	58.47	59.98	0.67	123.73	0.27	1331.37	7.12	32.60
50	45.11	6252	25.32	1500	26.96	58.44	57.99	0.90	149.58	0.32	1763.15	6.11	33.66
51	45.79	6325	26.19	1459	25.21	57.73	80.76	1.23	213.96	0.45	2479.85	8.44	48.01
52	43.42	6252	25.33	1274	27.74	59.35	100.35	1.24	234.84	0.50	2690.01	11.35	58.37
53	55.18	6853	29.99	1290	33.06	65.28	99.66	1.32	225.75	0.53	2569.15	13.14	59.73
54	57.85	6723	29.1	1774	33.35	63.75	102.61	1.62	255.38	0.53	3192.61	13.42	61.44
55	46.5	5187	27.9	1547	28.04	65.37	114.47	1.34	242.83	0.53	2645.90	13.80	68.17
56	56.2	5767	29.01	1361	29.86	65.89	86.15	1.03	184.77	0.39	2076.80	11.02	50.58
57	56.96	6230	28.32	1397	30.34	67.19	113.10	1.35	235.61	0.52	2734.04	14.98	67.59
58	49.96	6250	23.97	1314	26.95	60.28	88.61	1.44	253.74	0.53	2852.28	9.16	57.95
59	52.76	6044	23.59	1666	22.33	58.15	84.53	1.44	284.03	0.56	2909.94	8.21	58.91
60	47.24	5935	23.45	1885	26.28	61.37	69.56	0.99	201.24	0.40	2020.36	7.63	43.81
61	40.08	5564	22.68	1460	26.23	60.65	83.71	1.08	225.75	0.44	2287.26	8.74	51.56
62	35.89	5218	22.45	1326	21.92	57.65	54.14	0.72	163.02	0.33	1533.97	5.09	35.59
63	37.12	6332	21.25	1421	24.77	54.28	60.06	0.96	189.86	0.41	1862.99	5.62	40.37
64	36.97	6659	21.46	1400	23.45	53.41	52.90	0.84	163.75	0.32	1780.56	4.70	33.21
65	35.84	5989	21.22	1345	23.71	56.7	57.47	0.72	150.32	0.30	1535.62	5.46	34.32
66	38.93	6148	22.37	1396	27.25	61.9	58.13	0.86	159.18	0.32	1690.11	5.75	35.51
67	36.88	5835	21.98	1267	23.42	57.6	61.76	0.95	189.37	0.37	2034.78	5.31	37.54
68	36.53	6373	21.53	1420	24.49	59	60.29	0.82	186.55	0.37	1848.74	5.10	37.75
69	38.86	7527	23.35	1602	27.47	59.42	42.32	0.74	139.23	0.29	1590.67	3.78	27.11
70	38.66	7248	21.33	1514	28.06	61.66	68.63	1.16	209.88	0.42	2316.98	6.63	44.92
71	40.61	7978	22.72	1542	26.02	60.25	61.63	1.10	198.38	0.39	2406.46	5.73	40.27
72	36.84	7151	22.59	1755	34.03	61.82	45.45	0.78	133.73	0.27	1538.79	5.06	28.92
73	40.14	7939	23.51	1829	31.25	62.57	38.94	0.73	136.00	0.27	1554.26	3.99	26.69
74	38.88	8036	21.82	1989	33.77	61.21	61.86	1.11	198.33	0.40	2221.90	6.88	40.73
75	39.17	7793	23.02	1965	37.25	63.08	71.01	1.06	200.28	0.40	2152.10	9.02	45.63
76	39.71	7293	21.68	2097	37.6	65.06	44.10	0.70	129.82	0.25	1359.37	5.46	28.44
77	39.55	6806	21.53	2713	37.33	66.35	43.18	0.78	133.36	0.27	1382.68	5.28	27.77
78	44.33	7476	24.68	3675	41.91	71.58	39.27	0.82	124.95	0.27	1371.06	5.06	24.52
