The Carbon Dynamics of East Lake, Newberry Volcano
Oregon
by
Lena Rose Capece
Class of 2016

A thesis submitted to the
faculty of Wesleyan University
in partial fulfillment of the requirements for the
Degree of Bachelor of Arts
with Departmental Honors in Earth and Environmental Science

Middletown, Connecticut April, 2016
Table of Contents

List of Figures ........................................................................................................ iv
List of Tables ........................................................................................................... v
Acknowledgments ................................................................................................... vi
Abstract ................................................................................................................... vii

1. Introduction ........................................................................................................ 1
   1.1 Purpose of Research ..................................................................................... 1
   1.2 Limnology ..................................................................................................... 1
   1.3 Volcanic Lakes ............................................................................................. 4
   1.4 Volcanic Hydrothermal and Geothermal Systems ...................................... 7
   1.5 Carbon Cycling in Volcanic Lakes ............................................................... 9

2. Geological Setting .............................................................................................. 12
   2.1 Newberry Volcano ..................................................................................... 12
   2.2 Geothermal System at Newberry Volcano ............................................ 14
   2.3 Hydrology of the Newberry Caldera ......................................................... 15

3. Previous Work at the Newberry Crater Lakes .............................................. 17

4. Methods ............................................................................................................. 19
   4.1 Field Methods ........................................................................................... 19
      4.1.1 Water Samples .................................................................................... 19
      4.1.2 CO₂ Flux Data Collection .................................................................. 20
      4.1.3 Gas Chamber and Air Samples ....................................................... 21
      4.1.4 Sediment Cores ................................................................................ 21
      4.1.5 Organic Matter .................................................................................. 23
      4.2.1 Biogenic Silica .................................................................................... 23
      4.2.2 Carbon and Nitrogen Analysis ......................................................... 25
      4.2.3 XRF .................................................................................................... 25
      4.2.4 Mercury ............................................................................................... 26
      4.2.6 pH, Alkalinity, DIC ......................................................................... 27
      4.2.7 IC and ICP .......................................................................................... 27
      4.2.8 Stable isotopes O, H, and C ............................................................... 28
4.2.9 CO₂ Flux Data .............................................................................................................. 28

5. Results ............................................................................................................................... 30

5.1 Field Data ........................................................................................................................ 30

5.1.1 Temperature ................................................................................................................ 30

5.1.2 Dissolved Oxygen (DO) ............................................................................................ 31

5.1.3 Conductivity ................................................................................................................ 32

5.2 Water chemistry .............................................................................................................. 33

5.2.1 Major Anions ............................................................................................................... 33

5.2.2 Alkalinity .................................................................................................................... 34

5.2.3 Major Cations ............................................................................................................. 35

5.2.4 pH ............................................................................................................................... 37

5.2.5 Phosphorus ............................................................................................................... 38

5.3 Stable Isotopes ............................................................................................................... 39

5.3.1 Stable Isotopes of Oxygen and Hydrogen (Water) .................................................... 39

5.3.2 δ¹³C DIC ...................................................................................................................... 40

5.4 Gas and Air Data ............................................................................................................ 41

5.4.1 Flux Data .................................................................................................................... 41

5.4.2 δ¹³C of Lake Gas and Ambient Air Samples ................................................................. 43

5.5 Sediment Cores and their Chemical Composition ....................................................... 44

5.5.1 General Description .................................................................................................. 44

5.5.2 Bulk Dry Density (BDD) ............................................................................................ 44

5.5.3 Major and Trace Elements ......................................................................................... 45

5.5.4 Incompatible Elements ............................................................................................. 51

5.5.5 Mercury ..................................................................................................................... 53

5.5.6 Biogenic Silica ........................................................................................................... 54

5.5.7 Carbon and Nitrogen Content .................................................................................. 55

5.5.8 δ¹³C and δ¹⁵N of Sediment Core Samples ................................................................. 58

6. Discussion ......................................................................................................................... 61

6.1 Physical Characteristics of East Lake Waters ................................................................. 61

6.1.1 General ....................................................................................................................... 61

6.1.2 δ¹³C DIC Time Trends ............................................................................................... 63

6.1.3 Compositional Trends in East Lake Waters ............................................................... 65

6.1.4 Comparison to Paulina Lake ..................................................................................... 70

6.2 Carbon Dioxide Degassing .......................................................................................... 73
List of Figures

2. Geological Setting
   Figure 2.1.1 13

4. Methods
   Figure 4.1.4.1 22
   Figure 4.2.1.1 24

5. Results
   Figure 5.1.1.1 30
   Figure 5.1.2.1 31
   Figure 5.1.3.1 32
   Figure 5.2.1.1 33
   Figure 5.2.1.2 34
   Figure 5.2.2.1 35
   Figure 5.2.3.1 36
   Figure 5.2.3.2 36
   Figure 5.2.4.1 37
   Figure 5.2.5.1 38
   Figure 5.3.1.1 39
   Figure 5.3.2.1 40
   Figure 5.4.1.1 41
   Figure 5.5.2.1 44
   Figure 5.5.3.1 48
   Figure 5.5.3.2 49
   Figure 5.5.3.3 49
   Figure 5.5.3.4 50
   Figure 5.5.4.1 51
   Figure 5.5.4.2 52
   Figure 5.5.5.1 53
   Figure 5.5.6.1 54
   Figure 5.5.7.1 55
   Figure 5.5.7.2 56
   Figure 5.5.7.3 57
   Figure 5.5.8.1 59
   Figure 5.5.8.2 60

6. Discussion
   Figure 6.1.1.1 62
   Figure 6.1.2.1 64
   Figure 6.1.3.1 66
   Figure 6.1.3.2 67
   Figure 6.1.3.3 68
   Figure 6.1.3.4 69
   Figure 6.1.4.1 71
   Figure 6.1.4.2 72
   Figure 6.2.1.1 73
List of Tables

4. Methods
   Table 4.1.3.1  21
   Table 4.1.3.2  21
   Table 4.1.4.1  23

5. Results
   Table 5.2.3.1  36
   Table 5.4.1.1  42
   Table 5.4.2.1  43
   Table 5.5.3.1  45
   Table 5.5.3.2  47
   Table 5.5.7.1  58
   Table 5.5.8.1  58

6. Discussion
   Table 6.2.1.1  77
   Table 6.3.2.1  82
   Table 6.3.3.1  85
Acknowledgments

My absolutely genuine and sincere gratitude go to Johan Varekamp. Thank you for providing me with this incredible experience. Your immeasurable dedication to the ongoing research at the Newberry caldera and to my success is staggering. Not to mention your expertise, encouragement and tomfoolery! You have truly inspired me to further my career in the geosciences and seek opportunity.

A special thanks goes to Ellen Thomas and Tim Ku for their help and expertise during various stages of this project. I also thank Cindy Flores, Ning Ouyang and my fellow Keck researchers Heather Upin, Julia Horne, and Sam Caldwell. Also thank you to the Keck Consortium for providing the funding for this project.

