High Resolution geochemical XRF data from Elk Lake, Minnesota: A Holocene paleoclimate record from varved lacustrine sediments

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Dedication

This thesis is dedicated to my friends and family that have supported me in this journey, especially Megan R. Desmarais.

Abstract

The study of Holocene climate change is vital to understanding present and future climate conditions in the Upper Midwest region of the United States. Varved sediments from Elk Lake, Clearwater County, Minnesota provide an archive of multiple climate sensitive proxies and past climate conditions, particularly related to the balance of precipitation and evaporation (available moisture) for the North Central United States. Studies conducted in the past using Elk Lake sediments have established large scale and long term changes in the climate history of the region, but were done at a resolution that only allowed for a discussion of events on time scales of hundreds to thousands of years.

Scanning XRF is a new analytical technique that allows for much higher resolution, geochemical data to be gathered from sediment cores for the characterization of climate variability with resolution on the order of decades to inter-annual changes. This study seeks to repeat, using new analytical and higher resolution methods, the work done by previous researchers. One centimeter resolution XRF scans were used to describe changes that occurred during the Holocene, and 200 micron scans were used to identify the nature of varve deposition during major periods in the Holocene and to characterize the timing and relationships between the laminations that make up individual varves. With higher resolution data with which to work, time series analysis provides insight into high frequency cycles during the Holocene record including El Nino Southern Oscillation (ENSO) and solar activity cycles.

With the addition of the first known geophysical data set from Elk Lake, this study also illustrates the usefulness of obtaining multiple records from an individual lake.

Through the use of both geochemical and geophysical data, it is shown that events seen separately in each data set can be correlated to one another and an accurate estimate for the timing of major climatic events can be obtained.

Table of Contents

List of Tables

List of Figures

1. Introduction

The study of past climates in any region of the world is of particular importance to gaining knowledge of how, why, and when changes have occurred and to identify possible mechanisms for those changes. Knowledge of the past prepares us for current and future changes that may take place. Many studies have looked at the past climatic conditions of the Upper Midwestern region of the United States, but changes and advances in analytical techniques are constantly occurring, allowing researchers greater insight into the timing and duration of events while also providing greater resolution. Studies of Holocene climate change in the state of Minnesota have included work done on Elk Lake in Itasca State Park, Clearwater County, Minnesota.

One significant improvement in the ability to analyze data sets from lacustrine sediments includes the Scanning XRF (X-ray Fluorescence) which allows non-destructive, high resolution geochemical information to be gathered. This technique also allows for the characterization of variability over shorter term time scales that were not available to researchers who studied Elk Lake in the past. With this method, it is possible to tell not only the general, long term changes that have occurred in the Midwest since the end of the last glaciation, but also to describe cycles and changes that have occurred on the scale of decades or even individual years.

Itasca State Park, at the head waters of the Mississippi River, has been recognized for decades as an important location for the study of paleoclimatology due to its position relative to the prairie forest boundary and proximity to the triple junction of three major airstreams (Wright 1976; Anderson 1993). Elk Lake sits within the boundaries of Itasca

State Park and has several characteristics that make it an excellent location for sediment core investigations with respect to paleoclimatology. The varved sediments preserved in Elk Lake contain several climatically sensitive proxies that are affected by shifts in the ecosystem and climatic boundaries, and they provide a high resolution record of climate change throughout the Holocene. Elk Lake is located within the boundaries of Itasca State park and thus it is has undergone minimal anthropogenic disturbance.

While the Elk Lake sedimentary record has been widely studied by the paleoclimatology community, analytical techniques have continued to improve and Elk Lake has not been revisited in quite some time. Thus, this study seeks to continue the research by attempting to develop a high resolution data set that will allow for the identification of annual and inter-annual changes in the climate of the region during the Holocene.

The non-destructive, high-resolution technique known as Scanning X-ray Fluorescence (XRF) provides the ability to analyze the sediments of Elk Lake without the time and labor intensive processes that were required to gain geochemical data in the past. The Itrax XRF core scanner (Cox Analytical Systems), located at the Large Lakes Observatory (LLO), Duluth, MN was able to run one meter of sediment at 1cm resolution in under 4-5 hours, whereas past techniques would have taken substantially more time and energy to gain the same resolution (approximately 100 hrs/meter at 1cm resolution).

The following chapters will present a dataset that is both higher in resolution and better able to provide information of time scales down to decades, and even individual years, than any previous dataset collected from Elk Lake. The main difference in the new dataset from Elk Lake was the timing of phases and events, and a more detailed record of climate dynamics. While it was difficult to determine conclusively that the age scale developed for the XRF record is lacking error, there is a fairly strong argument that the varve year chronology originally used for Elk Lake includes substantial error and the use of bulk organic radiocarbon dating techniques on a lake such as this is greatly influenced by the “hard-water” effect. Thus the age scale was developed by tying into data presented from Steel Lake by Wright (2003) that utilized terrestrial macrofossils and AMS ^{14}C dating methods.

1.2 Location

Elk Lake (figure 1-A and 1-B) is a kettle lake located in Itasca State Park, Clearwater County, MN (lat. 47º 12” N, long 95º 15” W) and is part of the Itasca Moraine. Elk Lake drains into Lake Itasca through a small creek, at the northern end of the lake, known as Chambers Creek and is part of the headwaters of the Mississippi River.

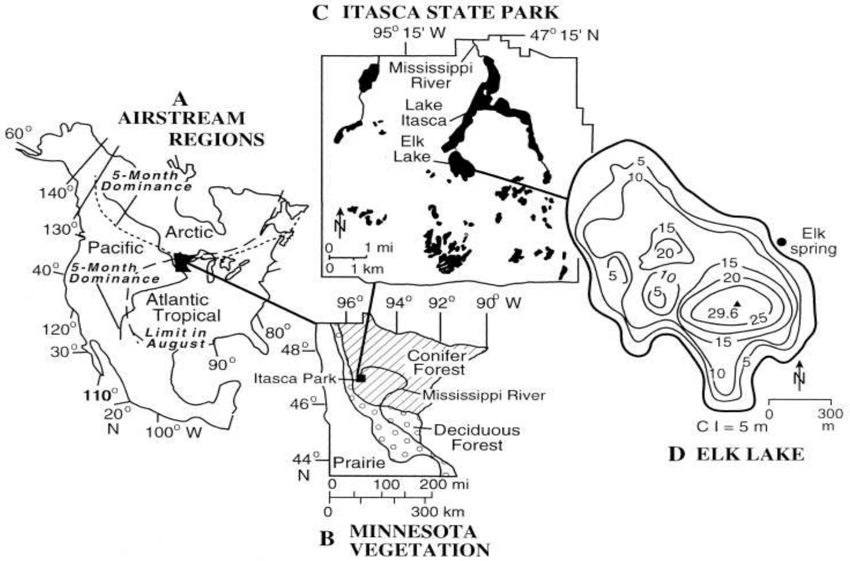


Figure 1-a Location. Maps of (A) Major regional airstreams of North America (B) Minnesota including vegetation zones, (C) Itasca State Park, and (D) Elk Lake (from Dean, 2009).

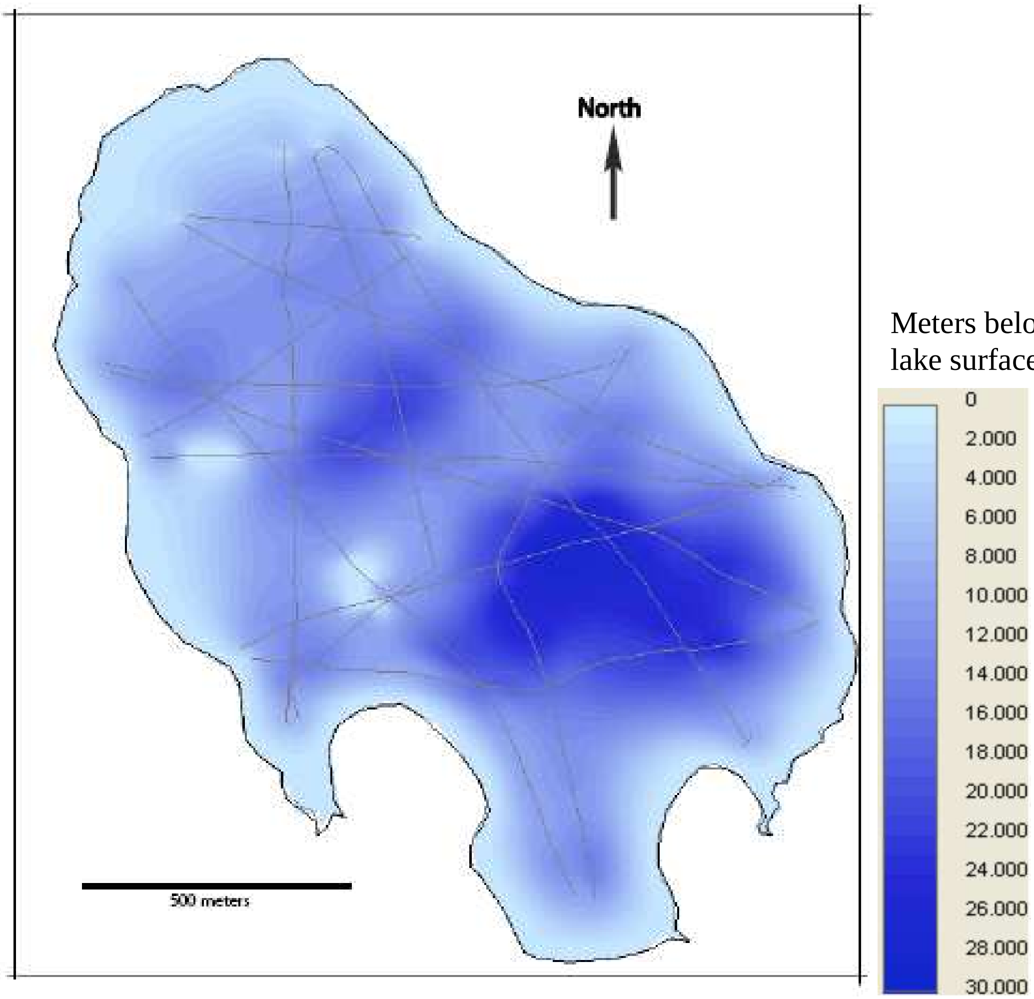


Figure 1-b Bathymetric Map of Elk Lake developed from geophysical CHIRP data recovered on August 25, 2009 (see methods and results).

Land use in the watershed of Elk Lake is minimal with less than one percent of the land developed, cultivated, or open pasture land and almost one hundred percent forest and water. This means the Elk Lake watershed has had little anthropomorphic disturbance. The basin of Elk Lake, because of its origin as a kettle lake, is very small and thus there is little surface runoff into the lake.

Elk Lake is a dimictic lake, over-turning twice a year in spring and autumn, with a maximum depth of 30 meters. Hills surrounding the lake generally rise approximately 25 meters above the lake surface. Due to the large depth of Elk Lake relative to the surface area, the hypolimnion becomes seasonally anoxic, preventing bioturbation of the sediments by benthic organisms.

1.3 Climatic Proxies

1.3.1 Carbonate Deposition:

As is the case with most lakes underlain by calcareous glacial drift, Elk Lake contains a large amount of dissolved alkaline-earth cations (e.g. calcium, magnesium, strontium) and is typically saturated with respect to calcium carbonate, particularly during the summer months (Dean and Megard, 1993). For the purposes of this study, it is assumed that the carbonate fraction of the Elk Lake sediment cores are represented by the amount of calcium (Ca) within the record as well to a lesser extent magnesium (Mg) and strontium (Sr) which geochemically behaves much like magnesium. Previous studies of carbonate precipitation in Elk Lake have shown (through water chemistry, carbonate saturation, and sediment-trap samples) that the deposition of calcite occurs during the summer months as a response to algal photosynthesis in the epilimnion and is, for the most part, authigenic in origin (Dean and Megard, 1993). As primary productivity increases after the spring over turn, photosynthetic removal of CO_2 leads to an increase in the pH of the waters and they become oversaturated with respect to calcite. Epilimnetic depletion of calcite is proportional to the increase in pH and the rate of photosynthetic carbon fixation.

A study of the environment of deposition of calcite within Elk lake (Dean and Megard, 1993) showed that the mole percent of dissolved magnesium in $CaCO_3$ increases as the ratio of magnesium to calcium increases as predicted by the Eugster and Jones model (1979). The Mg:Ca ratio was also shown to increase as more calcite is precipitated from the water, leading to an increase in the Mg:Ca ratio of both the residual water and the precipitating calcite. The ratio is also affected by the relationship between precipitation and evaporation—the ionic strength of the lake. As the balance of precipitation to evaporation moves toward drier conditions, the water becomes enriched in carbonates and depleted in Ca leading to an increase in the Mg:Ca ratio (Dean and Megard, 1993).

While the XRF is unable to directly measure magnesium, we do have a record of strontium within the core. Strontium behaves much like magnesium; as salinity within the lake increases, the amount of strontium precipitated and preserved within the carbonates of the sediment also increases (E. Brown, personal communication, 2010). Although the process by which strontium replaces Ca within the calcite structure is not well know within Elk Lake (S. Colman, personal communication, 2010), the ratio of Sr:Ca can be used empirically as a measure of the salinity of the lake through time. It was assumed that the ratio of Sr:Ca is a measure of salinity within the record, but it must be noted that some of the Sr and to a lesser extent Ca could enter the lake as eolian clastic material.

1.3.2 Ground Water Input, Iron/Manganese Oxyhydroxides and Carbonates:

Iron and manganese are particularly abundant during some of the main geochemical phases of the Elk Lake record (which will be defined later). The presence of these elements is particularly important during the last four thousand years where very large concentrations are seen in the sediments. The precipitation of these Fe and Mn oxyhydroxides is likely related to intense redox cycling within the water column and the sediments. Because these compounds are relatively unstable under reducing conditions, most of the precipitated Fe and Mn oxyhydroxides are probably recycled back into the water column after raining to the bottom, but there is also significant net burial as shown by the XRF data. During the summer months when stratification takes hold and bottom waters become anoxic, some of the Fe and Mn may be removed from the sediment under anoxic conditions and cycled back into the water column, but a great deal of this material must be returned to the sediment during periods of overturn. This “pump” of iron and manganese seems to have been increasing in efficiency during the last four thousand years as evidenced by the increasing concentrations of Fe and Mn shown in the XRF data and previous studies (Dean 1993). It is possible that in any given iron and manganese oxyhydroxide layer, the concentrations of Fe and Mn are representative of the several years preceding the deposition of a specific lamination rather than that of an individual year

The possibility, due to the reducing conditions of the sediments, that iron and manganese from the oldest sediments (those older than 4000 cal yrs BP) could have been removed in full and diffused upward into the youngest sediments exists. Previous researchers suggested that this was not the case (Dean, 1993) and rather the iron and manganese were present in the form of oxyhydroxides. With little evidence from the data to support the idea that the Fe and Mn records represent long term diagenetic diffusion of these elements, it was assumed for the purposes of this study that the Fe and Mn are in the form of oxyhydroxides and possibly carbonates.

Another process to note is that unlike Fe oxyhydroxides, which form colloids and are relatively stable in the reducing conditions present in the bottom waters and sediments of Elk Lake, manganese oxyhydroxides are inherently unstable in these conditions (Dean and Megard, 1993). While some of the Manganese preserved in the cores could be present in the form of manganese oxyhydroxides that survived sedimentation to the bottom, some portion is probably present in the form of rhodochrosite ($MnCO_3$). Rhodochrosite has been shown to be a constituent of the sediment rain throughout the year (Dean and Megard, 1993), but most of this mineral is probably deposited in the sediments when anoxic bottom waters mix with carbonate rich surface waters during spring and autumn over-turning periods. It is possible that some of the Mn oxyhydroxides raining on the bottom of the lake survive, but more likely that most is converted to rhodochrosite within the anoxic hypolimnion and sediments (Dean and Megard, 1993). Similar processes likely affect the nature of Fe deposition as well. Even though Fe oxyhydroxides form more stable colloids than the Mn oxyhydroxides, they are also probably altered diagenetically in the reducing conditions of the sediments and hypolimnion. During the formation of rhodochrosite, Fe is probably altered to form siderite ($FeCO_3$) under the reducing conditions of the sediments. Unfortunately, whether the Fe and/or Mn are present in the sediments as oxyhydroxides or carbonates was difficult to determine. Smear slides from Fe and Mn rich layers within the cores did not show any significant quantities of siderite or rhodochrosite in the sediments.

While there is little direct evidence for the original source of the Fe and Mn, it likely reaches the lake by ground water flow through the surrounding sediments. One small iron-rich spring flows into the lake from the east and likely represents the composition of the ground water (Dean, 1993). Groundwater monitoring wells near LaBaugh Lake and Williams Lake just south of the Itasca Moraine also show high concentrations of Fe and Mn (Dean, 1993). A possible hypothesis could be made that changes in the amount of iron and manganese in the sediments could potentially represent changes in the amount of groundwater flowing into the lake although these elements are certainly influenced by a number of other processes that can affect the amount of each element that is deposited and preserved in the sediments of Elk Lake—particularly in relation to limnologic processes in the lake that are not well documented.

1.3.3 Weathering and Eolian Processes: Detrital Clastics

During the Early and Modern stages of Elk Lake's history, detrital clastic minerals were minor constituents of the sediment. During the mid-Holocene, the amount of clastic material entering the lake increased dramatically. Elements such as titanium (Ti), potassium (K), and to some extent silica (Si), and other trace elements represent clastic materials entering the lake (Dean, 1993).

There are two possible explanations for the presence of feldspathic elements (K and Ti especially) and clay minerals within the sediments of Elk Lake—particularly during the mid-Holocene as will be discussed later on. One is that when conditions within the basin become drier, the rate and degree of chemical weathering of feldspars in the basin will decrease due to a lack of available moisture (resulting in an increase in K:Ti;

decrease in Ti:K ratios, see results);Ti and K bearing minerals can be transported and preserved in the sediments of the lake. There is a relatively high amount of Ti and K in the sediments deposited between 4000-9000 cal years BP suggesting a decrease in available moisture. This change in the amount of available moisture is supported by pollen records that indicate the presence of prairie vegetation during the same time period (Dean, 1993; Wright, 2003). Clastic indicators can potentially be used to discuss changes in the rates of feldspathic decomposition/erosion and available moisture in the watershed of Elk Lake and the surrounding region.

Due to a generally limited understanding of the rate at which feldspars decompose within the general climatic regime of the region and thresholds that need to be met in order to weather feldspar at a rate sufficient to produce a record of weathering within the Elk Lake basin, it is likely that the record is not long enough to adequately address the weathering of feldspar (i.e. chemical weathering of feldspars occurs at a rate too slow for a Holocene record to show appreciable changes in the degree of chemical weathering). If this is in fact the case, the record of clastic elements within the sediment could be explained through eolian transport of minerals from the High Plains region to the west of Elk Lake, including the area formerly covered by Lake Agassiz. This second process would almost certainly be a signal of available moisture in the region because drier conditions are needed to facilitate wind driven transport of minerals. While the clastic elements most likely represent the interplay between both processes, they are dominated by wind borne clastic material. Therefore, for the purposes of this study, it will be assumed that the clastic elements within the sediments of Elk Lake represent eolian processes and not chemical weathering within the lake's basin.

1.3.4 Other Clastic Elements: Si, Cr, Cu, Rb

There are a number of other elements associated with the clastic fraction of the lake sediments, but none are as descriptive of processes in and around the lake as Ti and K are. Silica can be used to discuss clastics, but, unfortunately, it is difficult to discern clastic Si from biogenic Si using the XRF alone. Copper (Cu), chromium (Cr), rubidium (Rb), and other trace elements show similar trends to the major clastic elements (Ti, K, etc.), but for the most part have low XRF counts. Considerable noise results from data with low XRF counts and thus many of the trace elements found in the sediments of Elk Lake have not been deemed sufficiently reliable or noteworthy to be used as indicators of past climate conditions.

1.4 History and Setting of Elk Lake

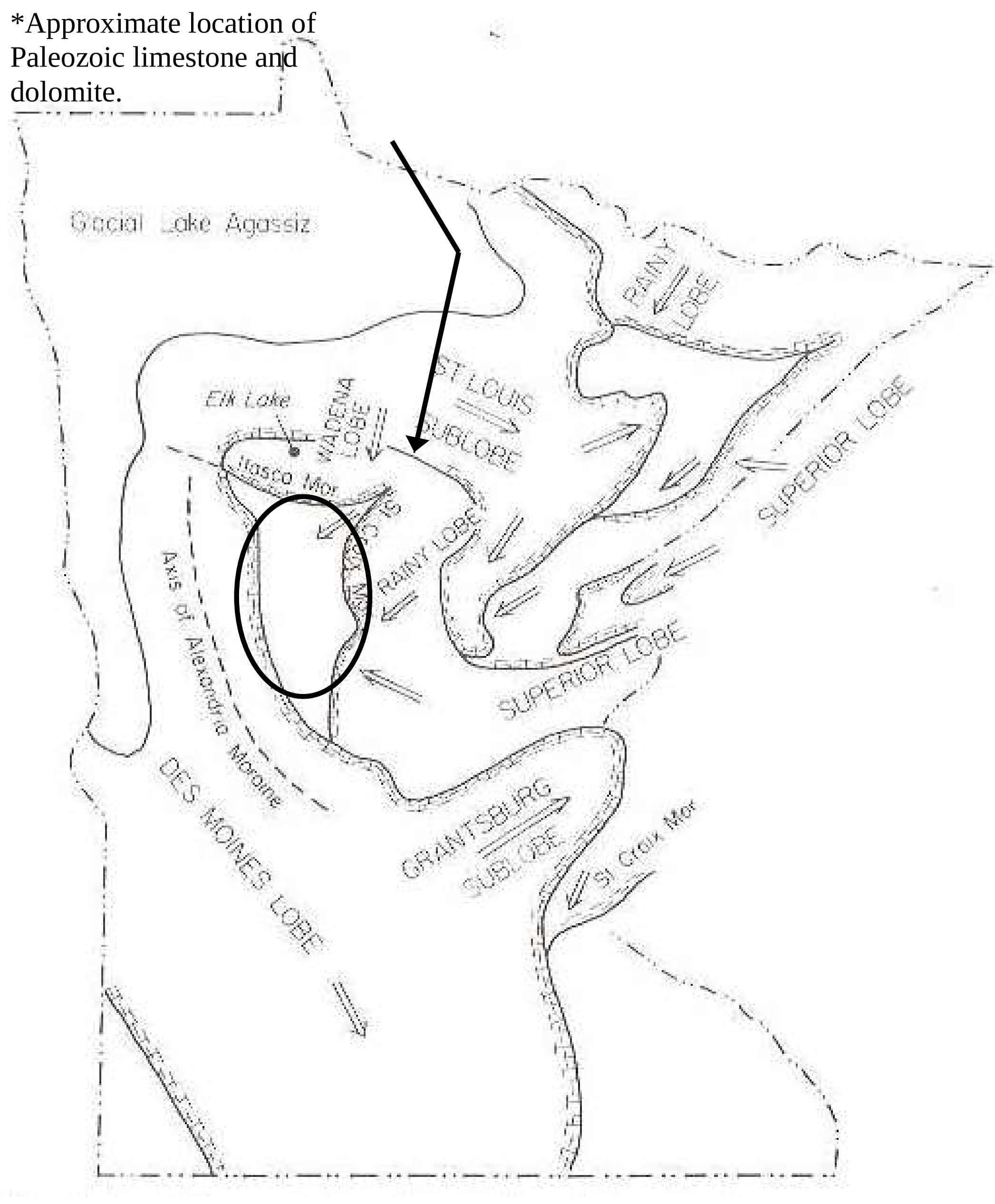
1.4.1 Glacial History and the Origin of Elk Lake:

The Itasca moraine is one of the most prominent features of the region surrounding Elk Lake and trends in the east to west direction north of the town of Park Rapids, MN. It is assumed that due to the very large amount of material contained within the Itasca moraine that the ice margin responsible for deposition of the feature must have remained at this location for an extended period of time, on the order of hundreds of years (Wright 1993). Also, due to the high amount of relief within the Itasca moraine, the ice that created it must have been relatively heterogeneous with some sections containing large amounts of debris and other parts of the ice margin being relatively pure ice. This is consistent with the presence numerous kettle lakes and wetlands in and around the moraine (Wright 1993).

Elk Lake is currently about 30m deep and contains approximately 20m of sediment (Wright 1993). Hills surrounding the lake rise about 25m above the lake surface, suggesting the original local relief was approximately 75m. The basin developed from an area within the ice margin that was almost pure ice. The hills were created by parts of the glacial ice that contained large amounts of material (Wright 1993).

Based on the composition of the tills associated with the Itasca moraine it is thought to have formed as a result of deposition by the Wadena lobe. The tills of the Itasca moraine contain mostly carbonate material that is not found in areas to the northeast of the moraine. The composition of the Wadena tills are mostly dolomite and limestone likely derived from Paleozoic rocks only exposed to the northwest of Elk Lake in southern Manitoba. Due to the orientation of the Wadena Drumlin field (indicates southwesterly ice flow)—just south of the Itasca Moraine— it has been hypothesized that the Wadena ice lobe, coming into the area from the northwest must have been diverted and forced to flow to the south west by the Rainy Lobe moving in from the Lake Superior basin (Wright 1993).

The Wadena lobe then retreated some unknown distance only to re-advance to the location of the Itasca Moraine, where it remained for a long period of time .The fact that the Wadena lobe remained at the position of the Itasca moraine for an extended amount of time represents relatively stable climatic conditions (Wright 1993). On the basis of radiocarbon dates taken on bulk organic sediment from a marsh (Wolf Creek) behind the moraine (Birks, 1976), the creation of the Itasca moraine is thought to have occurred at approximately 20,000 (calibrated radiocarbon) yrs. BP and lasted for several hundred years (Wright 1993). This date may be an upper limit because it was taken on bulk fine-grained lake sediment that could contain ^{14}C deficient organic matter, or lignite particles from Cretaceous rocks. Because of this issue it can only be assumed that the lake is older than 14,000 (calibrated) years BP (the date of the Des Moines lobe advance as established by basal wood analysis) (Wright 1993).



*Approximate location of Paleozoic limestone and dolomite.

Figure 2 Ice lobes that affected Elk Lake. Map of Minnesota showing the relations of different ice lobes that affected the area through time, during the Late Wisconsin glaciation (From Wright, 1993). Also shown: the approximate location/direction of the Paleozoic rocks found in the Wadena Lobe tills, Black arrow shows the approximate flow direction of the Wadena lobe, Circle indicates the approximate location of the Wadena Drumlin Field.

While the Wadena lobe remained in the Itasca area, a large series of sub-glacial troughs were created as melt-water moved beneath the ice sheet. The flowing water in these troughs needed tremendous power in order to both carry any sediment falling out of the ice and be capable of maintaining an open channel underneath a large volume of ice. Most of the linear lakes in the area are in such tunnel valleys (Wright 1993). Lake Itasca and Elk Lake each rest within these tunnel valleys and even the Mississippi River utilizes a tunnel valley as it flows from Lake Itasca (figure 3).

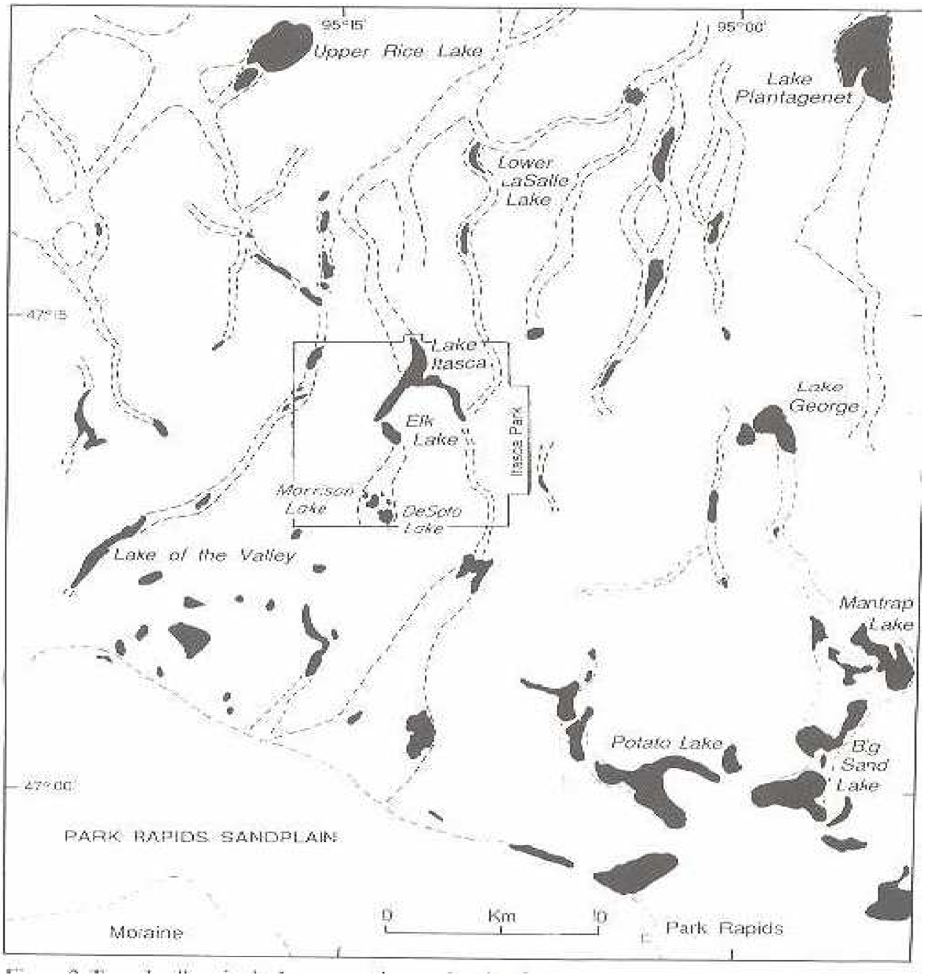


Figure 3 Tunnel valleys in the Itasca Moraine as determined from topographic maps including Elk Lake (From Wright, 1993).

The Wadena lobe eventually retreated leaving behind numerous stagnant ice blocks, which would later become the kettle lakes of the Itasca moraine. The Des Moines Lobe to the west re-advanced and an arm of the ice known as the St. Louis sub-lobe moved into the region. Outwash channels from the sub-lobe utilized the tunnel valleys created by the Wadena Lobe. The valley now occupied by Elk Lake was one of the pathways for material washing out of the St. Louis sub-lobe. The ice block responsible for the Elk Lake basin was, at this time, still present and further buried by outwash material from the St. Louis sub lobe (Wright 1993).

Even with the final retreat of the ice margins from the area at approximately 14,000yrs ago, the ice blocks left by the Wadena lobe and buried by successive events were still present in large numbers within the Itasca moraine (Wright 1993). The amount of time needed to melt a stagnant ice block completely varies depending on the location of a block and the amount of debris with which it is covered. It is postulated, based on basal sediments in Elk lake containing datable terrestrial organic detritus that the lower most sediments are approximately 11,000 years old (Wright 1993). Because the active Wadena lobe had to have left the site more that 14,000 years ago, the ice block that created Elk Lake must have remained buried for at least 3000 years (Wright 1993).

1.4.2 Vegetational History of Elk Lake:

The Elk Lake region is adjacent to the boundary of the Prairie-Forest transition and the sharp moisture gradient between these two ecosystems types. Because the boundaries between vegetational bands in the region are relatively narrow (figure 4) they are particularly sensitive to slight changes in climate and move readily as parameters such as the balance between precipitation and evaporation are altered (Wright 1993). The first of the vegetational bands for the Itasca region (white and black spruce, balsam fir, tamarack, white pine, jack pine, birch and aspen) extends from Itasca to Ontario (Wright 1993). Thirty kilometers to the west of Itasca Park is presently the western most limit of this mixed coniferous deciduous forest (Wright 1993). The pure temperate deciduous forest containing sugar maple, basswood, elm burr-oak, ironwood, and hazel begins 10 kilometers to the west of the limit of the mixed coniferous –deciduous forest. Further to the west, the vegetation transitions into oak-land and prairie savanna. Today, this vegetational zone is composed mostly of burr-oak because of its resistance to fire, but before the European settlement and the suppression of forest fires, this band would have consisted of prairie grasses with disconnected stands of oak. These three vegetational bands are controlled by a strong moisture gradient that exists between the southwest and northeastern parts of Minnesota with increasing moisture, snow, and lower summer temperatures to the northeast (Wright 1993).

Earlier studies of pollen sequences from sediment cores in numerous Minnesota lakes show that herbaceous pollen was dominant, suggesting a tundra-like ecosystem followed by spruce in the late-glacial forest of northeastern Minnesota (McAndrews

1966). After the final deglaciation of the region, the spruce forest was succeeded by pine, then deciduous forest, and finally prairie conditions took hold approximately 9400-8000 cal yrs BP (Wright 2003; Wright 1993). The timing of the prairie making its way into the Itasca region is consistent with steadily increasing temperatures during the Holocene. By the time the warming trend peaked (approximately 7200 cal yrs BP) the prairie forest boundary is thought to have moved as much as 100km east of Elk Lake (Wright 1993). After peaking, the forest boundary began moving back to the west as the climate became wetter and cooled slowly, eventually reaching the mean regional conditions seen today (Wright 1993).

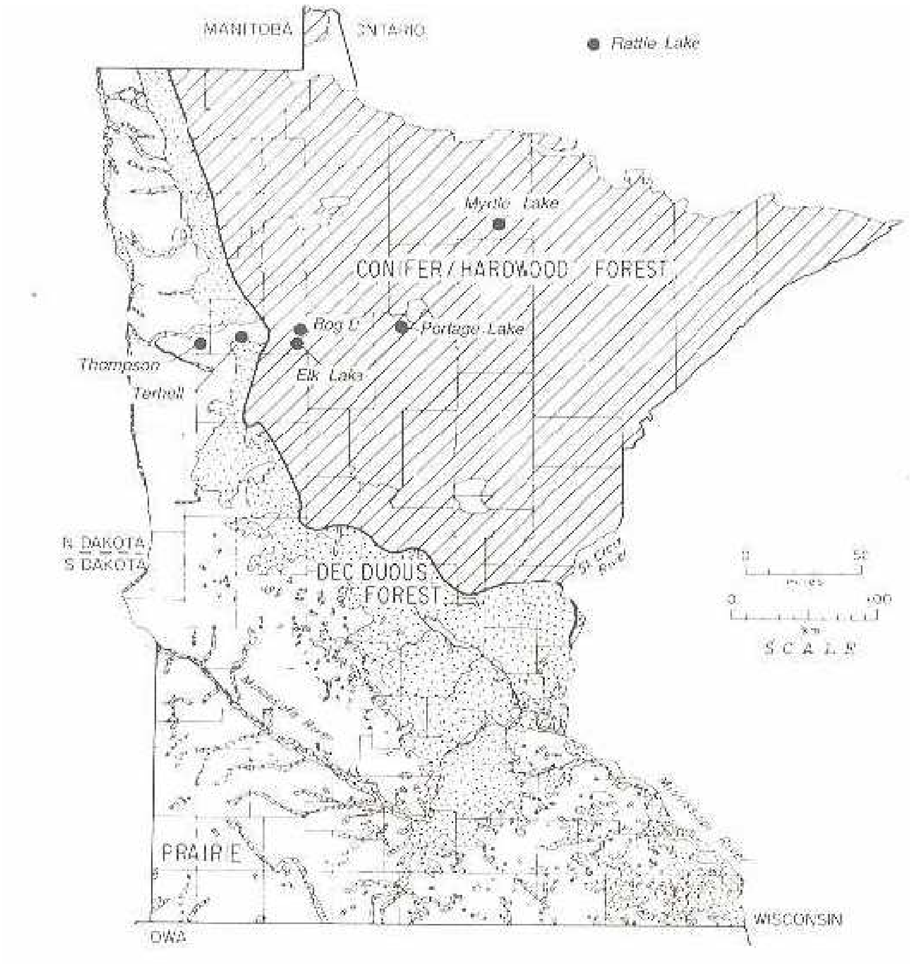


Figure 4 Map of vegetation zones of Minnesota showing the location of pollen sites used to infer the vegetation history. From (Wright, 1993).

1.5 Climatic and Limnologic Setting

1.5.1 Airstreams and Regional Climate

Elk Lake is located near the mean annual junction of three major airstreams, each of which has a distinct influence on the regional climate (figure 5). The Arctic air-stream moves south into the area from the Canadian Shield. The Pacific air-stream follows the path of the strongest westerlies as it moves into Western North America. The third air-stream that influences Elk Lake is the Tropical air-stream that moves in from the Gulf of Mexico. The Pacific airstream typically loses most of its moisture as it crosses the Coastal and Rocky Mountains of the United States and thus brings relatively dry air to the Elk Lake region. The Tropical air-stream is responsible for most of the precipitation that the area receives, especially during the summer when circulation around low pressures systems moving to the east causes the northward flow of Gulf air (Megard, Bradbury, Dean 1993).

The interaction of these three airstreams changes seasonally, during the winter the Pacific airstream forms a wedge that points to the east and occasionally can entrain and lift the Tropical air-stream creating heavy snowfall. This is usually followed by at incursion of Arctic air and can lead to blizzard conditions (Megard, Bradbury and Dean 1993). In the summer, low pressure systems moving from west to east can capture tropical gulf air and bring it north to the Elk Lake region creating thunderstorms when the gulf air runs into Arctic air moving south (Megard, Bradbury and Dean 1993). Put simply, today the eastward moving Pacific air represents the typical atmospheric movement of the region with periodic incursions from the two other major airstreams.

The interaction of these airstreams has changed over the course of the Holocene as will be shown. At various times throughout the record, the Elk Lake sediments indicate the dominance of one air-stream over the others leading to changes in the regional climatic system and the types of material preserved in the sediments of lakes.