79	43.46	7312	24.7	2732	35.38	69.6	57.25	0.94	154.11	0.33	1719.12	6.94	33.93
80	39.83	6607	23.81	1872	32.4	65.89	64.76	0.76	164.09	0.32	1682.91	7.27	38.26
81	40.25	6543	25.36	1621	32.54	66.46	68.66	0.97	176.63	0.37	1992.41	6.75	38.98
82	35.71	5346	23.66	1202	26.93	64.45	55.60	0.58	125.98	0.26	1318.22	5.30	30.13
83	34.65	5034	24.04	1061	30.58	67.42	86.16	0.79	195.60	0.40	1811.31	9.06	49.89
84	35.51	5796	21.19	1367	29.71	61.15	66.41	0.75	178.45	0.36	1623.88	6.15	39.94
85	34.38	6107	21.32	1130	27.3	58.36	62.61	0.75	176.99	0.35	1703.79	5.38	38.13
86	38.46	7442	22.02	1502	34.15	61.4	60.00	0.77	168.18	0.32	1798.00	5.70	36.83
87	38.96	8441	24.15	1558	39.75	65.73	63.48	0.87	156.18	0.32	1811.80	7.38	36.04
88	37.11	6714	23.28	1330	34.37	63.36	64.37	0.82	166.12	0.33	1845.39	6.88	36.49

Depth	Ni con	P con	Pb con	S con	Ti con	Zn con	Al influx	As influx	Ca influx	Cu influx	Fe influx	K influx	Mg influx
89	36.64	7224	22.69	1529	32.54	66	52.00	0.72	151.58	0.28	1621.22	4.74	31.02
90	40.23	9037	23.19	1536	32.49	62.35	46.76	0.74	156.28	0.29	1698.05	4.05	29.31
91	38.71	8127	21.52	1581	37.14	62.96	52.15	0.73	157.28	0.26	1745.08	5.09	33.35
92	38.85	8178	22.13	1533	37.66	61.2	48.29	0.76	141.23	0.24	1700.69	4.77	29.25
93	38.59	8133	21.21	1896	42.26	66.21	61.65	0.83	158.59	0.28	1740.94	6.95	35.53
94	39.68	8405	21.46	2190	38.92	65.21	30.89	0.53	104.90	0.18	1160.85	3.28	21.22
95	39.11	8467	20.17	2348	41.91	61.39	32.21	0.61	111.03	0.20	1234.77	3.83	22.02
96	37.32	8314	19.67	2165	44.66	58.41	43.16	0.76	132.15	0.26	1410.02	5.86	29.04
97	40.33	9314	20.27	2107	48.46	58.4	37.41	0.66	109.87	0.21	1315.50	5.50	24.64
98	41.22	9755	21.1	2149	43.44	56.68	29.84	0.56	94.51	0.19	1205.41	3.93	19.87
99	43.95	10211	23.17	2081	45.93	56.89	31.48	0.64	98.57	0.20	1318.70	4.29	21.43
100	39.81	8795	20.3	2096	49.39	59.2	39.48	0.63	103.95	0.20	1229.12	5.89	25.21
101	38.34	7779	23.4	662	57	62.13	59.80	0.89	136.73	0.31	1616.52	9.03	35.14
102	41.35	9297	24.21	712.6	52.98	63	58.40	1.02	142.26	0.36	1880.38	8.07	35.96
103	38.61	7429	22.83	732.2	48.15	62.67	63.39	0.89	136.99	0.31	1712.68	9.28	35.40
104	38.83	7192	23	710.6	45.47	67.68	64.81	0.71	115.87	0.25	1255.13	10.47	36.13
105	44.45	8236	24	786.4	50.73	65.71	45.30	0.67	105.98	0.23	1301.09	6.67	26.85
106	51.19	9004	27.08	914.2	60.16	68.19	47.20	0.87	121.45	0.27	1736.52	8.02	28.84