Thank you to Daniele McKay and her students at the University of Oregon Cascades, and to Bob Reynolds from Central Oregon Community College. And finally thank you to the amazing staff at the East Lake Resort, who were always accommodating and friendly.
Abstract

East Lake is one of two twin-crater lakes located in the Newberry Volcano, 30 miles south of Bend, Oregon. It has volcanic geothermal inputs largely composed of CO$_2$, but also including H$_2$S and Hg. These volcanic inputs establish unique sediment and water chemistries in the lake and the surrounding ecosystem. Sediment analyses reveal that East Lake sediment is predominantly composed of biogenic silica (~60%) followed by organic carbon (8-12%) with the remainder consisting of volcanic ash. East Lake is terminal. Its water level is dependent upon meteoric water inputs and evaporation. The surface water pH varies between 6.5 and 7 and waters are HCO$_3^-$ dominant with an average concentration of about 130 ppm. East Lake has a higher internal P$_{CO_2}$, compared to the atmospheric P$_{CO_2}$, producing a diffusive loss of CO$_2$ from the surface of the lake. Data collected from CO$_2$ measurements taken from the surface of the lake during the summer of 2015 in conjunction with sequential Gaussian simulation, estimate a lake surface loss of about 44 tonnes of CO$_2$/day. The diffusive CO$_2$ loss at the lake surface is the main cause of an exaggerated $\delta^{13}C$ gradient of dissolved carbon with depth. East Lake is a moderately productive lake with CO$_2$ and silica volcanic inputs providing nutritive reactants to photosynthetic organisms. Such organisms consist of phytoplankton, various Nostoc species (cyanobacteria) and aqueous vegetation. All new data collection for this study occurred during the summer of 2015.
1. Introduction

1.1 Purpose of Research

Most lakes recycle atmospheric CO$_2$ through a photosynthetic loop where the resulting organic matter is cycled through the ecosystem and partially buried in the sediment. As a result of the partial oxidation of imported terrestrial carbon, lakes also evade CO$_2$. In some volcanic lakes, CO$_2$ enters from below the lake instead of entering through the atmosphere. This volcanic CO$_2$ is then cycled through the ecosystem and buried in the sediment while a portion is evaded through diffusion at the lake surface. This study, through the implementation of physical and geochemical analyses, endeavors to define and quantify carbon fluxes and their isotopic signatures in East Lake in central Oregon.

1.2 Limnology

The interplay between the physical, chemical, and biological characteristics of lakes and their environment is crucial in understanding the role that these bodies of water have on a global scale. Lakes have considerable roles in biogeochemical cycles because they regulate the regional circulation of carbon, nitrogen, and phosphorus. Various processes such as photosynthesis, bacterial respiration, and the sedimentation of organic matter all mediate these cycles. Lakes are the libraries of earth’s past. They create unique depositional environments that preserve an archival history, which can be analyzed for a variety of proxies and indicators in order to reproduce past geological ecosystems and settings (Meybeck, 1995; Cohen, 2003).
In general, lakes are formed through glacial, tectonic, fluvial, and volcanic processes. Over the last twenty thousand years glacial retreat has resulted in the formation of many lakes and has redistributed their location across the globe. Glacial retreat causes: 1) glacial melt and scouring of continent, 2) ice dam formation, 3) changes in sea level, and 4) changes in humidity (Meybeck, 1995), which aid in the formation lacustrine environments. Tectonic processes, such as faulting or uplift, have dominated more recent lake formation (Wetzel 2001). Fluvial lakes are the third most abundant lake type (Wetzel 2001). They can form through action by a flowing body of water that results in the creation of topographical depressions or depositional sediment dams (Cohen, 2003). Lakes can also result from landslides since they cause a sudden influx of sedimentary material that may lead to the damming of streams or rivers. Landslides typically create large lakes formed through mudflows, rockfalls or ice slides (Wetzel, 2001).

Various types of volcanic activity also have the ability to form lakes. Volcanic material released from eruptions can create cavities or depressions, creating a space, where meteoric or groundwater discharge can collect. Violent magma ejections or the entire collapse of volcanic structures above magma chambers can create crater and caldera lakes (Wetzel, 2001).

The geomorphology of lakes also has a substantial effect on a lake’s physical and chemical state. Geomorphology can govern the distribution of sediments, gases, and nutrients, as well as life. The relationship between the surface area of a lake and its depth is critical in determining a lake’s biological potential. For example, the size and depth relationship has an effect on the ability of a lake to receive light. Deeper,
larger lakes will receive less overall light than small, shallower lakes. Therefore, deep lakes generally experience less productivity than shallower lakes, solely based on the interactions between the sediment surface area and the water itself (Wetzel, 2001).

The hydrologic cycle also plays a crucial role in lake formation and their global distribution (Cohen, 2003). Patterns of precipitation and evaporation, in combination with surface and ground water runoff, dictate the water budget of lakes. Water inputs can include direct precipitation on the surface of lakes, groundwater seepage or surface runoff, and outputs can include seepage through lake walls, evaporation from the lake surface and evapotranspiration from biota (Wetzel, 2001).

The distribution of heat in lakes is important in the establishment of “lake water layers”, which ultimately regulates lake mixing. Typically the temperature of lake surface waters varies seasonally. During prolonged periods of decreased temperature, many lakes experience ice cover. During spring, when ice cover melts, turnover occurs when colder, denser water near the surfaces of a lake descends and displaces warmer, less dense water mixing the lake. However, as lake temperatures increase, the resistance to mixing also increases (Wetzel, 2001). Turnover is usually followed by a period of summer stratification. The epilimnion is the uppermost stratum and is the most sensitive to external conditions, such as temperature. It is also the most exposed to thermal radiation (Christenson et al., 2015). The metalimnion is characterized by the thermocline, which is defined by a dramatic decrease in temperature with depth. The hypolimnion rests below the metalimnion. It receives the least amount of light and experiences the lowest temperatures that are largely determined by spring lake turnover (Christenson et al., 2015).
As mentioned before, lakes serve as regulators in several biogeochemical cycles, including the nitrogen and phosphorus cycles; however, their exposure to ambient conditions means they are also exposed to pollutants. Both nitrogen and phosphorus are regulators of biological productivity, especially in lakes, as they are necessary reactants in photosynthesis. Nitrogen is most abundant in the form of N\textsubscript{2} and through various fixation processes it becomes available in lake environments for uptake by biota (Wetzel, 2001). Phosphorus in most lake environments is available as dissolved phosphate and forms from weathering rock or recycling of organic matter (Cohen, 2003; Wetzel, 2001). The phosphate can react with cations in the water column but also may be taken up by life forms through photosynthesis (Wetzel, 2001). Dissolved substances and particulate matter enter lakes through groundwater, rivers, gas or atmospheric exchange, and precipitation. Depending on the location of a lake, pollutants or excess nutrients have varying degrees of effects ranging from slight shifts in trophic states to severe eutrophication with toxic algal blooms (Cohen, 2003).

1.3 Volcanic Lakes

Volcanic lakes are found all over the world. They are extremely diverse in chemical composition and physical characterization. These lakes serve as surface expressions, or “blue windows”, into their underlying hydrothermal systems (Christenson et al., 2015). The residence times of water in lakes is defined by the mass of lake water divided by its total input or output, which are equal at steady state (Varekamp, 2003). Volcanic lakes are frequently monitored because volcanic inputs
impact lake water quality. Additionally, compositional lake water monitoring provides a glimpse into the subsurface processes that may occur with volcanic activity (Rouwet et al., 2014).