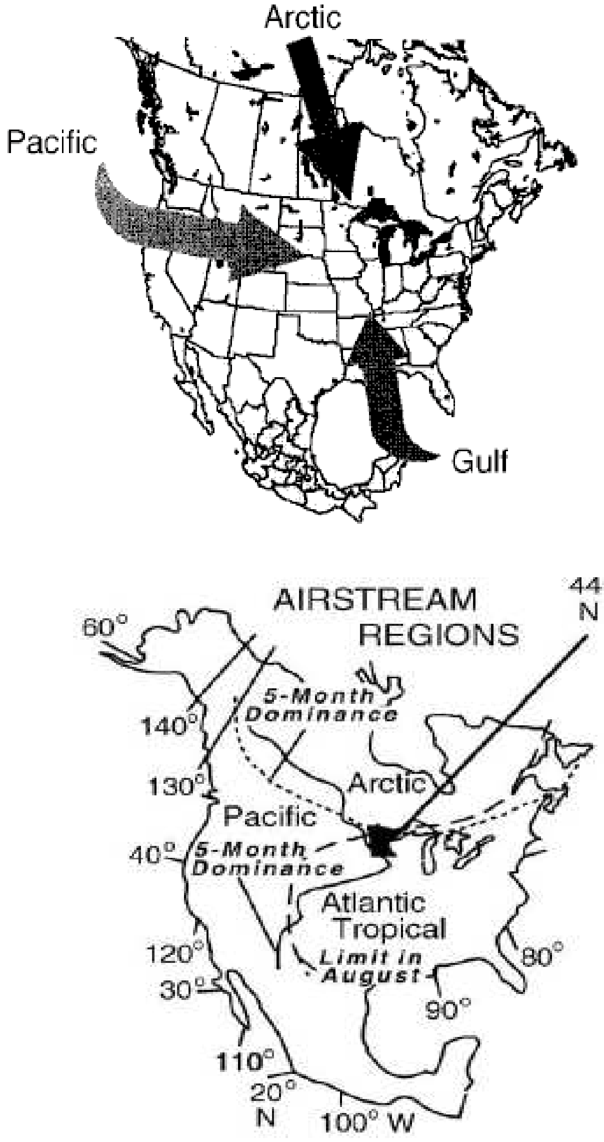


Figure 5 Regional airstreams of North America that affected the climatic environment of Elk Lake. From (Clark, Grimm, Lynch, and Mueller, 2008; Dean, Forester, and Bradbury, 2001)

1.5.2. Temperature and Precipitation

The regional climate around Elk Lake is one of typically cold winters and mild to hot summers. Seasonal averages for the region for the period from 1951 to 1980 are presented in Table 1 (Megard, Bradbury and Dean, 1993).

Average Seasonal Temperatures (ºC)

Mean Annual Temperature	3.64
Mean Spring Temperature (MAM)	3.6
Mean Summer Temperature (JJA)	18.16
Mean Fall temperature (SON)	5.53
Mean Winter Temperature (DJF)	-11.55

Table 1 Average Seasonal Temperature for Itasca State Park for the period between 1900 and 2008. Spring: March to May, Summer: June to August, Fall: September to November, and Winter: December to February. From Minnesota Climatology Working Group (http://climate.umn.edu/).

Variability in temperature and precipitation are illustrated by figure 6 showing data for Itasca State Park— mean annual precipitation 1900-2008=65cm; mean annual temperature 1900-2008=3.7ºC. The timing and duration of ice cover, stratification, turnover events, nutrient fluxes and several other limnological processes are going to be greatly influenced by the dynamics of the regional climate. Unfortunately, consistent and continuous measurements that would allow for the evaluation of the relationship between regional climate dynamics and limnologic processes in the lake have not been.

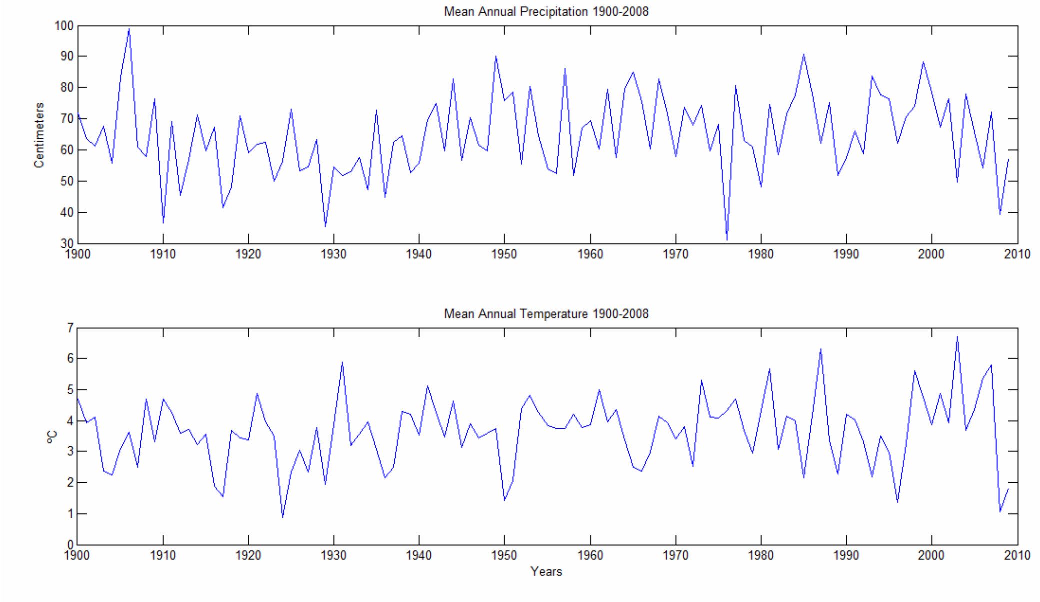


Figure 6 Mean Annual Precipitation and Temperature for Itasca State Park, Clearwater County, Minnesota from 1900-2008. From Minnesota Climatology Working Group (http://climate.umn.edu/)

1.5.2 Modern Limnology:

While a great deal of paleoclimatic research has been done on Elk Lake in the past, there continues to be a distinct lack of data on modern processes in the lake. Data concerning processes such as ice cover, turnover events, and stratification are limited with little data covering continuous periods over long time spans. Nonetheless, the data that are available show processes that have been assumed to be broadly applicable to interpreting the lake’s history by previous and current researchers.

Long term records of ice cover for Elk Lake do not exist, but data from Lake Itasca have been collected regularly for many decades. Elk Lake generally thaws within a day or two of Lake Itasca but freezes one to two weeks after Itasca due to its smaller surface area to volume ratio (Megard, Bradbury, and Dean, 1993). Typically, extremely early or late ice out dates are single year events occurring every 3-7 years and it has been suggested that this is related to El Nino cycles (ENSO) (Megard, Bradbury and Dean 1993; Diaz and Pulwarty 1992). Based on the fact that Elk Lake generally freezes and thaws close to the dates that Lake Itasca does, ice cover forms in mid to late November and thaws in April to early May with an average of 152 days of cover per year (table 2, Figure7). Ice thickness often reaches 1m and the clarity of the ice varies greatly from year to year depending of snow fall and other processes that can effect light transmission through the ice (Megard, Bradbury and Dean 1993).

Ice Up Date	Ice Out Date	No. Days Ice Cover
11/10/78	5/7/79	175
11/9/79	4/21/80	164
11/15/80	4/9/81	145
10/25/83	4/19/84	177
11/17/84	4/20/85	154
11/11/85	4/12/86	152
11/13/86	4/11/87	149
12/2/87	4/17/88	137
11/18/88	4/29/89	162
11/17/89	4/24/90	158
11/26/90	4/18/91	143
11/4/91	4/11/92	159
11/14/92	4/19/93	156
11/8/93	4/18/94	161
11/26/94	4/26/95	151
11/11/95	5/6/96	177
11/12/96	4/27/97	166
11/16/97	4/12/98	147
12/7/98	4/14/99	128
11/29/99	4/9/00	132
11/27/00	4/27/01	151
12/2/01	4/18/02	138
11/13/02	4/16/03	153
11/10/03	4/19/04	161
11/29/04	4/13/05	136
11/25/05	4/14/06	141
11/30/06	4/23/07	146
11/27/07	5/7/08	162

Table 2. Ice up and ice out dates for Lake Itasca. From Itasca Biological Research Station (www.cbs.umn.edu/itasca/research/).

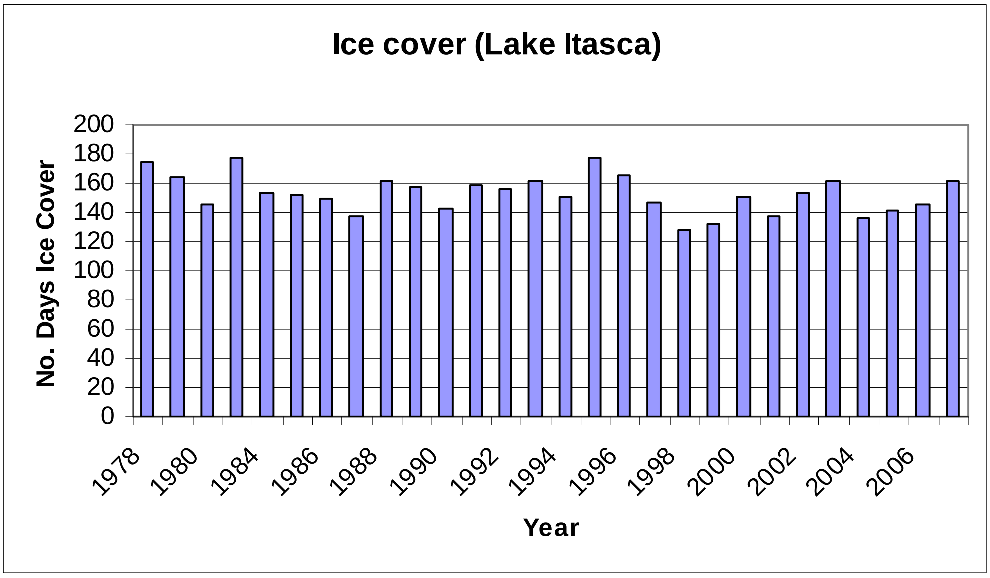


Figure 7 Number of Days of Ice Cover for Lake Itasca, Minnesota for the period of 1978 to 2007 (from the Itasca Biological Research Station www.cbs.umn.edu/itasca/ research).

Since 2008, the SLICE (Sustaining Lakes In a Changing Environment) program run by the Minnesota Department of Natural Resources has begun to gather data on dissolved oxygen (DO), temperature (T) and pH within Elk Lake. The following data, while lacking coverage over a long enough period to make distinct conclusions about the nature of Elk Lake, provides insight into the processes that dominate the lake today.

Concentrations of DO are particularly important to the preservation of varved laminations (by preventing the presence of benthic organisms) and the cycling of elements such as Fe and Mn which are major constituents of the sediments in Elk Lake.

After reviewing the oxygen profiles for Elk Lake in the years 2008 and 2009 (figure 8 and 9), it is clear that early in the spring, after ice out, the lake was relatively oxygenated down to the bottom (~30m) in 2008, but in 2009, anoxia had begun to occur much earlier, with the possiblity that the hypolimnion may have remained anoxic through the winter. By the end of June, the lake had become fully anoxic in the hypolimnion. Once the lake was well stratified, it was close to or fully anoxic in the hypolimnion at depths of approximately 10m or greater. During the earlier months of the spring, oxygen concentrations in the epilimnion were around 12 mg/L, by mid-summer the oxygen concentrations in the upper water column dropped due to decreased oxygen solubility at higher temperatures. As autumn approaches, the lake began to show signs that a turn-over period was beginning, with oxygen mixed to greater depths.

Profiles of temperature vs. depth for 2009 and 2008 (figure 8 and 9), help to describe how the lake becomes thermally stratified over the course of the summer months. The lake generally begins to turn over during April, soon after ice cover has disappeared. It is clear from figures 8 and 9 that the lake was fairly well mixed during May, but by early to mid-June, the lake was becoming thermally stratified. The thermocline was at approximately 5-10m depth which is consistent with the depth profiles of dissolved oxygen. Stratification begins to weaken in response to cooling temperatures during October in both years presented here. There is no data to suggest whether or not stratification may occur during the winter months but it is certainly a possibility. In some years (2009), the hypolimnion is anoxic very early in the season after ice out which may suggest that stratification had taken place during the winter.

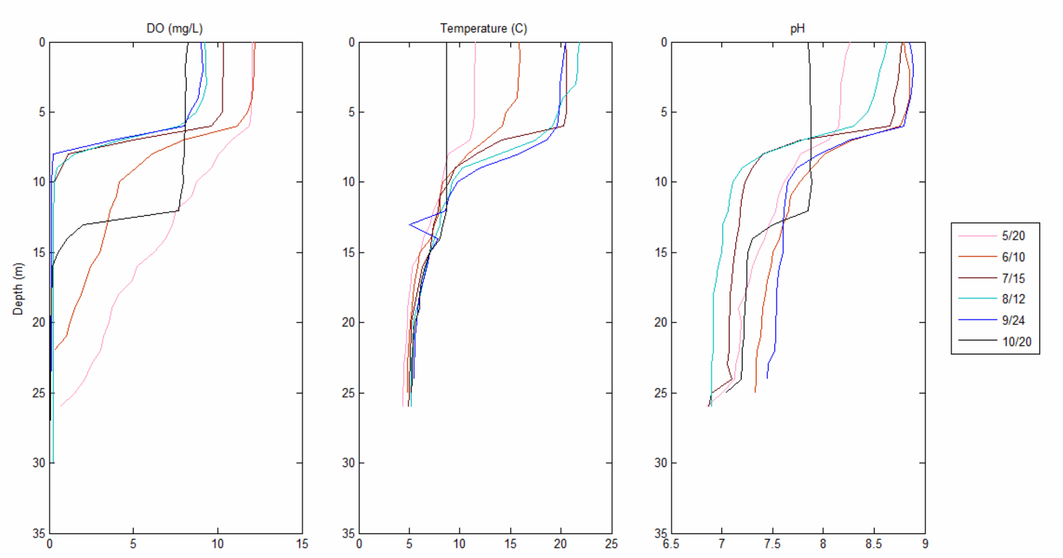


Figure 8. DO, Temperature, and pH for Elk Lake in 2009. Data from the Minn. DNR SLICE program. (www.dnr.state.mn.us/fisheries/slice/sentinel.html)

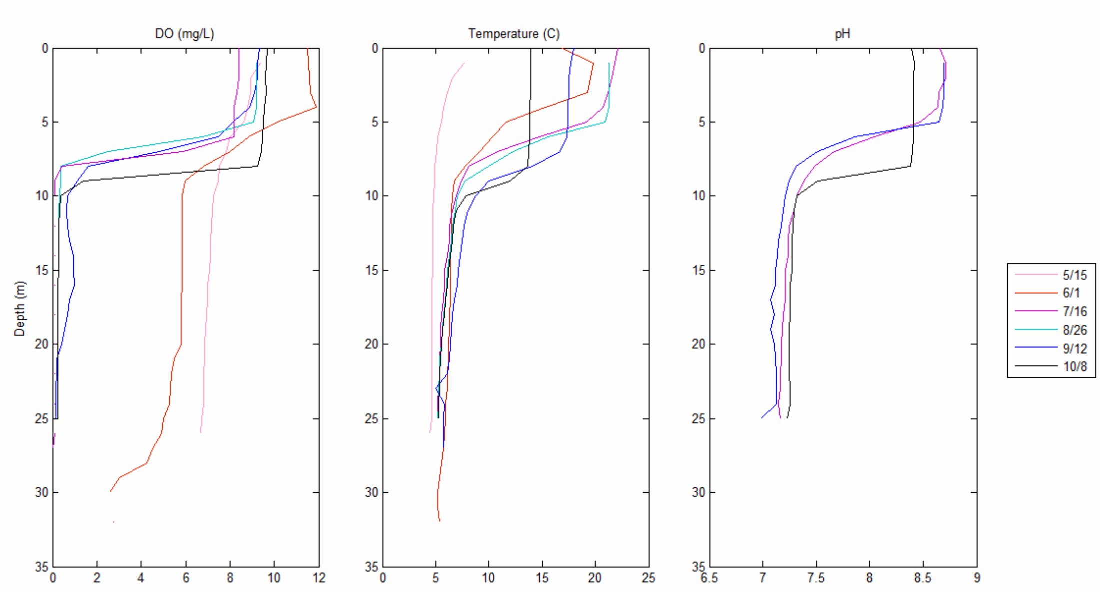


Figure 9. DO, Temperature, and pH for Elk Lake in 2008. Data from the Minn. DNR SLICE program. (www.dnr.state.mn.us/fisheries/slice/sentinel.html)

The pH vs. depth profiles of Elk Lake (figure 8 and 9) help to illustrate processes that influence the precipitation and deposition of carbonate minerals in the lake. Algal photosynthesis in the upper water column leads to the removal of CO_2 and a subsequent increase in the pH (less acidic). The rise in pH can allow the water to become saturated with carbonate minerals and precipitate materials such as calcite. Bacterial respiration in the bottom waters leads to a release of CO_2 and thus a decrease in pH (more acidic) of the hypolimnetic waters. With a decrease in the pH of the bottom waters, some or most of the precipitated carbonates can be dissolved back into the water. As primary productivity increases in the lake, more carbonates will be precipitated in the epilimnion and more will be dissolved in the bottom waters as respiration increases due to a larger flux of organic material available for bacterial respiration. While the pH of the bottom waters presented for 2008 and 2009 does not show that the bottom waters were acidic enough to dissolve calcium carbonate, it is certainly a possibility that this process could have taken place in Elk Lake in the past.

Processes associated with primary productivity are vital to the nature of the sediments within Elk Lake; unfortunately little has been done to study primary productivity. Carbonate deposition is directly related to how productive the lake is in any given year and within the varves, dark laminations rich in organic matter are seen each year that contain considerable amounts of biogenic materials such as siliceous cells of diatoms. Thus the thickness and composition of annual laminations is related to how productive Elk Lake is in any given year. A few measurements taken in 1967 and 1968 found a net integral rate of carbon assimilation of 0.5 g C/m^2 per day and that this rate of productivity was in general much lower than other lakes in the region but the data as mentioned is limited to this brief study (Megard, Bradbury and Dean, 1993).

1.5.3 Objectives of this Study

There is a considerable body of information available on Elk Lake through earlier studies which began in the 1970’s (Bradbury, Anderson, and Dean, 1993). Due to the fact that analytical techniques have improved since this previous work was published, this study seeks to utilize the large knowledge base on Elk Lake to determine (1) the usefulness of the Scanning XRF and its ability to repeat geochemical studies of lacustrine sediments and (2) create a higher resolution data set from which to discuss climate variability during the Holocene. Other objectives include (3) using both geochemical and geophysical data to determine the nature and timing of major climate events in the past and (4) use high resolution geochemical XRF data to discuss the nature and timing of varve deposition.

2. Methods

2.1 Field Methods

In February of 2009, a group of professors and students from the University of Minnesota Duluth (UMD) and members of LacCore from the Twin Cities campus, recovered sediments from Elk Lake, Clearwater County, Minnesota. Coring activities were performed in mid winter in order to have a stable platform, in the form of ice, on which to work. Casing was used in order to direct the Bolivia coring device into or close to the same hole for each drive. The case consisted of 2m sections of 4 inch aluminum pipes and was placed down the entire water column and approximately 1m into the sediments.

Three separate cores were recovered over the course of three days (table 3). Core PBR (Paleoclimate-Biomaker-Research)-ELK09-1A consisted for 10 core sections and ended at approximately 13m into the sediment with the recovery of glacial outwash. Cores PBR-ELK09-2A and PBR-ELK09-2B were taken in close proximity to one another and would be used as a duplicate core set for the construction of a continuous record. We recovered approximately 12-13m of sediment at each of these sites but did not reach glacial outwash and were unable to penetrate to the depth of sediment recovered in previous work (approximately 20m). Two M.U.C.K. (Multi-Use Core Kit) surface cores were also taken in order to sample the sediment-water interface of the lake.

Core site information

Core	Lat/Long	Water Depth (m)	Approx. Total Core Length (m)
1A	N 47º 11.233', W 95º 12.97'	25	13
2A	N 47º 11.254', W 95º 12.981'	28.75	13
2B	N 47º 11.254', W 95º 12.982'	28.75	13

Table 3. Core locations and information.

Cores were transported to the LaCore storage facility in the Twin Cities. In June of 2009, the cores were split and underwent initial processing to prepare them for transport to the Large Lakes Observatory (LLO) for Scanning XRF analysis. At LaCore each core was split in half longitudinally—the working half and the archival half. High resolution (100micron) optical images were taken of each individual core section to be used later in the construction of the duplicate core record and for the identification of horizons of interest.

Whole core data, including GRAPE gamma ray density, magnetic susceptibility, and natural gamma ray activity were gathered from each of the core sections via the Geotek system, as well as high-resolution (1cm) magnetic susceptibility. Once each of these steps was completed the cores were ready for transport back the Large Lakes Observatory where the analysis could begin.

On August 25 of 2009, high resolution geophysical data from Elk Lake were collected using a 4-24 kHz Edgetech 424 pulsed frequency CHIRP system which uses acoustics to identify reflectors within the sediments. The CHIRP, pulled behind a 16ft outboard motor Lund fishing boat, sat approximately 0.5-1m below the water surface and was set up to pulse at 5ms at a frequency of 4-20 kHz. Each line was taken at an approximate survey speed of 2 knots, which is relatively slow for such a study and is likely the reason for the high-quality data collected. The CHIRP and survey lines were located using GPS and the data were processed using the Kingdom software suite. Based on the properties of the cores recovered (specifically the gas content as evidenced by the need to drill holes in core sections in order to prevent the loss of end caps as well as the presence of expansion cracks as seen in the radiographic images of the cores) earlier in the year, it was initially thought that little useful data would be gained from the geophysical expedition, but while on the lake it was found that the sedimentary stratigraphy of Elk Lake was visible in many areas with the exception of the deeper basins where the concentration of gases were too high for distinct reflectors to been seen.

2.2 Continuous Record Construction using Corewall

Optical and Radiographic images from all three core-sites were loaded into the COREWALL software (Electronic Visualization Laboratory, University of Illinois at Chicago). Sections from site 2A and 2B (the duplicate cores) were aligned using visible and characteristic sets of laminations. Specific horizons including the base of the disturbed layer (dated, through varve counting, at 1904) and a distinctive 1cm thick clay layer (790 cal yrs BP, dated through varve counting) were used to identify initial boundaries and dates (Anderson, Dean, and Stuiver, 1993). Further tie points between the cores sites were matched using both characteristic laminations and initial XRF data. This allowed for the development of a continuous dataset by splicing together various sections from each site to eliminate any gaps in the record. Site 1A was also aligned with the other two sites, but differences in sedimentation rates and potential hiatuses at the shallower site made it difficult to develop unambiguous and unique stratagraphic tie points between the sites (figure 10).

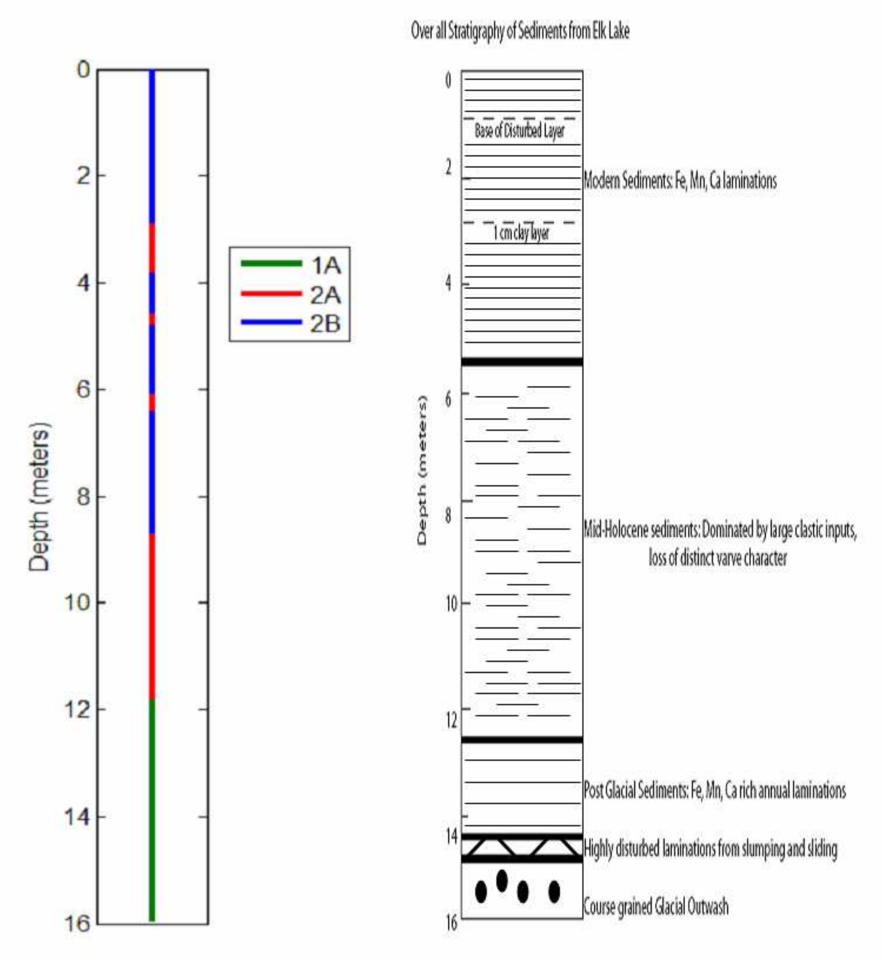


Figure 10. Continuous core construction and general lithology.

The site 2 cores did not reach the bottom of the sediment pile, so in order to obtain a full Holocene record the assumption was made that there were no significant hiatuses in the lowest 4m of the site 1A core and data from this section were spliced onto the 2A/2B record.

The continuous record developed and built from pieces of each core was utilized in all subsequent analysis. An important first step was the comparison and correlation of this data set with Dean et. al. (1993), Anderson and Bradbury (1993), and Wright et. al. (2003).

2.3 Analyseries and Chronology

Once a continuous data set was created, the XRF data were imported into the Analyseries software program (Paillard, Labeyrie, and Yiou, 1996). Analyseries was utilized to convert depth scales to age scales. This was done by creating tie points between the XRF data (on a depth scale) and the geochemistry data from previous studies (on an age scale) (Dean, 1993). The program was then able to provide us with an age scale that could be used to discuss the timing and duration of events seen in the XRF data.

Initially the XRF data was tied into the Varve Year counts/chronology made by Dean et. al. (1993) and Anderson et. al. (1993), but it was later realized that there is likely significant error within the chronology due to the difficulty in visually identifying individual varve lamination sets and hard water effects on radiocarbon dates taken on bulk lacustrine organic matter—the incorporation of old carbon from the calcareous glacial till surrounding Elk Lake (Hu et.al. 1999, Wright 2003). It was noted by Wright (2003), that the age difference at the bottom of the cores between the age provided by Varve Years (Dean et al, 1993, Anderson et. al., 1993) and the age as determined by

AMS radiocarbon dating in Steel lake (Wright, 2003) was off by 1000 years with varve years showing a date that was too young. This could be explained by uncertain interpolations between core segments and/or the poor quality of varves within some sections leading to errors in the counting of annual laminations in Elk Lake (Wright, 2003). Between two individual varve counters, there was a 10% difference in the varve age assigned to the bottom most varves of the cores taken by the researchers in the 1970's (Dean, personal communication, 2010). This alone would lead to a 1000 year difference in varve counts for the oldest laminations when dealing with a record that covers the entire Holocene and it is apparent that bulk organic mater radiocarbon dates are not sufficient for developing a high resolution age scale.

Steps for Age Scale Development

1. Tie pollen data from Elk Lake to pollen data from Steel Lake.
2. Replace Elk Lake varve years with corresponding Steel Lake ^{14}C dates (based on Pollen).
3. Interpolate between dates to develop full age scale for Elk Lake geochemical data (Dean 1993).
4. Tie XRF data to Adjusted Elk Lake Chronology using elemental data

Box 1. Steps for applying Steel Lake AMS radiocarbon dates (Wright et. al. 2003) to Elk Lake geochemical data (Dean1993), and then developing an age scale for the XRF data.

In order to develop a more accurate chronology, 26 AMS radiocarbon dates on terrestrial macrofossils from Steel Lake (47 km to the southeast of Elk Lake) were applied to the original Elk Lake geochemical data (Dean 1993; Wright 2003)). Because terrestrial macrofossils are far less likely to incorporate old carbon from the soil or carbonate rocks than bulk organic matter, which can contain algae growing in water with old dissolved inorganic carbon (DIC), the radiocarbon dates from Steel Lake provide a more reliable chronology. Dates for stratigraphic horizons defined by various pollen zones and assemblages as well as significant peaks in certain pollen types within the sediments of both Elk and Steel Lakes were used to adjust the varve year chronology of the original Elk Lake geochemical data (figure 11 and 12, table 4) (Dean 1993; Whitlock, 1993; Wright, 2003). The adjusted age scale showed that the varve counts on Elk Lake sediments were too young by approximately 700-1000 years as Wright et. al. (2003) had predicted. During this process, a significant gap at the top of the Elk Lake varve record was produced and in order to bring the top of the XRF data back to zero years before present, two distinct horizons in the record were used—the base of a highly disturbed layer created during clear cutting in the region dated at 1904 and a 1 cm thick clay layer dated at 1180 A.D (790 cal yrs BP) with a simple linear interpolation between the points. The uppermost 1000 years of the age scale developed for this study rely on varve counts, which likely contain less inherent/cumulative error than would the varve counts at the base of the cores. Zero calendar years before present represents the year 1904 (base of the disturbed layer).

With an adjusted record from which to work, the XRF data was then tied into the previous Elk Lake data (now with Steel Lake radiocarbon dates rather than varve years) and a more accurate chronology was developed and used for all further analysis (figure 13). The rest of this study will refer to the age scale as the Steel Lake chronology to avoid confusion, but the data tied into the original varve year age scale can be seen in the appendix.

High resolution (200 micron) sections from various periods in the history of Elk Lake were chosen based on initial XRF data (1cm resolution) and centered on specific ages. Approximate age scales for this data were created by counting geochemical peaks in elements such as calcium (Ca), authigenic iron (Fe) and other varve constituents that are deposited seasonally in annual laminations. These varve counts were then referenced to a known age from the Steel Chronology.

Steel Lake Pollen Record

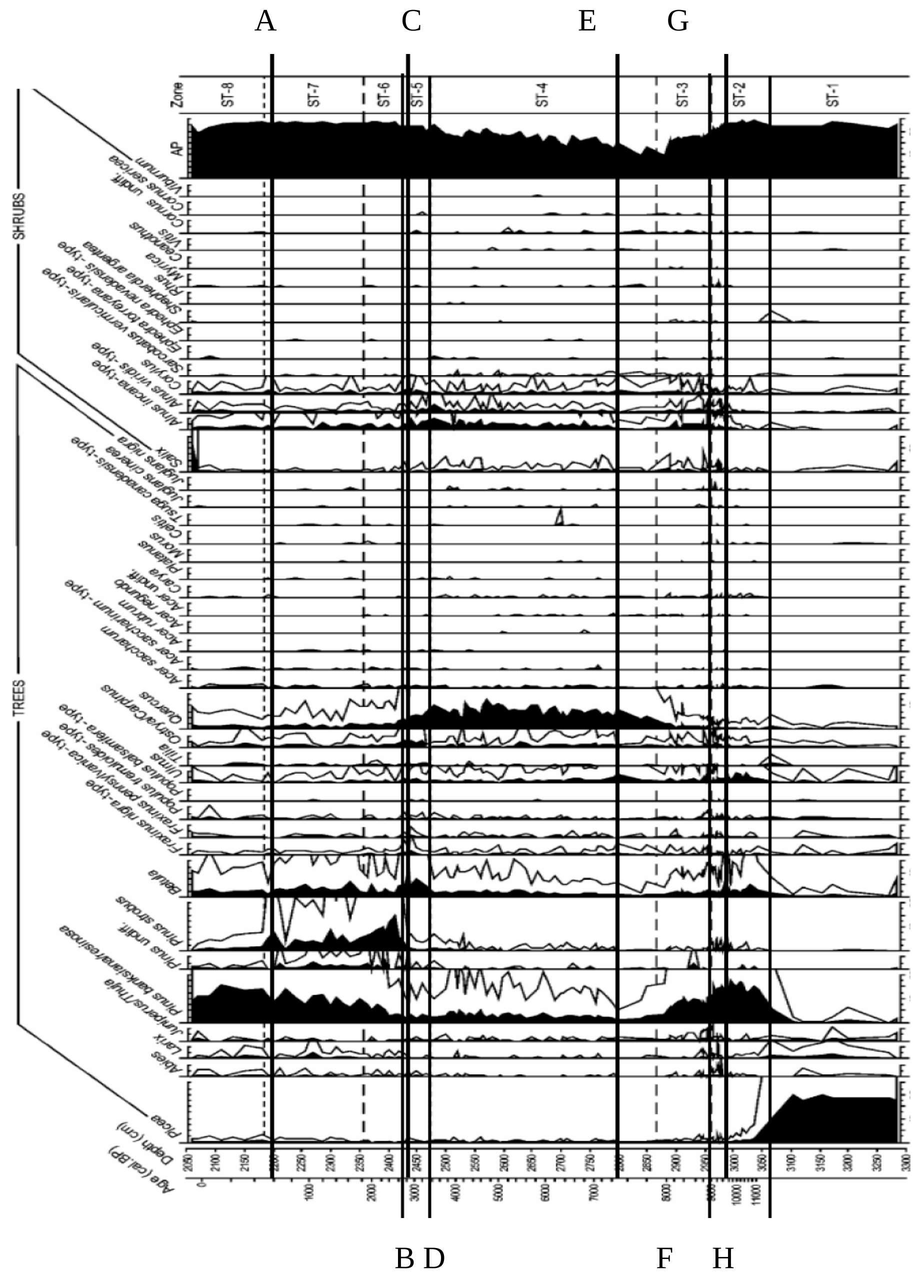


Figure 11 Steel Lake Pollen Record. Pollen is plotted in % ∑ P= AP+ NAP. Lines and Letter A-H indicated tie points between Steel and Elk Lake Pollen records used for the application of Steel Lake radiocarbon dates to the Elk Lake varve chronology and refer to Table 3. (From Wright 2003).

Elk Lake Pollen Record

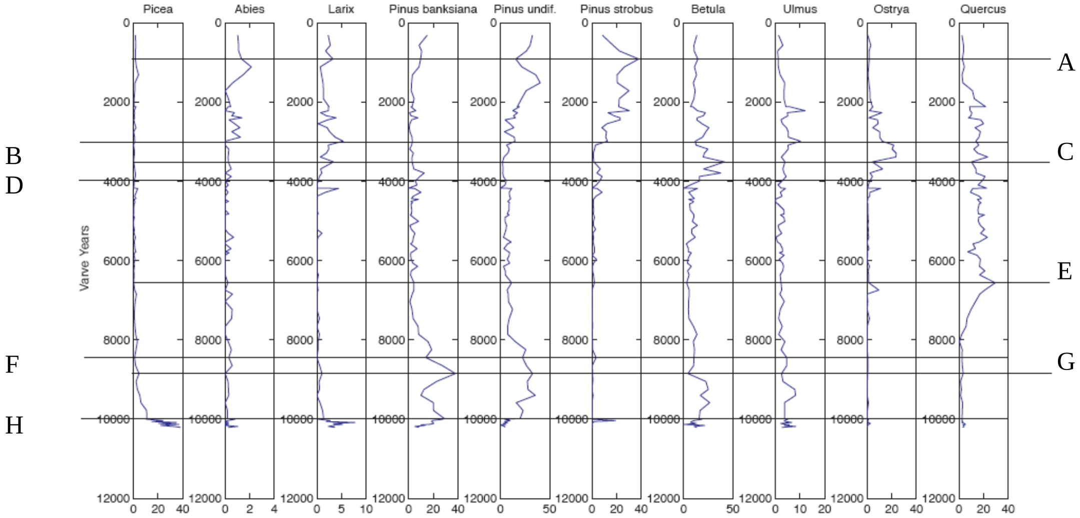


Figure 12 Elk lake Pollen record plotted in % ∑ P= AP+ NAP. Letters A-H refer to tie points between the Elk and Steel Lake pollen records for the development of the age scale for this study and and the application of Steel Lake AMS radio carbon dates to the Elk Lake geochemical record in Dean (1993). Letters/tie points refer to table 2.3-1. (From Dean 1993).

Tie Point	**Pollen Type/Assemblage**	**Steel Lake Age (yrs. BP)**	**Elk Lake Age (Varve yrs. BP)**
A	Peak: Pinus Strobus	2,100	900
B	Stage: 6 (start): Pinus Strobus	2,700	3,000
C	Peak: Betula	2,800	3,500
D	Stage 2 (end): Quercus-Gramineae-Artemisia	3,400	4,000
E	Peak: Quercus	7,400	6,500
F	Stage 2 (start): Quercus-Gramineae-Artemisia	9,000	8,500
G	Peak: Pinus Banksiana	9,400	8,800
H	Stage 1 (end): Picea	11,200	10,000

Table 4. Tie points between Steel Lake and Elk Lake pollen records with corresponding Pollen types/assemblages and both Steel and Elk Lake ages.