107	50.31	8277	26.37	906.7	48.55	65.21	35.02	0.64	91.47	0.18	1266.50	5.29	21.18
108	57.28	8606	27	1191	36.79	65.65	47.74	1.09	161.13	0.28	2116.33	5.32	30.73
109	67.07	11205	32.1	1557	44.34	69.87	32.85	0.98	117.12	0.20	1848.56	4.03	22.08
110	50.06	8015	28.2	1093	34.83	67.79	49.15	0.84	129.11	0.21	1753.33	6.43	31.39
111	44.56	7094	26.25	1023	44.55	63.13	42.00	0.70	104.67	0.18	1347.34	5.95	26.11
112	49.82	8405	27.71	786.1	51.26	60.77	47.02	0.87	123.31	0.20	1698.02	6.85	30.66
113	45.18	7847	24.58	809.5	30.49	61.23	36.17	0.65	104.61	0.19	1302.48	3.56	24.81
114	50.11	6349	26.39	927.1	33.88	62.53	45.12	0.84	126.34	0.23	1675.38	4.92	30.32
115	46.64	7725	26.23	1071	50.01	64.64	43.27	0.80	103.83	0.21	1411.36	6.08	25.27
116	37.54	6802	21.78	890.3	38.89	64.8	49.53	0.58	97.72	0.18	982.80	6.57	27.15
117	33.11	5639	20.12	773.8	33.8	64.91	63.10	0.66	132.87	0.22	1262.98	7.37	34.87
118	40.69	6670	23.33	937.1	34.96	63.85	41.27	0.74	112.10	0.19	1491.12	4.21	23.21
119	48.66	7850	24.59	1130	41.5	63.92	45.13	1.07	147.20	0.24	2046.13	5.14	29.40
120	49.7	10395	24.3	1105	46.96	76.21	49.69	1.32	160.84	0.35	2359.70	6.54	30.71
121	53.92	11494	25.94	1255	46.46	69.25	45.29	1.35	152.77	0.34	2198.96	5.56	28.00
122	49.05	8919	25.22	1176	33.8	69.8	25.78	0.64	86.31	0.17	1159.43	2.61	16.74
123	61.79	10346	27.6	1558	37.27	75.04	23.48	0.89	94.95	0.18	1353.11	2.45	16.17
124	58.66	10372	27.99	1382	39.6	92.04	23.43	0.78	96.55	0.18	1456.08	2.59	16.18
125	46.01	9525	22.71	1083	39.78	72.19	42.40	0.73	108.79	0.19	1279.58	5.75	25.31
126	57.86	10482	25.4	1316	41.33	76.74	44.11	0.97	137.08	0.27	1879.98	5.35	26.25
127	52.68	8560	25.32	1243	39.64	79.5	39.69	0.77	113.77	0.23	1277.34	5.16	24.88
128	72.15	6588	29.96	851.1	37.02	74.11	34.59	0.87	131.71	0.21	1683.80	4.18	24.26
129	63.01	9514	30.36	1126	34.87	76.99	20.66	0.91	119.42	0.24	11.39	2.44	17.17
130	55.71	8228	28.09	1281	36.72	79.55	23.05	0.74	104.28	0.21	1410.68	2.56	18.81
131	51.57	9979	24.84	1094	42.07	74.71	28.35	0.68	104.47	0.21	1328.06	3.34	21.82
132	50.57	8811	27.2	1032	43.29	71.93	20.05	0.52	74.59	0.16	969.92	2.39	15.44
133	55.22	10461	25.42	955.9	40.57	69.12	27.69	0.70	107.87	0.25	1361.98	2.90	21.75
134	48.18	8672	25.23	921.4	42.87	62.26	25.42	0.64	89.75	0.20	1092.83	2.97	19.60