Volcanic lakes are classified into six sub-classes (Christenson et al., 2015) based on their chemical and physical constraints: erupting (Class 1), peak activity (Class 2), high activity (Class 3), medium activity (Class 4), low activity (Class 5), and no activity (Class 6). Erupting lakes are characterized by varying lake volume, high temperatures, and hyperacidic waters. Volume varies more frequently in these lakes, because evaporation due to volcanic activity is typically greater than the recharge of meteoric water. Peak activity lakes share common characteristics with erupting lakes; however, instead of just being hyperacidic they are highly saline with concentrations of total dissolved solids (TDS) higher than 300 g/L. Erupting lakes and peak activity lakes are not considered to be in steady state equilibrium, setting them apart from the other sub-classes of volcanic lakes. High activity lakes are divided into further classifications based on concentration of TDS and temperature. All high activity lakes have low pH values and high concentrations of salts, but hot acidic high activity lakes have higher TDS concentrations and higher temperatures than cool acidic high activity lakes. Medium activity lakes do not have the same obvious volcanic inputs that high activity lakes have. Instead, their volcanic inputs are the result of hydrothermal systems and volcanic vapor inputs, such as CO₂ and H₂S. Again, these lakes are subdivided into two other classes, but they generally have low pH values, and are above environmental temperature. Low activity lakes are either characterized as either acid sulfate lakes with a TDS concentration below 10 g/L or
CO₂-dominated lakes (shallow or deep which are referred to as Nyos-type lakes). All other volcanic lakes fall under the classification of no activity lakes, which contain waters of meteoric origin and are generally neutral (Rouwet et al., 2014; Pasternack and Varekamp, 1997).

Volcanic lakes can be classified more simply using four main criteria to describe their origination: 1) the geotectonic setting in which the lake is found; 2) the relationship between volcanism and lake formation; 3) the timing of lake formation and the relationship to volcanism; 4) the location of the lake in relation to the volcanic center (Christenson et al., 2015). Classification through this method may include lakes that may not have a direct volcanic association such as lakes of the East African Rift system or lakes that have been damned by volcanic deposition, like Spirit Lake in Washington, which is still recovering from the eruption of Mt. St. Helens in 1980 (Christenson et al., 2015).

Additional classifications are based on lake origin, lake setting and chemical composition of lake waters. The first class is defined by lakes that reside in active volcanic craters or craters of recently active volcanoes and that directly interact with volcanic gases via magmatic-hydrothermal systems that may only several kilometers from the lake bottom contaminating groundwater. Lakes receiving substantially processed fluids from hydrothermal systems associated with active volcanoes define the second class. However, since the fluids that interact with the lake are substantially processed, these lakes receive fewer volcanic contaminants than the previous class. Volcanic lakes representing the third class are still characterized by volcanic fluid input, but these inputs have lost their reactive components and are primarily CO₂ or
carbonate by nature. The last class contains lakes that are controlled by meteoric contributions due to the lack of volcanic geothermal inputs or the size of the lakes (Christenson et al., 2015). Fundamental differences between the various classes of volcanic lakes and potential classification parameters are further discussed by Varekamp (2015) and Varekamp et al., (2000).

1.4 Volcanic Hydrothermal and Geothermal Systems

Volcanic hydrothermal systems can occur in a range of tectonic settings, and often accompany many active and dormant volcanoes (Arnórsson, 2007; Henley and Ellis, 1983). For instance, converging plate boundaries are usually associated with andesitic volcanoes, which may heat geothermal systems indirectly through magma tendrils. In contrast, diverging plate boundaries are associated with sheeted dyke complexes that may more directly provide the heat for geothermal systems (Arnórsson, 2007). Geological structures such as deep fractures, fissures, hot springs, calderas and ring structures may all be associated with thermal systems (Arnórsson, 2007; Henley and Ellis, 1983). These systems can be composed of a mixture of meteoric water, seawater, or a combination of both and volcanic inputs. Water may reach depths of 8km below the surface of the earth where temperatures could be as high as 400°C. Fluid circulation is mainly density driven because magma heats fluids and they are then transported to shallower depths, displacing denser fluid which eventually gets reheated (Arnórsson, 2007).

Geothermal systems can be classified as high temperature or low temperature, hot water or vapor dominated, and volcanic or non-volcanic. Hot water systems are
found where sedimentary or volcanic rock is able to hold fractures or faults open (White, 1971). Vapor dominated systems mature from hot water systems, formed when the heat supply becomes greater than the rate of water recharge to the system and a large portion of the circulating fluid is vaporized (Arnórsson, 2001; White, 1971).

Despite the various types of systems that exist, uniformity still occurs. In all systems, water is the dominant fluid component (Arnórsson, 2007). Low or moderate temperature hot springs associated with geothermal systems are chemically similar to the local groundwater; however, higher temperature hot springs are more similar to their circulating fluid, which is enhanced in alkali chlorides, SiO$_2$ and As.Rarely do volcano-hydrothermal systems have a large component of juvenile waters and very low pH values, or high TDS and high temperatures (e.g., Copahue, Argentina, Varekamp et al., 2010).

The composition of fluids is ultimately determined by mineral equilibria; however, tectonic setting—the mineralogy and chemical composition of parent rock—also affects the type of fluid produced (Arnórsson, 2007; Henley and Ellis, 1983). The circulating fluid may be composed of H$_2$O, CO$_2$, SO$_2$, H$_2$, HCl, and HF. Salts are common solutes and often define thermals fluids since the pH of thermal systems is dependent on salinity (Henley and Ellis, 1983). There are two types of fluids: primary fluids and secondary fluids. Primary fluids may undergo separation and mixing processes in order to form secondary fluids. These processes include mixing of CO$_2$ from a deep source with heated groundwater, boiling of a fluid until it reaches the steam phase, and mixing of geothermal fluids with cooler shallower
For primary fluids, NaCl waters are the most common component and have chloride concentrations from 100s ppm to 1000s ppm. The only conservative element in NaCl waters is chloride. Acid sulfate waters, which are most often associated with andesitic volcanoes, are acidic with pH values ~2. Their acidity is attributed to concentrations of HCl and HSO$_4^-$.

High salinity waters, which are formed by the dissolution of evaporites or magmatic interactions with HCl, are geothermal brines. Carbon dioxide waters are a common secondary fluid and can be thermal or be non-thermal. They are typically high in carbonate concentrations and usually are not fixed to hot springs or vents near volcanoes. They are formed by the interactions of ground or surface waters with magmatic, metamorphic, or mantle CO$_2$ (Arnórsson, 2007).

1.5 Carbon Cycling in Volcanic Lakes

Lakes are active sites for carbon cycling, specifically the transformation, transportation and sequestration of carbon. The dominant carbon inputs in lakes are dissolved inorganic carbon, dissolved organic carbon, particulate inorganic carbon, and particulate organic carbon (Tranvik et al., 2009). Carbon dioxide has an important role in many aspects of carbon cycling. Dissolution of carbon dioxide in lake water leads to the formation of carbonic acid, which then dissociates into bicarbonate (HCO$_3^-$) and H$^+$. Depending on pH, the bicarbonate may further dissociate into carbonate (CO$_3^{2-}$) and H$^+$. In most lakes, the pH is dependent on the buffering capacity of suspended matter or surrounding rock, which is largely conditional on the type of bedrock, but also the quantity of bases available (Cohen,
2003). The availability of CO$_2$ and other forms of carbon is dependent upon how carbon is cycled through photosynthesis, organic matter burial and carbon mineralization. Both internal and external differences amongst lakes may lead to variations in the proportions of carbon forms in the water column and sediment. Carbon may enter a lake system through the atmosphere, groundwater or upstream flow and it may leave a system through downstream export, groundwater, sedimentation or diffusive escape (Tranvik et al., 2009). However, not all lakes cycle carbon the same.

Carbon dioxide, in a volcanic lake setting, can be of thermal or non-thermal origin and may enter as a gas phase, CO$_2$ or carbonate. Degassing of CO$_2$ may occur through bubbling and diffusion from the water-atmosphere interface depending on its concentration in the lake system (Mazot and Bernard, 2015). Degassing, as well as the associated chemical and physical properties of volcanic lakes, is particularly important as more lakes with such geothermal inputs could evolve overtime and present problems if not monitored, or regulated (Kling et al., 2015).