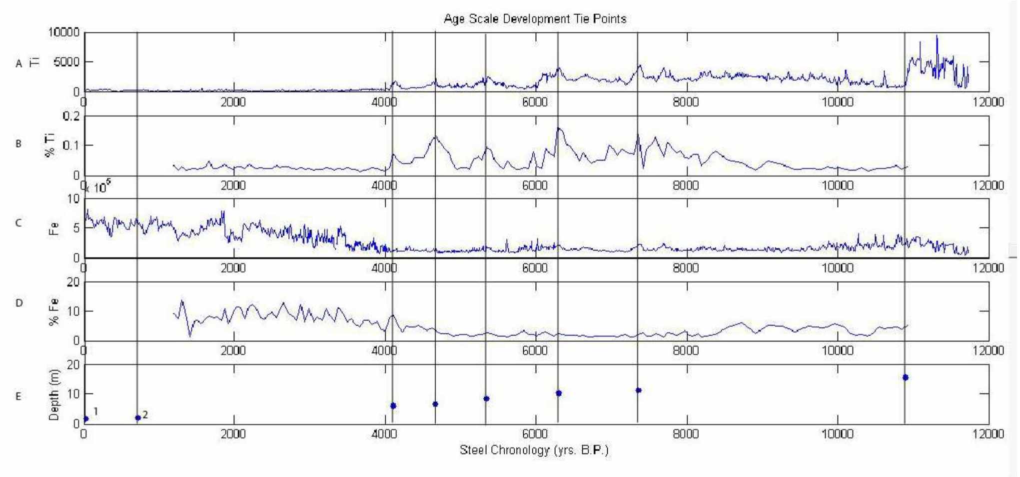


Figure 13 Tie points between Elk Lake geochemical data and the XRF data. Ti (A) and Fe (C) are plotted in XRF counts against the age scale developed for this study. %Ti (B) and % Fe (D) are from Elk Lake geochemical record (Dean 1993). Vertical lines represent tie points made between the Dean (1993) Elk Lake data plotted on the age scale developed using Steel Lake AMS radiocarbon (Wright 2003), and the XRF data for this study. Plot E is the age/depth model for this study with points indicating the tie points made with previous research. The gap at the top of the XRF data was accounted for using two known and dated lithologic layers in the core sections. Point 1 is the base of the disturbed layer (1904) and point 2 is a 1 cm clay layer dated at approximately 750 cal yrs BP. Elk lake data is from (Dean 1993).

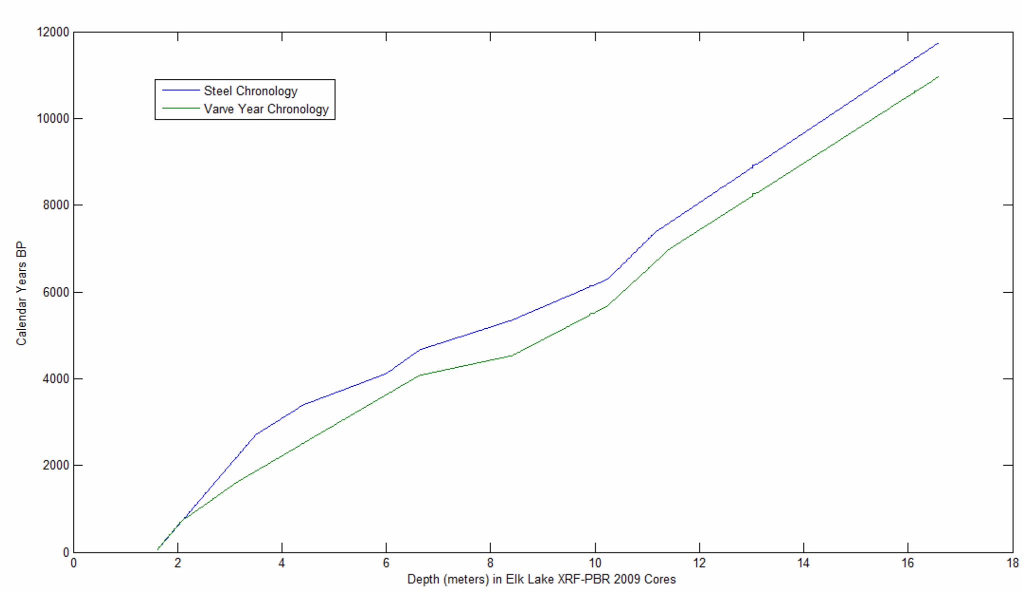


Fig 14 Two age scales developed for this study by tying into the Elk Lake geochemical data from Dean (1993). In blue, the XRF age model using the Steel Lake AMS radiocarbon dates (Wright, 2003) and in green the XRF age model using the Varve Year Chronology from Anderson, Bradbury and Dean 1993; Dean 1993.

2.4 X-ray Fluorescence:

The main goal of this research was to use the Scanning XRF located at the Large Lake Observatory to develop a high-resolution geochemical data set and determine if and how much inter-annual variability occurred during the Holocene. While working with the core images and developing a method for matching up the cores and creating a continuous record, each section recovered from Elk Lake was run through the Scanning XRF.

The Scanning XRF uses X-rays to excite the electrons of atoms within the sediments and force them into higher energy states. When the electrons move back into their lower energy state, energy is released in the form of fluorescence. Each element within in the XRF's detection range fluoresces at unique energies allowing for counts to be made of various elements.

Every section was initially run through the XRF at 1cm resolution to develop the main curve that was used to describe the major changes that took place in and around Elk Lake. Specific sections (approximately 20cm long) from each of the main geochemical phases of Elk Lake were run at 200micron resolution to get a better understanding of the inter annual climate variability during these times. While a 200micron data set for the entire record would prove very useful, the time and cost of gaining such a dataset is impractical.

3. Results

3.1 Physical properties of Elk Lake sediments

Results from previous research suggested changes in the water content (%) and dry bulk density (g/cm3) show the effects of compaction on the sediments. Water content in the sediments decreased from 80% in the sediments beginning at a depth below the sediment-water interface of ~1.5m to <60% at the base of the cores (Dean, 1993). Dry bulk density increased form 0.2-0.3 g/cm3 at the top to 0.6g/cm3 at the base of the cores (Dean, 1993). Changes in the water content and density of the sediments during the Holocene (figure 15) represent shifts in the dominance of various processes such as diatom abundance (lower density and higher water content) and the influx of clastic material (higher density and lower water content).

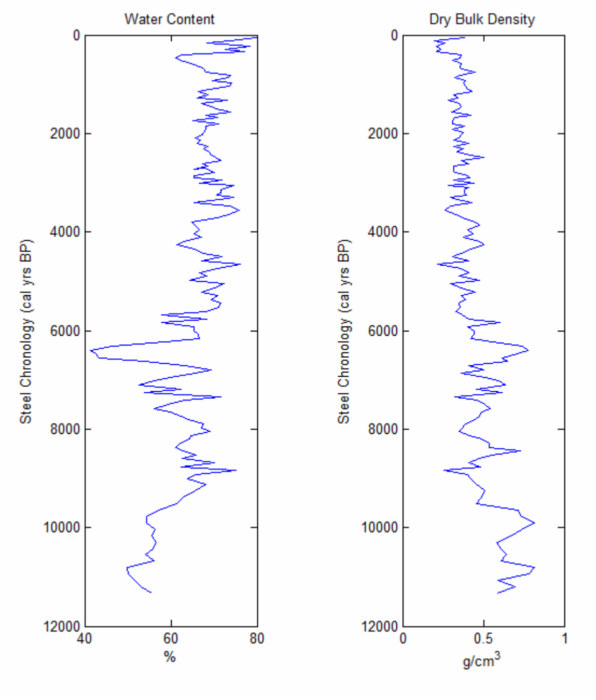


Figure 15. Water content (%) and density (g/cm^3) of Elk Lake sediments.

The mineralogy of the cores as determined by XRD analysis (figure 16 and 17) showed that the dominant carbonate in the sediments is calcite. The second most dominant carbonate is dolomite which shows the highest abundances during the mid-Holocene. Both of the major carbonate minerals in the sediments are most likely formed as primary precipitates from the water column (Dean, 1993). The clastic fraction is composed almost entirely of quartz and orthoclase feldspar as well as albite with some additions of quartz (Dean, 1993).

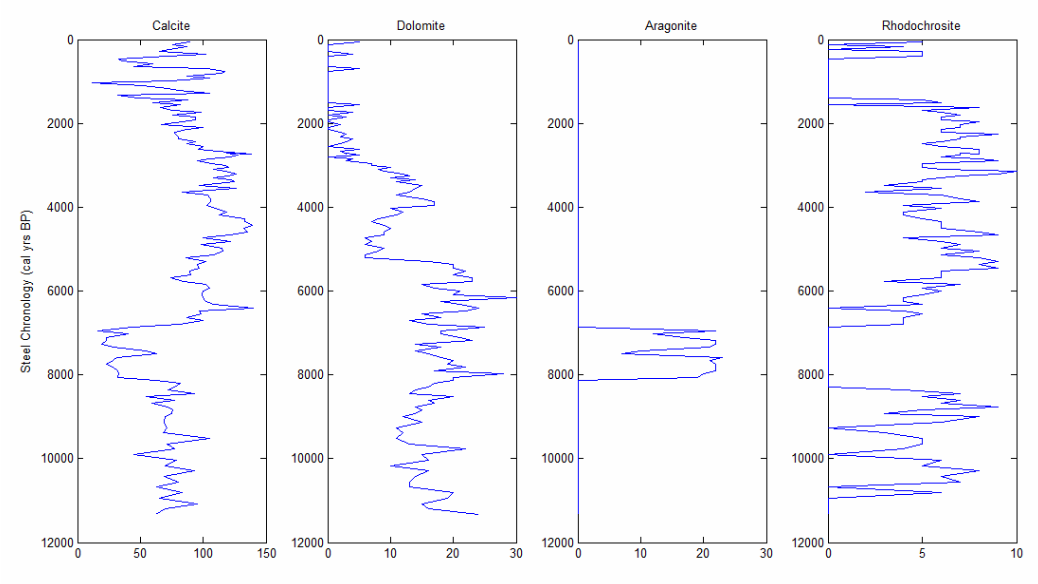


Figure 16. Major carbonate mineral components of sediments (Dean,1993). Plotted in relative XRD peaks in mm.

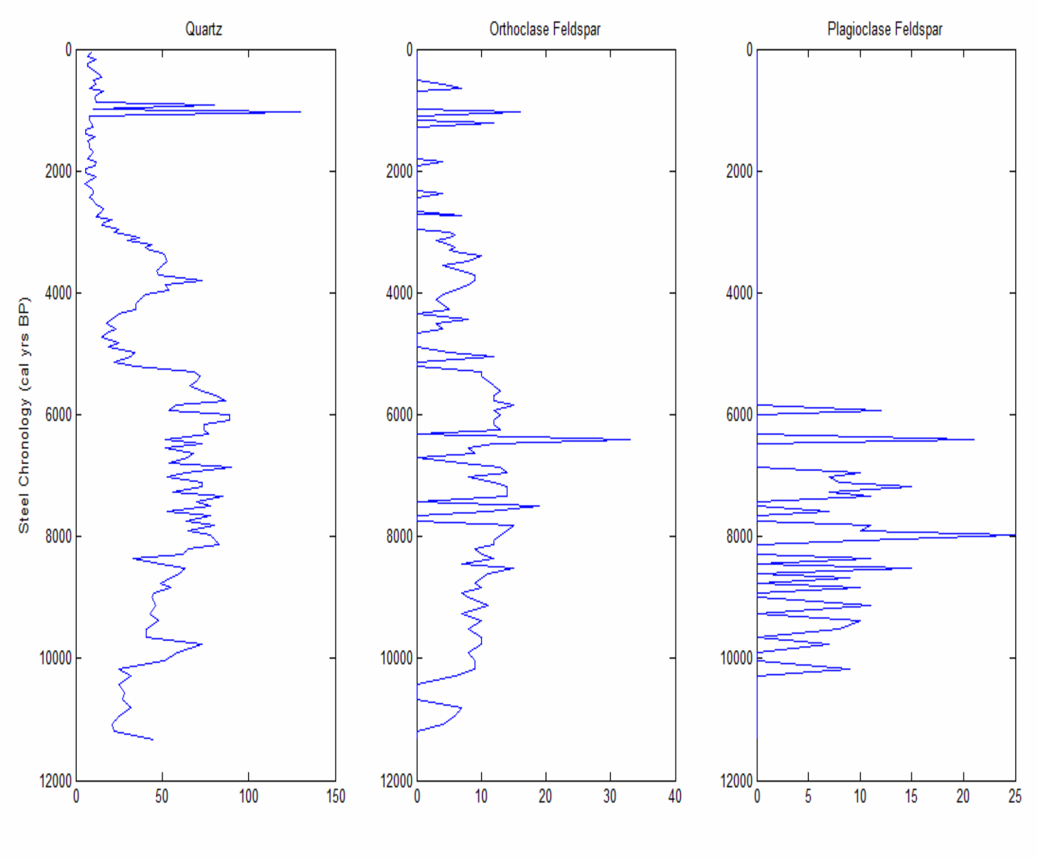


Figure 17. Major detrital mineral components of sediments (Dean 1993).Plotted as XRD peaks in mm.

The following are plots of all useful data gained from the Scanning XRF that will be used to discuss the nature of Elk Lake's evolution during the Holocene as well as processes that have taken place within the lake over time. Some data were found to lack significant meaning in reference to climate dynamics and change over time and will be presented only in the Appendix. Varve-year chronologies of each element where created, but as discussed, the Steel Lake Chronology was determined to have greater accuracy so varve year plots can be found in the Appendix. All of the following plots are those which will be used in the Discussion section of this report.

3.2 Carbonate Elements:

The following figures are plots of elements related to carbonate deposition within Elk Lake (figure18 and 19). For a discussion of processes related to the deposition and preservation of these materials see the proxy section of the introduction.

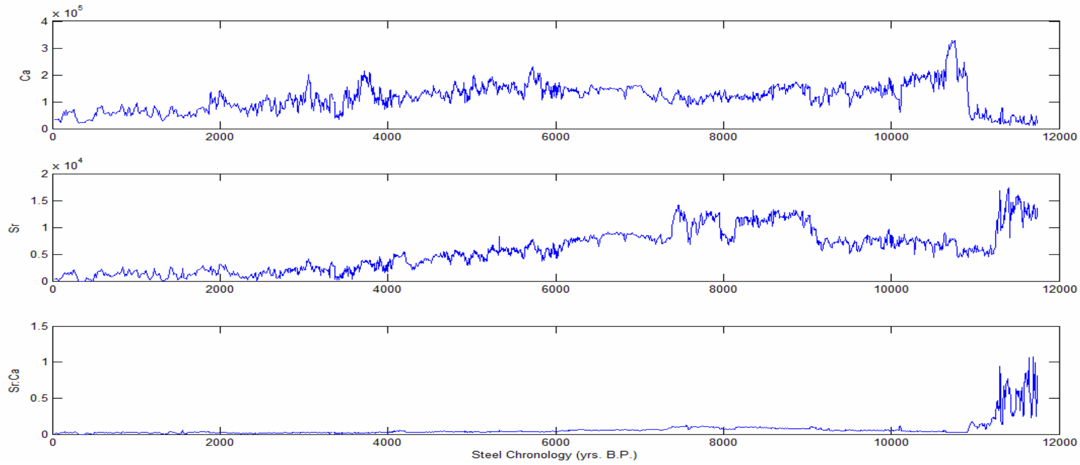


Figure 18 plots of relevant carbonate minerals. Ca and Sr plotted in XRF counts and Sr:Ca ratio (unitless) are all plotted against the Steel Chronology.

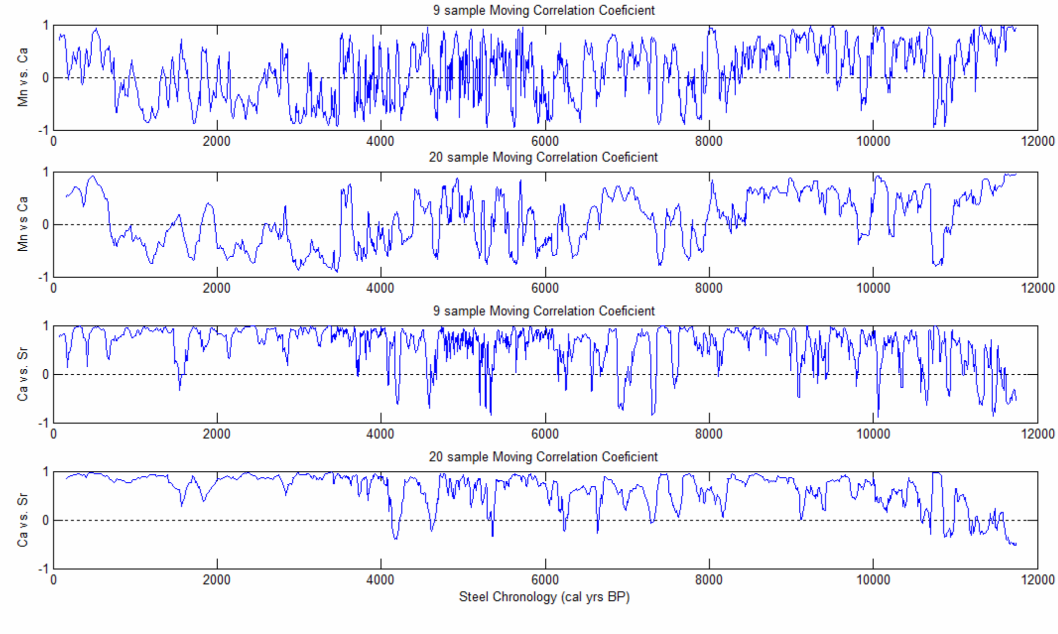


Figure 19 Nine and twenty sample moving correlation coefficients for the carbonate elements plotted against the Steel Chronology.

Moving correlation coefficient (MCC) plots are a method of assessing how two elements are correlated over time. Each MCC plot was calculated using nine and twenty sample moving windows throughout the entire Holocene record. Nine sample moving windows were used to describe elemental associations with a resolution of approximately 100 years, while twenty sample moving windows were calculated to discuss changes in the nature of associations over broader time scales (hundreds of years). A correlation coefficient of 1 suggests that two elements are behaving similarly/in phase while a value of -1 indicates that the elements are not in phase with one another. Zero correlations means there is no relationship between the elements. These plots have been made to assess the relationships between several elements.

Based on the moving correlation coefficient plot (figure 19) of Ca vs. Sr, it is clearly indicated that for the vast majority of the record the two elements are strongly related. Times when the relationship between Ca and Sr are out of phase are likely due to the influx of detrital Sr and/or Ca. The relationship between Mn and Ca as indicated by the moving correlation coefficient plot (figure 19) is highly variable when compared to the relationship between Sr and Ca, but shows that at times Mn is likely present in the carbonate fraction as manganese carbonate.

The portion of the Sr signal that is detrital in origin was estimated using a scatter plot of titanium (Ti) vs. strontium (Sr) and determining the slope of a line that represented the data where there was a strong relationship between these elements (figure 20). It was determined that there were approximately 1.9 Sr counts for every Ti count. This ratio was used to estimate and split the Sr signal into its authigenic and detrital portions. It is clear from this method as well as the moving correlation coefficient plot of Ca vs. Sr, that the vast majority of Sr within the sediments of Elk Lake is authigenic in origin and likely present in the carbonate fraction (figure 20 and 21).

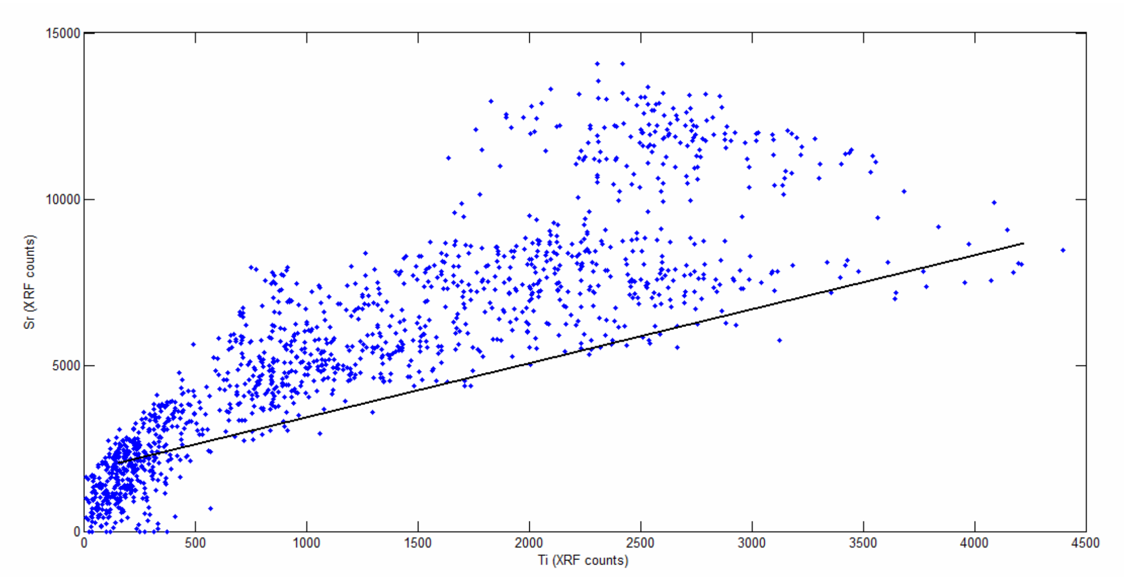


Figure 20. Scatter plot of Ti vs. Sr (both in XRF counts). Black line represents the ratio used to determine the authigenic and detrital portions of the total Sr signal.

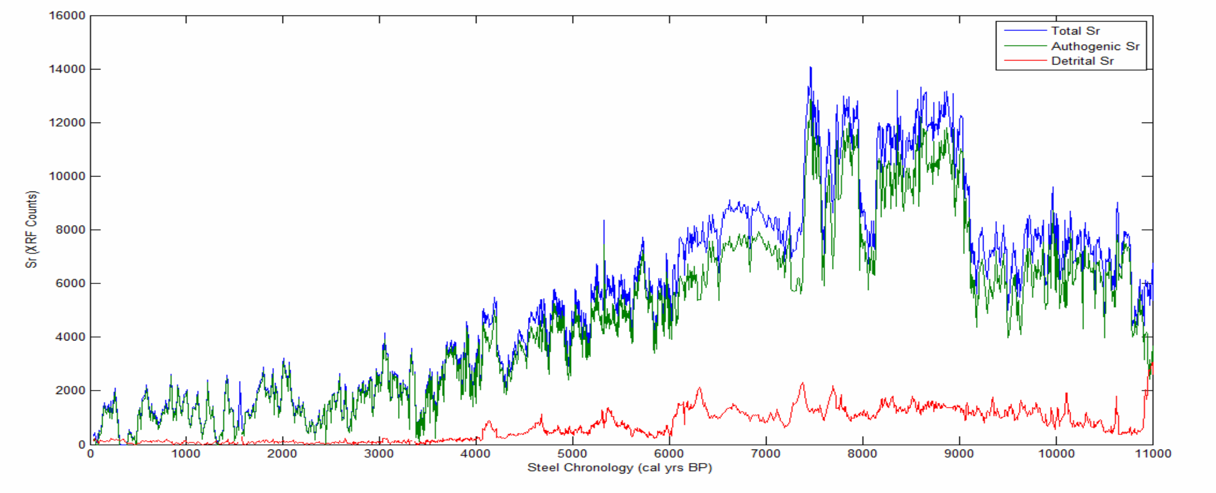


Figure21 Plot of authigenic, detrital and total Sr in XRF counts (bottom).

The same method was applied to the Ca signal in order to determine what portion of the Ca in the sediments might be related to eolian clastic deposition in the lake. It was found (figure 22) that there are approximately 7.2 Ca counts for each Ti count. Using this ratio, it is clear that, just like Sr, the vast majority of the Ca in the sediments of Elk Lake is present in the carbonate fraction (figure 23).

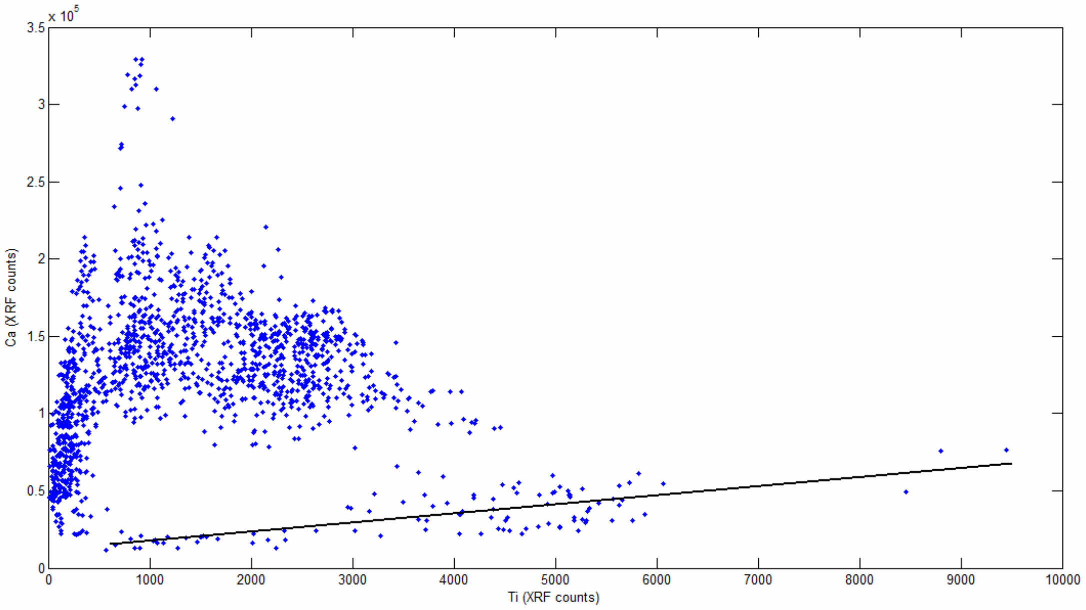


Figure 22. Scatter plot of Ti and Ca used to determine the authigenic and detrital portions of the total Ca signal. The black line was used to estimate the Ti:Ca ratio which was used for the calculation of each fraction (Ca_{total}=Ca_{authi}+$Ca_{detrital}$; Ca_{authi}=Ca_{total}-(Ti*Ti:Ca); $Ca_{detrital}$=Ca_{total}-Ca_{authi}).

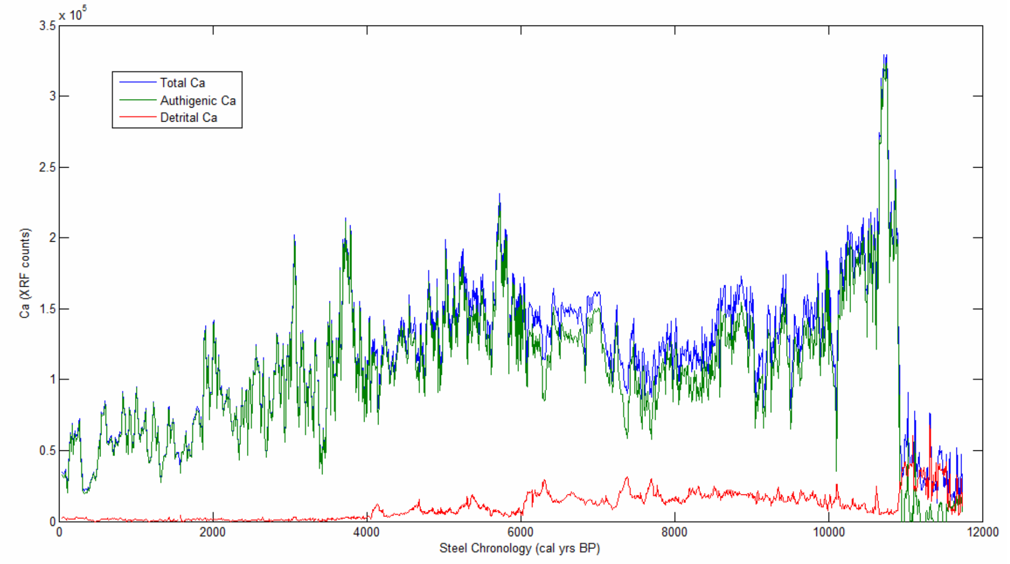


Figure 23. Plots of authigenic, detrital and total Ca in XRF counts vs. time

3.3 Fe and Mn Oxyhydroxides/Carbonates:

The following are plots of elements within the varved sediments of Elk Lake that represent the deposition of Fe and Mn oxyhydroxides/carbonates within the lake (figure 26). For description of processes related to these materials, see the climate proxy section of the introduction and iron and manganese geochemistry section of the discussion. Some portion of the Fe signal was determined to represent detrital wind borne iron and was differentiated from the total Fe signal by using the Ti to Fe ratio of approximately 40 (see equation 3.2.1 and 3.2.2, figure 24).

$$Fe_{authigenic} = Fe_{total} - (Ti*40) \qquad \text{eq.} \quad 3.2.1$$
$$Fe_{detrital} = Fe_{total} - Fe_{authogenic} \qquad \text{eq.} \quad 3.2.2$$

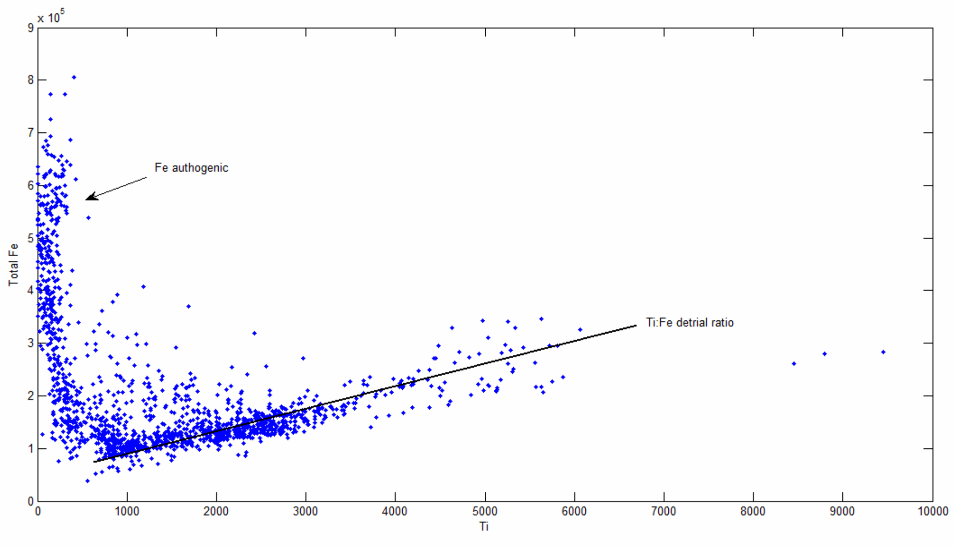


Figure 24. Scatter plot of Ti and Total Fe used to determine the amount of authigenic and detrital iron in the signal. The black line indicates the portion of the Fe signal that is related to clastics (Ti). The slope of this line was used in equations 3.2.1 and 3.2.2 to determine how to divide the iron signal.

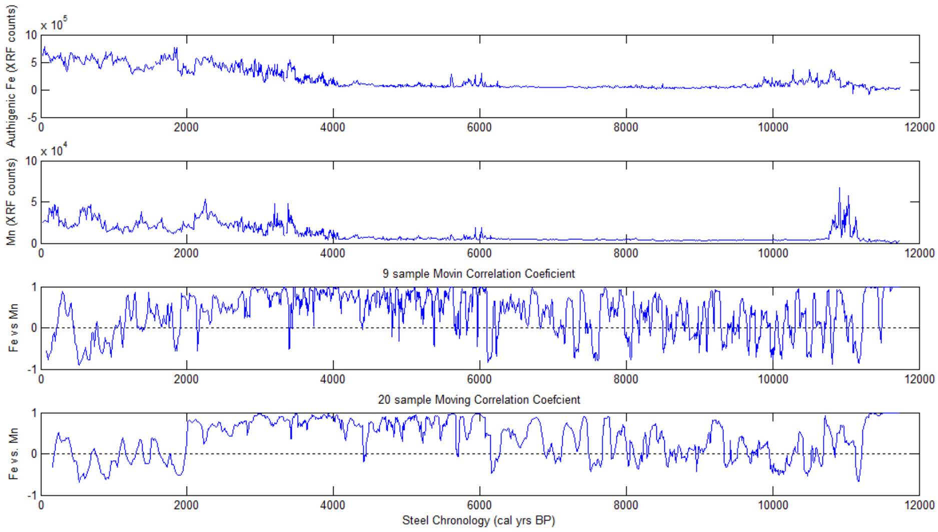


Figure 25. Plots of Fe (authigenic) and Mn are in XRF counts, a nine sample moving correlation coefficient of Fe vs. Mn and twenty sample moving correlation coefficient (from top to bottom) all plotted against the Steel Chronology.

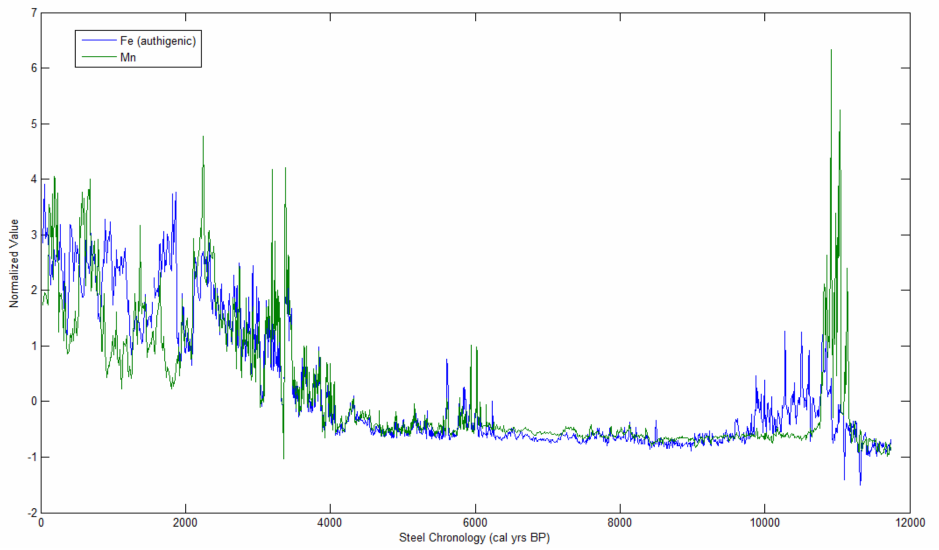


Figure 26 Normalized Fe (authigenic) and Mn XRF data plotted against the Steel Chronology. Data has been normalized in order to plot elements with different count rates on the same y-axis (in Standard Deviations).

3.3 Major Clastic Materials and Indicators of Eolian processes/activity:

The geochemical record preserved in the sediments of Elk Lake is likely not long enough to properly address the chemical weathering of minerals within the lake basin and even if some portion of the clastic signal is related to chemical weathering/soil development in the watershed, it will affect the record of Ti, K, and the Ti:K ratio in the same direction as eolian dust during arid times. Thus it is assumed that the concentration of clastic materials in the sediments of Elk Lake is dominated by transportation and deposition related to eolian processes. These elements include titanium (Ti), potassium (K), detrital iron (Fe), silica (Si), and some trace elements. The most useful and descriptive elements in the record are Ti, K, and Fe (detrital). Other elements may be mentioned, but the records of these trace elements are not as useful for describing climatic changes during the Holocene.

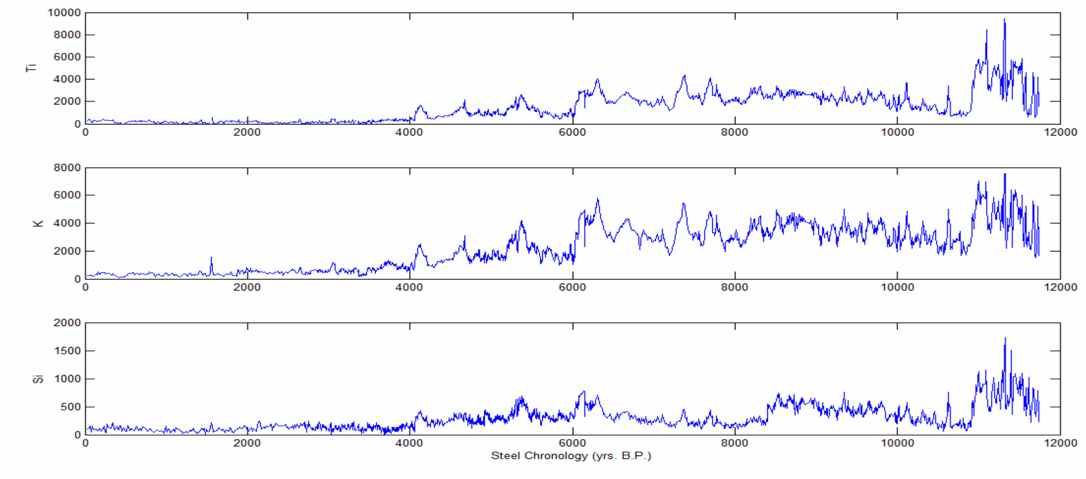


Figure 27 Plots of the major clastic indicators in the Elk Lake sedimentary record. Ti, K, and Si are all plotted in XRF counts vs. the Steel Chronology.