135	48.38	8335	23.1	908.4	39.57	62.82	29.76	0.67	124.22	0.22	1116.47	3.49	22.68
136	56.77	7529	28.14	1126	27.45	62.62	21.01	0.55	84.94	0.15	1130.86	1.61	15.32
137	47.89	7522	26.02	1071	32.74	76.81	55.40	0.86	157.79	0.32	1695.67	5.69	37.70
138	48.08	7343	27.4	1212	31.89	67.84	35.93	0.72	114.66	0.22	1470.05	3.08	23.87
139	42.04	7485	21.44	1036	34.9	69.9	28.57	0.55	92.18	0.19	986.40	2.94	19.28
140	45.89	7264	22.92	844.2	28.74	60.19	32.29	0.81	123.91	0.27	1588.26	2.55	24.04
141	45.43	8355	24.41	865.1	34.46	62.3	27.54	0.71	93.33	0.19	1197.83	2.54	19.08
142	43.67	7753	23.32	913.3	36.94	65.76	43.59	0.76	120.52	0.25	1340.20	4.81	28.74
143	43.52	8156	24.78	958.1	39.6	77.53	45.81	0.67	107.28	0.22	1123.10	6.14	29.69
144	56.34	8857	27.86	1108	30.17	67	36.65	0.84	123.80	0.24	1565.69	3.60	24.83
145	57.96	6568	26.26	947.7	27.05	64.28	44.72	0.79	139.89	0.27	1705.28	3.97	31.08
146	62.48	7315	28.09	1212	26.92	66.71	32.71	0.75	109.70	0.22	1247.90	2.99	23.18
147	45.29	6800	25.83	1038	32.52	62.89	53.06	0.82	127.36	0.26	1560.19	5.46	35.02
148	45.42	6711	24.2	851.6	29.26	64.79	49.72	0.79	130.70	0.28	1465.03	5.43	36.02
149	48.18	7207	25.55	1051	37.43	65.7	42.26	0.93	129.89	0.31	1508.39	4.93	30.26
150	44.9	7466	24.4	976.2	38.22	70.1	48.68	0.87	120.57	0.24	1402.18	6.16	34.83
151	49.21	7681	26.57	1183	38.54	65.33	46.64	0.84	112.54	0.23	1362.85	6.37	33.18
152	61.36	8003	26.92	779.1	34.42	59.48	21.20	0.67	95.41	0.21	1152.05	2.28	17.17
153	46.68	7623	24	685.8	33.43	58.79	34.77	0.64	108.29	0.24	1175.54	3.94	28.54
154	51.09	7610	26.77	764	33.59	56.9	33.99	0.76	116.84	0.25	1535.18	3.81	27.26
155	48.9	7238	22.5	728.3	32.15	55.5	34.92	0.74	124.78	0.25	1348.27	4.11	29.38
156	54.61	7367	24.52	729.5	23.78	56.83	31.71	0.78	139.72	0.27	1658.75	2.94	30.26
157	44.44	6743	21.84	708.4	26.63	52.59	31.93	0.70	131.57	0.23	1325.91	3.29	30.03
158	49.98	6791	22.64	753.8	29.56	57.25	44.20	1.11	176.98	0.50	1820.89	4.98	42.76
159	50.88	7549	22.96	879.5	33.42	55.79	43.66	1.27	169.60	0.34	1760.36	5.72	39.48
160	42.73	4858	23.53	871.4	28.1	66.65	38.16	0.81	122.19	0.26	1382.82	3.96	29.52
161	51.45	5159	28.64	888.3	28.6	64.66	41.41	0.91	173.98	0.32	1701.37	3.92	36.44
162	51.34	8087	24.34	833.7	32.25	59.31	45.41	1.29	187.58	0.40	1911.58	4.81	41.41
163	59.71	7394	26.13	835.1	30.71	52.06	24.19	0.76	118.68	0.22	1329.15	2.55	23.93