After the limnic eruptions that occurred at Lake Nyos and Monoun in Cameroon, Africa during the 1970s and 1980s, the study of carbon dynamics in volcanic lakes progressed. These limnic eruptions released large amounts of carbon dioxide and suffocated, in the case of Lake Nyos, 1800 people in the surrounding area (Kusakabe, 2015). It became evident that further research on these lakes, and volcanic lakes in general, needed to be carried out in order to determine what factors determined the evolution of these lakes and what lead to their limnic explosions (Kling et al., 2015). Scientists studied the chemical evolution of carbon within the
lakes and their carbon recycling efficiency. They hypothesized that both Cameroonian lakes had a “density wall” that formed due to stratification. As geothermal CO₂ rose from the lake bottom, it became trapped by this density wall and ultimately lead to a dangerous accumulation of CO₂ which could have been released by an sudden shift in its state, such as a landslide, seismic activity or and internal wave (Kusakabe, 2015). Degassing pipes were installed in Nyos and Monoun to mitigate the possibility of another explosion, allowing for the steady and controlled degassing of CO₂ from the lake bottom (Kling et al., 2015).
2. Geological Setting

2.1 Newberry Volcano

Newberry Volcano is located in central Oregon east of the Cascade Range, near the western edge of the Columbia plateau lavas also known as the High Lava Plains (Williams, 1935; MacLeod and Sherrod 1988). Newberry is a shield volcano that spans 60km north-south and 30km east-west. It has an average caldera rim height of 1000m, with its highest point, Paulina Peak, reaching 2434m. Newberry caldera is ~ 5km north-south and ~7km east-west, and is host to two crater lakes: Paulina Lake and East Lake (Williams, 1935; MacLeod and Sherrod, 1988). Paulina Lake is the larger of the two lakes and the surface of the lake sits lower in elevation than the water surface of East Lake. The lakes are surrounded by a variety of volcanic features, including the Big Obsidian flow and a pumice cone that separates both lakes dating back 6 thousand years (MacLeod and Sherrod, 1988). Newberry was probably active more than 500,000 years ago, with its most recent eruption in the Holocene 1,300 years ago. The Newberry caldera has probably collapsed twice, but younger eruptions have filled it in with flows and breccia (Fitterman, 1988). Three fault zones meet at Newberry Volcano. The Sisters fault zone intersects Newberry from the northwest direction crossing older flows. The Brothers fault zone joins in from the southeast direction, but does not intersect any flows (Fitterman, 1988). The Brothers fault zone extends into the Blue Mountains and the Basin and Range province, just passing Newberry and may potentially have an effect on the volcano (MacLeod and Sherrod, 1988). The Walker Rim fault zone enters from the southwest and like the Sisters fault zone, offsets early flows (Fitterman 1988; MacLeod and Sherrod, 1988).
Figure 2.1.1: Location of Newberry Volcano in relation to the Sisters fault zone, Brothers fault zone, and the Walker Rim fault zone (Fitterman, 1988).

The shape of the Newberry volcano implies that it could be primarily composed of olivine basalt and andesite however, the type of underlying bedrock is unknown. The main shield was primarily formed by basaltic eruptions, alternating with rhyolitic domes and flows. The oldest flows are composed of rhyolite and appear less glassy than younger ones. They are found along the northeast side of East Lake and appear platy and blue-grey in color. Violent eruptions covered these rhyolites with basaltic ash, which have formed tuff, and scoria. Volcanic activity along fissures on the outer banks of the shield probably accompanied or followed the violent eruptions (Williams, 1935). More than 150 parasitic cinder cones have formed on the outer flanks of the volcano as well as several parasitic rhyolite hills. Younger basalt
flows are located outside the extent of caldera activity on the northwest part of the shield (Williams, 1935).

The most recent volcanic activity occurred during the Holocene and is split into episodes based on the creation of certain volcanic formations. The first episode occurred before the eruption of Mt. Mazama, and is characterized by an obsidian dome. The second episode is characterized by east rim fissure activity that produced cinder cones, flows, scoria, and potentially, rhyolitic eruptions. The third episode of Holocene activity resulted in the formation of a central pumice ring and other less extensive pumice rings, occurring some time after the eruption of Mt. Mazama. The forth episode was andesitic and basaltic in composition and the fifth episode consisted of obsidian flows and deposits of pumice. The most recent episode of eruptive volcanic activity produced pumice deposits along the southern edge of the caldera, the Paulina Lake ash flow, and the Big Obsidian Flow which currently covers an area of ~20km² just south of the lakes (MacLeod and Sherrod, 1988).

2.2 Geothermal System at Newberry Volcano

Several studies have been conducted at Newberry volcano in order to reveal its geothermal potential. The caldera water table is maintained by meteoric recharge. The water is heated through conduction and by geothermal fluids of a volcanic source (Sammel et al., 1988). Geological evidence provides insight into the probability of the existence of an active magma chamber beneath the volcano that was present over the last 10,000 years (MacLeod and Sherrod, 1988). Evidence for this chamber is based on the consistent Holocene silicic rock composition, the occurrence of basalt-rhyolitic
Holocene rocks at the boundary of an area characterized by silicic vents which are surrounded by basaltic vents, and a high conductive thermal gradient (MacLeod and Sherrod, 1988). Seismic imaging suggests that this magma body could exist ~3 km below the surface of the caldera (Sammel et al., 1988). Evidence for this magma chamber may be provided by the temporal repeat pattern of caldera eruptions. The period or repose, or semi-dormancy, of Newberry is around 2-3 thousand years. Since the last eruption occurred 1300 years ago it’s very likely that a magma chamber still exists at depth and will likely erupt again (MacLeod and Sherrod, 1988). Geothermal fluids observed at 932m in the Newberry-2 drill hole located in the southern central section of the caldera, had a temperature of 265°C. In addition, hydrothermal mineralogy indicates thermal fluxes from a deeper source, like a magma chamber (Fitterman, 1988). The structural location of Newberry volcano also makes the presence of geothermal activity plausible: the fault zones that intersect at Newberry contribute to increased permeability, setting the stage for more effective thermal energy transfer (Fitterman 1988).

2.3 Hydrology of the Newberry Caldera

Paulina Lake and East Lake are located in the summit caldera of Newberry Volcano. Paulina Lake has a surface altitude of ~1930m and a maximum depth of ~77m while East Lake is higher in altitude at ~1940m, and has a maximum depth of ~55m. The caldera floor is covered by volcanic structures including pumice cones, andesitic and rhyolitic flows and domes (Sammel and Craig, 1983; Williams, 1935). The caldera summit run also creates its own climate relative to the surrounding area.
These differences are most evident in the precipitation patterns as well as temperature. The average annual precipitation at Newberry caldera is \(~90\text{ cm}\) a year. Paulina Lake has a surface outflow in the form of Paulina Creek, which is regulated through a gate. The average annual outflow from Paulina Creek is \(0.51\text{ m}^3\text{ sec}^{-1}\). Since the average annual evaporation for the general Newberry area is \(~77\text{ cm}\), the average annual evaporation from Paulina and East Lake is probably less than \(~77\text{ cm}\) due to higher elevations and the effects of decreased pressure and temperature. The USGS hydrologic survey of Newberry volcano in 1983 calculated the average annual evaporation at Paulina Lake to be \(~48\text{ cm}\) and \(~71\text{ cm}\) at East Lake (Sammel and Craig, 1983).