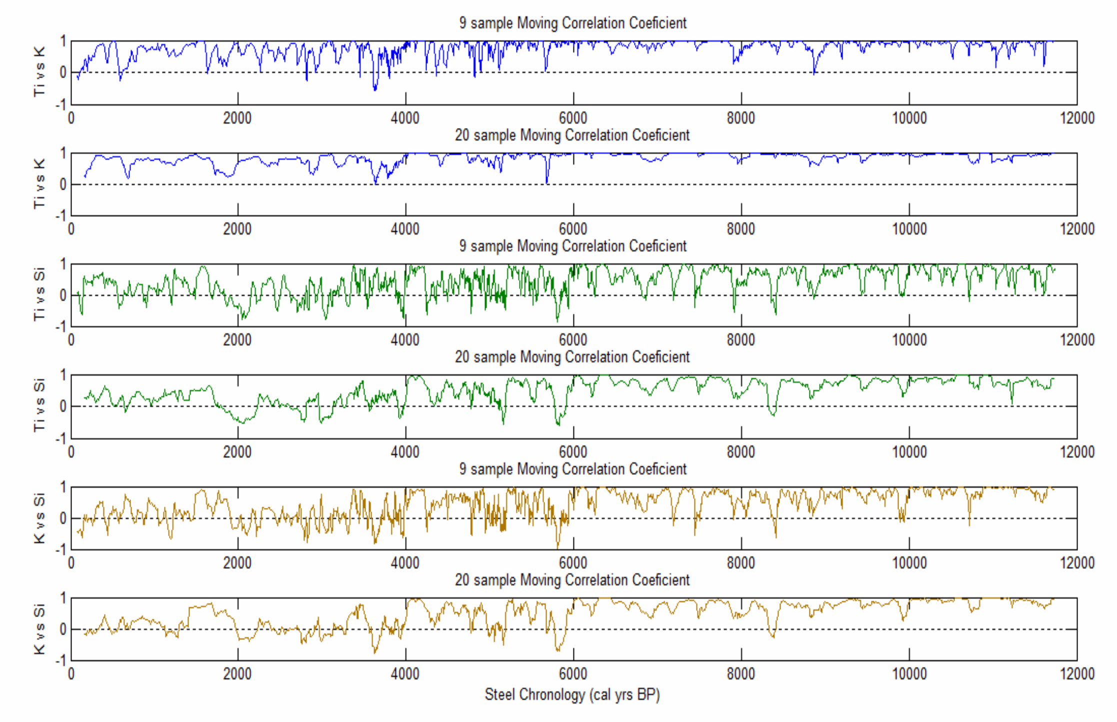


Figure 28 Nine and twenty sample moving correlation coefficient plots for major clastic elements showing the relationships between the major clastic indicators, Ti vs. K, Ti vs. Si, and K vs. Si.

A scatter plot of titanium and potassium shows a clear relationship between the two elements. Data in figure 29, box A is form the glacial outwash found at the base of the core. The vast majority of the titanium and potassium found in the rest of the signal suggest that the source area of the clastic feldspar/clays did not change considerably at any time in the history of Elk Lake indicated by a single, relatively stable slope. Two other interesting characteristics of the scatter plot are shown by lines B and C of figure 29. Line B represents data from the base of the core, just above the glacial outwash found at the bottom of the lake. Line C is data points representing a 1 cm clay layer dated at approximately 790 calendar years before present (cal. yrs. B.P.).

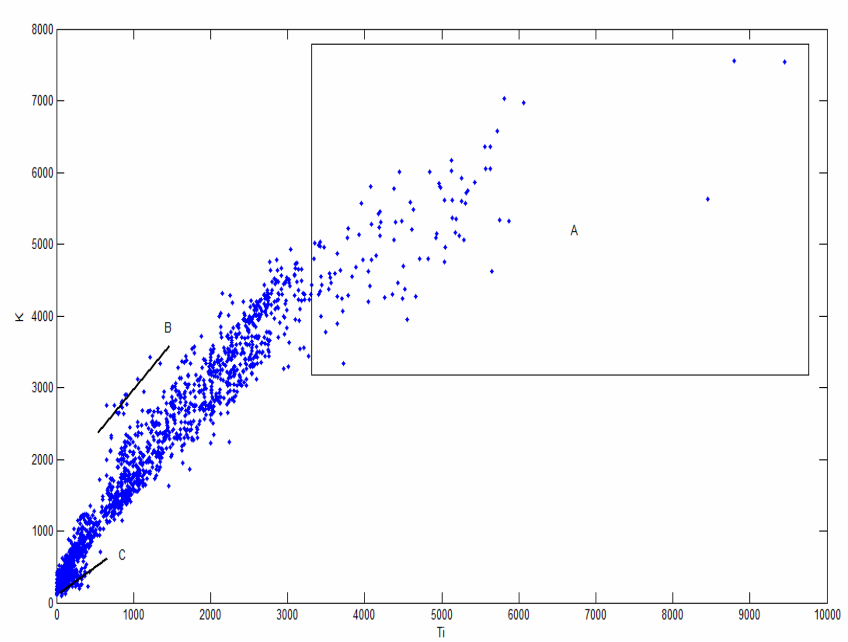


Figure 29 Scatter Plot of Ti vs. K (in XRF counts). Box A: Glacial Outwash, Line B: early Post Glacial sediments, Line C: 1 cm clay layer approximately 750 cal. yrs. BP.

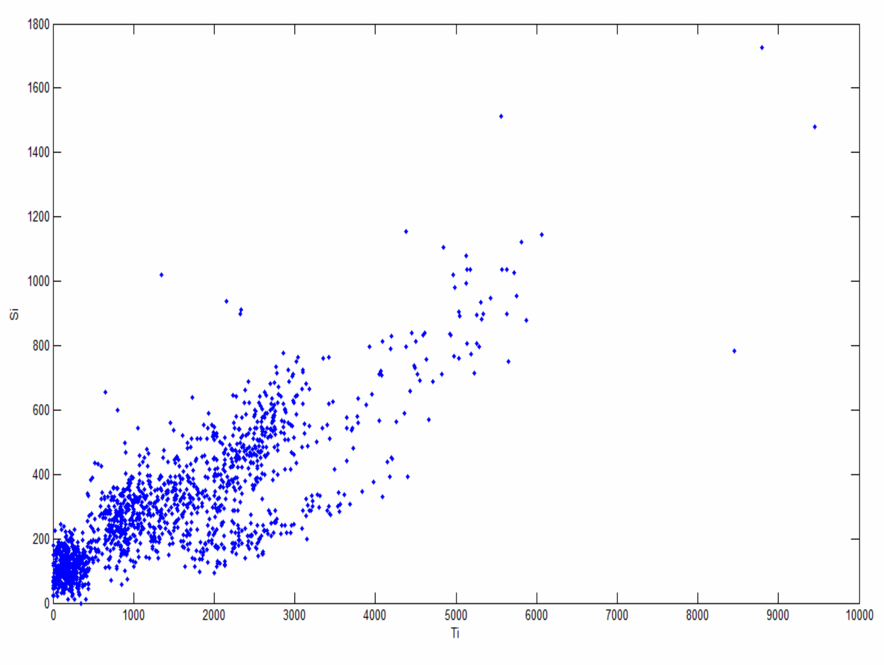


Figure 30 Scatter plot of Ti and Si (in XRF counts).

Some of the iron signal in the Elk Lake sediments is also detrital, especially during the mid Holocene when detrital clastic material is a major constituent of the sediments. The portion of the Fe signal associated with the clastics was determined by using the ratio of Ti to Fe from figure 31. A ratio of approximately 40 Ti counts for every Fe count (see figure 31). By multiplying the Ti data by this ratio and then subtracting the subsequent value from the Fe signal, it is possible to estimate what portion of the total Fe is authigenic and what portion is detrital. This shows that during the mid-Holocene when calstic material was a dominant fraction of the sediments, that Fe tracks Ti and other clastics.

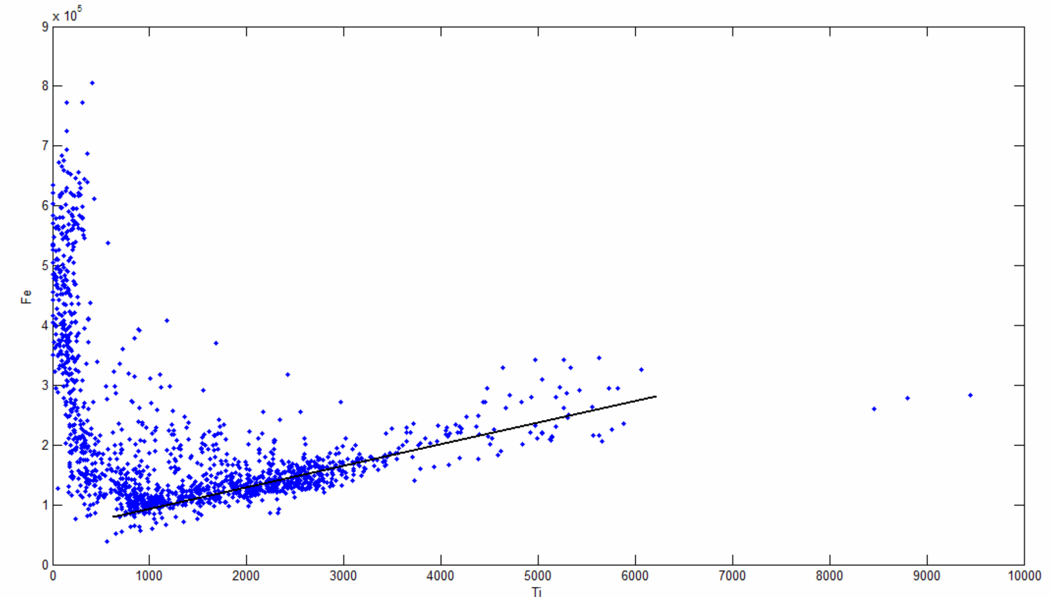


Figure 31 Scatter plot of Ti vs. Fe. Black line represents the sediments of the mid-Holocene; the slope of this line was used to determine what portion of the Fe signal was authigenic and detrital using equations 3.2.1 and 3.2.2.

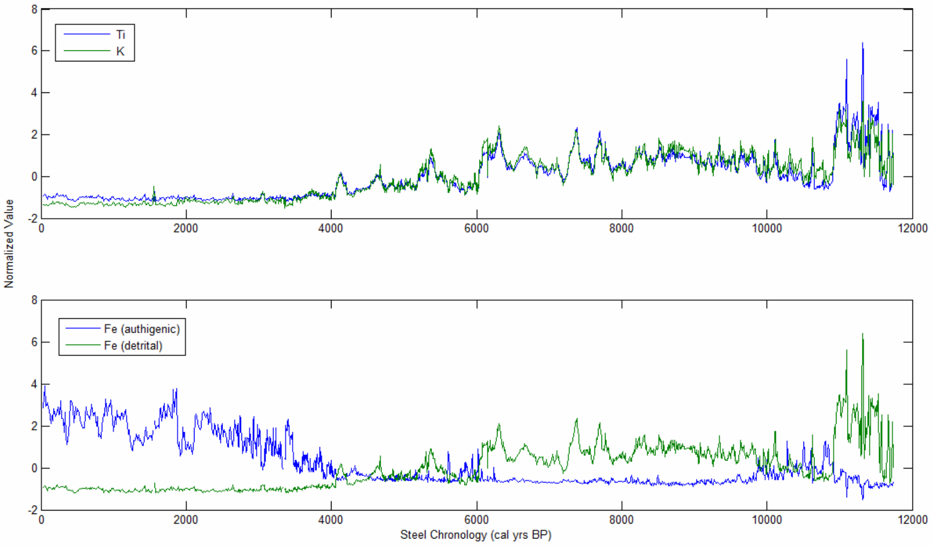


Figure 32 Plots Ti, K, Fe (detrital) and Fe (authigenic). All data has been normalized in order to plot different elements on the same y-axis and thus is plotted in Standard Deviations against time (Steel Chronology).

3.5 Qualitative Measure of Organic Carbon:

The XRF is unable to take direct measurements of organic carbon within the sediment cores from Elk Lake. As a qualitative measure, the ratio of incoherent to coherent scatter can be used to discuss the amount of organic carbon measured the sediments. This is not a perfect method especially when a lake contains sediments related to more that two processes such as Elk Lake.

During the XRF core scanning process, scattering occurs when an X-ray photon interacts with the electrons of a target atom. If the interaction is elastic (no loss of energy) the scattering is called coherent (Rayleigh) scatter. When the interaction involves the loss of energy the scatter is referred to as incoherent (Compton) scatter. The intensity of the scatter is dependent on the average atomic number of an element. Incoherent scatter occurs with greater intensity when measuring elements with lighter atomic numbers, whereas, coherent scatter is stronger when measuring elements with a larger atomic number. Thus the ratio of incoherent to coherent scatter (Inc:Coh) will have a greater value when the sediments contain more organic matter and a lower value when measuring materials such as primary minerals (Jenkins 1999).

While the use of the incoherent to coherent scatter (Inc:Coh) is not a particularly robust means of determining the amount of organic matter/carbon in sediments, a comparison between the Inc:Coh ratio from the XRF data and the total organic carbon (TOC) curve from Dean (1993) shows similar trends over time (figure 33). Thus, this ratio of Inc:Coh will be used as a qualitative measure of the amount of organic carbon within the sediments of Elk Lake.

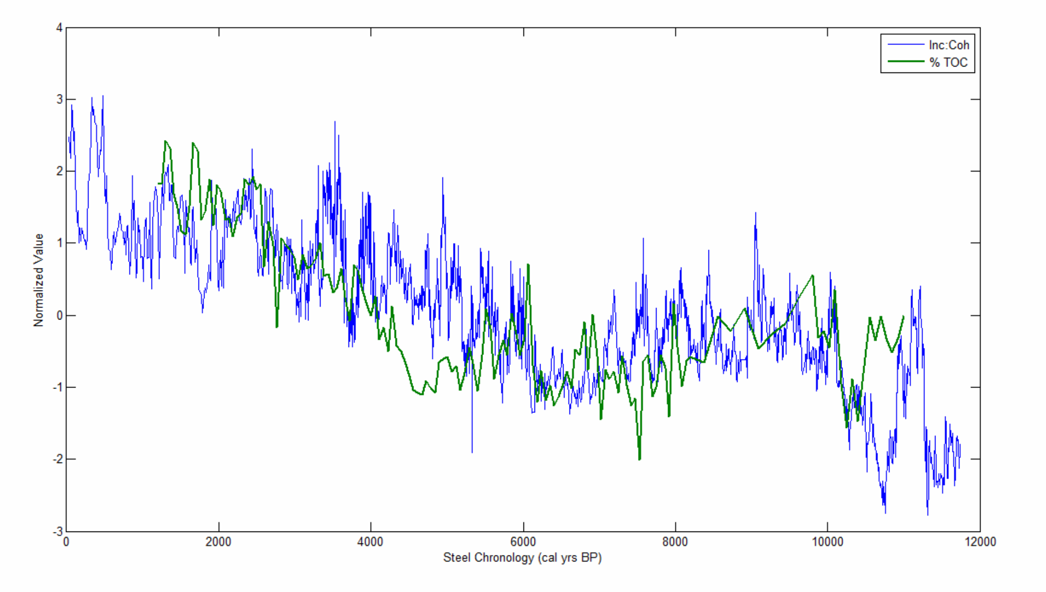


Figure 33 Plots of the XRF Inc:Coh scatter ratio (blue) and %TOC from Dean (1993) in green. Data has been normalized and is plotted in standard deviations against time.

3.6 Geophysical Data:

On August 25 of 2009, the first known geophysical data set ever taken in Elk Lake was collected (figure 34a and 34b). Before entering the field it was initially thought that, based on field observations while coring Elk Lake, the sediments contained far too much gas to allow for reliable geophysical results. While the distribution of gases in the lake's sediments varies widely around the lake, in general sediments below a water depth of 15-20m contain too much gas to allow for reliable geophysical results. Occasionally laminated sediments can be seen below this depth, but the persistent presence of gas makes it difficult to trace distinct layers into the deeper areas of the lake. Upon retrieving and reviewing the data, it was found that in fact the data showed some interesting characteristics of the lake's sedimentation that had not before been directly observed.

Things such as the focusing of sediment into the deep basin of the lake, a distinct and intriguing unconformity within the sediments, and the possibility of confirming a drop in lake level that had been interpreted in the past (figure 35) (Dean and Anderson, 1993; Stark, 1976; Forester and other, 1987).

During the initial description of the cores retrieved for this study, it was noted that the core from site 1A (water depth of 25m) showed much lower sedimentation rates than the cores taken from site 2A and 2B (water depth of 27.85m). Site 1A contained a full record of Holocene sediments (including outwash) down to a depth of approximately 13m while cores 2A and 2B penetrated to the same approximate depth into the sediment but did not contain material further back in time than around 8000 cal yrs BP. This all suggested that there was a difference in sedimentation between the two sites—one at a shallower water depth and the other closer to the deepest part of the Elk Lake basin. With the acquisition of our geophysical data set, it is now clear that the focusing of sediment is an important process in Elk Lake and is responsible for the differences in sediment accumulation at various sites. Sediment focusing also accounts for the difference in total core length covering the entire Holocene between the cores taken for this study and those from previous research which were approximately 5m longer in total length than the 2009 PBR cores (Anderson, Dean, and Stuiver, 2993).

Sediment focusing is the process by which sediment may be re-suspended and transported from shallower to deeper parts of a lake leading to greater net accumulation in the deeper basins of a lake (Davis and Ford, 1982). It is not uncommon for sediment focusing to take place within a lake, but while the processes behind this phenomenon are well understood, it can be difficult to determine which of them dominated at any given time in the record. This is due to the fact that various processes can govern at different times and multiple processes can occur at the same time (Hilton 1986). The actual means by which sediment is preferentially deposited in the deep basin and the process by which sediment is moved from shallower areas to the deep is not particularly evident in Elk Lake. As many as ten processes have been suggested that could produce the results seen in the sediments of lakes—among the likely possibilities in Elk Lake are sliding or slumping on slopes, intermittent complete mixing (ICM), peripheral wave action (PWA), and random redistribution(RR), (Hilton, 1985). The most probable causes for the greater net accumulation of material in the deep basin of Elk Lake are ICM and PWA.

In the earliest sediments deposited at the bottom of the core section there is clear evidence for the slumping of material into the deeper part of the lake in the presence of highly disturbed laminations (seen from core evaluation) that likely resulted from slumping associated with over-steepened slopes in the lake basin, but these disturbed laminations cease soon after the final disappearance of the ice block and are not likely a major process taking place in the lake today. Random redistribution requires that a lake be shallow enough for wave energy to be transferred directly to the bottom of the entire lake creating a redistribution of sediments over the full lake bed, particularly during times of weak or no stratification (Hilton, 1985). With as much as 25-30m depth, Elk Lake is far too deep with too small a fetch for this process to explain the trends we see in the geophysical data from the lake. Although this process could certainly be acting to re-suspend sediment in the shallower, near-shore zones of the lake.

The lake behaves as a dimictic lake with two main turn-over periods each year. During these times, the deposition of Fe and Mn oxyhydroxides form distinct layers that are used in the description of varve sets. It would seem that the deposition of these oxides during spring and autumn turn-over would indicate the possibility that intermittent complete mixing is the dominant focusing processes during these seasons. Sediment trap studies from Belham Tarn showed that almost four times more material was deposited during fall overturn than at any other time during the year (Hilton 1986). While this process could certainly contribute to the focusing of sediment in Elk Lake, further studies of the modern limnlogical processes taking place today would be needed in order to confirm the degree to which this is taking place.

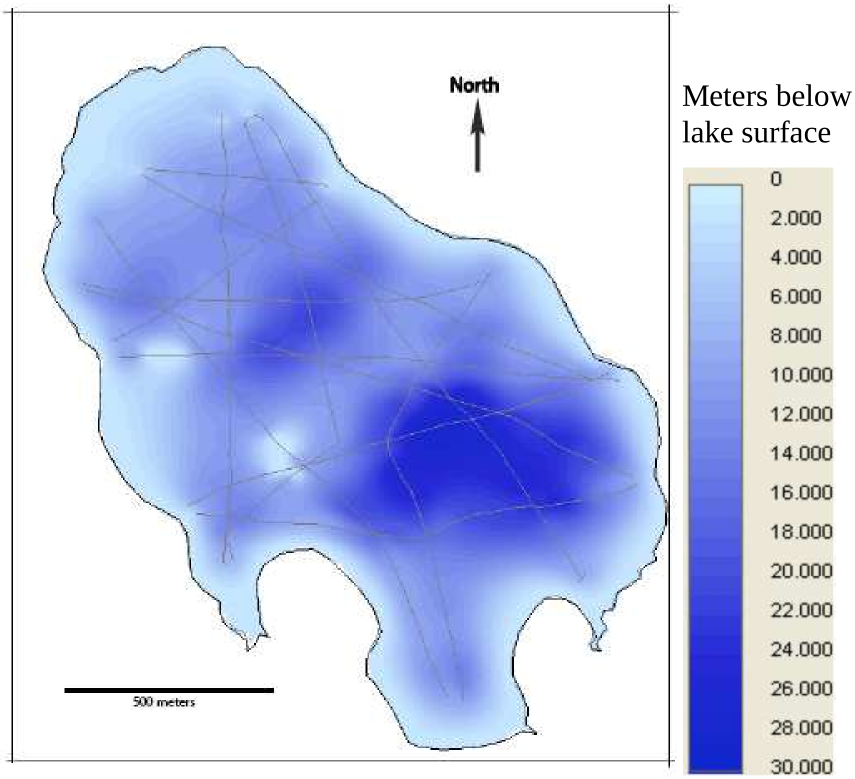


Figure 34a Bathymetric Map of Elk Lake developed for geophysical CHRIP data recovered on August 25, 2009.

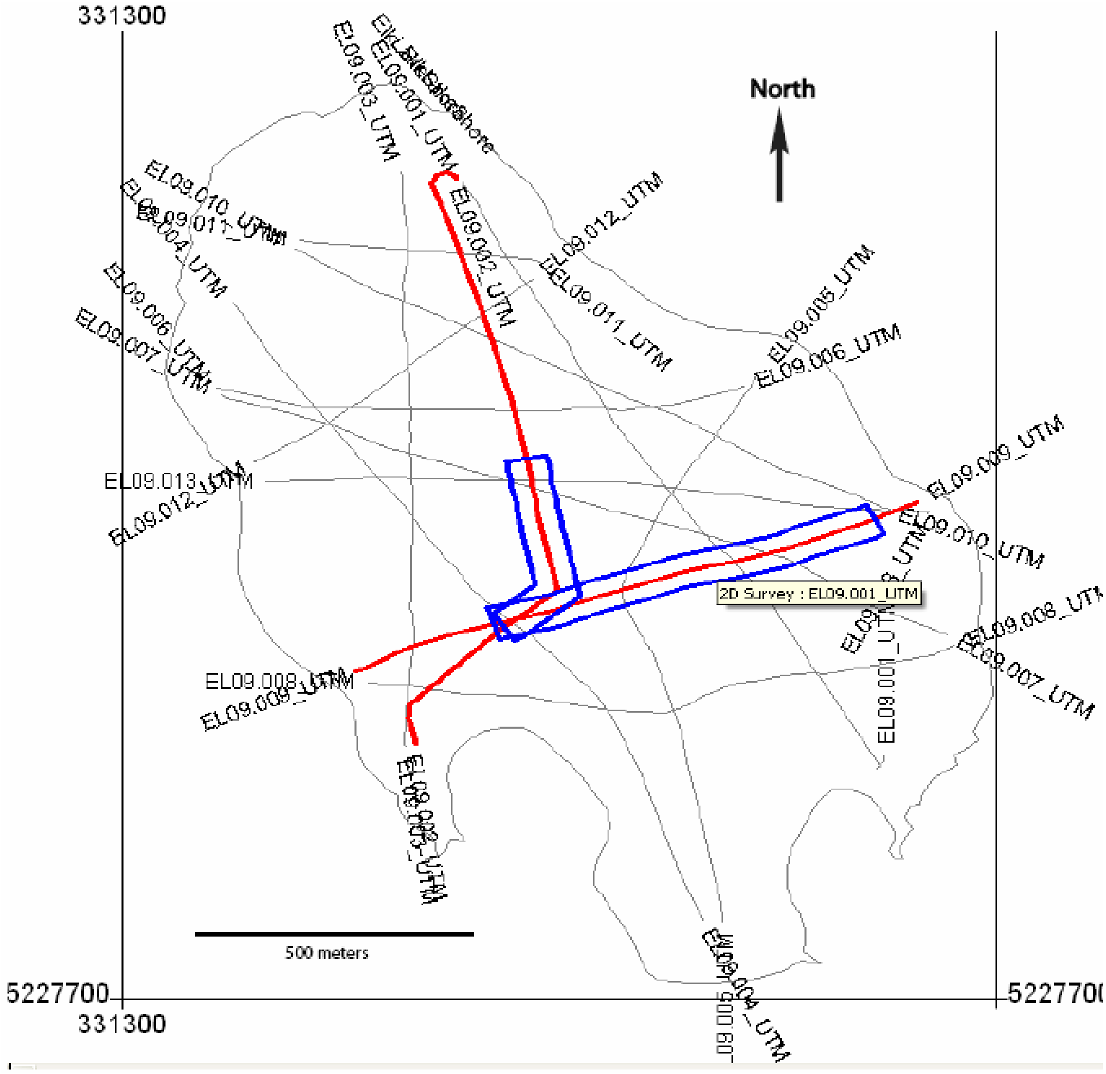


Figure 34b Map of Elk Lake showing (in black) the geophysical lines with their corresponding labels. In red are Lines 2 and 9 .Blue boxes indicate the portions of lines 2 and 9 that are presented in figures 36 and 37.

The only sediment focusing process for which there seems to be direct evidence is peripheral wave action (PWA). It is easy to imagine that wave action in the near shore zones of a lake can produce sufficient energy to re-suspend sediment in these areas and redistribute it to the deeper parts of a lake. There is evidence within the geophysical data that this is in fact taking place. A clear pinch out of the upper most sediment can be seen in the shallower depths of most of the profiles taken in Elk Lake (figure 35). These pinch out zones seem to occur around the entire lake (thus they are not localized to one area within the lake) at a uniform depth of approximately 8m and indicate the point where the lake bed transitions from erosional processes.

Diggerfeldt (1986) and Shuman et. al. (2001, 2005) used a method of comparing sediment cores and geophysical sub-surface profiles within lakes to discuss changes in lake level by tracking the position of near-shore sediments. This method relies on the assumption that peripheral wave action in littoral zones prevents the deposition/accumulation of sediments in the shallower areas around the lake. Thus, a pinch out is created where processes transition from depositional in the deeper areas to erosional in the shallows. As lake level changes, the location of the zone of deposition/pinch out in littoral areas will move toward the center of the basin as lake level falls and away from the center of the basin as levels rise. These researchers showed that infilling of a basin cannot explain the shoreward expansion of fine grained sediment accumulation. Thus near shore sediments can be used to infer both high and low stands in a lake (Shuman et. al., 2009). In Elk Lake a pinch out can be seen in several of the geophysical lines (figure 35 and 36) and is at a fairly uniform depth of approximately 8-9m. Utilizing the depth at which an unconformity becomes conformable (i.e. the depth of the pinch out during a low stand) and assuming the depth of the transition (unconformable to conformable) represents the same depth as the modern pinch out during a low stand, an estimate of the amount of lake level fall that occurred during a low stand can be reached.

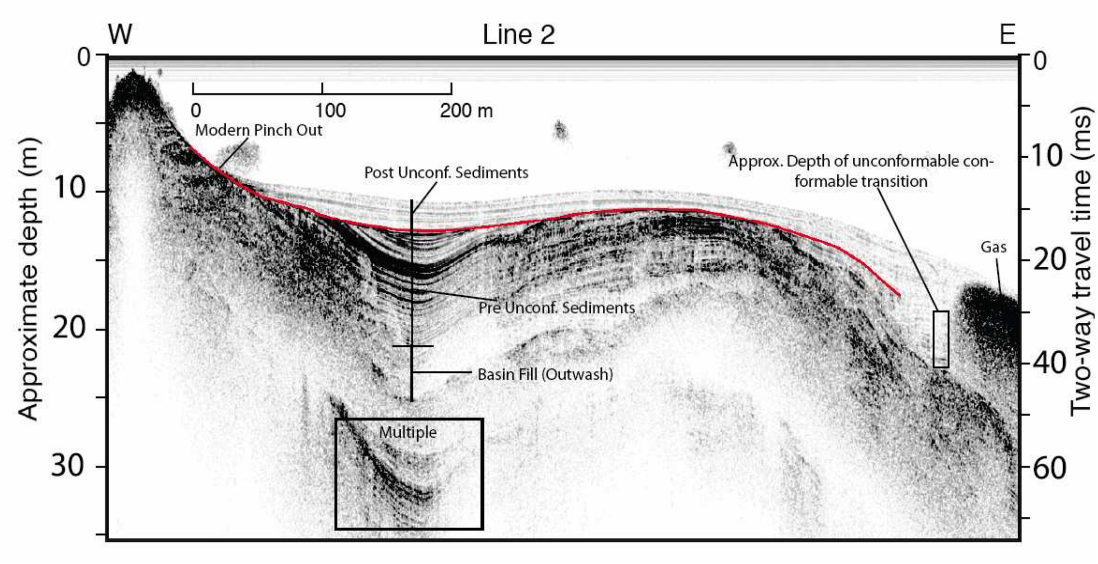


Figure 35 Line 2 annotated to show major features of the geophysical data. In red is the unconformity. Depths calculated using two way travel time and assuming sound velocity of 1500m/s.

The most striking feature of the geophysical data is the presence of a distinct unconformity within the sediments (figure 35 and 36). Previous researchers have postulated that there was likely a low stand during the mid Holocene associated with drier conditions and a change in the hydrologic budget of Elk Lake (Dean and Anderson, 1993; Stark, 1976; Forester and other, 1987). This conclusion was only based on observations made through the study of geochemical data from sediment cores (specifically the clastic signal and the Mg:Ca ratio within the sediments), but with the addition of this new geophysical dataset, it is now clear that a low stand occurred during the Holocene. This low stand and unconformity indicate a fairly important climatic event that took place causing the lake level to drop significantly. Unfortunately, the gas content of the deeper sediments obscures the depositional layers in the location where the cores were taken. This means that a clear view of where and at what depth the unconformity becomes conformable is difficult to locate which limits our ability to determine the exact timing of the event and an accurate correlation with the geochemical dataset.

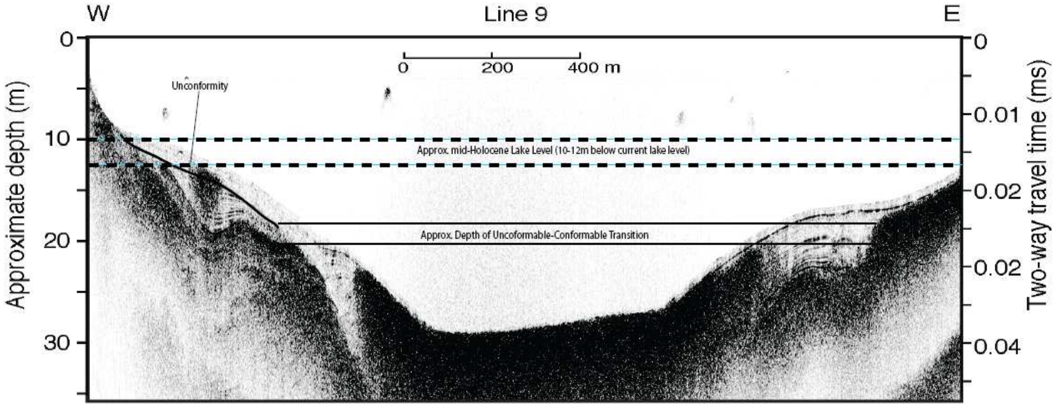


Figure 36 Line 9 annotated to show the unconformity, the approximate depth of the transition from unconformable to conformable sedimentation. Sediment focusing can be seen to some extent. Also depicted is the approximate lake level during the low stand that created the unconformity. Depths calculated using two way travel time and assume sound velocity of 1500m/s.

In most of the geophysical lines the transition from unconformable to conformable sedimentation is difficult to distinguish. One of the few places where the transition seems to be visible is in Line 9 (figure 36). The depth at which the transition becomes obscured by gas provides an upper limit and based on estimates from line 9, the unconformable-conformable transition is approximately 18-20m (calculated using two-way travel time and a sound velocity of approximately 1500m/s) below the current lake surface. As will be discussed later on, the mid-Holocene sediment proxies in Elk Lake also suggest aridity and closed basin conditions. Assuming, based on the depth of the modern pinch out, that the transition zone from erosional to depositional processes occurs at 8m below the surface, the lake level could have dropped by as much as 10-12m during the mid-Holocene (figure 36). This estimate of course assumes that wind driven turbulence and wave action in a shallower Elk Lake will affect the littoral sediments the same way these processes do today. Obviously there would probably be slight differences in the thickness of the upper mixed layer and depth to which wave action penetrates as the lake becomes shallower and the fetch decreases. If there was a significant decrease in the depth to which the wave base interacted with the sediments, then the estimate of 10-12m drop in lake level is too high.

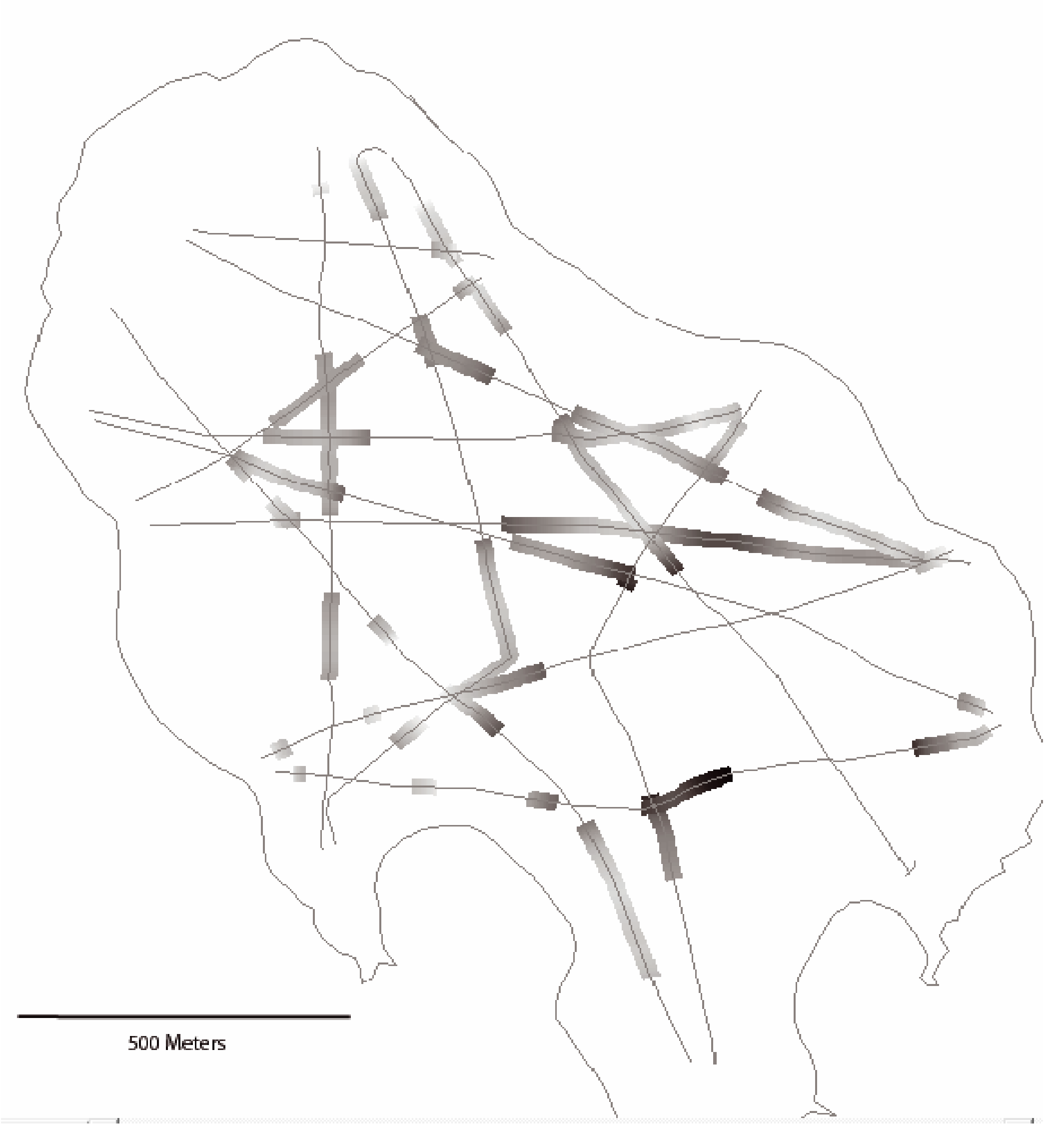


Figure 37a Depth to the unconformity. Map of Elk Lake showing the geophysical lines and depicted with grey scale is the depth to the unconformity as seen in each line. Darker colors represent deeper areas while lighter grey represents shallower depths to the unconformity.

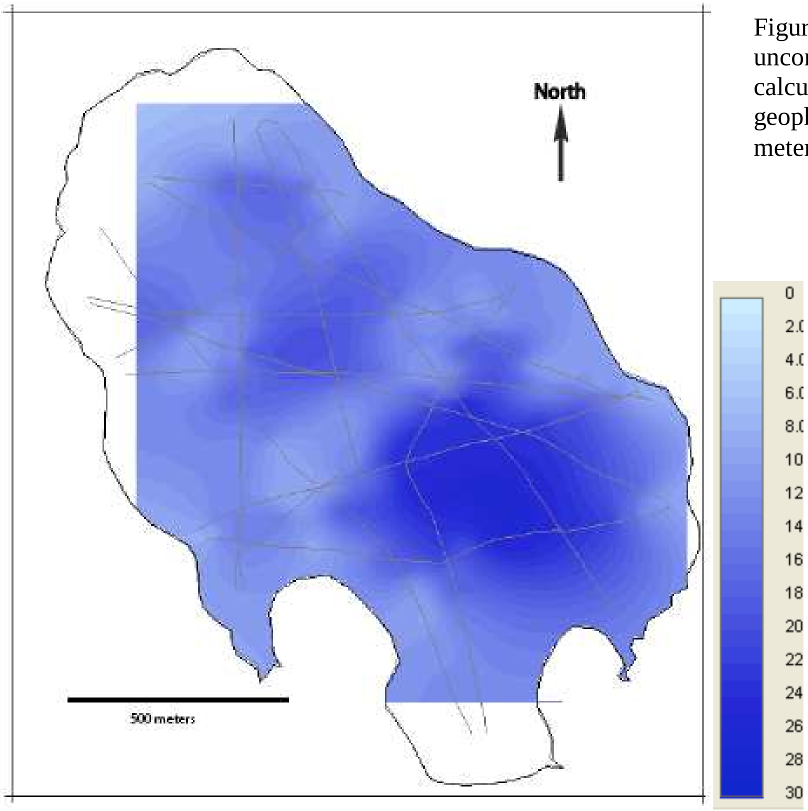


Figure 37b Interpolated depth to unconformity based on depth calculated from individual geophysical lines. Scale is in meters below the surface.