164	77.59	7799	28.62	1002	31.98	57.27	28.71	0.92	160.90	0.26	1500.67	3.25	27.01
165	61.15	4616	25.27	874.3	30.85	57.67	69.97	0.98	239.77	0.40	1964.16	9.32	56.64
166	43.21	4837	22.39	682.5	30.79	55.8	46.12	0.68	129.85	0.25	1097.94	6.29	40.64
167	49.82	5037	19.56	647.1	21.4	43.45	30.39	0.69	114.04	0.21	1047.95	3.26	27.27
168	79.46	8309	31.38	1254	32.86	76.32	29.21	1.35	159.03	0.29	1839.46	3.06	25.09
169	53.28	7209	28.86	1078	34.19	60.49	44.41	1.25	166.40	0.34	2037.74	4.62	30.82
170	42.19	5829	24.33	765.1	31.63	61.88	99.75	1.14	227.64	0.45	2023.22	12.77	72.81
171	43.96	7088	25.17	821.2	31.8	60.22	59.40	0.87	149.17	0.30	1766.09	6.10	38.79
172	43.6	6708	24.63	808.9	35.13	61.95	69.47	0.88	155.87	0.31	1736.90	8.20	44.88
173	49.99	6346	27.69	1056	33.31	63.31							
174													

Depth	Mn influx	Na influx	Ni influx	P influx	Pb influx	S influx	Tl influx	Zn influx
1								
2	1132.21	6.43	3.03	124.14	0.66	46.00	1.00	1.12
3	1490.96	8.25	4.02	144.39	1.00	60.55	1.07	1.48
4	880.00	5.10	2.48	84.50	0.63	46.47	0.81	1.13
5	1014.58	4.88	2.89	102.46	0.82	46.07	0.89	1.21
6	661.38	5.72	2.01	160.83	0.95	53.12	1.56	1.76
7	423.79	3.71	1.31	132.49	0.70	35.87	1.11	1.25
8	341.43	2.58	1.09	94.93	0.61	29.56	0.76	0.90
9	417.18	3.37	1.34	130.33	0.76	38.62	0.95	1.29
10	298.29	2.84	1.00	108.07	0.62	26.81	1.02	1.23
11	303.08	2.90	1.04	123.35	0.72	31.83	1.05	1.33
12	195.90	3.01	0.70	99.28	0.46	30.37	0.78	0.93
13	276.02	3.31	0.96	203.81	0.61	38.95	1.01	1.47
14	394.85	3.29	1.65	190.56	0.64	39.51	0.98	1.40
15	615.09	5.06	2.64	236.10	1.02	60.97	1.36	2.21
16	643.95	5.34	2.79	249.48	1.19	79.33	1.55	2.37
17	308.38	3.12	1.40	155.51	0.59	58.79	0.98	1.37
18	246.93	3.52	1.22	155.88	0.62	52.80	1.14	1.71
19	445.42	5.50	2.12	264.89	0.97	66.59	1.87	3.01
20	283.02	2.83	1.28	152.59	0.54	32.07	0.92	1.28
21	401.69	4.01	1.83	195.01	0.80	45.15	1.31	1.85
22	267.06	4.01	1.26	136.93	0.68	32.45	1.18	1.58
23	201.07	3.09	0.99	116.37	0.49	26.90	1.01	1.33
24	174.59	2.98	0.89	99.51	0.51	30.67	0.91	1.24
25	221.38	3.13	1.11	126.31	0.58	43.28	1.06	1.45
26	259.45	3.71	1.31	160.43	0.65	44.95	1.27	1.72
27	401.13	6.56	2.11	248.73	1.11	60.14	1.92	3.25
28	389.14	5.26	1.94	241.67	0.95	40.34	1.37	2.77
29	322.83	3.76	1.55	183.01	0.72	29.35	1.04	1.94
30	399.01	3.89	1.87	165.50	0.71	34.18	1.10	2.02
31	347.51	3.66	1.59	140.72	0.60	30.50	1.01	1.61
32	493.43	4.84	2.25	176.92	0.74	53.40	1.34	2.13