The stable isotopes of O and H (\(\delta^{18}\text{O}\) and \(\delta^2\text{H}\) values) in the crater lake waters, plot on an evaporation line that intersects the meteoric water line at the composition of local meteoric waters. This strongly suggests that the bulk of the fluid composition is meteoric water. The \(\delta^{18}\text{O}\) and \(\delta^2\text{H}\) from Paulina Lake hot springs, as well as the \(\delta^{18}\text{O}\) and \(\delta^2\text{H}\) of East Lake hot springs show a mixing relationship between lake waters and meteoric waters (Sammel and Craig, 1983).
3. Previous Work at the Newberry Crater Lakes

In the years 2009-2012, 2014 and 2015 students from Wesleyan University collected samples and field data from the two Newberry crater lakes. Surveying of the lakes occurred during the months of June, July and August. These data from sediment and water analyses, largely collected by Lefkowitz, 2012 and Lefkowitz et al. 2016, provide a brief history of Paulina Lake and East Lake. The data suggest distinct and persistent chemical differences between the two lakes. East Lake waters have pH values between 6 and 7 while Paulina Lake waters have values greater than 8. These values vary with depth and with season. Both lakes have different concentrations of anions and cations. Paulina Lake has ~400 ppm of HCO$_3$ while East Lake waters contain ~130 ppm of HCO$_3$. Cation concentrations in Paulina Lake are generally higher than those in East Lake. Dissolved carbon in East Lake is very heavy in $\delta^{13}$C while Paulina Lake has lower $\delta^{13}$C DIC values that barely vary with depth. East Lake has a high internal $P_{CO_2}$ compared to ambient partial pressure of CO$_2$, whereas in Paulina Lake the internal partial pressure is much more modest. Sediment chemistries between the two lakes also vary. East Lake has 8-12% organic carbon while Paulina Lake has 2.5-5%. Paulina Lake has up to 14% Fe$_2$O$_3$ while East Lake has 1-2%, and both lakes have silica rich sediments. East Lake sediments have relatively high concentrations of mercury and low arsenic, whereas Paulina Lake is characterized by high arsenic concentrations and low mercury in its sediment. Disparities between water and sediment chemistry suggest different types of geothermal inputs into each lake: a geothermal fluid at Paulina Lake and a fluid dominated by geothermal gases in East Lake. Another fundamental difference between the two lakes is their
morphology. Paulina Lake more or less resembles a deep bathtub while East Lake is mainly shallow with a single, deep funnel-shaped crater zone. These two morphologies lead to distinct differences in their mixing behavior (Lefkowitz et al., 2016).
4. Methods

4.1 Field Methods

4.1.1 Water Samples

Vertical water profiles were taken at Station 1 (43.73299 N, 121.20098 W) in East Lake. The YSI Model 52 Dissolved Oxygen Meter measured temperature and dissolved oxygen (DO) to 30m depth and the 3000 T-L-C Meter measured temperature and conductivity to 45m depth. Before going into the field, each instrument was calibrated with standard solutions at Wesleyan University. Lack of certainty in measurements stems from errors in vertical depth as strong lake currents might have caused a more angled or inclined probe descent into the water column.

Water profiles with depth were taken from two sites during the summer of 2015 (KELA 43.73286 N, 121.20525 W; EL 43.73338 N, 121.207221 W). These sites were in the deepest part of East Lake. A bulk water sample was collected at 10m vertical increments, using a teflon van Dorne water sampler. The KELA profile started at 0m and went to 40m depth. The EL profile went from 5m to 45m depth. Each bulk water sample was subsampled for: 1) $\delta^{13}$C (DIC) determination using an exetainer vial; 2) alkalinity using a serum vial with compression lid; 3) trace elements that were placed in an ultra clean amber bottle and acidified and; 4) stable isotope analysis using 5ml glass tight vials. The remainder of water from the bulk sample was stored in HDPE bottles of 125ml and 175ml. Both bottles were used for IC and ICP analyses for anions and cations. All samples, except for the water that was extracted from the bulk sample for trace elements, were filtered in the field using 30-50ml Luer-Lock syringes and 0.45um filters. One hot spring was sampled (43.71995 N,
121.20060 W) for a similar set of analyses. For each analysis that was subsampled, 11 samples were collected in the field.

4.1.2 CO₂ Flux Data Collection

CO₂ flux surveys were conducted on East Lake during the summer of 2015 over a 7-day period from June 26th to July 2nd at approximately 40 different locations on the lake. Location was determined using a GPS on the boat. A floating accumulation chamber was used (West Instruments, Pisa, Italy) to measure the increase in CO₂ concentration over time upon deployment onto the surface of the lake. Most initial CO₂ concentrations were close to atmospheric values (~400 ppm) and increased over the 30-60 second interval in which a LICOR CO₂ Analyzer LI-6252 and a laptop measured and recorded concentrations of CO₂. The analyzer measures CO₂ concentrations by employing infrared absorption spectroscopy. Prior to field use, the CO₂ analyzer was calibrated at Wesleyan University using two standard gases at 350 ppm and 500 ppm CO₂. The CO₂ flux value for each site was calculated using the time-dependent concentration data, water temperature, atmospheric pressure, and the surface area to volume (dimensions) of the accumulation chamber. Air and water temperature were not measured during data collection because water temperature remained relatively stable at ~20°C during the survey. During a few days of surveying, remaining at the initial GPS location was difficult due to varying wind speed and drifting. The contents within the accumulation chamber were sampled by inserting a syringe into a septum, collecting a sample and then injecting the sample into a pre-evacuated exetainer for δ¹³C CO₂ measurement.
4.1.3 Gas Chamber and Air Samples

During the summer of 2015, 8 gas samples were extracted from the accumulation chamber using a 30ml syringe with a 26-gauge needle. In the field, samples were dispensed into pre-evacuated 12ml extainer vials. In late August and early October of 2015 several air samples from around East Lake were collected and dispensed into extainers vials. Several of those samples had been dispensed into ‘blood serum vials’ which then needed to be transferred into extainer vials.

<table>
<thead>
<tr>
<th>Sample Label</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>ELIS1</td>
<td>43.72446 N, 121.19607 W</td>
</tr>
<tr>
<td>ELIS2</td>
<td>43.72446 N, 121.19608 W</td>
</tr>
<tr>
<td>ELIS3</td>
<td>43.72076 N, 121.12164 W</td>
</tr>
<tr>
<td>ELIS4</td>
<td>43.72076 N, 121.12164 W</td>
</tr>
<tr>
<td>ELIS5</td>
<td>43.72342 N, 121.20913 W</td>
</tr>
<tr>
<td>ELIS6</td>
<td>43.72342 N, 121.20914 W</td>
</tr>
<tr>
<td>ELIS7</td>
<td>43.72087 N, 121.20256 W</td>
</tr>
<tr>
<td>ELIS8</td>
<td>43.72087 N, 121.20257 W</td>
</tr>
</tbody>
</table>

Table 4.1.3.1: Gas chamber sample and their GPS location at East Lake. The CO₂ concentration at the time of gas extraction from the chamber was also recorded.