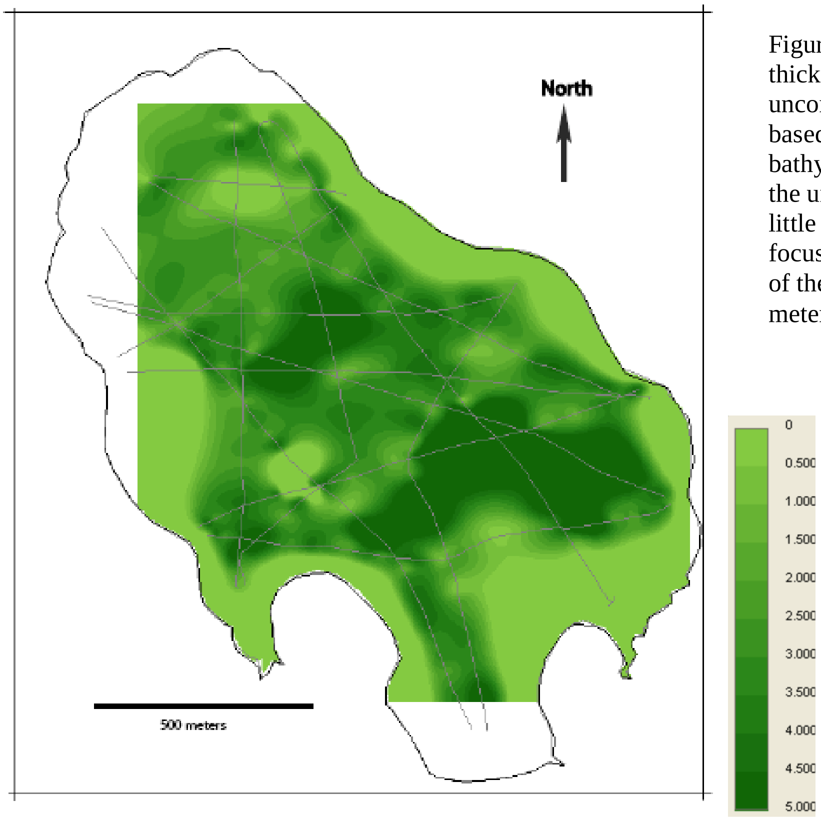


Figure 37c Interpolated thickness of post-unconformity sediments based on difference between bathymetric data and depth to the unconformity. Suggests little regularity to sediment focusing with the exception of the deep basins. Scale is in meters below the surface.

Finally the geophsical data show a change in the degree of sediment focusing before and after the unconformity was created. Based on profiles from the lake, there is clear sediment focusing taking place in the sediments below the unconformity but the degree to which this process is visible in the younger sediments is much less distinct. The best plausible explination is that there was a significant change in the nature of deposition and the major constituents of the sediment after the unconformity was created. During the mid-Holocene, conditions were very dry and there was a significant influx of clastic material and higher sedimentation rates. The increased abundance of clastic material entering the lake would have provided more sediment for focusing process to affect and redistribute to the basins of the lake, leading to higher sedimentation rates and greater focusing of sediments into the deep basins. After the proposed age of the unconformity (approximately 6100-6300 cal yrs. BP, based on geochemical XRF data as will be discussed in the following chapter), the amounts of clastic material entering the lake decrease significantly and the modern sediments of the lake contain little detrital material. This would have led to less material avaialbe in the shallower, near shore areas for foucusing processes to affect. Changes in the types and amounts of material entering the lake after the creation of the unconformity/low stand meant that the degree of foucsing decreased within the modern sediments and is evident in both the profiles from geophysical lines and interpolated maps of Elk Lake (depth to unconformity figure 37a and 37b, thickness of post-unconformity sediments 37c).

4. DISCUSSION

4.1 Elemental Associations and Major Processes:

Elements measured by the Scanning XRF, show similarities in trends and variation through time, related to processes taking place within the lake. These groups show minima and maxima at different periods in the Elk Lake record and help to describe changes in the regional climate. In many cases, data has been normalized (Normalized data=(Raw data-Mean of data)/Standard deviation of data) in order to depict elements that have very different XRF count rates yet contain valuable signals for the description of past climatic events and show similar trends over time.

4.1.1 Iron and Manganese geochemistry:

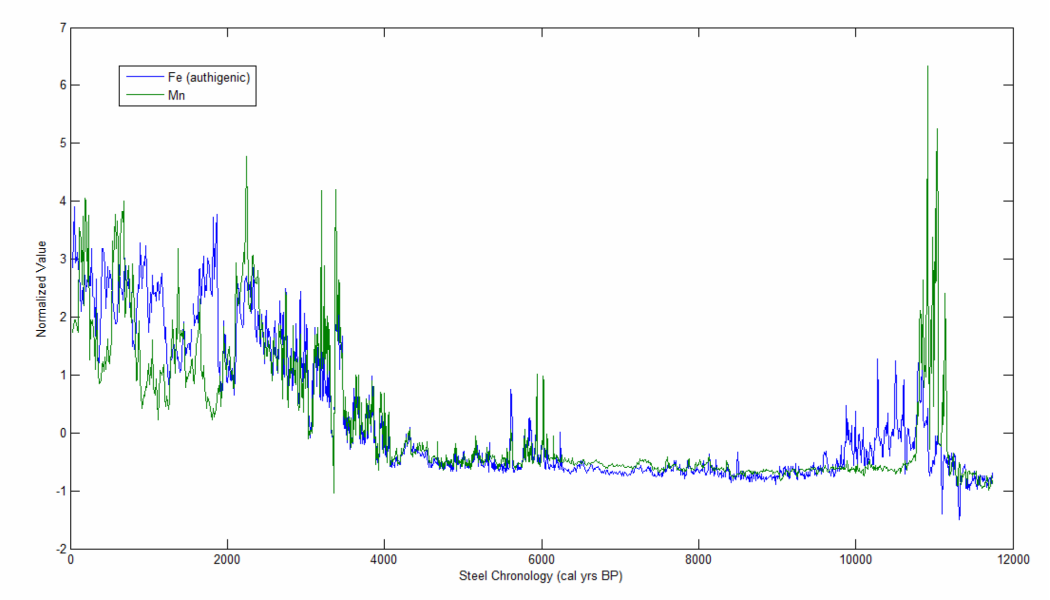


Figure 38 Normalized Fe (authigenic) and Mn plotted against time (Steel Chronology).

The Fe and Mn signals are among the most prominent features of the Elk Lake sediment record showing particularly high concentrations during the very early and more recent periods of the lake's history—approximately 11,000-10,000 cal yrs BP and 4,000 cal yrs BP to present respectively (figure 38). The abundances of these two elements are especially high during the last 4000 yrs. of the lakes evolution. As mentioned in the climatic proxies section of the introduction, Fe and Mn are mostly likely present in the sediments as authigenic oxyhydroxides or carbonates and are related to redox cycling in the eplimnion, hypolimnion, and sediments (Dean 1993). It was shown in some Labrador lakes that the rapid transition from tundra to coniferous forests in the basins of lakes leads to the increased mobilization of organometallic complexes through humus accumulation in coniferous forests and a subsequent increase in the deposition of authigenic iron and manganese in the sediments (Engstrom and Wright, 1984). This process may explain the higher abundances of Fe and Mn during the early Holocene—just after the final melting of the ice bock (Dean, 1993). The high abundances of these elements during the final stage of the lake's development are likely related to changes in vegetation from prairie to forest species around the basin and increases in the amount of ground water feeding the lake as the climate in the region became wetter.

Reducing conditions within the hypolimnion and sediments of Elk Lake certainly lead to the release or alteration of much of the Fe and Mn oxyhydroxides present in the sediments. Nonetheless, there is a significant net burial of this material as seen in figure 38, particularly during the final stage of the lake's history. While large amounts of Fe and Mn may be released from the sediments during stratification and the onset of seasonal anoxia in the summer months of any given year, it is probably returned to the sediment during fall overturn. Due to the nature of this pump, it is possible that the concentrations of Fe and Mn at any given point in the record could be an average of conditions during the previous years, but none the less, it seems that the efficiency of this pump has been increasing with time as evidenced by the increasing abundance of Fe and Mn in the sediment record (Dean 1993).

Scatter and moving correlation coefficient plots (figure 39 and 40) show relationships between Fe, S, P, and Incoherent to Coherent Scatter (Inc:Coh)—used as a measure of organic carbon (OC) in the sediments (E. Brown, person. comm., 2010). There is a distinct lack of correlation between Inc:Coh (OC) and sulfur in the record. This is to be expected in freshwater systems where sulfate is limited and there is little reduction of sulfate and limited formation of iron sulfides (Brener and Raiswell 1984, Dean, 1993). The sulfur concentrations throughout the majority of the record are very low, with the exception of the first two thousand years (~9,000-11,000 cal yrs BP) of the Holocene. During the period from 10,900 to 9,000 cal yrs. BP., the correlation between Fe and S and to some extent the correlation between Inc:Coh vs. S, are much stronger than at any other time. This suggests that at this time sulfur was not limiting and allowed for the formation of iron sulfides (including Pyrite). The ultimate source of the sulfate is probably from Cretaceous Gypsum which is an important component of the calcareous glacial drift that underlies the region (Dean 1993, Ackroyd et al 1967, Shultz et al 1980).

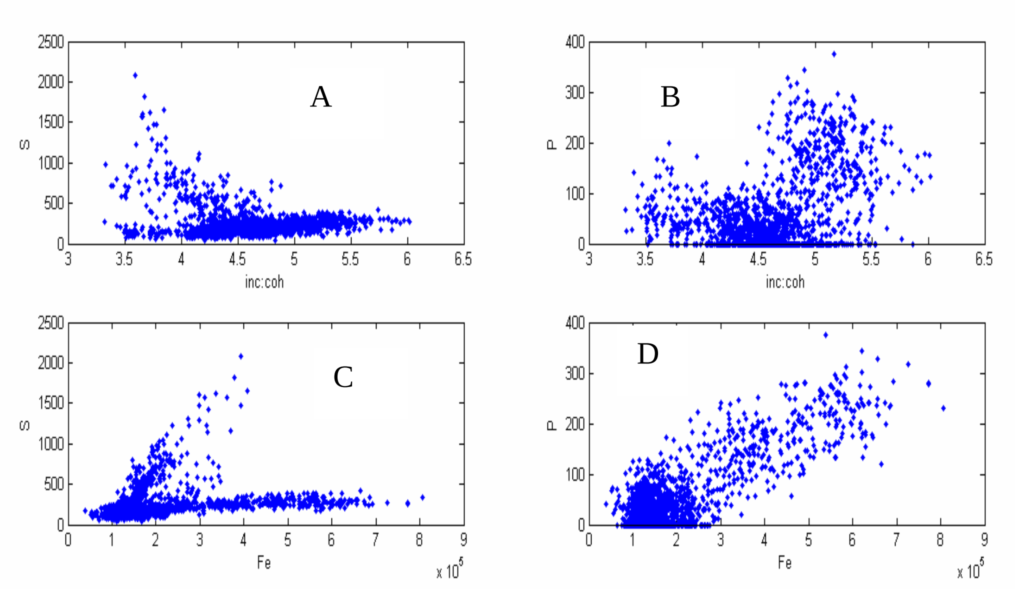


Figure 39 Scatter plots of (A) Inc:Coh vs S, (B) Inc:Coh vs. P, (C) Fe vs. S, and (D) Fe vs. P all plotted as XRF counts.

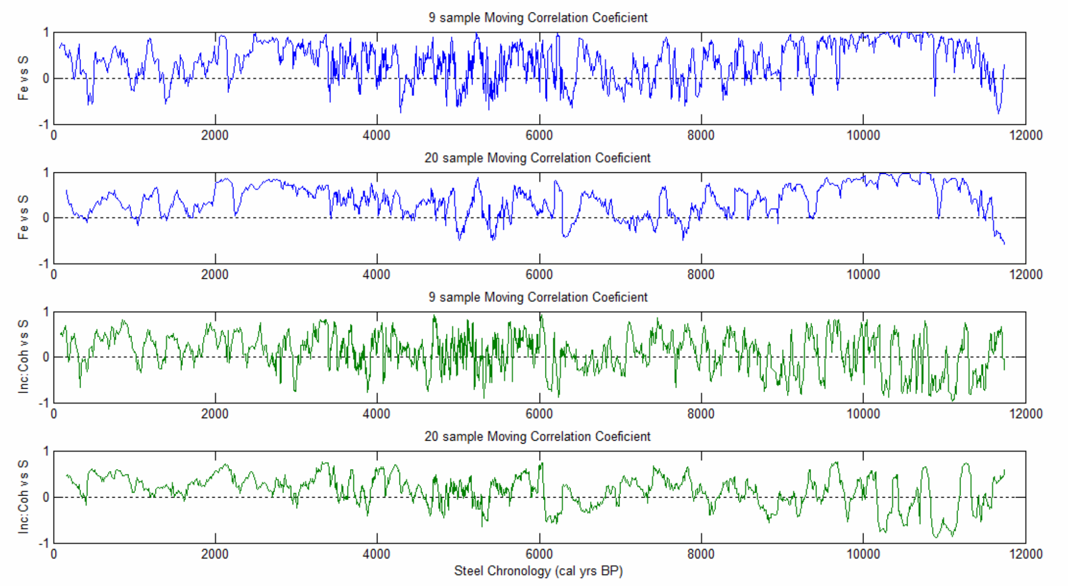


Figure 40 Nine and twenty sample moving correlation coefficient plots against time.

There does seem to be a relatively good correlation between Fe vs. P and Inc:Coh vs. P suggesting a possible control on primary productivity through the formation of iron phosphates making phosphorus a limiting nutrient on productivity in the lake. This is particularly true for the last 3,500 to 3,000 years where the burial of P increases dramatically as opposed to the rest of the Holocene. Prior to this modern period, there was little to no P buried in the sediments whereas in the modern lake (4,000-0 cal yrs BP), the amount of phosphorous preserved in the sediments has increased markedly and shows similar trends to Fe. This correlation between Fe and P points to the formation of iron phosphates as a possible control on the amount of phosphorous available for primary producers making P a limiting nutrient. This would explain why eutrophication has not occurred in Elk Lake and its current classification as an oligitrophic lake (Dean, 1993).

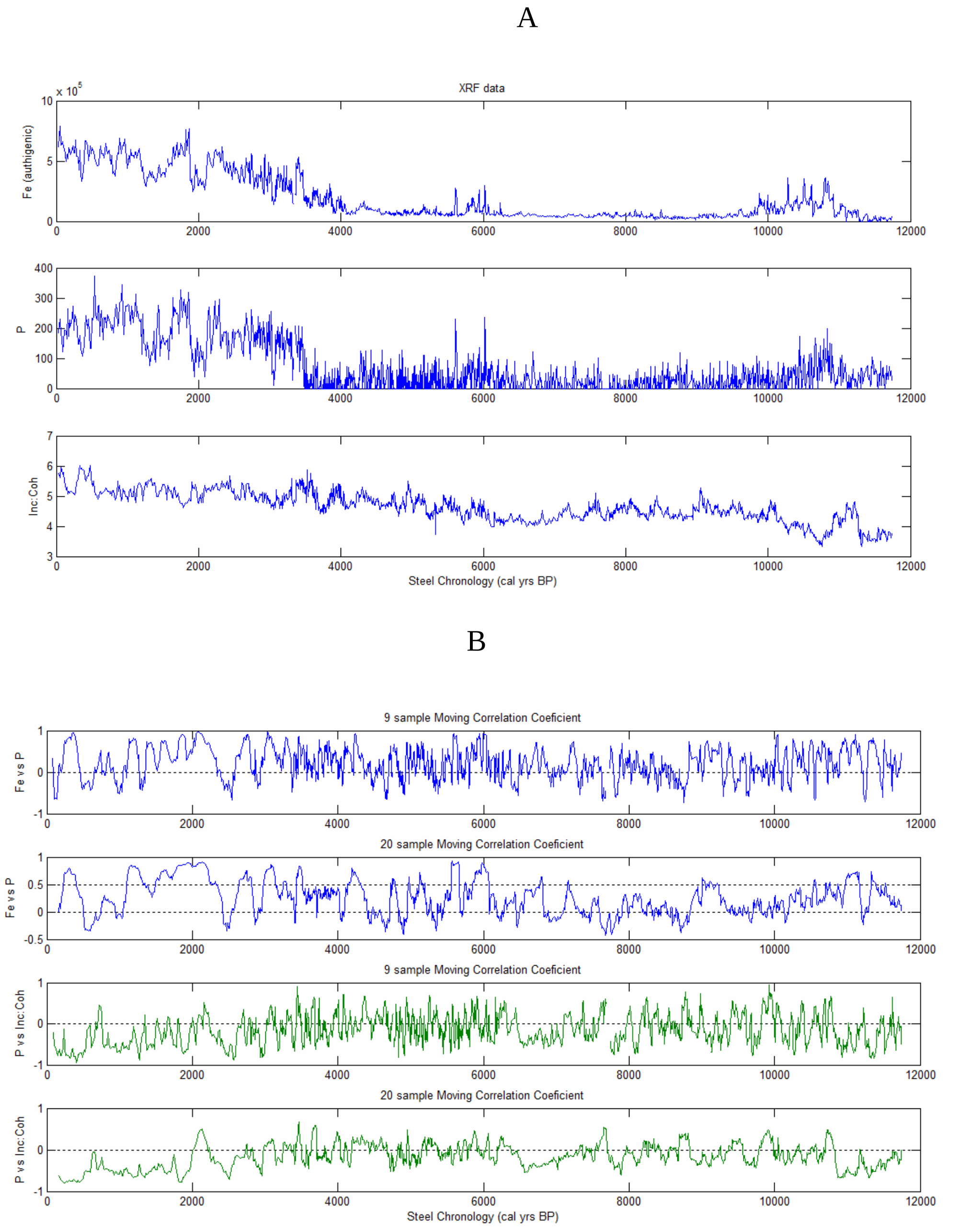


Figure 41 (A) Plots of Fe (authigenic) and P in XRF counts, Inc:Coh, and (B) nine and twenty sample moving correlation coefficients of Fe vs. P, P vs. Inc:Coh showing the relationships between these elements.

Work done on sediments from Elk Lake in the past have shown similar trends in relationships between Fe, P and organic carbon and suggested that when there was a negative correlation between Fe and organic carbon, the correlation between Fe and P had broken down (Dean 1993). While it is sometimes the case that the two relationships are in phase with one another, it is also possible for these parameters to occur out of phase as well. It would seem that during the last 500-700 years, negative correlations between Fe and organic carbon (Inc:Coh) are preceded by a breakdown in the correlation between Fe and P rather than an in phase relationship between the elements (figure 42).

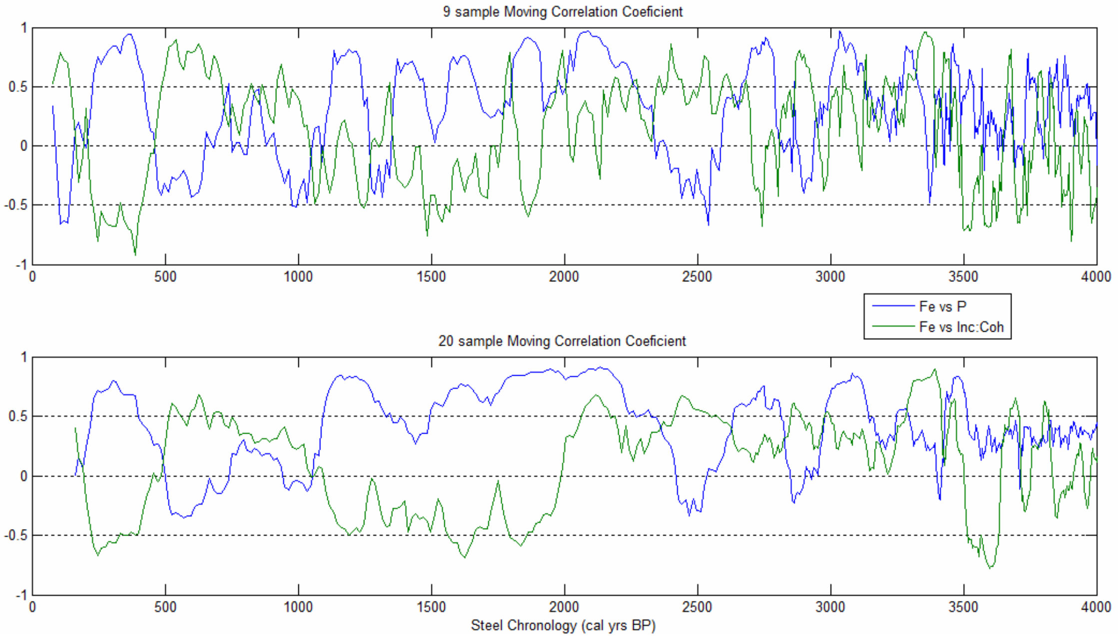


Figure 42 Nine and twenty sample moving correlation coefficient plots of Fe (authigenic) vs. P and Fe (authigenic) vs. Inc:Coh

4.1.2 Carbonate Geochemistry:

The description of processes related to the deposition of carbonate minerals within Elk Lake is somewhat difficult without a comprehensive study of the modern limnology within the lake and the processes that influence the formation and deposition of minerals such as calcite. None the less, it is assumed that the non-silicate Ca curve developed form the XRF data is representative of carbonate deposition through time (figure 43).

As mentioned in the proxy section of the introduction, the most likely process by which carbonates are precipitated is through interactions related to primary productivity in the upper water column of Elk Lake. As photosynthesis takes place in the epilimnion, CO_2 is removed from the water, increasing the pH and allowing for the precipitation of authigenic calcite and other carbonates. While there is definitely some evidence for an increase in salinity during the mid Holocene—which will be discussed in further detail in later chapters—the dominant process resulting in the net burial of Ca during the Holocene is certainly related to primary productivity in the lake.

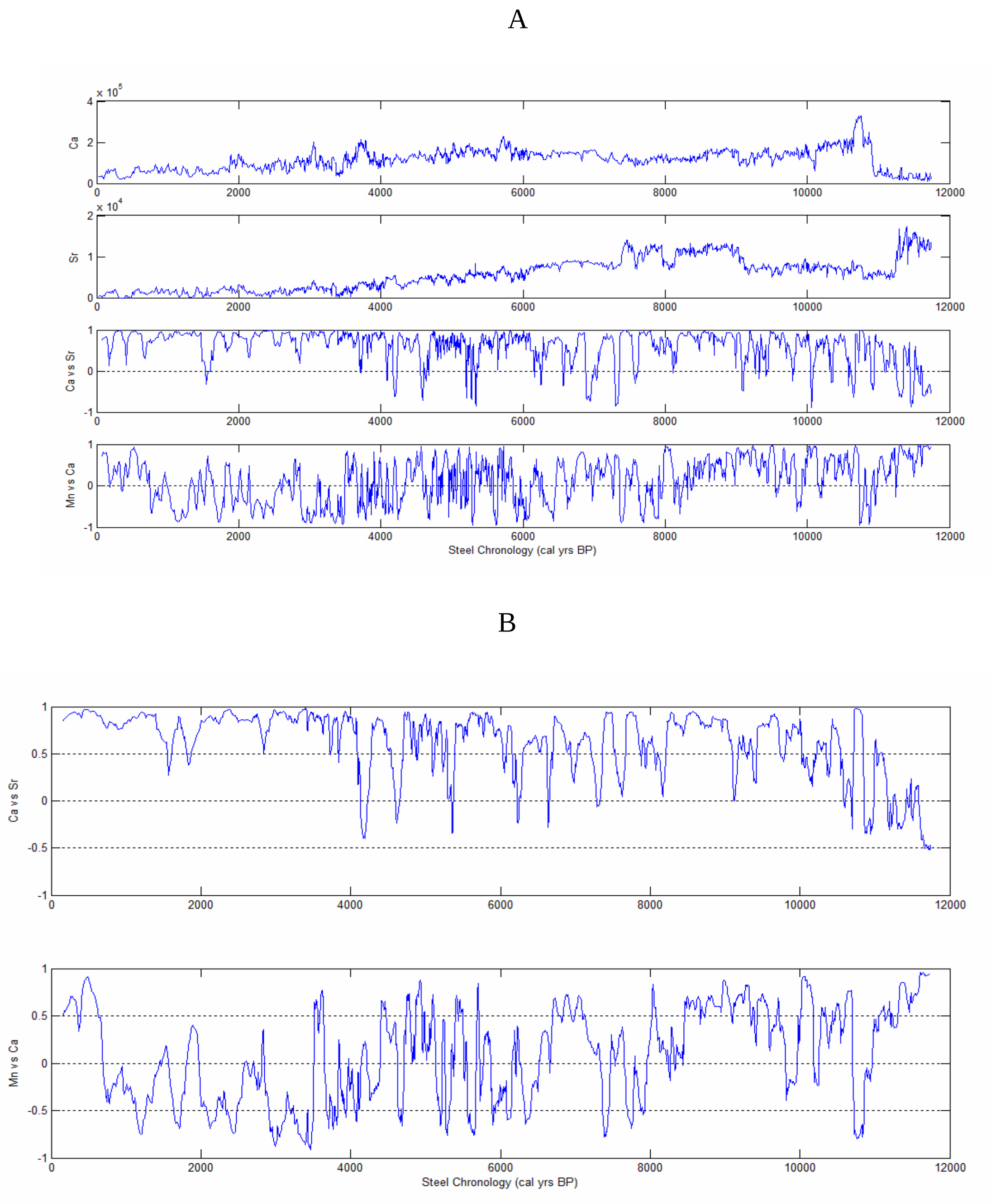


Figure 43 A: plots of non silicate Ca and Sr in XRF counts, and nine sample moving correlation coefficients of Ca vs. Sr and Mn vs. Ca. B: twenty sample moving correlation coefficient plots of Ca vs. Sr and Mn vs .Ca.

It has also been mentioned in previous chapters that the ratio of Sr to Ca could, to some extent, be used as a measure of salinity within the lake. It is difficult to determine the proper ratio of these elements needed in order to begin replacing Ca with Sr due to increases in the salinity of the lake. Empirically, the relationship seems particularly strong as based on the moving correlation coefficient plot of Ca vs. Sr (figure 43). Some of the strontium has been estimated to be derived from clastic sources entering the lake through eolian transport with the other major detrital elements. Due to the strong correlation (figure 43) between these two elements over the vast majority of the Holocene and the estimated portion of the Sr signal related to the detrital and authigenic fractions of the sediment, it is likely that much of the strontium preserved in the sediments of Elk Lake is present in the carbonate fraction. Unfortunately, without direct measurements and evidence of the process by which Sr enters the carbonate structure, a quantifiable measure of salinity through time remains illusive using the XRF alone.

Rhodochrosite (manganese carbonate, $MnCO_3$) is a minor constituent of the sediments, as shown by sediment trap studies (Dean and Megard, 1993), but none the less represents an important process and interaction between elements within the lake. During times when the Sr:Ca ratio and the correlation between these elements suggest increased salinity within the lake, the correlation between Mn and Ca also seems to be particularly strong. During the period between 4000 and 6000 cal yrs BP for example, it would seem that the correlations between Ca vs. Mn and Ca vs. Sr are in phase with each other suggesting that a significant portion of the Mn preserved is in the carbonate fraction.

Intellectually this seems to be a valid statement, while the correlation between Mn and Ca is far more variable than Sr and Ca as a result of the deposition of Mn oxyhydroxides, at this time we would have expected to see an increase in salinity due to the drier conditions of the mid Holocene. Geophysical evidence for a significant drop in lake level will be discussed later, but it suggests a drop in lake level (unconformity in sediments) and it would make sense that the lowest stand preserved would come near the end of the drier Prairie period due to an extended episode (thousands of years) of decreased precipitation.

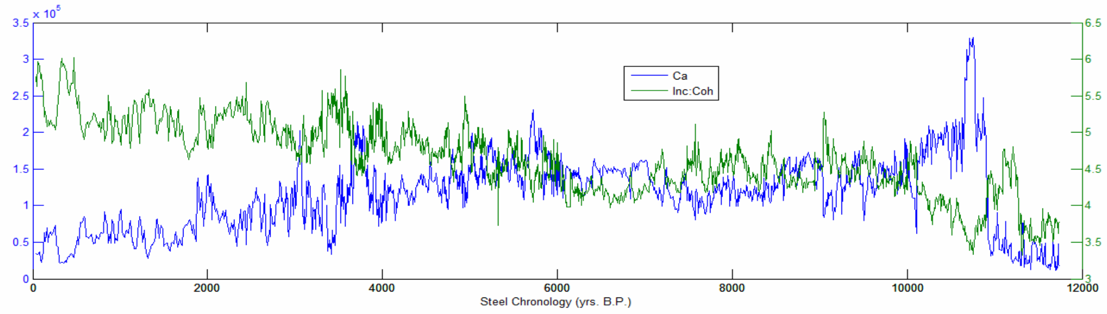


Figure 44 Authigenic Ca (XRF counts) and Inc:Coh ratio (OC) showing the relationship between carbonate preservation and organic carbon content of the sediments. Plotted against the Steel Chronology.

Due to the nature of carbonate precipitation and its relation to primary productivity, it would be expected that as productivity increased in the lake, so should the deposition of carbonate minerals. Figure 45 shows a plot of Ca and Inc:Coh (OC) which would suggest otherwise, at least as far as the preservation of carbonates is concerned. Over the course of the Holocene, the ratio of incoherent to coherent scatter (OC) increases with time suggesting the lake has become more productive. While higher productivity would certainly affect the pH of the upper water column and allow for greater precipitation of calcium carbonate, the increased amount of organic matter in the bottom waters and sediments of the lake would allow for greater bacterial respiration and a decrease in the pH at depth. This process is illustrated by figure 44, showing that over time, particularly since 6000 cal yrs BP, productivity has been increasing and the amount of preserved Ca has been decreasing, most likely the result of increased bacterial respiration in the bottom waters causing a decrease in the pH and the preservation potential of carbonate minerals. But it is also possible that the trend seen in these parameters is simply a result of dilution as other elements increase in their contribution to the sediments of Elk Lake.

4.1.3 Clastic Signal, Weathering, and Eolian activity:

One of the more intriguing parts of the Elk Lake record is present in the clastic signal. Elements such as Ti, K, Si, and Fe (detrital) all tell a chapter in the history of the region that sheds light on some of the more dramatic events of the past. These clastic elements help to describe the transition of the lake from the Post Glacial period through the mid Holocene and the drier conditions associated with changing atmospheric patterns and vegetation in the region. In the following discussion, major periods in the lake's history related to changes in the amounts of clastic material and other geochemical signals will be revealed.

4.1.4 Relationship between XRF data and past studies of pollen stratigraphy:

Previous studies of Elk Lake sediments determined the timing of various stages of the lake's evolution through the study of pollen stratigraphy. In order to tie into this pollen data, the Steel Chronology was applied to the pollen data from these studies (Bradbury, Dean, and Anderson, 1993). The following plot (figure 45) shows the relationship between the major elements used for this study and the pollen data from previous research. The fit is not entirely perfect due to the application of the Steel Lake radiocarbon dates to the pollen data which is at a fairly low resolution. Nonetheless, the major periods as will be described in the following sections show that there is a generally reliable relationship between the pollen types entering the lake at various times during the Holocene and the geochemical data from the XRF.

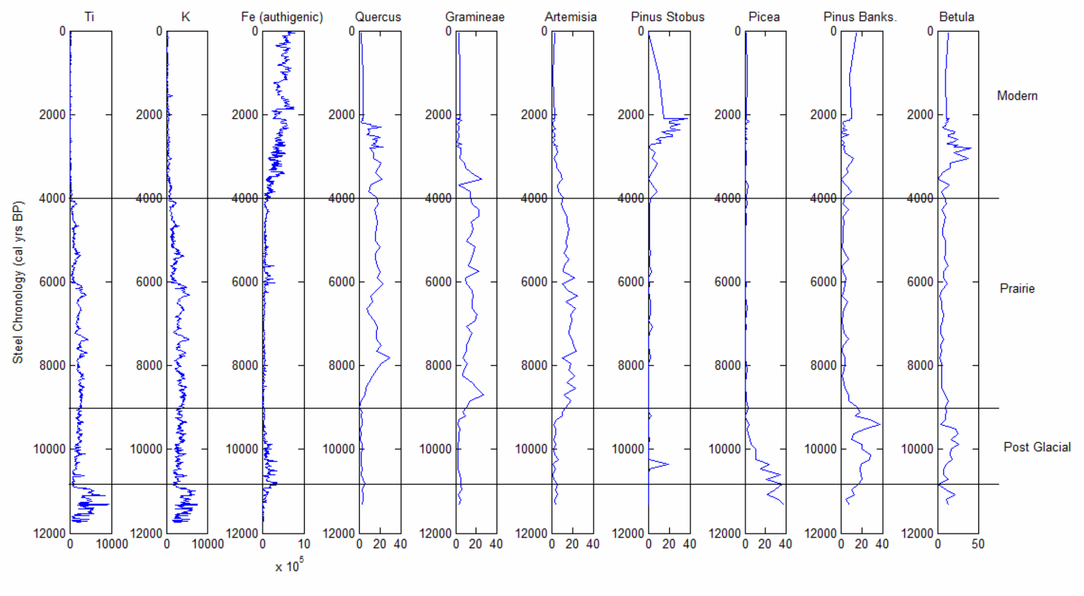


Fig 45. Comparison of geochemical and pollen data. Ti, K, and Fe (authigenic) plotted in XRF counts. All pollen types plotted as mass accumulation rates (MAR in mg dry sediment/cm2/yr). Period names and duration for this study are based on the geochemical data, and only indirectly on the pollen data. This figure is used to illustrate that the two datasets provide similar, although not perfect, results for the timing of different periods in Elk Lake's history.

4.2 Major Periods in Elk Lake's history: Geochemical Evolution:

The three major periods in the Elk Lake record as presented in previous research (Bradbury, Dean, and Anderson 1993) are reflected in the more recent XRF data. The Post Glacial period began with the complete melting of the ice block, the Prairie period is associated with the drier conditions of the mid-Holocene and the final Modern period covers the last few thousand years. While these periods are present in the data, the timing and duration of these events are slightly different due to the age scale developed for this study and the use of the Steel Lake chronology (Wright 2003).

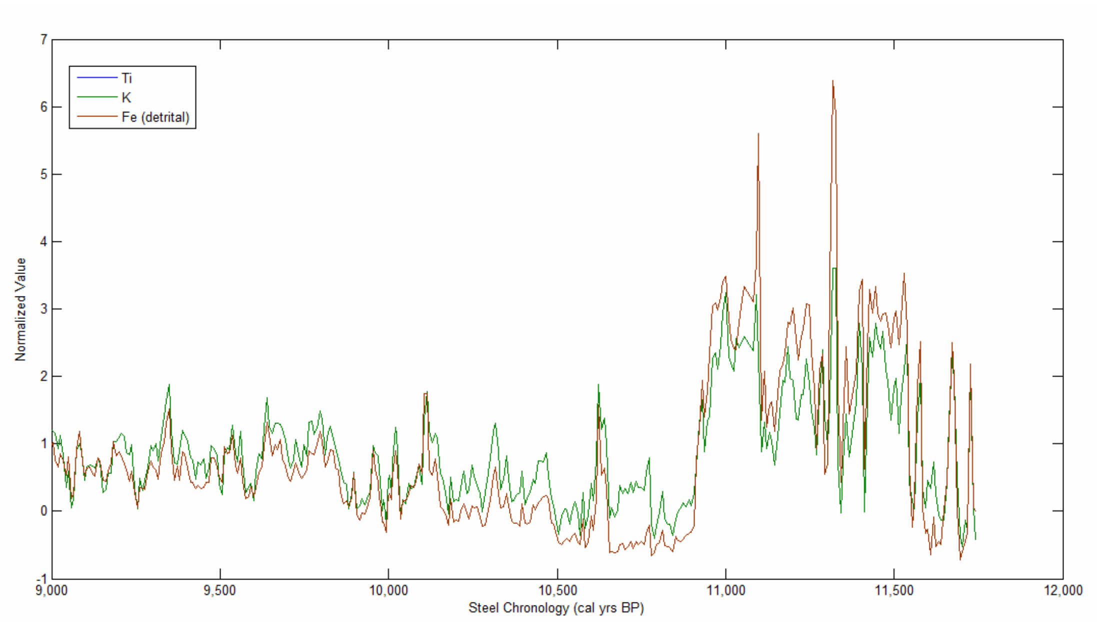
Higher resolution (200micron) runs were done on 20cm section from each of the three main phases of Elk Lake's history in order to evaluate inter-annual variability within the periods.

4.2.1 Post Glacial Period: 12,000-11,000 cal yrs. BP

The very bottom of the cores recovered and used in the development of the continuous record contain glacial outwash sands and gravels and are marked by high concentrations of clastic indicators including Ti which has its highest XRF counts of the entire record at this depth/age (figure 46). Outwash would have been deposited both below and on top of the ice block as it was melting. The material on top of the ice was deposited by the St. Louis sub-lobe during the re-advance of the Des Moines lobe.

Approximately 11,200 cal yrs BP, the concentrations of Mn and Fe began to increase dramatically, presumably due to increased groundwater flow into the lake as the ice block was nearing the end of its melting process. At this time, Ti levels remained high. It is possible that these elevated levels were caused by high runoff or wind driven transport of clastic material into the lake, but turbidity currents and slumping/sliding as a result of over steepened slopes created by the boundaries of the ice within the basin are more likely (figure 46).