33	461.97	4.71	2.21	162.40	0.82	72.57	1.31	2.30
34	399.05	4.43	1.92	153.22	0.66	90.16	1.19	2.08
35	497.01	5.90	2.43	187.42	0.73	113.82	1.59	2.45
36	364.84	2.74	1.68	89.59	0.50	68.46	0.69	1.28
37	470.42	4.45	2.27	194.70	0.84	98.20	1.14	2.27
38	269.44	3.24	1.37	144.07	0.63	65.93	0.83	1.57
39	371.17	5.61	1.98	245.31	1.01	106.13	1.54	2.33
40	236.95	3.54	1.30	173.07	0.74	42.20	0.77	1.72
41	249.20	4.29	1.45	232.49	0.87	38.20	1.08	2.08
42	226.43	4.05	1.30	183.86	0.79	33.78	0.77	2.03
43	250.12	4.98	1.48	215.92	0.96	35.61	1.15	2.59
44	283.83	4.99	1.63	225.37	0.97	39.11	1.16	2.55
45	204.69	3.44	1.17	145.38	0.76	33.24	0.87	1.74
46	188.57	3.01	1.07	135.70	0.69	33.21	0.65	1.49
47	195.73	3.30	1.15	127.15	0.70	35.32	0.66	1.68
48	208.08	3.56	1.25	138.25	0.76	39.05	0.75	1.77
49	153.98	2.67	0.92	96.26	0.57	29.02	0.59	1.33
50	216.23	2.99	1.19	164.94	0.67	39.57	0.71	1.54
51	311.45	4.19	1.73	238.93	0.99	55.11	0.95	2.18
52	331.76	4.87	1.86	268.12	1.09	54.64	1.19	2.55
53	378.80	4.86	2.05	254.07	1.11	47.83	1.23	2.42
54	446.00	5.32	2.35	273.53	1.18	72.18	1.36	2.59
55	328.12	5.08	1.89	211.37	1.14	63.04	1.14	2.66
56	330.05	3.95	1.72	176.24	0.89	41.59	0.91	2.01
57	419.70	5.29	2.20	240.48	1.09	53.92	1.17	2.59
58	418.64	4.92	2.15	269.11	1.03	56.58	1.16	2.60
59	492.45	5.21	2.50	286.69	1.12	79.02	1.06	2.76
60	288.90	3.89	1.55	194.93	0.77	61.91	0.86	2.02
61	271.52	4.35	1.53	211.71	0.86	55.55	1.00	2.31
62	178.05	3.04	1.01	147.15	0.63	37.39	0.62	1.63
63	217.85	3.48	1.25	213.04	0.71	47.81	0.83	1.83
64	196.22	3.03	1.09	197.11	0.64	41.44	0.69	1.58
65	168.21	2.86	0.97	161.60	0.57	36.29	0.64	1.53
66	184.82	3.04	1.06	166.78	0.61	37.87	0.74	1.68
67	215.39	3.41	1.23	194.37	0.73	42.21	0.78	1.92
68	199.20	3.16	1.16	202.02	0.68	45.01	0.78	1.87
69	168.64	2.50	0.93	180.90	0.56	38.50	0.66	1.43
70	246.74	3.96	1.39	261.11	0.77	54.54	1.01	2.22
71	254.54	3.83	1.42	279.83	0.80	54.09	0.91	2.11
72	157.33	2.65	0.88	171.50	0.54	42.09	0.82	1.48
73	164.72	2.59	0.93	183.13	0.54	42.19	0.72	1.44
74	235.11	3.89	1.32	273.42	0.74	67.68	1.15	2.08
75	227.40	4.17	1.31	261.26	0.77	65.88	1.25	2.11
76	146.17	2.69	0.85	155.83	0.46	44.81	0.80	1.39
77	145.20	2.71	0.87	148.94	0.47	59.37	0.82	1.45
78	137.98	2.41	0.85	142.79	0.47	70.19	0.80	1.37
79	174.05	3.03	1.05	177.07	0.60	66.16	0.86	1.69
80	174.94	3.46	1.03	170.68	0.62	48.36	0.84	1.70