<table>
<thead>
<tr>
<th>Sample Label</th>
<th>Location</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>RELAIR-1</td>
<td>43.72371 N, 121.19602 W</td>
<td>8/31/15</td>
</tr>
<tr>
<td>RELAIR-2</td>
<td>43.72328 N, 121.19661 W</td>
<td>8/31/15</td>
</tr>
<tr>
<td>RELAIR-5</td>
<td>43.72321 N, 121.19389 W</td>
<td>8/31/15</td>
</tr>
<tr>
<td>RELAIR-1 (blood vial)</td>
<td>43.73732 N, 121.20840 W</td>
<td>9/10/15</td>
</tr>
<tr>
<td>RELAIR-4 (blood vial)</td>
<td>43.72917 N, 121.20197 W</td>
<td>9/10/15</td>
</tr>
<tr>
<td>RELAIR-6 (blood vial)</td>
<td>43.72382 N, 121.19604 W</td>
<td>9/10/15</td>
</tr>
</tbody>
</table>

Table 4.1.3.2: Air samples and their GPS locations at East Lake.

4.1.4 Sediment Cores

A total of 7 sediment cores were extracted, using a percussion corer, from various sites in East Lake. There were 2 long cores, with a length greater than 100cm
at the time of extraction, and 5 short cores less than 100 cm long at the time of extraction. Cores were kept vertical to minimize disturbance. The majority of the cores were collected at water depths around 15 m (KCEL3, KCEL4, KCEL5, KCEL6, KCEL7). KCEL1 was taken at a water depth of 51 m and KCEL2 was taken at water depth 50 m. Two cores (KCEL5, KCEL2) were extruded in the laboratory. These cores were sliced at 2 cm increments, placed on Styrofoam plates and allowed to dry in order to calculate bulk dry density. Once dry, sediment was homogenized using a mechanical grinder as well as a mortar and pestle. They were then placed into plastic containers and used for further sedimentary analysis.

Figure 4.1.4.1: East Lake 2015 core sites (Google Maps).
Table 4.1.4.1: Locations, water depths and lengths of each core collected.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Location</th>
<th>Lake Depth (m)</th>
<th>Core Length (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCEL1</td>
<td>43.73306 N, 121.20811 W</td>
<td>49</td>
<td>50</td>
</tr>
<tr>
<td>KCEL2</td>
<td>43.73306 N, 121.21429 W</td>
<td>50</td>
<td>105</td>
</tr>
<tr>
<td>KCEL3</td>
<td>43.72608 N, 121.20145 W</td>
<td>10</td>
<td>47</td>
</tr>
<tr>
<td>KCEL4</td>
<td>43.72427 N, 121.20326 W</td>
<td>13</td>
<td>85</td>
</tr>
<tr>
<td>KCEL5</td>
<td>43.72498 N, 121.20485 W</td>
<td>9</td>
<td>110</td>
</tr>
<tr>
<td>KCEL6</td>
<td>43.72832 N, 121.20759 W</td>
<td>9</td>
<td>43</td>
</tr>
<tr>
<td>KCEL7</td>
<td>43.72516 N, 121.21667 W</td>
<td>20</td>
<td>51</td>
</tr>
</tbody>
</table>

4.1.5 Organic Matter

Several types of organic matter were collected from East Lake. Samples included multiple small *Nostoc* algal spheres about 0.5 to 1 cm in diameter, large *Nostoc* colonies with individuals ~5-7 cm in diameter, sections of “phytobergs”, and other algal species living near the shores of East Lake. Filters used for taking water samples were saved for diatom analyses. Some fish samples were taken for Hg analysis.

4.2 Laboratory and Analytical Methods

4.2.1 Biogenic Silica

Biogenic silica (BSi) analysis was carried out on a total of 48 samples from two sediment cores (KCEL5 and KCEL2). The analysis consisted of a two-part process as outlined by the LabCore SOP handouts following DeMaster (1992). The objective of this analysis was to differentiate between biogenic silica and the other silica fractions such as volcanic glass or silicate. The opaline silica that comprises the biogenic silica portion dissolves faster than other silica fractions. The time-
concentration line for the extracted silica is initially curved and becomes linear when silicate is the only material left dissolving. Time versus silica concentration graphs can be extrapolated to time zero, providing the biogenic silica portion. The first part of this process consisted of sample digestion in hot NaOH, where samples were treated with a pH close to 15 and subsampled at timed intervals. The second part consisted of the actual silica analysis through colorimetry. The visible-light UV spectrophotometer was calibrated with dissolved silica standards of 30 ppm, 60 ppm, 120 ppm, 480 ppm, 600 ppm, 900 ppm, 1200 ppm, 1500 ppm, and 2000 ppm. The absorbance of samples was applied to a calibration curve and silica concentrations were then recorded. The stepwise extraction method and extrapolation routine carries some inherent uncertainty with concentration values.

Figure 4.2.1.1: Silica concentrations over time for core KCEL5 sediment samples.
4.2.2 Carbon and Nitrogen Analysis

Carbon and nitrogen analyses were carried out on samples from cores KCEL5 (24 samples), KCEL2 (16 samples) and CLE12 (16 samples). A total of 24 samples were analyzed for C and N from KCEL5, 16 from KCEL2 and 16 from CLE12 using a Flash 1112 Series Elemental Analyzer (EA). Finely ground 15 mg sediment samples were wrapped in tin cups that were 11mm x 12mm. These samples were placed into circular trays, which were then mounted onto the sample holder of the EA. Each tray contained a blank that was a tin cup wrapped into a spherical shape with no sediment sample, 3 standards of l-cystine, 4 of aspartic acid and 2 to 3 standards, either l-cystine or aspartic acid, mixed amongst the unknown samples. Each sample required ~320 seconds to be analyzed. Organic matter samples were analyzed separately.

4.2.3 XRF

X-ray fluorescence (XRF) spectrometry for 8 major elements and about 25 trace elements was carried out on 19 samples from the KCEL5 core from East Lake. For each sample, 6g of finely ground sediment was pressed into a cylindrical briquette using a wax additive as a binder. The samples were used for trace element analyses against Geoquant analytical software of Bruker on the Bruker Pioneer S-4 XRF instrument at Wesleyan University. Standards were run concurrently and precision and accuracy for most elements was ~4%. Major element analyses were run on 0.5g samples, fused in a Li-tetraborate flux into thin discs. The discs were analyzed against elemental standard lines based on the SRMs of basalts, andesites and
rhyolites. Several sediment SRM were run as unknowns and reproduced within 1-2% precision. Many East Lake samples have silica concentrations >75% SiO$_2$, which is the highest silica standard for the Si calibration line. A silica correction equation was generated but, errors remain at ~2-3%. The BSi analyses, discussed above, were carried out on bulk samples, which contained 8-12% organic carbon. The XRF samples undergo combustion (LOI) prior to fusion, so XRF results are assumed to be on a volatile-free basis and Fe is assumed to be all Fe$_2$O$_3$. Comparison of the reported BSi and XRF analyses take these sample differences into account.

4.2.4 Mercury

Mercury concentrations were determined in 28 samples from KCEL5 and in 16 samples from KCEL2. Sediment samples were finely ground and the Hg was introduced through pyrolysis into the furnace of the DM-80 Hg analyzer at Wesleyan University. Detection was done using atomic absorption spectrophotometry. Sediment standards and SRMs were used to calibrate the instrument. Precision is within ~5% and routine lower detection limits are around 25 ppb of Hg.