I postulate that around 10,900 cal yrs BP the ice block had completely melted as indicated by the deposition of discrete and undisturbed laminations and the initiation of varved sediments in the cores recovered. The rapid decrease in Ti concentrations suggest a distinct decrease in clastics entering the deep hole of the lake—thus drop in the occurrence of turbidity currents— and the disturbance of laminations associated with slumping and sliding. The decrease in clastic material is concurrent with increases in Mn and Fe as a result of increased groundwater flow into the lake that was blocked or greatly reduced by the presence of the ice block (figure 46). The timing of the complete melting of the ice block is consistent with radiocarbon dates taken from terrestrial organic material at the base of the lake (Wright 1993). At the same time as the increases in Mn and Fe occur there is a dramatic increase in the concentration of Ca (assumed to represent $CaCO_3$). All three of these elements are likely derived from the fresh calcareous tills of the area and soil development in the basin.



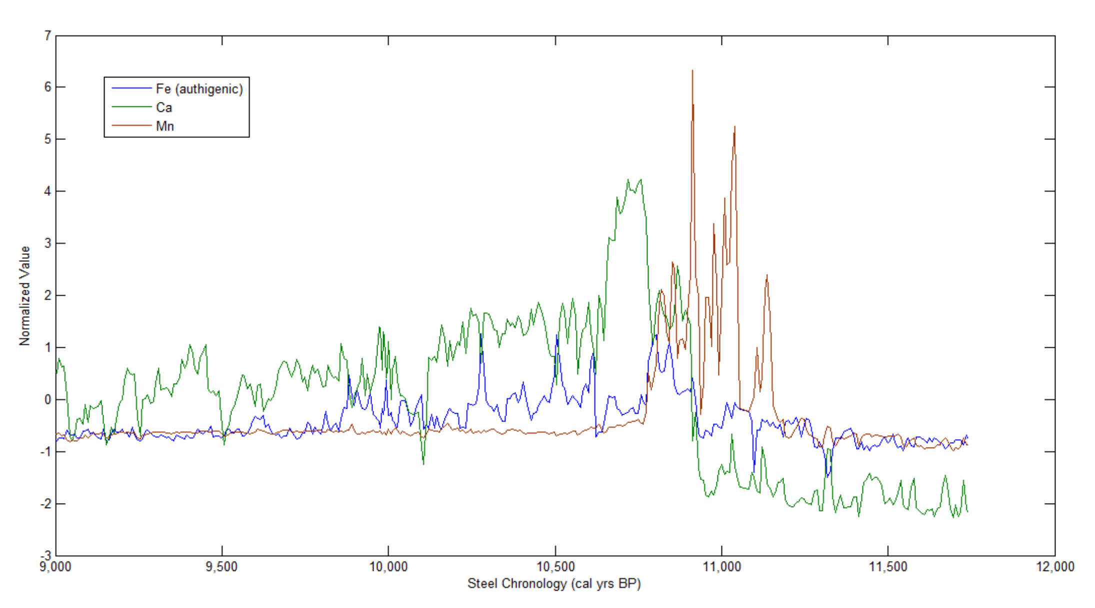


Figure 46 Plots of major elemental constituents of the Elk Lake sediment cores. All data has been normalized and is plotted in Standard deviations against the Steel Chronology.

4.2.2 Post Glacial: 11,000-9,000 cal yrs BP:

Between 10,900 and 10,850 cal yrs BP, varves begin to develop and the presence of disturbed laminations and deposits related to turbidity currents decrease. Beginning at 10,900 cal yrs BP Ti is at is lowest level while Mn and Fe (authigenic) remain at relatively high values for this period, but within about 100 yrs, the conditions of the lake change fairly dramatically. From a minimum, Ti begins to gradually transition to higher values while ions that were being brought into the lake by ground water flow decrease (authigenic Fe, Mn, Ca). This would suggest a rapid change in the amount of available moisture coming into the region and a portent of the dry conditions associated with the mid-Holocene. During the period between 10,700 and 9,400 cal yr BP, the Ti curve shows gradually increasing counts with several peaks in concentration. Authigenic Fe, Mn, and Ca seem to be mostly, although not entirely, in phase with Ti suggesting alternating periods of calm and dry conditions with periods of storminess (higher rate of mixing) and higher precipitation (increased ground water flow) leading to increased deposition of oxyhydroxides. The same stormy periods would have led to greater deposition of wind borne clastic material. Previous researchers noted that climate models during this time suggested a decrease in the strength of anticyclonic winds associated with the ice sheet (as it retreated and decreased in size), and a low pressure system that was moving to the northeast (Bradbury, Dean, and Anderson, 1993). Time series analysis of the period between 10,700 and 8,000 cal yrs BP suggests a frequency for the alternating wind patterns of approximately 153-170 years which is consistent with the timing between peaks in the clastic signal (figure 47). The relationship between these two air masses could have led to the alternating stormy and calm conditions that could produce the signal we see in Ti, Fe, Mn, and Ca during this time period. It is possible that this approximately 150-year cycle is related to variability in solar activity having an effect of the strength of both westerly zonal winds and the anticyclonic southerly winds, but there is little evidence to support this claim. All other peaks in the time series analysis are of frequencies that are too long and the selected period in the record does not contain enough of these cycles for them to be statistically valid.

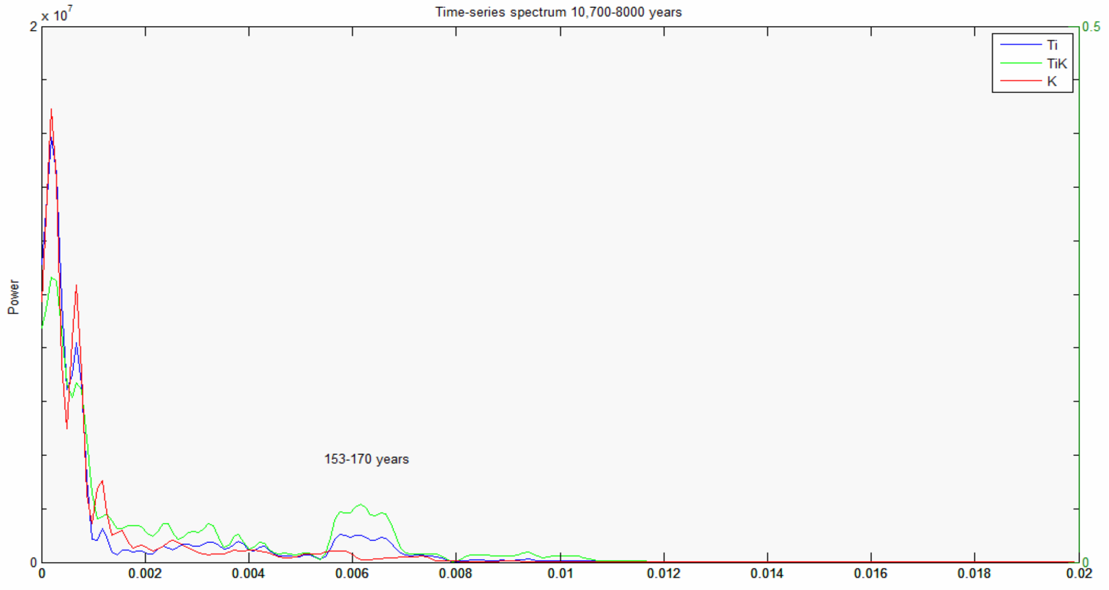


Figure 47 Time series analysis of the Ti, K, and Ti:K data for the period between 10,700 and 8000 yrs. BP. Shows a particularly strong cycle related to the interplay of the Pacific air-stream and the anticyclonic winds associated with the Laurentide ice sheet. Time period of 10,200 to 8000 was chosen in order to capture enough cycles to make a statistically valid assessment of the periodicity of the atmospheric interactions between the Pacific and anticyclonic (Arctic) airstreams during the post glacial period.

The ratio of Ti to K during this period suggests that, due to the high amount of potassium relative to titanium (see figure 36), the material entering the lake in the clastic fraction was fresher than the material that would be deposited later on in the Holocene. This fresh clastic material was likely derived from the glacial margin of the Laurentide ice sheet and transported by southward moving winds.

Around 9.4 ka the “peakiness” of the Ti record decreases and levels out while Fe (authigenic) and Mn are at some of the lowest values seem in the entire record. This could be explained by an end to the arctic anti-cyclonic air patterns as the Laurentide ice sheet neared the end of its existence and the zonal, westerly air movement coming from the Pacific moved northward, bringing more dry air to the region, stabilizing the climate as one atmospheric system became dominant over the other (Pacific over the Arctic anticyclonic winds). During this same time, as shown by pollen assemblages from Steel Lake, there was a transition from Pine to prairie grassland pollens like those seen today in western Minnesota (Wright 2003). This marks the beginning of the so called Prairie period.

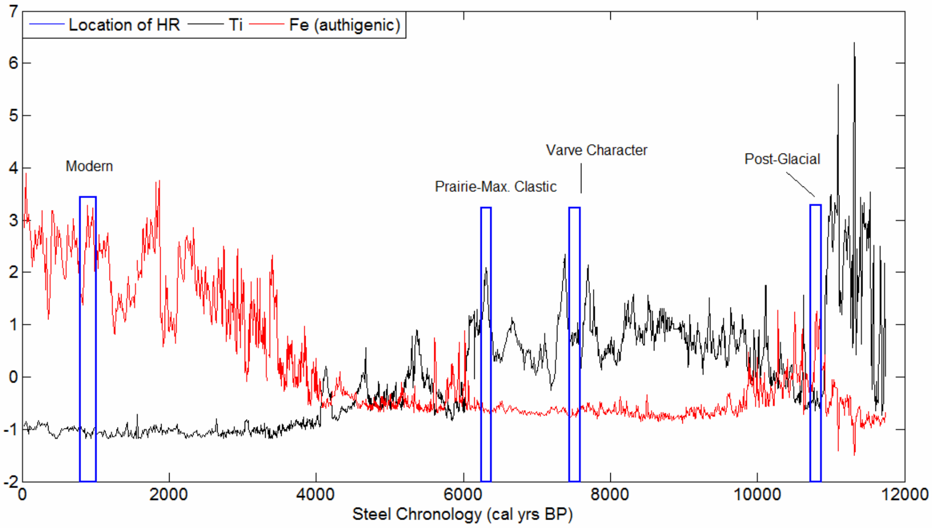


Figure 48 Location of high resolution runs. Ti and Fe (authigenic) data plotted in normalized values (y axis) of the entire Holocene record showing the location of all high resolution 200 micron runs including Post Glacial High Resolution.

Time series analysis and concentrations through time of elements (1 cm resolution data) within this period of the lake's development help to illustrate variability on the scale of the Holocene and long term changes, but high resolution 200 micron scans of 20cm of sediment within this time period help us to describe climatic changes on the scale of individual years. The varves during the post glacial period are fairly simple compared to what is seen in the modern lake consisting of a two component system that includes mostly authigenic iron and calcium carbonate with some inputs of clastic material (figs. 49 and 50).

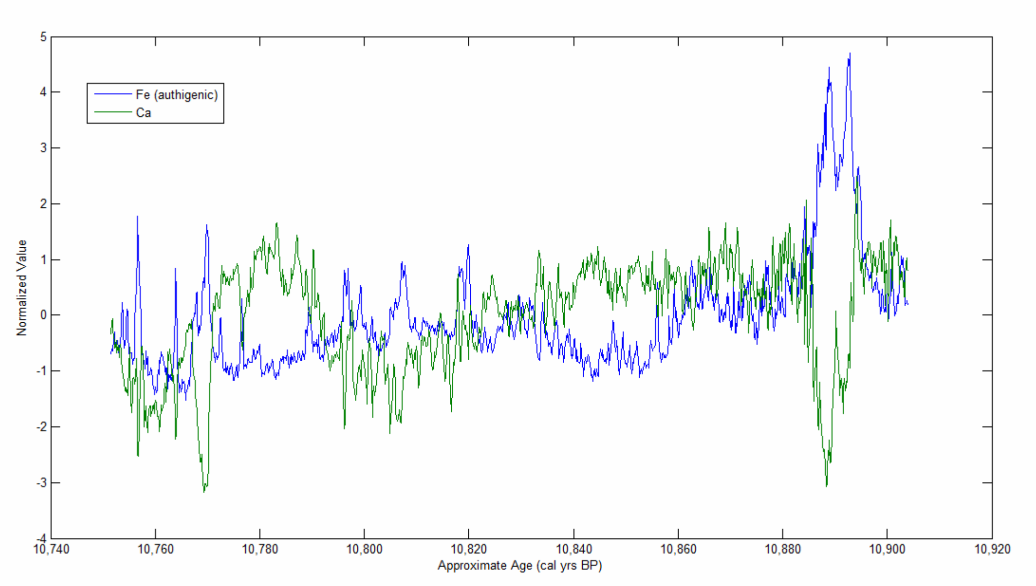


Figure 49 Normalized Post glacial Fe (authigenic) and Ca data plotted against an approximate age scale developed by counting varves using the geochemical signal of Ca (calcium carbonate) that has one major seasonal peak each year related to algal photosynthesis.

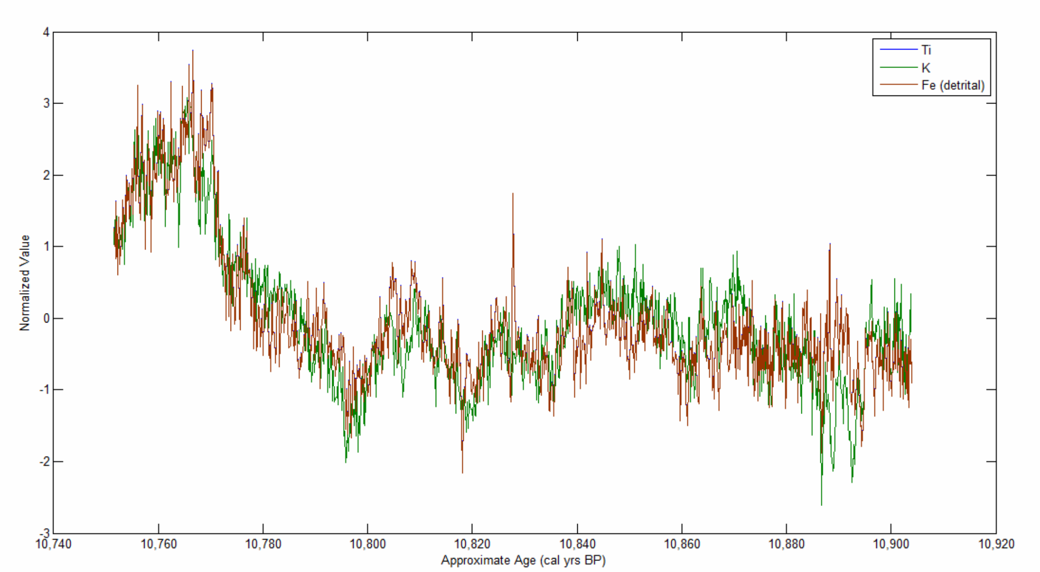


Figure 50 Normalized Post glacial Fe (detrital), Ti and K data plotted against an approximate age scale developed by counting varves using the geochemical signal of Ca (calcium carbonate) that has one major seasonal peak each year related to algal photosynthesis.

It is clear that calcium and authigenic iron are certainly out of phase with each other due to the seasonality of their depositional conditions and over the course of the entire high resolution data there is significant change in the relative contributions of these elements (figure 51). Calcium carbonate would have precipitated and been incorporated into the sediments during the summer months in response to algal photosynthesis. Iron oxyhydroxides, while a constituent of the sediment rain year round (Dean, 1993), would have formed distinct gel like laminations during the winter months and specifically during autumn and spring overturning periods (Dean, personal comm., 2010). It is also evident, form figure 49 that there was significant variability in the nature of these elements’s deposition over the course of a short time period and an interesting overprint of clastic material showing increasing concentrations (figure 50) later in the high resolution record of post glacial sediments (likely related to the interplay between atmospheric systems associated with anticyclonic winds and low pressure systems in the southwest shown by climate models for this time period).

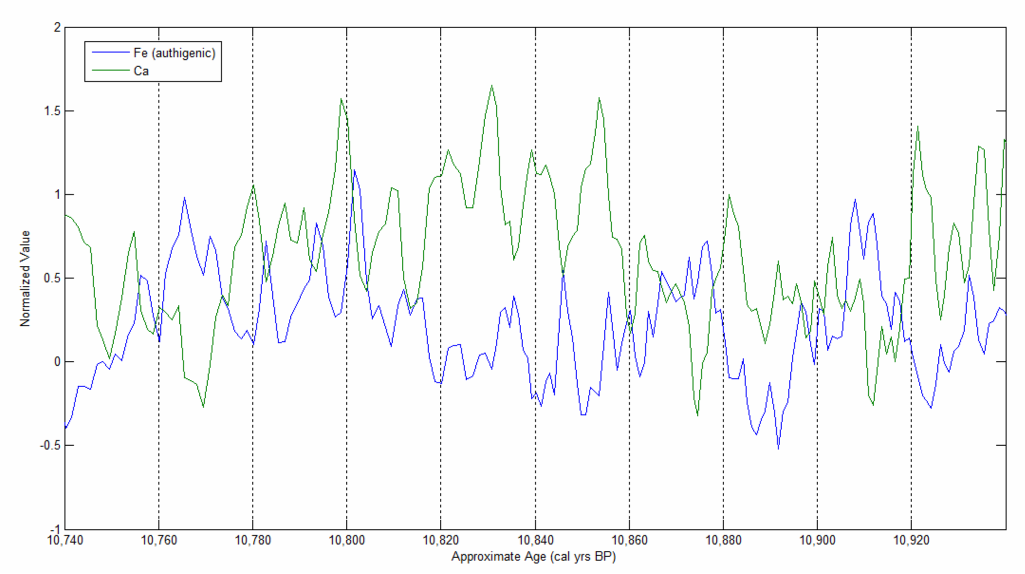


Figure 51 Normalized Post glacial Fe (authigenic) and Ca data plotted against an approximate age scale developed by counting varves using the geochemical signal of Ca (calcium carbonate) that has one major seasonal peak each year related to algal photosynthesis. Zoomed in to facilitate the discussion of varve characteristics during the post glacial period of Elk Lake's history.

Figure 51 shows alternating peaks of Ca and Fe (authigenic). In any given year there tends to be one major and occasionally minor seasonal peaks in the concentrations of carbonates (Ca) bounded by a peak in authigenic iron. This would be expected based on the nature of deposition for each of these elements. Where, calcium carbonate is incorporated into the sediments during the summer months when productivity is highest in the lake and iron oxides would be deposited when anoxic bottom waters rich in dissolved iron mix with oxygenated surface waters during fall and spring overturning as well as the winter months. While the relationship does not always hold true, it would seem that these processes typically occurred in Elk Lake during the post glacial period just as they do today.

The clastic signal within this high resolution section from the post glacial period, shows high variability, which is be expected for elements entering the lake through eolian transport. This is expected due to the nature of wind and the processes that determine the strength, speed, direction, and duration of any given wind pattern as well as the seasonal nature of clastic influx which will be greatly reduced during periods of ice cover.

Time series analysis of the post Glacial high resolution data was done using a Single Spectrum Analysis (SSA) to filter the data (for frequencies of interest) and the Multi Taper Method (MTM) described as the most useful combination of methods for the identification of cyclicity and climate variability (Gihl et al, 2001). SSA is useful for the identification of modes of interest and filtering out others. This enhances the signal to noise ratio of the data for subsequent time series analysis (Gihl et al, 2001). Through filtering the data researchers can identify frequencies that would other wise be drowned out by lower frequency cycles. The MTM method of time series analysis uses fewer assumptions and is generally more robust than other methods of spectral analysis (Gihl et al, 2001). Plots of the filtered frequencies and cycles/periodicities associated with various frequencies are shown in figures 52 and 53.

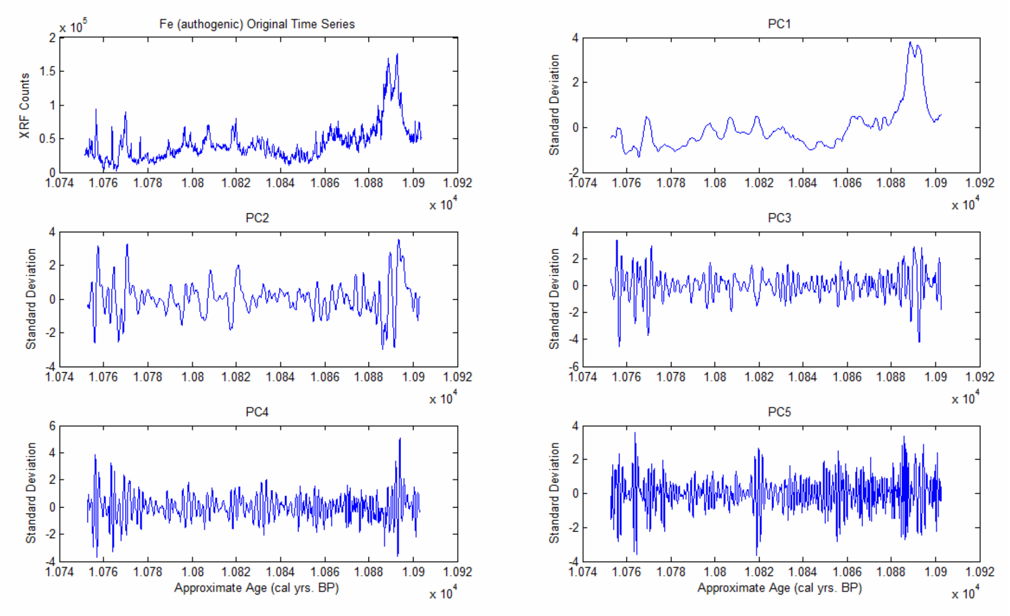


Figure 52 Authigenic iron signal from the post glacial high resolution data (top left). All other plots are the PC (principle component frequencies) as determined through Single Spectrum Analysis (SSA) using Analyseries. All PC data has been normalized and is plotted as standard deviations. Everything is plotted against the approximate age scale based on counting annual peaks in Ca concentration.

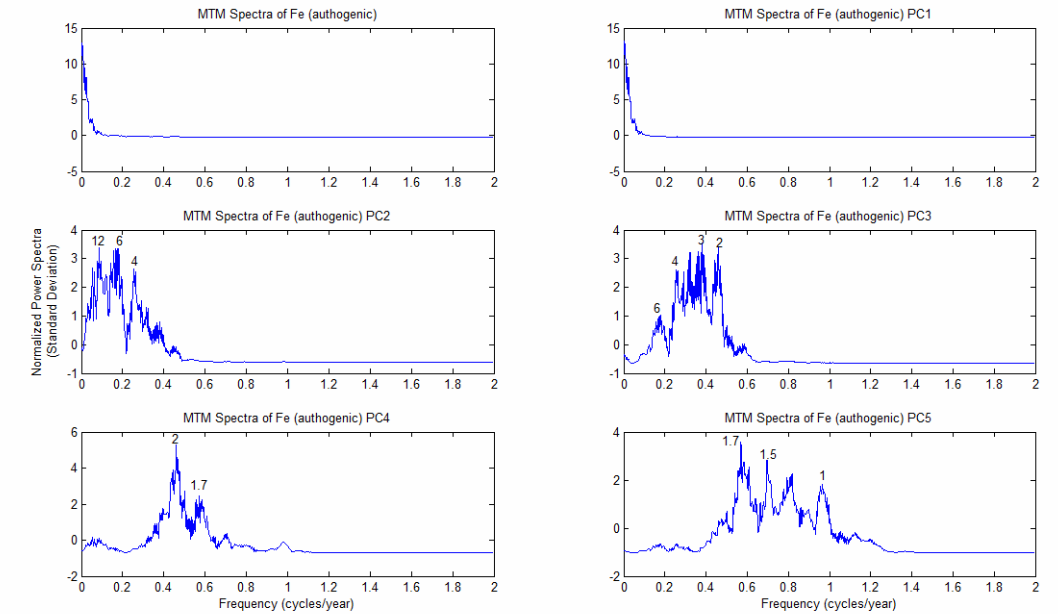


Figure 53 Authigenic iron time series analysis of the entire high resolution post glacial section and each of the PC frequencies showing various cycles within data and inter annual variability.

The filtered data (PC1 through PC5) for authigenic iron samples various ranges of frequencies and periodicity allowing for higher frequency cycles to become visible during time series analysis. Fe (authigenic) shows almost identical spectra to Ca, Ti, and K for the high resolution post glacial data. The fact that all these elements, despite their different origins and depositional requirements, show strong similarities in time series analysis supports the idea that the climate was influenced by variability in the dominance of the Arctic and Pacific air-streams. When the Pacific air-stream entered the region it brought storms following the strongest westerlies, leading to increased wind turbulence on the lake and thus more oxygen to create Fe and Mn oxyhydroxides (as well as increased groundwater flow due to increased precipitation). The same winds would also bring with them influxes of clastic materials (Ti, K, etc.).

It is plausible that the 12 year period seen in the MTM spectra of PC2 could be related to cycles of solar activity which have been shown to have a periodicity of approximately 11 years. The 3 and 6 year cycles could be related to El Nino Southern Oscillation (ENSO). Unfortunately, there is little direct evidence to support either of these claims. The strongest cycles seen in the time series analysis of the post glacial high resolution data is the 2-year cycle suggesting significant inter annual variability in the data during this time (figure 53).

The obvious variability seen in both the 1 cm and 200 micron data sets for the early Post Glacial Elk Lake is supported by the time series analysis which suggests some longer term variability such as the interplay seen between the anticyclonic winds and the

Westerlies, as well as short term inter annual variability with periodicities ranging from 12 year cycles to 2 year and sub annual periodicities.

4.2.3 Prairie Period: 9,000-6,000 cal yrs BP:

From 9,000 to 6,000 cal yrs BP, the conditions remained relatively dry and dominated by eolian fluxes into the lake as evidenced by the high concentrations of Ti, K, and other elements associated with the eolian clay fraction (figure 55). This period would likely have had the driest conditions seen since the end of the last glaciation showing low concentrations of elements/ ions that are brought into the lake through groundwater flow which would have decreased as precipitation decreased. There is a significant drop in authigenic Fe and a subsequent increase in the amount of detrital Fe entering the lake. The Prairie phase is the only major period in the Elk Lake Holocene record when the sediments of the lake were composed of less than 90% authigenic material (Dean 1993). The peaks in the clastic signal are presumably related to an increase in the amount of wind driven clays and silts entering the lake from the plains to the west of the region.

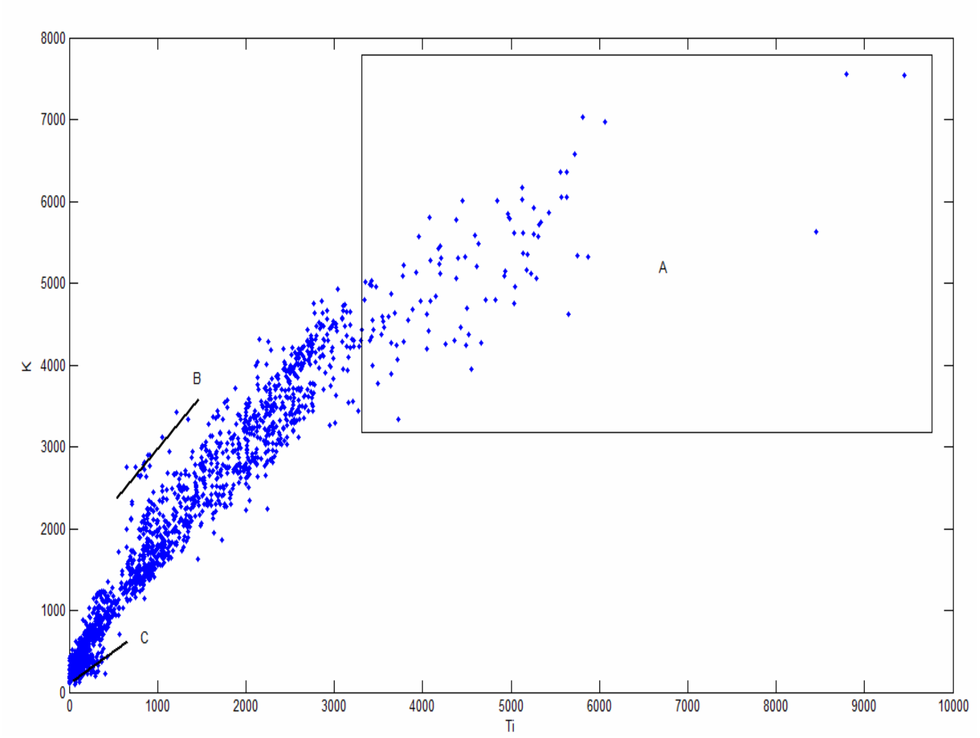


Figure 54 Scatter Plot of Ti vs. K (in XRF counts). Box A: Glacial Outwash, Line B: early Post Glacial sediments, Line C: 1 cm clay layer approximately 750 cal. yrs. BP.

The K:Ti ratio (figure 54) shows that there was little to no change in the source area of the clastics throughout the majority of the mid Holocene. The best possible source for the solid phase material entering the lake is from the plains to the west of the Lake, particularly the Lake Aggassiz lake bed which would have been recently exposed by the retreat of the ice sheet allowing the glacial lake to drain into the Atlantic through Hudson Bay.

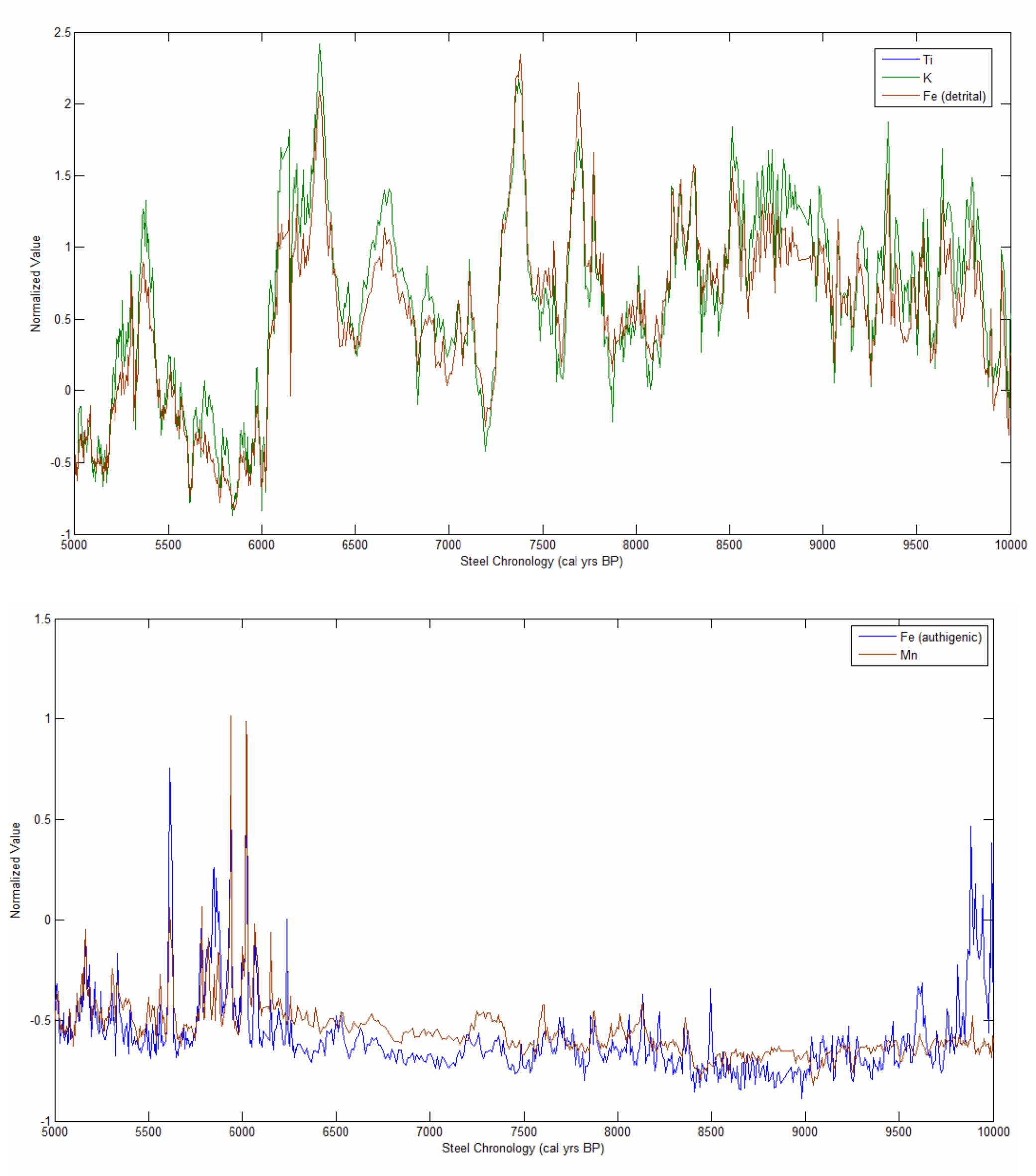


Figure 55 Plots of major elemental constituents during the period from 5,000 to 10,000 cal yrs BP. All data has been normalized and is plotted in standard deviations vs. time.

Previous researchers have suggested that a change in atmospheric circulation occurred over North America causing the so called "8.2 cold event" seen in Greenland ice cores and other data sets from around the North Atlantic (Dean, Forester, and

Bradbury 2001). The 8.2 event seen in Atlantic proxy records has been attributed to the catastrophic flooding of the North Atlantic by fresh melt water including Lake Aggassiz and Ojibwa which, while dating these drainages is difficult, occurred at approximately 8.2 cal ka BP. Changes in the geography of the area—the loss of a major ice sheet and the exposing of large areas of land that had been covered with melt water—would have led to a significant changes in the atmospheric circulation patterns of the region and would have allowed for the northward expansion of the westerlies which had been pushed south by the presence of the ice sheet.

This event has been associated with changes in air movement dominated by the presence of the Laurentide ice sheet creating southward flowing wind patterns that brought Artic air to the location of Elk Lake to circulation dominated by the Pacific air-stream bringing dry eastward moving air to the region as the westerlies were able to move north and the Luarentide ice sheet diminished. In contrast, when the ice sheet was at a more southerly extent (see fig 56) winds moving south off of the ice sheet would have forced the jet stream further south than it is seen today. This would have made the Pacific air-stream also follow a more southerly route as it moved west across the North American continent. Thus, the dry Pacific air would have only entered the region of Elk Lake on occasion when the southward moving anticyclonic winds were weaker. As the ice sheet retreated northward, the jet stream and the Pacific air-stream would have moved further and further north, eventually reaching Elk Lake and becoming more dominant in their influence on the regional climate.

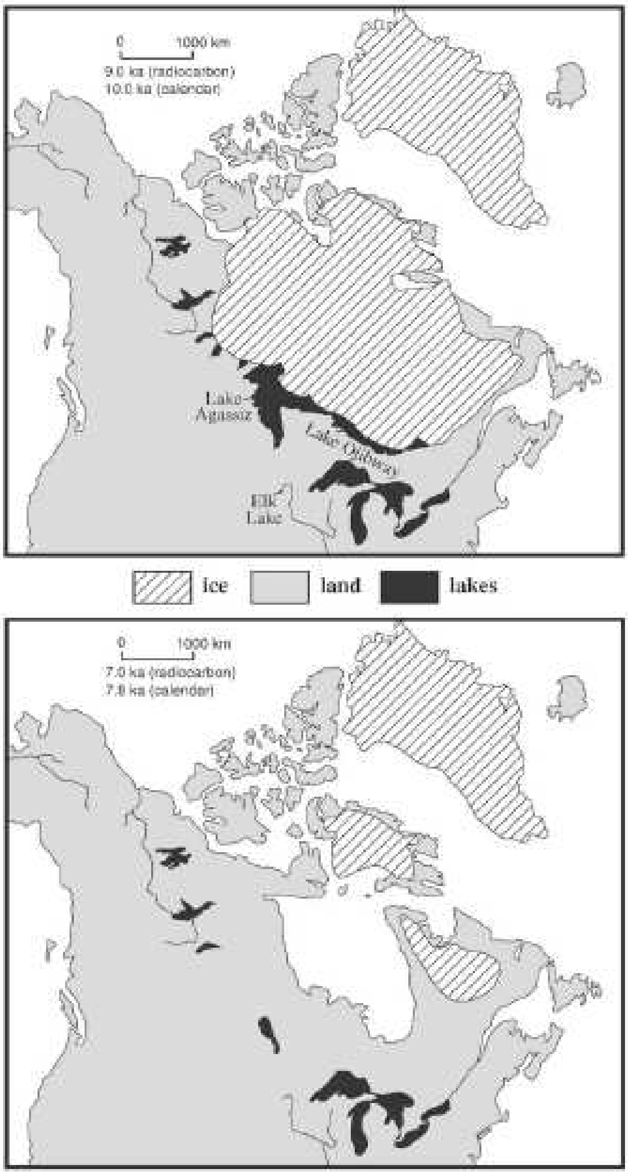


Figure 56 Map showing the relative distribution of land, water and ice at 10 and 7.8 ka cal. yrs BP. From Dean, Forester, and Bradbury (2001).

Climate shifts associated with the 8.2 event would be expected to be recorded by Elk Lake sediments by increased abundance of clastic material (wind borne) in the sedimentary record preserved in Elk Lake but there is no clear 8.2 event seen in the data set. This suggests that while the processes (changes in atmospheric circulation related to the demise of the ice sheet and the loss of large amounts of surface water) described by Dean (Forester, and Bradbury, 2001) may in fact have occurred; they did not produce a significant signal in this data. Thus, it is difficult to show that the 8.2 event seen in the Greenland ice core record was either a cause or effect of changes that occurred in the land cover of North America.

It is also possible that the error present in this dataset is such that there is a signal related to the 8.2 event but due to the nature of the age scale developed for this study, it is misplaced. Another, more plausible, explanation is that due to the lower resolution of previous work and the 1000 year offset in the age scale, a large change in elemental concentrations was seen because of a lack of data between samples when in fact the change was more gradual and time transgressive (Dean 1993, Wright 2003). None the less, the clastic signal suggests that the drying of the region occurred over an extended period of time rather than a quick and discreet event. The loss of the large pro-glacial lakes and the ice sheet certainly had an influence on the regional climate. As ice cover and large lakes decreased in size changes in the processes by which solar energy was absorbed and distributed throughout the region, as well as, changes in atmospheric dynamics led to a decrease in available moisture.