81	203.42	3.42	1.21	196.94	0.76	48.79	0.98	2.00
82	134.54	2.49	0.82	122.12	0.54	27.46	0.62	1.47
83	189.11	3.76	1.17	170.15	0.81	35.86	1.03	2.28
84	184.51	3.31	1.12	181.99	0.67	42.92	0.93	1.92
85	192.78	3.09	1.10	195.67	0.68	36.21	0.87	1.87
86	200.93	3.14	1.15	221.92	0.66	44.79	1.02	1.83
87	195.20	3.24	1.14	246.14	0.70	45.43	1.16	1.92
88	192.49	3.63	1.10	199.81	0.69	39.58	1.02	1.89

Depth	Mn influx	Na influx	Ni influx	P influx	Pb influx	S influx	Ti influx	Zn influx
89	175.83	2.92	0.95	187.34	0.59	39.65	0.84	1.71
90	195.72	2.82	1.05	235.26	0.60	39.99	0.85	1.62
91	187.47	3.11	0.98	206.56	0.55	40.18	0.94	1.60
92	178.86	2.93	0.94	198.04	0.54	37.12	0.91	1.48
93	194.69	3.53	1.04	219.43	0.57	51.15	1.14	1.79
94	137.39	2.27	0.71	149.37	0.38	38.92	0.69	1.16
95	145.15	2.64	0.75	161.58	0.38	44.81	0.80	1.17
96	167.91	3.35	0.89	199.37	0.47	51.92	1.07	1.40
97	157.38	2.87	0.82	190.32	0.41	43.05	0.99	1.19
98	146.47	2.36	0.73	173.50	0.38	38.22	0.77	1.01
99	161.74	2.57	0.80	185.26	0.42	37.76	0.83	1.03
100	143.30	2.68	0.75	166.23	0.38	39.61	0.93	1.12
101	175.51	3.06	1.02	206.77	0.62	17.60	1.52	1.65
102	203.90	3.32	1.10	247.11	0.64	18.94	1.41	1.67
103	179.57	3.41	1.03	197.46	0.61	19.46	1.28	1.67
104	142.96	3.05	0.86	159.30	0.51	15.74	1.01	1.50
105	153.96	2.66	0.84	156.37	0.46	14.93	0.96	1.25
106	212.31	5.93	1.13	199.44	0.60	20.25	1.33	1.51
107	157.54	3.14	0.84	137.50	0.44	15.06	0.81	1.08
108	283.34	3.38	1.52	228.75	0.72	31.66	0.98	1.74
109	253.27	2.41	1.27	212.73	0.61	29.56	0.84	1.33
110	208.92	3.09	1.11	177.53	0.62	24.21	0.77	1.50
111	153.61	2.53	0.85	134.68	0.50	19.42	0.85	1.20
112	212.68	2.74	1.10	186.17	0.61	17.41	1.14	1.35
113	158.64	2.11	0.86	148.98	0.47	15.37	0.58	1.16
114	218.09	2.75	1.11	140.63	0.58	20.54	0.75	1.39
115	156.25	2.68	0.89	146.66	0.50	20.33	0.95	1.23
116	114.84	2.37	0.71	129.14	0.41	16.90	0.74	1.23
117	149.67	3.08	0.88	149.88	0.53	20.57	0.90	1.73
118	168.85	2.68	0.90	147.74	0.52	20.76	0.77	1.41
119	245.04	3.14	1.29	208.65	0.65	30.04	1.10	1.70
120	264.47	3.44	1.42	296.66	0.69	31.54	1.34	2.17
121	252.25	3.15	1.43	304.42	0.69	33.24	1.23	1.83
122	138.20	1.78	0.75	136.76	0.39	18.03	0.52	1.07
123	174.06	1.95	0.96	160.22	0.43	24.13	0.58	1.16
124	179.36	2.03	0.93	164.09	0.44	21.86	0.63	1.46
125	164.92	2.54	0.92	190.13	0.45	21.62	0.79	1.44