Mercury was determined in a large sample of East Lake water at the University of Connecticut at Avery Point using a fluorescence Hg analyzer. The Hg was extracted from the water after HgCl$_2$ was added as a reductor, and purging of Hg from the fluid using Hg-free argon. Hg was amalgamated onto gold, which was placed in an oven and then transferred into the analyzer.
4.2.6 pH, Alkalinity, DIC

Alkalinity of water samples was determined at Wesleyan University using a Mettler DL12 auto-titrator. Alkalinities were determined in 16 water samples, 11 of which were from water profiles taken in the June/July of 2015, and 5 from a water profile taken in the October 2015. An initial pH reading was made at the onset of titration with 0.5 N HCl until a final pH of 4.320 was reached. Standard ocean water samples from Long Island Sound and Puerto Rico, with alkalinites of ~0.002 mol/L were used intermittently as informal standard checks. The pH values were determined at room temperature (~22°C) and were amended using Web-phreeq, an online program for aqueous speciation calculations, at field temperatures. In the first run on Web-phreeq, the alkalinity, lab pH and chemical composition of the water are entered at 22°C and charge balanced through manipulation of Cl contents, The total DIC was then recorded and used in the second run where field temperature and pH set to “floating” are used to calculate the pH at field temperature. A full carbon speciation is also calculated given the new parameters for pH and the temperature measured in the field.

4.2.7 IC and ICP

Ion chromatography (IC) analysis was carried out at Wesleyan University on both East Lake water profiles (KELA, EL). All filtered samples were analyzed for the anions chloride (Cl) and sulfate (SO4). The samples were evaluated against sets of 5 standard solutions that yielded calibration curves, with estimated errors of a few percent.
ICP analyses of water samples were run at Smith College in Massachusetts using a Teledyne Leeman Labs Inductively Coupled Plasma- Optical Emission Spectroscopy. The major elements Ca, Mg, Na, K and Si were analyzed in filtered bulk water samples. The standards used for ICP-OEC analysis were 1 ppm, 2 ppm, 5 ppm, 10 ppm, 20 ppm, and 60 ppm. They were made from 1000 mg/L stock solutions of Ca, Mg, Na, K and Si diluted with 2% nitric acid. Precision of these analyses were within 2%.

4.2.8 Stable isotopes O, H, and C

The δ18O and the δ2H of water samples were run on both water profiles (KELA, EL) collected in East Lake during the June/July of 2015. The water samples were analyzed at the UC-Davis stable isotope lab using a Lazer Water Isotope Analyzer V2 and final values are reported relative to VSMOW. The δ13C values of DIC in water samples were determined after gas evolution using phosphoric acid. The CO2 was then run on a trace gas-IRMS. The isotope values were satisfactory and were confirmed by hidden standards. However, the carbon quantities associated with measured δ13C values typically did not match quantities from our own analyses and tended to be lower. Therefore, we have not used these carbon analyses in any of our considerations as discussed later on.

4.2.9 CO2 Flux Data

The CO2 flux data were further analyzed at Wesleyan University through several statistical techniques. For each of the 40 sites, a CO2 concentration versus
time graph was created, providing a best-fit line for increase in CO₂ (ppm) per second. A K factor was determined with the equation: K = (86400*P/10^6*R*T_k) where P is the barometric pressure (820 mbar) expressed in HPa, R is the gas constant 0.0314510 bar L K⁻¹ mol⁻¹, T_k is the air temperature in Kelvin, and where 0.167702 is the net volume of the chamber over the area of the inlet chamber. The flux of CO₂ was then calculated from multiplying the slope of the best-fit line by the K factor and was expressed in moles of CO₂ m⁻² day⁻¹.

Sequential Gaussian simulation was run using the 40 calculated flux measurements and their GPS positions to establish a better spatial distribution of flux points. The 40 data points were first declustered and had inverse weighting interpolation performed on them to increase the data pool size to a grid of 7234 synthetic data points. A larger data pool allowed for a more complete variogram and histogram that would resemble the original data statistically and spatially. The SGS methodology used by Mazot and Bernard (2015) on a similar data set was not fully achieved. Typically after declustering, a normal score transform is run before SGS; however, this skewed data as a few of the flux measurements in the field dataset were outliers. Nonetheless, after retransformation of the data, a map was created giving the extended spatial pattern of CO₂ fluxes.
5. Results

5.1 Field Data

5.1.1 Temperature

Figure 5.1.1.1: Temperature depth profiles of East Lake (June 2015) showing the warm epilimnion and cold hypolimnion, separated by the thermocline at 10-20m depth.

Temperature profiles (Station 1: 43.73299°N, 121.20098°W) were taken using two different probes in June 2015. The data shows a slight decrease in temperature in the first 10m in the vertical profile. The thermocline exists at 10m to 20m depth, with a steady decrease in temperature from 20°C to ~5°C. Below 20m the temperature remains constant at around 5°C. The profile shows thermal stratification within the epilimnion largely affected by surface conditions. The temperatures in the hypolimnion are probably established during winter and after spring turnover. The
difference in the two measured profiles may be related to issues with staying “on station” during measurements due to strong winds or boat drift causing the temperature sonde to descend along an inclined path, not vertically. Given these uncertainties, Temperature2, is probably the better approximation of the temperature structure in the epilimnion and metalimnion, establishing the thermocline at ~15m depth. The presence of cold bottom waters in early summer indicates that mixing between the deep and shallow waters is limited.

5.1.2 Dissolved Oxygen (DO)

Figure 5.1.2.1 Depth profile of dissolved oxygen in East Lake in June 2015. All measured values are over saturated compared to water equilibrated with air 2km elevation.
A dissolved oxygen depth profile, taken at Station 1, shows moderate concentrations at 0-5m depth, whereas DO increases between 10m and 25m depth from ~10mg/L to ~15mg/L. As a result of the limited cable length, no data was collected below 30m in depth. The higher DO below 5m correlates with the decreasing temperatures of the lake water, indicating water equilibration with the air at low temperatures at the time of spring turnover.

5.1.3 Conductivity

![Conductivity Profile](image)

Figure 5.1.3.1: Depth profile of conductivity in East Lake in June 2015.

The measured conductivity profile taken at Station 1 consists of data that were corrected to 25°C. From 0m to 10m conductivity is in the range of 0.358μC/cm to 0.360μC/cm and below 10m, the conductivity drops from ~0.356μC/cm to ~0.353μC/cm. Conductivity then increases below 20m from ~0.353μC/cm to
~0.362m$\mu$/cm at 45m depth. Although differences are very small (1-2% variation), the bottom waters have a slightly higher conductivity and a layer of lower conductivity occurs at 15-20m depth.

5.2 Water chemistry

5.2.1 Major Anions

Figure 5.2.1.1: The SO$_4^{2-}$ concentrations in East Lake show some variation with depth, but are within a narrow range of 64.5 to 67.4 ppm.
Figure 5.2.1.2: The Cl⁻ concentrations in East Lake are very low and show minor variation with depth that are probably within analytical error.

The SO₄²⁻ concentrations are highest in the surface waters (66 to 67 ppm) and bottom waters show only minor variations with depth. The Cl⁻ concentration is uniformly low in the lake waters at ~0.8 ppm, with a potential slight enrichment in the surface water layer.

5.2.2 Alkalinity

Both profiles show a similar trend in alkalinity with depth. Alkalinity decreases with depth until about 20m where there is a gradual increase in alkalinity until about 40m. Surface values range from .00226meq/L to .00228meq/L and the
deepest waters have values that range from .00221meq/L to .00223meq/L. The total variation is limited to 3-4%, which is close to the analytical precision.

Figure 5.2.2.1: Vertical profiles of alkalinity with depth.

5.2.3 Major Cations

Major cation concentrations (Ca, Mg, K, Na, Si) range from several ppm (K) up to 29 ppm (Ca). All major cations have their highest concentration in the surface waters (less than 15m depth). East Lake hot spring had higher concentrations of K (9.3 ppm) and Ca (70.5 ppm). Concentrations of Mg and Na are also higher in the hot springs with values of 34.6 ppm and 55.4 ppm respectively. Dissolved silica concentrations are close to constant at ~6.4 ppm below 20m whereas the other elements show minor variations. East Lake hot springs (KES3) have cation
concentrations twice as high and silica concentrations 15x as high as lake waters. The high silica concentrations in the springs are related to the temperature of the springs.