Previous research showed that the maximum influx of detrital clastic material occurred at 5700 varve years B.P. (Dean, 1993). Based on the time discrepancies between the varve year counts of earlier work and the application of Steel lake radiocarbon dates (Wright 2003) to this work (that varve years are 700-1000 years too young), the maximum clastic peak in the XRF data is consistent with work done in the past—peaking at 6300-6400 cal years B.P(figure 55). An interesting note is the presence of two very large clastic peaks occurring before this maximum at 7300 and 7700 years B.P. Each of these two events is very similar in magnitude and duration to the maximum clastic influx of 6300 years B.P. Although, time series analysis did not find any statistically significant cycles in the period between 4000 and 8000 cal yrs BP, it appears that major peaks in clastic input seem to occur approximately every 1000 years during this time.

Inferences to a low stand in Elk Lake during the time of the maximum clastic influx have been made in the past. Presumably, the maximum deposition of clastic material should coincide with the driest conditions in the region of Elk Lake (Dean and Anderson, 1993; Stark, 1976; Forester and other, 1987). Because the wind borne transportation of clastic material requires that conditions be dry enough to mobilize the material, it is easy to imagine that when the final major influx—which happens to also be the largest influx of this material—occurs, the upper Midwest would have had to be significantly drier than in it had been previously. With the addition of the geophysical data collected for this study, it is now clear that there was certainly a low stand in the history of Elk Lake. While the XRF provides little direct evidence for the timing of this event in the cores recovered from Elk Lake, it would seem that 6300 yrs. BP. is the mostly likely timing for the lowest of low stands in the lake to occur.

While the Sr to Ca ratio does not directly record salinity within the lake, the ratio generally shows higher values in the years leading up to the maximum clastic influx in Elk Lake (fig 57). This helps to support the claim that the lowest of stands occurred around the time of the maximum clastic influx. Moving correlation plots seen in previous chapters show that the relationship between Ca and Sr imply, at least during this time, the two elements were both closely associated and present in the carbonate fraction of the sediments. While the timing of the highest Sr:Ca ratio occurs slightly before the maximum peak in clastics, it can be said with confidence that the lowest stand occurred within a 40 year period between 6300 and 6340 cal yrs BP and considering the nature of the age scale for this study, this is a fairly robust estimate for the formation of the unconformity as seen in the geophysical data set.

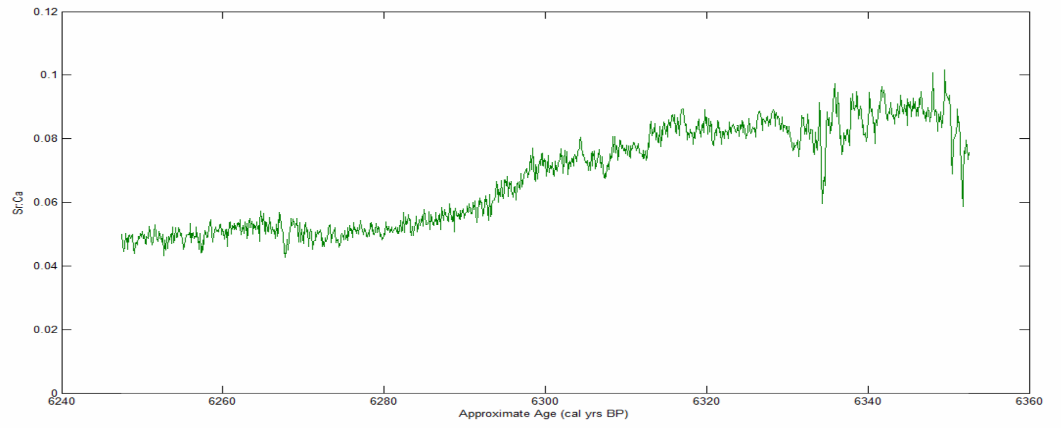


Figure 57 Plot of the authigenic Sr to Ca ratio for the 200 micron Prairie period XRF data plotted against time.

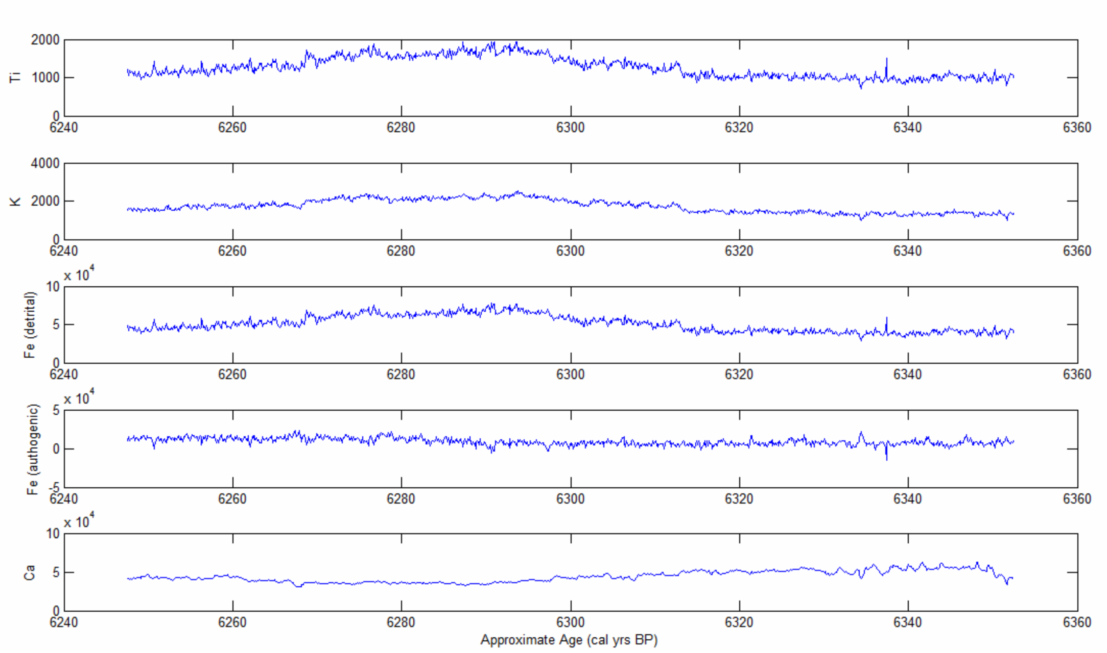


Figure 58 plots of Ti, K, detrital Fe, authigenic Fe, and Ca all plotted in XRF counts against time. Data if from the 200 micron Prairie period XRF data set.

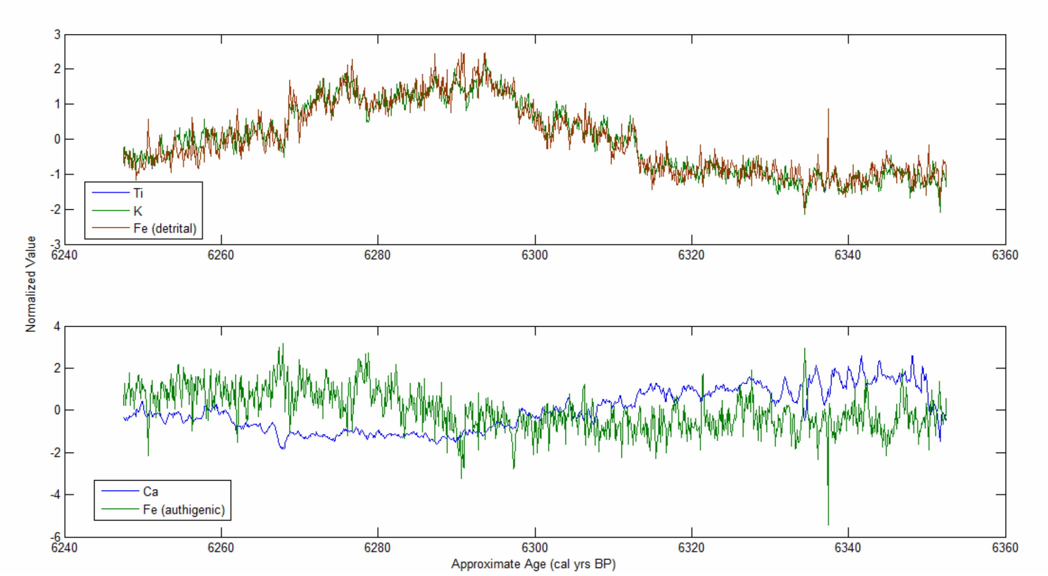


Figure 59 Normalized Ti, K, detrital Fe, authigenic Fe, and Ca data plotted in standard deviations against time.

High resolution (200 micron) data centered on the maximum clastic influx at 6300 cal years BP shows some of the variability that took place during this time (figure 59). On top of the general story, for the mid Holocene-Prairie Period, with a seemingly, but statistically vague cycle of major clastic peaks occurring approximately 1000 years apart, there is significant inter annual variability. Time series analysis using the SSA filter and the MTM methods (Ghil, 2001), suggests the strongest periodicities in the deposition of Ti (figure 60 and 61)—which are almost exactly like K, and detrital Fe— of 3-4 years as well as a distinct 1 year cycle. Both of these high frequency periodicities in the clastic record would be expected when discussing elements that are transported to the lake through eolian processes. Because of the nature of wind and the many variables that determine speed, direction, intensity and duration, it is not hard to imagine that during a time when the majority of sediment entering the lake is derived from wind borne process that there would be significant inter annual variability superimposed on the long term variability and changes in the record. There is also a notable loss of the 12-year (possibly solar activity) and 6-year (possibly ENSO) cycles/frequencies seen in the earlier, post glacial high resolution (200 micron). This could mark a decrease in the strength or influence of the ENSO band and/or solar forcing relative to the post glacial period.

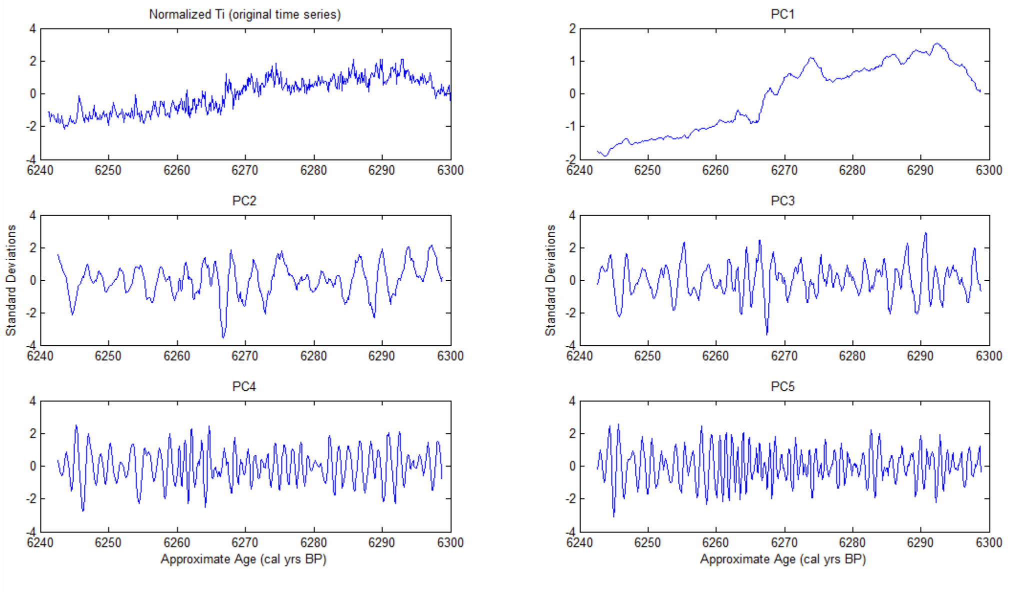


Figure 60 Single Spectrum Analysis (SSA) filtered Ti data for the Prairie 200 micron data set. PCs are principle component frequencies filtered from the data.

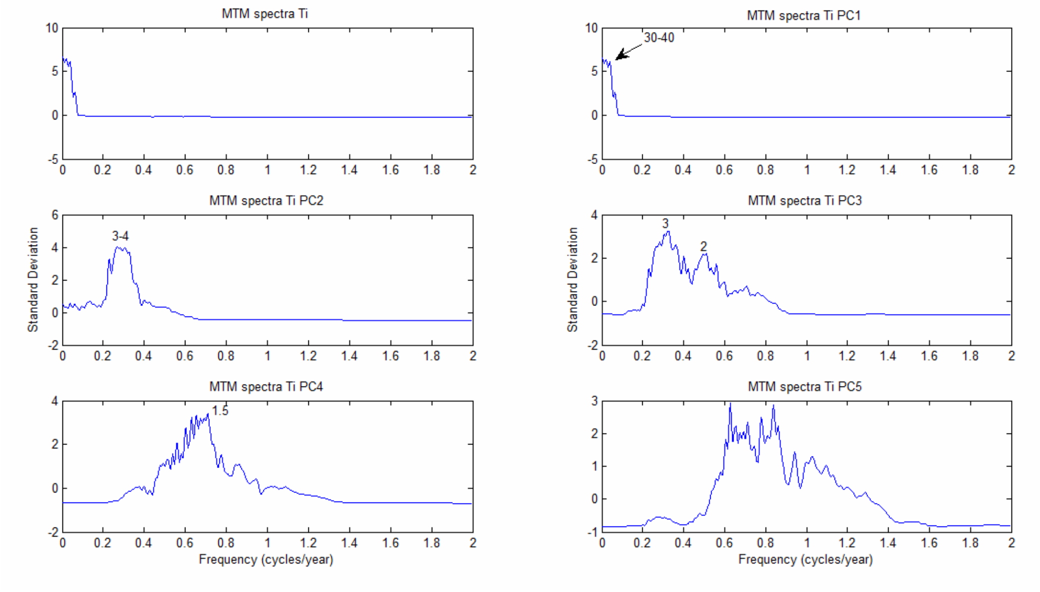


Figure 61 Multi-taper method time series analysis of Single Spectrum Analysis (SSA) filtered Ti data for the Prairie 200 micron data set, including PC's. Analysis shows significant frequencies and cycles in the high resolution 200micron Prairie period Ti data.

4.2.4 Prairie Period: 6,000-4,000 cal yrs BP:

From 6,100 to 6,000 cal yrs BP, the concentrations of clastic indicators drop dramatically to an intermediate level between the conditions seen during the mid-Holocene Prairie period and the Modern period. This, combined with peaks in Fe (authigenic) and Mn, suggests that the last 2000yrs of the prairie period were wetter than the time period before. None the less, because the counts of Fe and Mn during this time remain relatively low, there was still limited groundwater flow into the lake (figure 62).

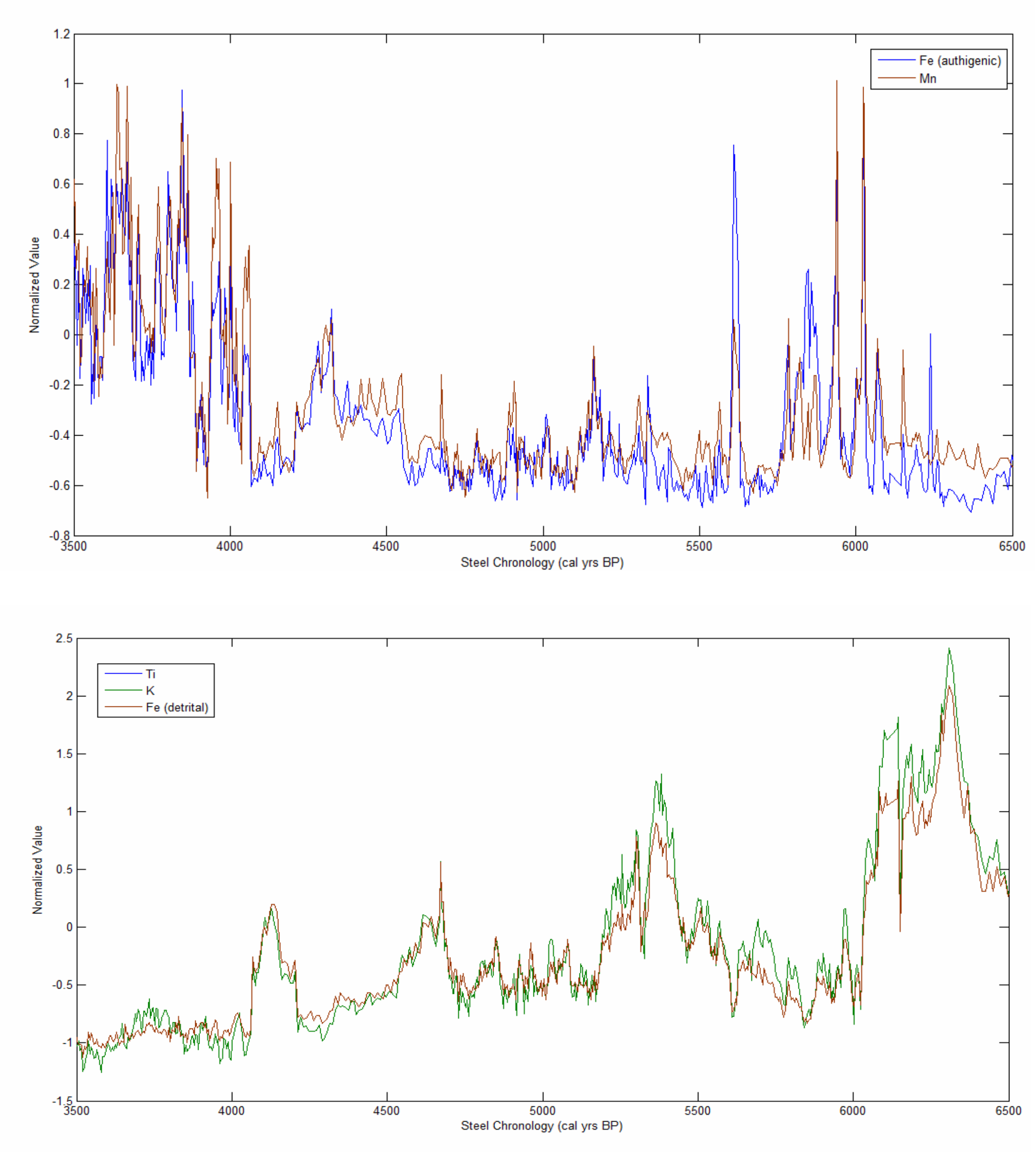


Figure 62 Plots of major elements in the Prairie-Modern period transition. Top: Major Authigenic components, Bottom: Major Clastic Components. All data has been normalized and is plotted in standard deviation against time.

Dean (1993) discussed an event occurred just after the maximum clastic boundary in which clastic indicators dropped off significantly and the lake appeared to head in to modern conditions only to revert back to prairie like conditions a short time later. There is a similar trend in the new XRF data, beginning at 6100 cal yrs BP the clastics dropped significantly and within 150-200 years the lake was heading toward modern conditions. For about 400 years the clastic counts remained low while Fe (authigenic), Mn and Ca concentrations increased, associated with possible increases in precipitation and groundwater input into Elk Lake. At 5,600 cal yrs BP the clastics began to rise and peak again as well as subsequent decreases in the groundwater transported ions. This pattern seems to have occurred multiple times during the period between 6,000 and 4,000 cal yrs BP. Its likely that the elements deposited in the lake were recording the interaction between the three main airstreams much like the sediments deposited during the transition between the post glacial lake and the mid Holocene prairie period.

When Elk Lake transitioned out of the post glacial period, there was a change in the pattern of atmospheric circulation from movement dominated by southward flowing anticyclonic winds to a dominance of the Pacific air-stream which follows the path of the strongest westerlies. It is most plausible that what we see in the record between 6000 and 4000 cal yrs BP is a change from patterns dominated by the Pacific air-stream to an interaction of the Pacific and Tropical air-streams (to some extent the Arctic) as is seen today. This would have brought more available moisture in to the region while leading to decreases in the amount of wind borne clastic material from the west.

4.2.5 Modern Period: 4000-present:

At 4000 cal. yrs. B.P., there is an abrupt and fairly significant change in the characteristics of Elk Lake's sediments. During this time, all of the major clastic indicators drop to their minimum values while Fe and Mn begin to rise and reach some of their highest values (figure 63). This all suggests that the processes in the lake began to change dramatically and that the regional climate changed abruptly within a very short time period. In general, Fe and Mn show an increasing trend as far as the amounts preserved in the sediments, but in detail, there is lots of variability on the time scale of decades to hundreds of years throughout this entire modern period. Some of the more interesting characteristics of this time period are the relationships between some of the elements including Fe, P, Mn, Ca, and the ratio of Incoherent to Coherent scatter (a general indicator of the amount of organic matter in the sediments. See earlier discussion section Fe and Mn geochemistry).

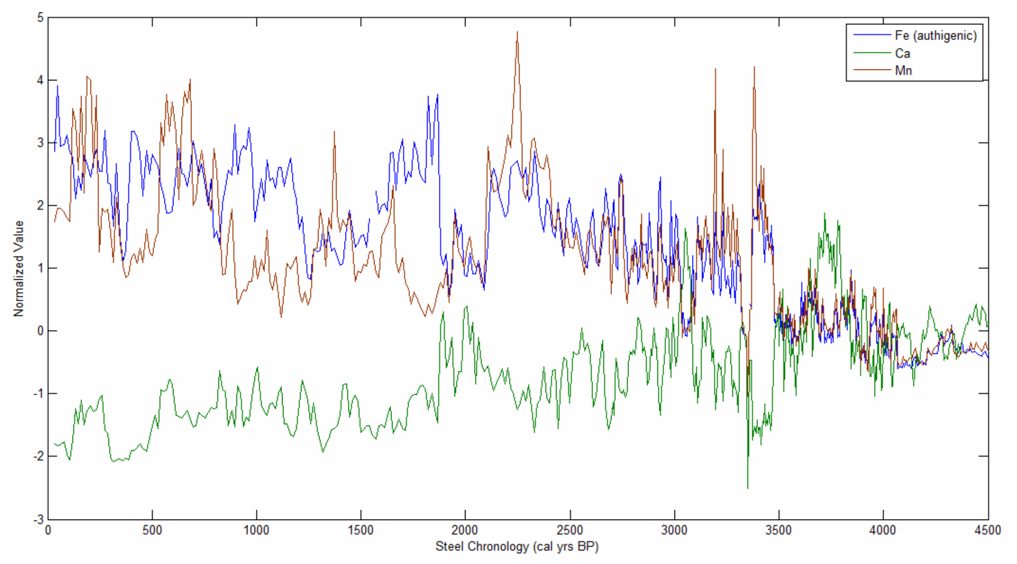


Fig 63. Plot of the major authigenic elements during the Modern period of Elk Lake's history. All data has been normalized and is plotted in standard deviations against time.

Overall, the later part of the Holocene is characterized by increased regional moisture. With increases in Fe and Mn, it can be assumed that Elk Lake has been receiving more groundwater flow over the course of the last 4,000 years and very little material is being brought to the lake by eolian transport, both of which indicate that the climate was becoming wetter than during the mid Holocene. This signals an increase in the dominance of the Tropical air-stream and rapid transition from prairie grasslands to the Mesic forest of today as the Prairie-Forest boundary moved back to the west from its position east of Elk Lake during the mid-Holocene. The transition back into a vegetation regime dominated by the forests as seen in the region today would have effectively cut the Elk Lake area off from major sources of wind driven clastic material from the west.

During the course of the Modern period, the cycling of Fe has become an important influence on the productivity of Elk Lake through the formation of iron phosphates that limit the availability P for primary producers. Vivianite is one such iron phosphate and qualitative assessment of the cores shows that it increases in abundance in the upper section of the sediments.

High resolution data (200 micron) shows that significant inter annual variability still remains in the Modern period. Plots of data filtered for certain frequencies and time series analysis (figure 54, 55, and 56) show that there is significant variability on the order of 1 and 3-4 year cycles. As well as a return of the 6 year cycle possibly related to an increasing influence of the ENSO band frequencies that were lost during the mid-Holocene. There is also a 14-16 year cycle seen in the analysis of both authigenic iron and calcium the explanation for which remains illusive.

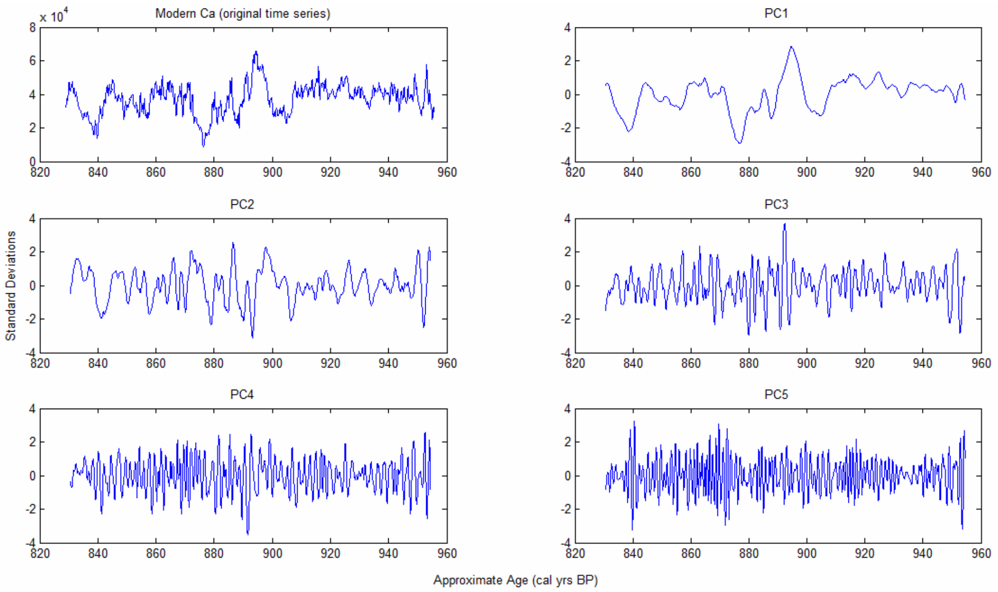


Figure 64. SSA filtered Ca data from the 200 micron run of during the modern period of the lake's history. PC's (principle component frequencies) are shown for the filtered data. All data is plotted against time.

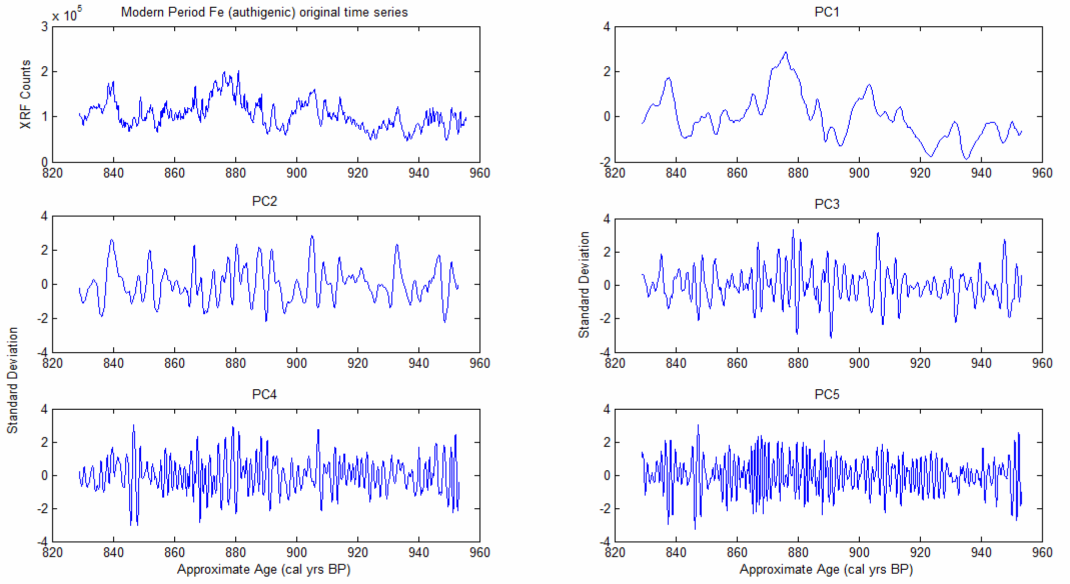


Fig 65 SSA filtered authigenic Fe data from the 200 micron run of during the modern period of the lake's history. PC's (principle component frequencies) are shown for the filtered data. All data is plotted against time

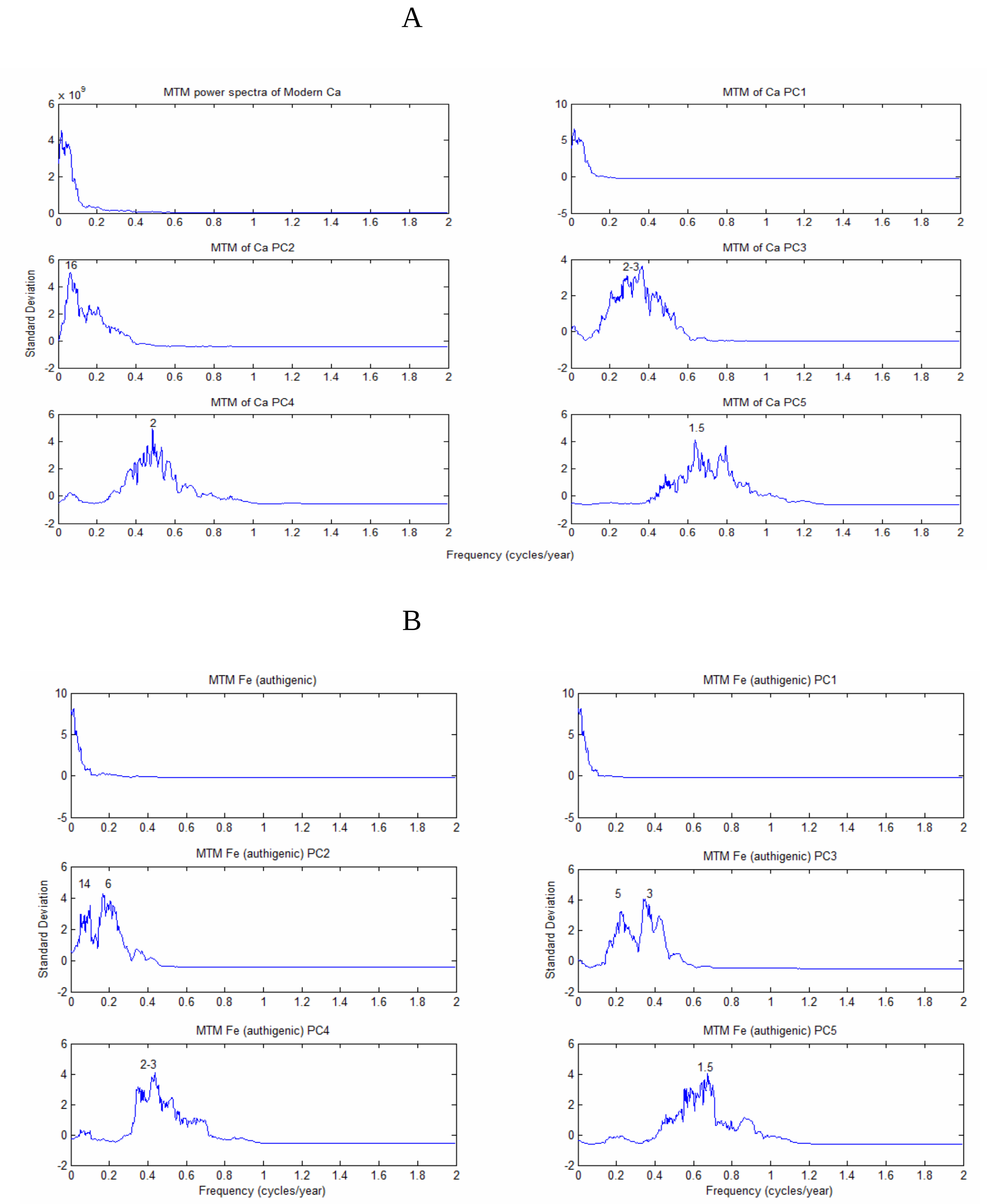


Figure 66 Multi-taper method time series analysis of Ca (A) and Fe (authigenic) (B) modern high resolution data including PC's, showing inter-annual variability in the records of the major authigenic elements.

4.2.6 Inter-annual variability:

In order to quantify variability in the deposition of the main elemental constituents during the major periods in Elk Lake's history, the coefficient of variance for Ca, Fe, Mn, and Ti was calculated. The data from each of the three high resolution (200 micron) runs were filtered (high-pass) using Analyseries to isolate variability related to high frequency cycles (on the order of sub-annual to decadal). The fifty highest and lowest values (~10% of the data) were excluded from calculation of variance and then the lowest (most negative) remaining value was subtracted from the entire data set for each element to adjust the mean value from zero. The standard deviation of each data set was divided by the mean in order to calculate the coefficient of variance; this allows for comparison of data sets with vastly different values/means and allows for a discussion of the amount of variation taking place during each of the main geochemical phases (Table 5).

	Coefficient of Variance (%)				
Period	**Ca**	**Fe**	**Mn**	**Ti**	**Average Variance**
Post-Glacial	43	42	40	47	43
Prairie	53	49	51	54	52
Modern	47	55	56	47	51

Table 5 Coefficient of variance for Ca, Fe, Mn, and Ti during each of the major periods in the history of Elk Lake. Presented as percentages (%).

The calculation of variance for each of the major periods suggests that the least amount of inter-annual variability, thus the most stable climate, took place during the Post Glacial period—average variance of 43%. Just after the initial formation of Elk Lake, the climate was dominated by the presence of the Laurentide ice sheet and would have experienced relatively stable climate conditions with little influence, initially, from the other two airstreams (Pacific and Gulf/Tropical airstreams). The variance increases during the Prairie period to 52% (average) which is the highest value for the entire record. An increase in the variability between individual years is expected when the system was dominated by inputs transported to the lake through wind driven processes which are inherently variable. Finally, the variance shows a slight decrease from the Prairie to Modern periods— from 52% to 51%— but is still higher than that of the Post Glacial period. The system during the last 4000 cal yrs BP, is one of decreasing dominance of the Pacific airstream and increasing influence of the Gulf/Tropical airstream.

Similar trends of low variability during the Post Glacial period, increasing variability during the Praire period, and finally intermediate to low values during the Modern period are seen for the individual elements Ca and Ti. Fe and Mn show generally increasing values for variability during the entire Holocene due to the increasing deposition of these elements over time and finally became the dominant constituents during the Modern period.

4.3 On the characterization of varves using the Scanning XRF:

There is little doubt that sediments of Elk Lake are varved, and it is clear that while the annual nature of varves provides an excellent opportunity for age scale development, there are a number of issues associated with visually counting individual sets of annual laminations. In fact, counts done by multiple researchers in previous work showed that there was a difference in varve counts of 10% at the bottom of the cores used (Dean, person. communication 2010). When dealing with a record that covers the entire Holocene, a 10% difference is approximately 1000yrs off from each individual's counts. Wright (2003) showed that there was also a difference of 1000 yrs. near the base of the records from Elk Lake varve counts and AMS radiocarbon dates form Steel Lake. This is a significant issue when using varve counts to develop an age scale for sediment cores.

The Scanning XRF provides an additional piece of data from which one can determine the boundaries between annual sets of laminations. High resolution 200 micron scans of specific sections of the cores taken for this study show that peaks in elements such as Ca, Fe, Mn, and others that are deposited on an annual basis can be used to effectively count individual years. While there are issues associated with this method such as changes in sedimentation rates and the thickness of varves which can lead to misleading geochemical signatures, the XRF certainly provides additional evidence that can be used to determine the age of an individual varve set during counting.

The following plots illustrate a 25cm, 200 micron run of sediments from the Elk Lake cores that showed some of the highest sedimentation rates and thicker varves in order to demonstrate the Scanning XRF's ability to measure and depict the geochemical nature of varves. This section covers 110 years of the record between 7455 and 7565 cal yrs. BP (figure 67). The age scale was approximated using Analyseries (Paillard, Labeyrie, and Yiou, 1996) and was sampled on a monthly basis for cross spectral analysis.

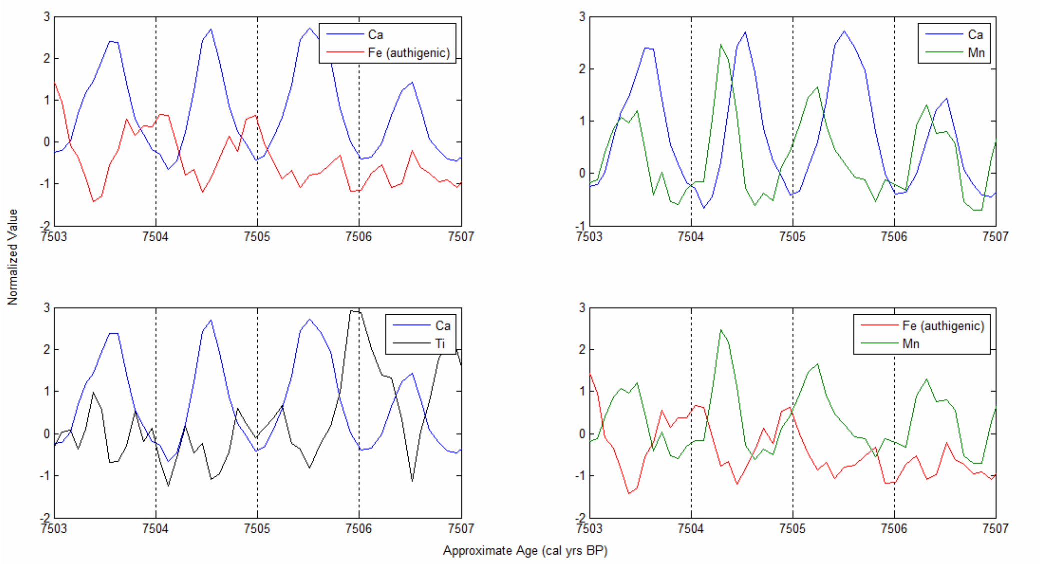


Fig 67 plots of the major elemental components of a typical varve set for Elk Lake showing the annual depositional relationships between them.