126	239.11	3.09	1.36	246.33	0.60	30.93	0.97	1.80
127	182.24	2.56	1.00	161.94	0.48	23.52	0.75	1.50
128	312.38	2.66	1.43	130.15	0.59	16.81	0.73	1.46
129	198.97	2.14	1.07	161.93	0.52	19.16	0.59	1.31
130	169.51	1.86	0.94	138.22	0.47	21.52	0.62	1.34
131	174.80	1.83	0.93	179.62	0.45	19.69	0.76	1.34
132	118.19	1.28	0.65	113.47	0.35	13.29	0.56	0.93
133	187.07	1.87	1.04	197.87	0.48	18.08	0.77	1.31
134	149.85	1.55	0.80	143.41	0.42	15.24	0.71	1.03
135	161.45	1.85	0.68	151.44	0.42	16.51	0.72	1.14
136	146.52	1.40	0.79	104.19	0.39	15.58	0.38	0.87
137	202.13	2.71	1.16	182.37	0.63	25.97	0.79	1.86
138	166.21	1.97	0.93	142.15	0.53	23.46	0.62	1.31
139	120.45	1.67	0.70	124.20	0.36	17.19	0.58	1.16
140	193.58	2.15	1.08	171.57	0.54	19.94	0.68	1.42
141	145.16	1.63	0.81	149.41	0.44	15.47	0.62	1.11
142	162.20	2.19	0.93	165.67	0.50	19.52	0.79	1.41
143	136.13	2.23	0.80	149.57	0.45	17.57	0.73	1.42
144	217.04	2.03	1.12	176.23	0.55	22.05	0.60	1.33
145	281.21	2.42	1.42	161.48	0.65	23.30	0.67	1.58
146	198.30	1.96	1.09	127.19	0.49	21.07	0.47	1.16
147	184.63	2.61	1.08	162.46	0.62	24.80	0.78	1.50
148	183.30	2.66	1.05	154.56	0.56	19.61	0.67	1.49
149	185.05	2.40	1.05	156.99	0.56	22.89	0.82	1.43
150	172.93	2.52	1.00	165.74	0.54	21.67	0.85	1.56
151	171.42	2.39	0.99	155.14	0.54	23.89	0.78	1.32
152	190.92	1.72	0.93	121.91	0.41	11.87	0.52	0.91
153	164.96	2.06	0.88	143.04	0.45	12.87	0.63	1.10
154	208.00	2.31	1.06	157.42	0.55	15.80	0.69	1.18
155	204.00	2.43	1.05	154.86	0.48	15.58	0.69	1.19
156	270.47	2.59	1.30	175.65	0.58	17.39	0.57	1.35
157	190.70	2.35	0.98	148.98	0.48	15.65	0.59	1.16
158	285.88	3.30	1.47	200.25	0.67	22.23	0.87	1.69
159	257.24	3.15	1.43	211.84	0.64	24.68	0.94	1.57
160	149.49	2.48	0.89	100.63	0.49	18.05	0.58	1.38
161	216.94	2.92	1.21	121.59	0.67	20.94	0.67	1.52
162	264.84	3.34	1.50	236.14	0.71	24.34	0.94	1.73
163	226.02	2.09	1.12	139.19	0.49	15.72	0.58	0.98
164	1048.15	2.46	1.59	160.04	0.59	20.56	0.66	1.18
165	411.15	4.37	2.02	152.64	0.84	28.91	1.02	1.91
166	166.25	2.62	0.94	105.69	0.49	14.91	0.67	1.22
167	232.97	1.88	1.16	117.11	0.45	15.05	0.50	1.01
168	1150.72	2.54	1.63	170.06	0.64	25.67	0.67	1.56
169	224.95	3.27	1.31	177.19	0.71	26.50	0.84	1.49
170	228.95	4.76	1.53	211.67	0.88	27.78	1.15	2.25
171	200.33	3.17	1.16	187.53	0.67	21.73	0.84	1.59
172	203.99	3.47	1.22	187.01	0.69	22.55	0.98	1.73
173								
174								