Figure 67 shows a selected section within the 200 micron run for the characterization of varves. It can be seen that there are specific times within any given year when the main varve components are deposited based on the limnologic processes within Elk Lake. While the nature of varves and the major constituents within them change over time depending on the dominant climatic processes taking place, Fe (authigenic), Ca, Mn, and especially during the mid Holocene Ti, make up the main laminations within any given varve through out the entire Holocene record.

Based on this high resolution section from the Elk lake cores, many of the limnologic processes that have been invoked to explain particular parts of the geochemical record are supported. For example, the idea that calcium is deposited mainly during the summer months in response to algal photosynthesis can be seen as one major peak, with occasional minor peaks each year. This calcium peak is, for the most part, bound by two peaks in authigenic iron which represent the deposition of iron oxyhydroxides during spring and fall overturns.

Manganese, surprisingly, shows only major peaks during what is likely fall overturn. The largest Mn peaks each year occur just after the major peak in calcium (presumably mid-summer) and before the major autumn peak in authigenic iron which would be expected in mid to late fall. The major authigenic components of the varves present the largest annual peaks at different times: Ca in mid summer, Mn in early fall, and finally authigenic Fe in late autumn. While this relationship is general and does not always hold true for every single varve deposited during the Holocene, for the most part, this high resolution geochemical data supports the ideas and theories about the deposition of varves in Elk Lake as presented by both past and current researchers. More limnologic data certainly would be needed to confirm these thoughts definitively, but it would seem that with the generally limited knowledge of processes taking place within the lake, that the XRF can provide a great deal of insight into the nature of varve deposition and would be a beneficial tool during the characterization of varve sets for the major periods in the lake's geochemical evolution as well as a significant improvement in the way varves are counted for the development of age scales.

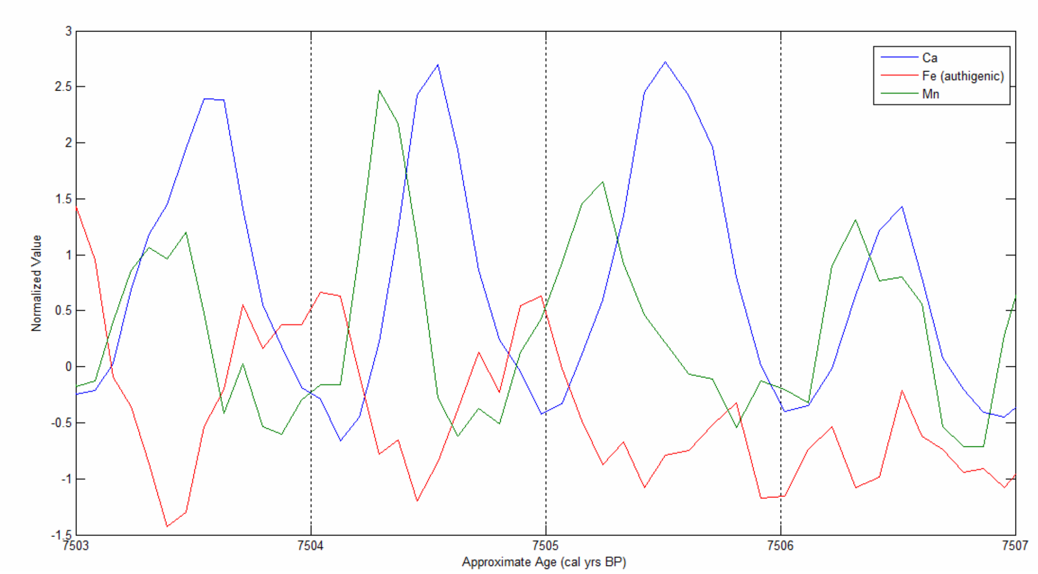
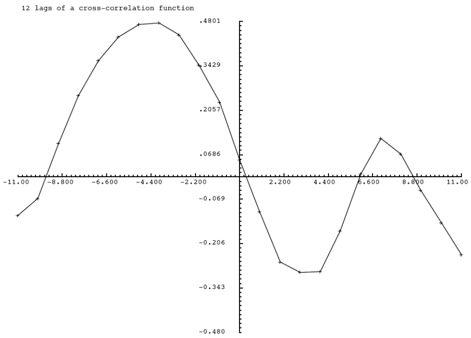


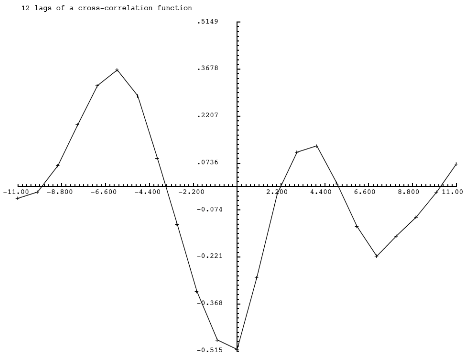
Figure 68 Normalized data for the three major authigenic components of the Elk Lake varves showing annual depositional timing.

In order to quantify the relationships between the depositional timing of the major authigenic varve components, cross correlations were preformed using the CROSPEC software available from the National Climate Data Center (Howell, 2001). This software allows for the description of leads and lags between the timing of peak deposition for elements such as Ca, Fe (authigenic), Mn, Ti and other major components of the annual varve sets. In order to identify the timing of events for a given year, the data was sampled on an approximately monthly basis (time step= .08 years). With approximately 7-8 XRF data points per varve (thus per year), sampling on a monthly basis is at a slightly higher frequency than the number of data points in a given varve year. Due to this difference in the sampling and the actual number of data points, the cross correlation done between various elements is not entirely accurate, but nonetheless is reasonable for the purposes of this study. The following figures show the relationships between these elements.

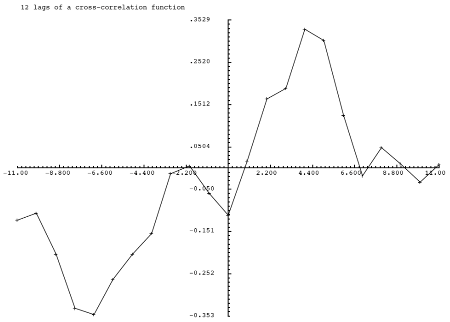
The cross correlation plots help to illustrate the timing of various events in the general, annual deposition of the elements shown. It is clear from both the cross correlation (figure 69) and the time series plots (element concentration vs. time) that the deposition of many of the authigenic components of the varves occur seasonally and lead/lag other elements. For example, carbonate deposition (Ca) leads the major peak in Mn deposition each year by approximately three to four months, which in turn leads the major autumn deposition of authigenic iron by four months. Ca and Fe (authigenic) cross spectral analysis shows that in fact, Ca deposition leads the major deposition of authigenic iron by approximately 6.5-7 months. This supports the claims that have been made that calcium carbonates will be deposited in the highest concentrations during the summer months due to changes in pH of the epilimnion during the height of algal photosynthesis and iron is deposited mainly during periods of over turn and forms distinct gel like laminations during the winter months (thus about approximately 0.5 years difference in the timing of Ca and Fe deposition).



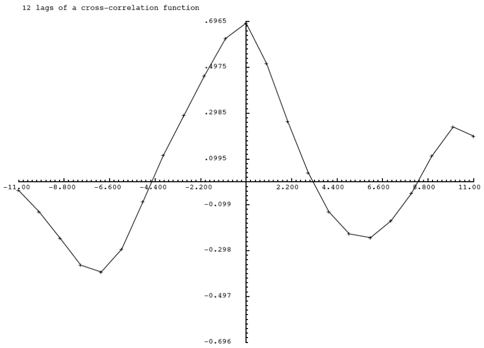
Ca vs. Mn



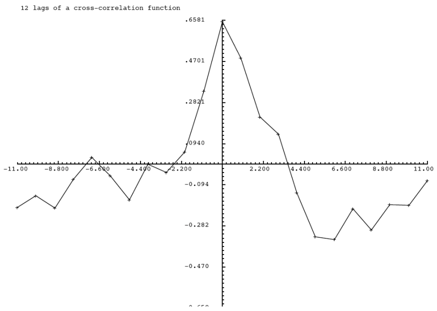
Ca vs. Fe (authigenic)



Fe (authigenic) vs. Mn



Ca vs. Sr



Ti vs. K

Figure 69 Cross correlation plots of various elemental leads and lags. Y axis shows the magnitude of a lead/lag (correlation), x axis indicates the number of time steps (0.08~ monthly); Number of lags=24. Created with CROSPEC software (Howell 2001).

Other cross correlation plots show the in phase nature of elements (figure 69). Ti and K for example have the strongest peak in correlation at a lag of zero years, supporting conclusions made based on the ratio of these elements and the original time series data that shows the two elements have very similar signals over time. Sr and Ca cross correlation also shows that these elements are in phase with major annual peaks in Sr occurring at the same time as Ca. A slight lag of about one month for Sr deposition vs. Ca deposition can be seen in the cross correlation plot of Ca vs. Sr. This small lag fits with the claim that Sr will begin to replace Ca in the carbonate structure as more calcium carbonate is precipitated and the ratio of Sr to Ca increases in the residual epilimnetic waters.

High resolution Scanning XRF data provides researchers with an advanced analytical technique for the description of varved sediments. It has been shown that both 1cm and 200 micron resolution scans of lacustrine sediments can provide insight into long term climatic changes as well inter annual variability within a geochemical data set. This same data can also be used to determine the nature of deposition of various elemental components of sediments such as the timing of deposition relative to other constituents and the relationships between them.

5. Conclusion

The varved sediments of Elk Lake provide an excellent and detailed archive of Holocene climatic change for the Upper Midwest region of the United States. It has been shown that the lake sediments contain multiple climate-sensitive proxies that have recorded changes in the amount of available moisture in the region through ground water influxes (Fe, Mn, Ca) and the presence of wind borne clastic material (Ti, Fe, K); these changes are related to the dominance of each of the three major airstreams that influence the region. The general story present in the Elk Lake sediment record is one of a maturing lake containing major inputs of Fe, Mn, and Ca related authigenic processes overprinted with clastic influxes related to changes in vegetation and the balance of precipitation and evaporation in the region.

The general story of climate change from the early post glacial period through the modern period is very much the same as what has been interpreted by previous researchers with a few differences in timing and duration of events due to the nature of the age scale developed. The major interpretive difference between this and previous studies are the lack of an 8.2 event seen in North Atlantic climate records. Rather than a distinct and abrupt change in the regional climate of the Elk Lake area at 8,200 cal yrs BP, we see a gradual change in climate sensitive elements suggesting that the changes in the region occurred over a much longer period of time. While it is possible that changes in atmospheric circulation and land cover over the North American continent could have been a result or cause of the 8.2 event, there is little evidence in the XRF dataset to support either claim. Instead the transition from a post glacial climate to the dry/windy climate of the mid-Holocene was time transgressive and gradual. As the Artic air-stream and anticyclonic north winds associated with the presence of the Laurentide ice sheet decreased in dominance, the Pacific air-stream moved into the region leading to drier regional conditions. Then, as the vegetational zones of Minnesota migrated back to the west after the major dry period of the mid-Holocene, the record shows the transition from a Pacific air-stream dominated atmospheric system to the increasing dominance of the Tropical air-stream that is responsible for the wetter conditions seen in the region today.

Other differences in the interpretation of this dataset and previous work are minor, usually consisting of discrepancies in the timing and duration of particular events rather than questions as to whether these events occurred or not. Periods such as the transition between the post glacial and prairie period, the maximum clastic influx, and the transition from prairie to the modern period are very distinct as in previous work.

The major contribution of this dataset is the high resolution that the scanning XRF is able to provide, both over the entire core record (1 cm resolution) and 200 micron runs of selected sections. Both the 1cm and 200 micron data provide an excellent record for interpreting changes in the dynamics of the climate over time and help to describe the subtle and high frequency characteristics of the regional climate. The high resolution of this type of geochemical data can also provide insight into the nature and seasonality of varve deposition and chemistry. It has been shown that XRF data can be used to determine the timing of seasonal elemental deposition and the relationships between various constituents of the sediments. For example, using cross correlation to determine leads/lag between elements such as Fe, Mn, Ca and others during any given year.

While the varved nature of sediments can provide an excellent means of age scale development, the XRF data shows that the seasonal deposition of varved laminations does not always behave reliably. There can be occasional years when a specific component of a varve may not be deposited in significant quantities or may be diluted by other components. This can lead to difficult to interpret annual laminations that can create error when counting varves. By utilizing both visual and geochemical information while counting varves in the development of an age scale, future researchers may be better able to develop more reliable varve-based chronologies.

Another of the more significant conclusions of this study is the use of both geochemical data from sediment cores and geophysical data. When these two methods are used in concert, a great deal of information about the nature of sedimentation and processes in a lake can be clarified. Geophysical data can show that events postulated by previous researchers, based on geochemical data, had in fact taken place in the lake—i.e. a drop in lake level during the mid-Holocene Prairie period. While it is difficult to determine the exact timing of the low stand in Elk Lake, by using the two datasets (physical and chemical) a strong argument can be made that the event most likely occurred during the maximum clastic influx at 6300 cal. yrs. BP. To confirm or deny this claim, it may be useful to core Elk Lake in an area with little gas, such as the small basin seen in Line 2 (see geophysical results section). This would allow for geochemical correlation between the sediment core record from the deep basin and an area that is known to contain the unconformity. In doing so, it could be determined what part of the

Holocene record was missing form the sediments known to contain the unconformity to estimate the timing of the event.

As is often the case with scientific research, there has been a great deal done to describe changes in the climate utilizing the sediments of Elk Lake, but questions still remain such as the timing of the unconformity/lake level drop, how to most appropriately develop an age scale that can provide insight into short term, inter-annual changes in climate, and a comprehensive study of the relationships between modern limnologic processes and their influence on various elemental proxies. None the less, this study provides a much higher resolution story of climate change for the North Central United States and helps to clarify the nature of this change on a much finer time scale than has been done in the past.

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7. Appendix

7.1 Appendix A: Plots of important data on the Varve Year Chronology from Dean (1993):

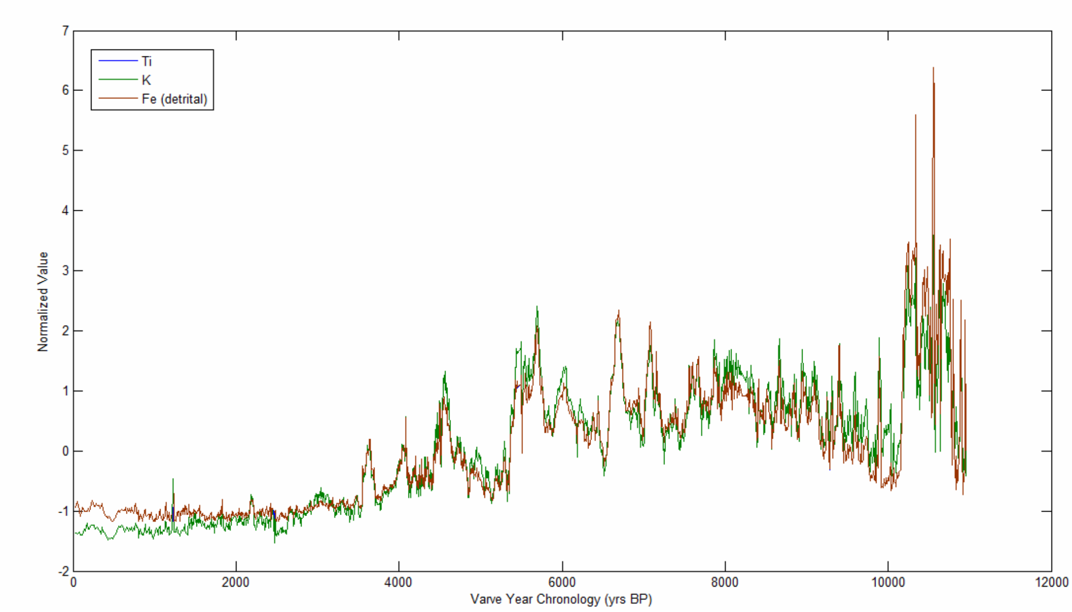

Figure A-1 Normalized Ti, K, and Fe (detrital) plotted against the Varve Year Chronology from Dean 1993.

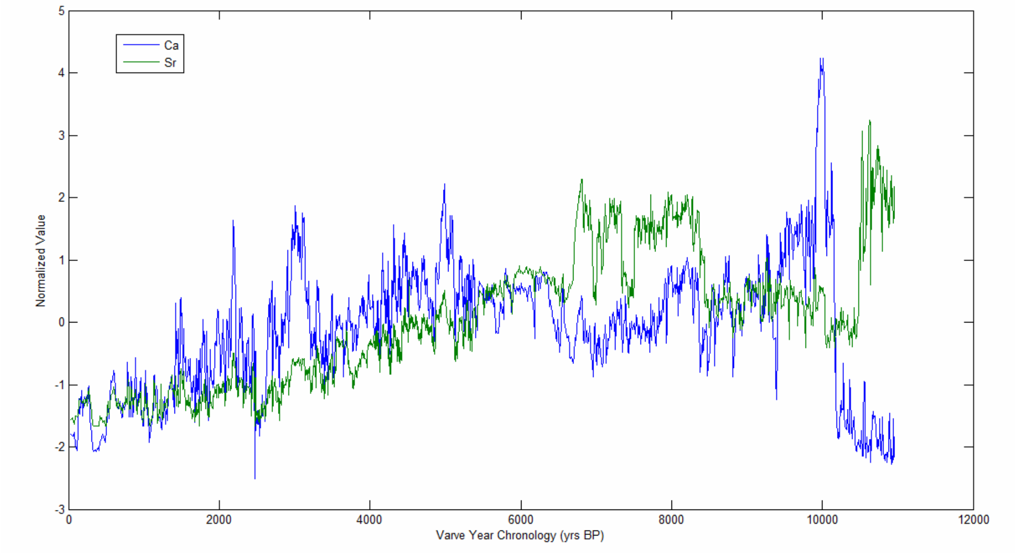

Figure A-2 Normalized Ca and Sr plotted against the Varve Year Chronology from Dean 1993.

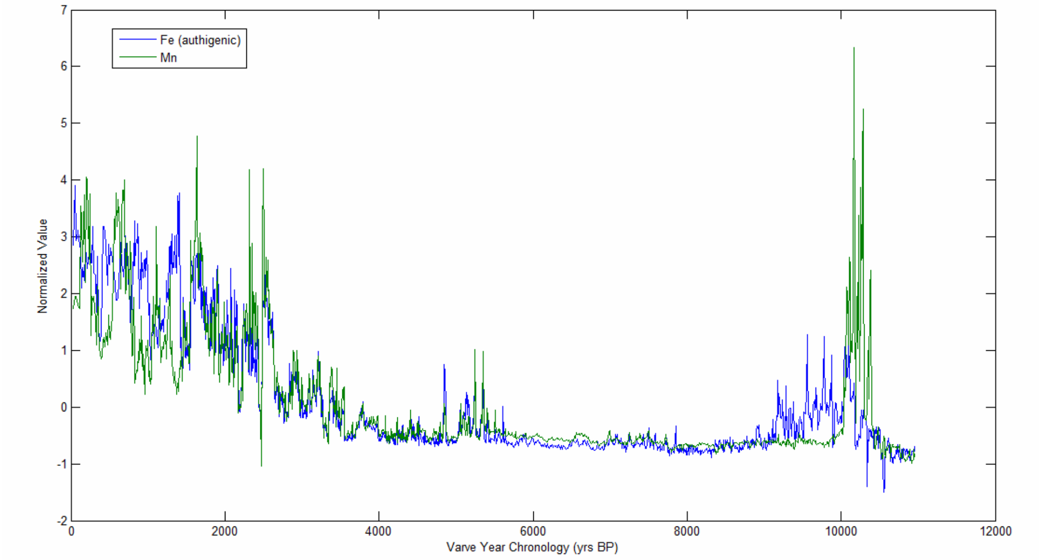

Figure A-3 Normalized Mn and Fe (authigenic) plotted against the Varve Year Chronology from Dean 1993.

7.2 Appendix B: Unused Elements

All of the following plots are of elements that were measured by the XRF but not used for the discussion of past climatic events for the Upper Midwest region of the United States. All plots are in XRF counts vs. both the Steel Chronology used for the study and Varve Years from GSA special report 276 (Anderson, Bradbury and Dean, 1993)

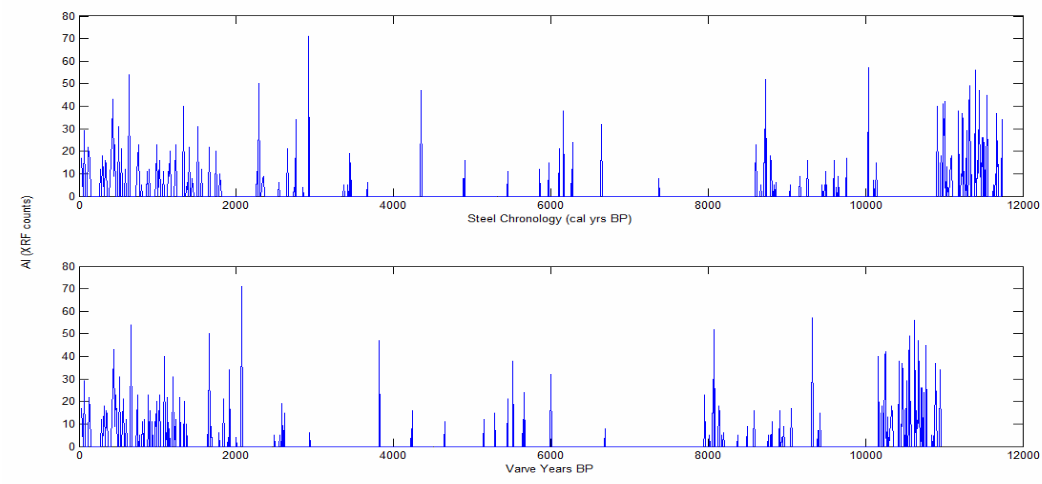

Figure B-1 Aluminum (XRF counts) vs. time (Steel Chronology and Varve Years).

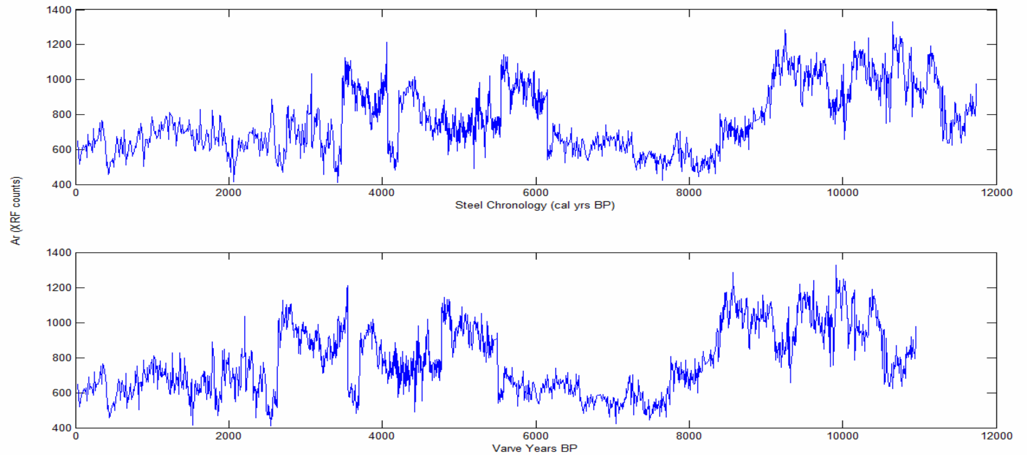

Figure B-2 Argon (XRF counts) vs. time (Steel Chronology and Varve Years).

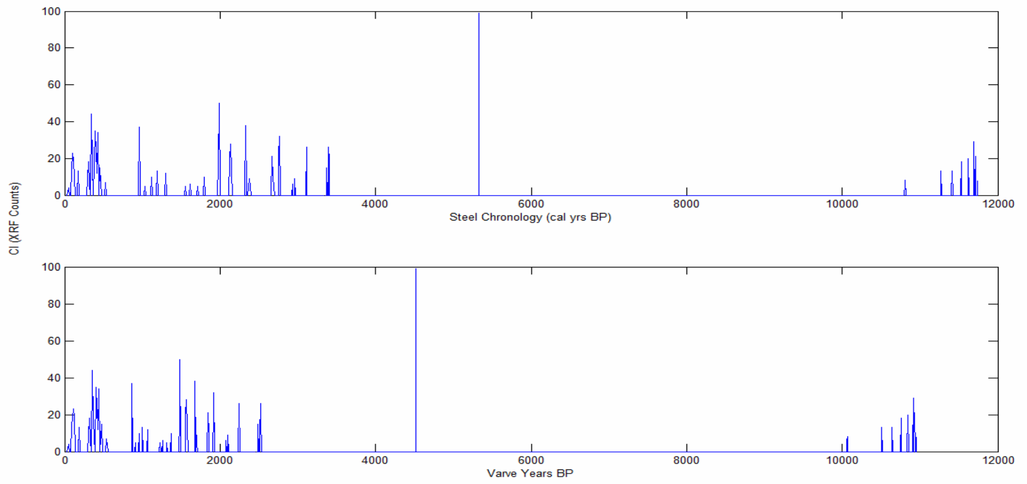

Figure B-3 Chlorine (XRF counts) vs. time (Steel Chronology and Varve Years).

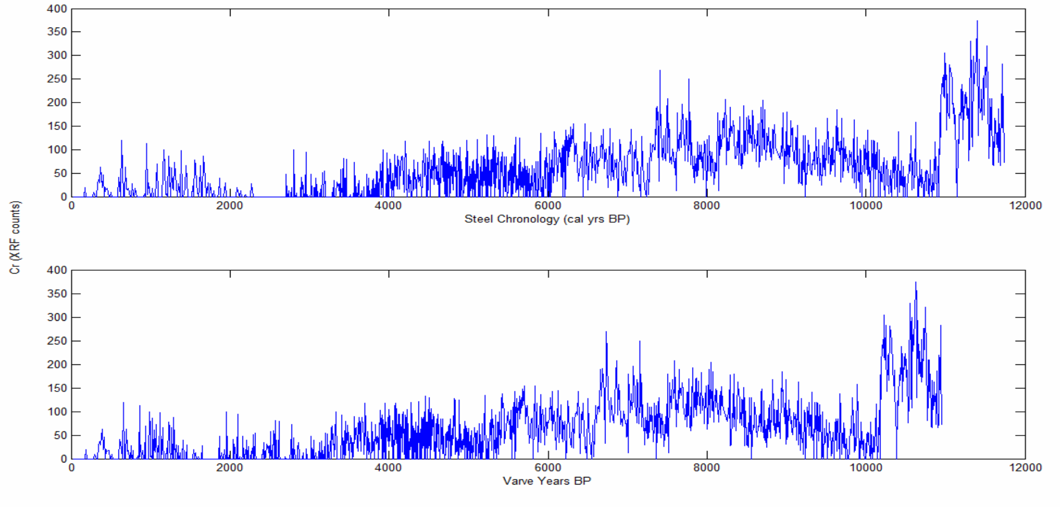

Figure B-4 Chromium (XRF counts) vs. time (Steel Chronology and Varve Years).

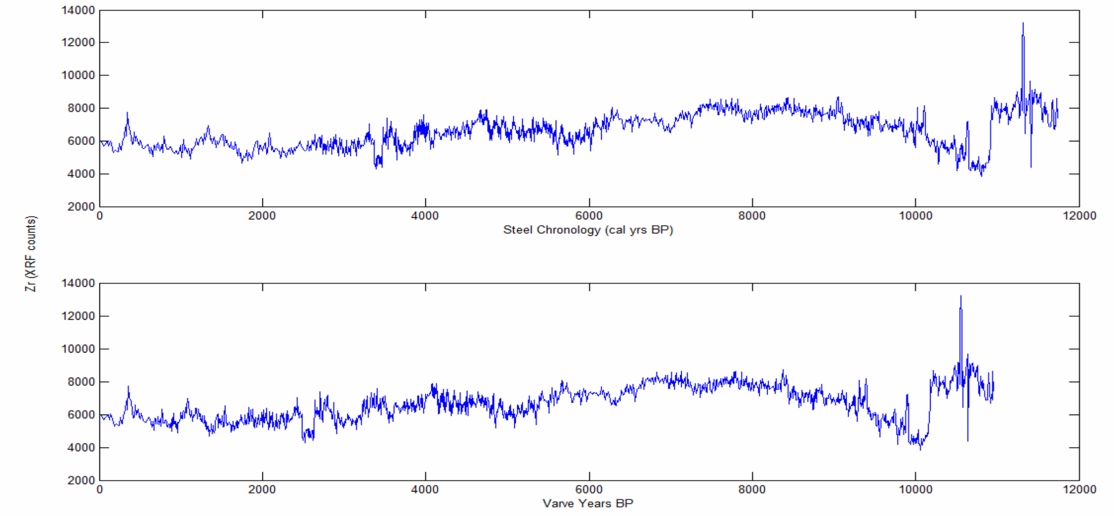

Figure B-5 Zircon (XRF counts) vs. time (Steel Chronology and Varve Years).

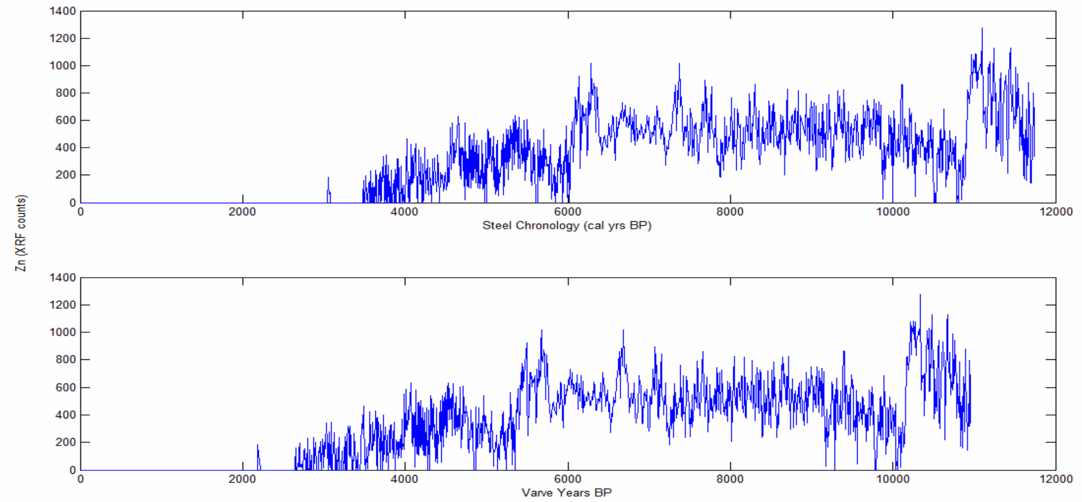

Figure B-6 Zinc (XRF counts) vs. time (Steel Chronology and Varve Years).

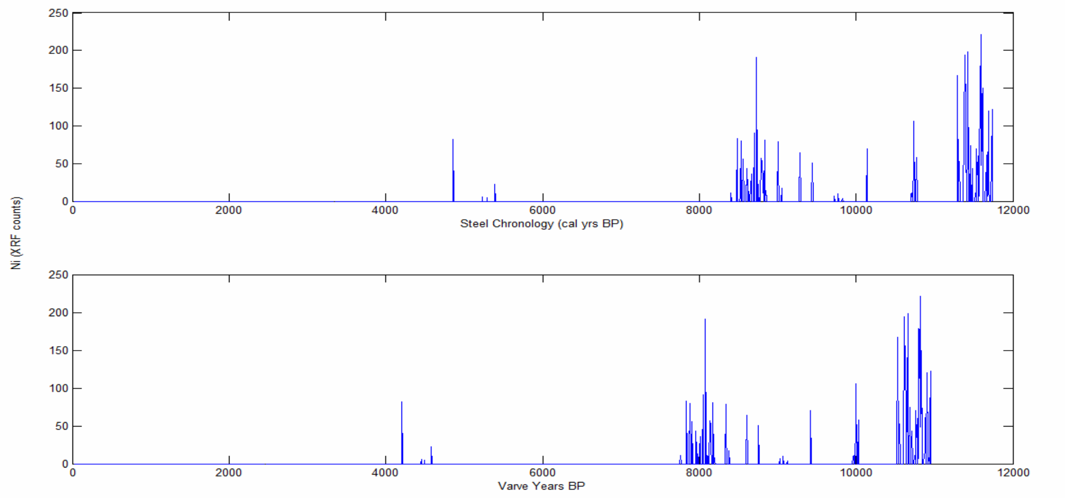

Figure B-7 Nickel (XRF counts) vs. time (Steel Chronology and Varve Years).

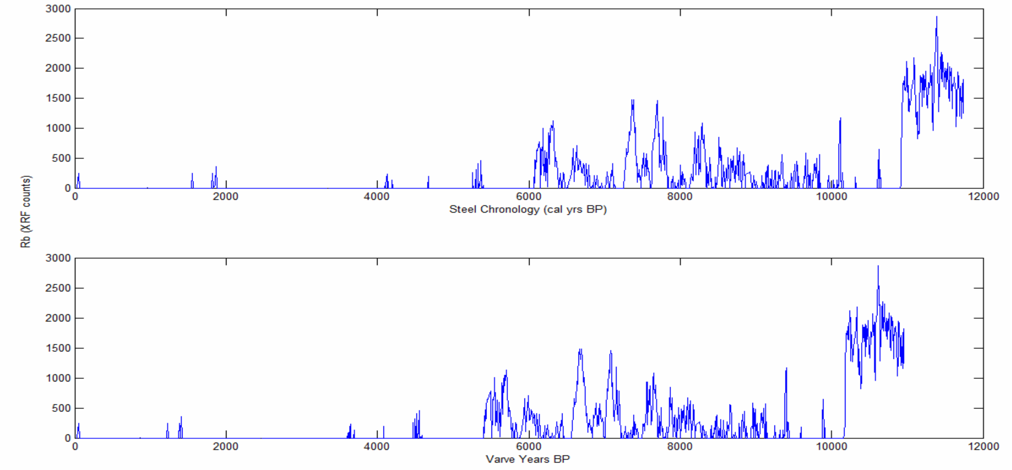

Figure B-8 Rubidium (XRF counts) vs. time (Steel Chronology and Varve Years).

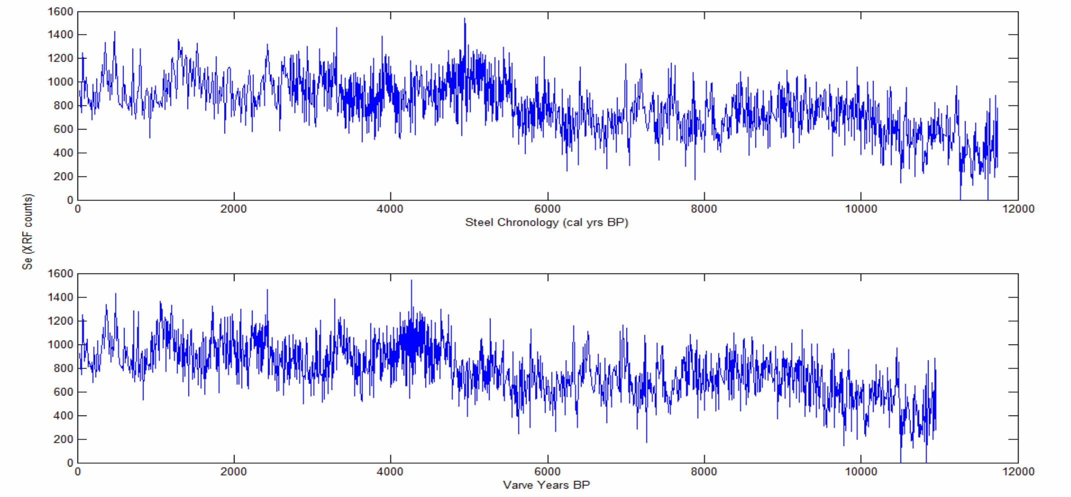

Figure B-9 Selenium (XRF counts) vs. time (Steel Chronology and Varve Years).

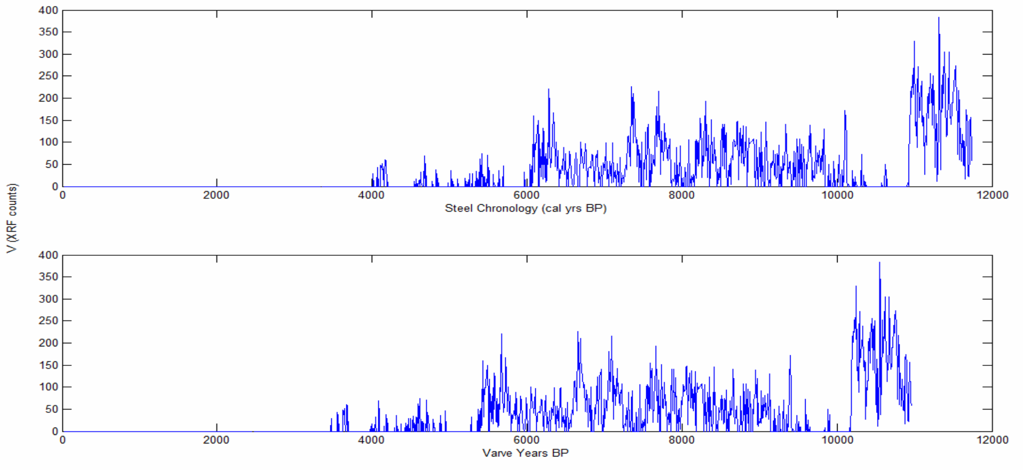

Figure B-10 Vanadium (XRF counts) vs. time (Steel Chronology and Varve Years).