Figure 5.2.3.1: Calcium, magnesium and sodium concentrations against depth for the two East Lake water profiles.

Figure 5.2.3.2: Silica and potassium concentrations against depth for the two East Lake water profiles.
Table 5.2.3.1: Major cation data from East Lake water profiles for June 2015. Includes data from two water profiles and one hot spring.

5.2.4 pH

Figure 5.2.4.1: Vertical pH profile created using data from the two East Lake water profiles. The “Measured” values were recorded as 22°C in the lab, while “Calculated” values have been corrected for the temperature difference between the lab and field using Web-phreeq.
Two vertical pH profiles were acquired at sites, EL and KELA, and measurements were carried out at Wesleyan University. The lab values were then converted into field pH values after correcting for the temperature difference. The EL and KELA water profiles display surface waters with pH values around 6.7, but exhibit opposite trends between 10 and 30m. At 45m in depth, both profiles have similar pH values once more.

5.2.5 Phosphorus

![Phosphorus concentrations against depth.](image)

Phosphorus was the only nutrient measured and concentrations are relatively low in East Lake. The surface layers show a depletion in phosphorus (~20 ppb), which is a typical trend for nutrients in lakes (Wetzel 2001). Bottom waters have 30-35 ppb phosphorus.
5. 3 Stable Isotopes

5.3.1 Stable Isotopes of Oxygen and Hydrogen (Water)

Figure 5.3.1.1: Stable isotope values in East Lake water with depth.
The $\delta^{18}O$ in water from East Lake shows values between $-7.8\%$ and $-8.45\%$ with the heaviest values found in the surface layer. Slightly lighter values occur between 10 and 30m depth with heavier values at the lake bottom. The $\delta^2H$ in East Lake generally becomes more negative with depth. Both profiles show this trend with depth. However, the KELA profile has a positive excursion from around $-76.5\%$ to around $74.5\%$ between 20 and 30m and a negative excursion from around $-74.5\%$ to around $-77.5\%$ between 30 and 40m depth. The opposite trends in $\delta^{18}O$ and $\delta^2H$ at 30m depth in the KELA and EL profiles are odd, and as of now unexplained.

5.3.2 $\delta^{13}C$ DIC

Figure 5.3.2.1: Depth profile of $\delta^{13}C$ (DIC) in East Lake. Note the heavier values in the surface waters.
The $\delta^{13}C$ (DIC) values in East Lake are heaviest in the surface waters with values that are unusually high (+3‰ to +5‰). The bottom waters have values of +0.3 to +3‰. The 2 to 2.5‰ gradient in the $\delta^{13}C$ (DIC) over a 50m depth interval is pronounced.

5.4 Gas and Air Data

5.4.1 Flux Data

$CO_2$ emission rates were measured in East Lake at 40 sites with a floating accumulation chamber. Most sites were devoid of rising bubbles, while at a few sites bubble activity was observed in the surface waters. The total range of measured values is from 0.03 to 0.9 moles of $CO_2$ m$^{-2}$ day$^{-1}$. The majority of measured $CO_2$ fluxes fall in the range of 0.1 to 0.2 moles of $CO_2$ m$^{-2}$ day$^{-1}$.

Figure 5.4.1.1: Map of East Lake with $CO_2$ flux measurement points collected in the early summer of 2015. The flux units are moles of $CO_2$ m$^{-2}$ day$^{-1}$. 
<table>
<thead>
<tr>
<th>Label</th>
<th>Date</th>
<th>°N</th>
<th>°W</th>
<th>Flux (mol m(^{-2}) day(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>EL6_27 S1</td>
<td>6/27/15</td>
<td>43.72762</td>
<td>121.20936</td>
<td>0.115014174</td>
</tr>
<tr>
<td>EL6_27 S2a</td>
<td>6/27/15</td>
<td>43.73364</td>
<td>121.21501</td>
<td>0.108661965</td>
</tr>
<tr>
<td>EL6_27 S2b</td>
<td>6/27/15</td>
<td>43.73414</td>
<td>121.21545</td>
<td>0.299421186</td>
</tr>
<tr>
<td>EL6_27 S3</td>
<td>6/27/15</td>
<td>43.72867</td>
<td>121.2103</td>
<td>0.046001137</td>
</tr>
<tr>
<td>EL6_28 S1a</td>
<td>6/27/15</td>
<td>43.73283</td>
<td>121.20961</td>
<td>0.10681387</td>
</tr>
<tr>
<td>EL6_28 S2a</td>
<td>6/27/15</td>
<td>43.73259</td>
<td>121.21398</td>
<td>2.280363902</td>
</tr>
<tr>
<td>EL6_28 S2b</td>
<td>6/27/15</td>
<td>43.73326</td>
<td>121.21275</td>
<td>0.425312669</td>
</tr>
<tr>
<td>EL6_28 S3</td>
<td>6/27/15</td>
<td>43.73355</td>
<td>121.21342</td>
<td>0.179248146</td>
</tr>
<tr>
<td>EL7_1 S1a</td>
<td>6/29/15</td>
<td>43.73237</td>
<td>121.20128</td>
<td>0.227329551</td>
</tr>
<tr>
<td>EL7_1 S1b</td>
<td>6/29/15</td>
<td>43.73352</td>
<td>121.20117</td>
<td>0.285788479</td>
</tr>
<tr>
<td>EL7_1 S1c</td>
<td>7/1/15</td>
<td>43.72115</td>
<td>121.20188</td>
<td>0.256979316</td>
</tr>
<tr>
<td>EL7_1 S1d</td>
<td>7/1/15</td>
<td>43.72091</td>
<td>121.20147</td>
<td>0.45618793</td>
</tr>
<tr>
<td>EL7_1 S1e</td>
<td>7/1/15</td>
<td>43.72075</td>
<td>121.20146</td>
<td>0.426928526</td>
</tr>
<tr>
<td>EL7_1 S1f</td>
<td>7/1/15</td>
<td>43.72037</td>
<td>121.20558</td>
<td>0.197302652</td>
</tr>
<tr>
<td>EL7_2 A</td>
<td>7/2/15</td>
<td>43.72062</td>
<td>121.20393</td>
<td>0.086455959</td>
</tr>
<tr>
<td>EL7_2 B</td>
<td>7/2/15</td>
<td>43.72063</td>
<td>121.19903</td>
<td>0.268051828</td>
</tr>
<tr>
<td>EL7_2 C</td>
<td>7/2/15</td>
<td>43.72589</td>
<td>121.20336</td>
<td>0.166320292</td>
</tr>
<tr>
<td>EL7_2 D</td>
<td>7/2/15</td>
<td>43.72111</td>
<td>121.20331</td>
<td>0.100629361</td>
</tr>
<tr>
<td>EL7_2 E</td>
<td>7/2/15</td>
<td>43.72091</td>
<td>121.20147</td>
<td>0.45618793</td>
</tr>
<tr>
<td>EL7_2 F</td>
<td>7/2/15</td>
<td>43.72075</td>
<td>121.20146</td>
<td>0.426928526</td>
</tr>
<tr>
<td>EL7_2 G</td>
<td>7/2/15</td>
<td>43.72037</td>
<td>121.20558</td>
<td>0.197302652</td>
</tr>
<tr>
<td>EL7_2 H</td>
<td>7/2/15</td>
<td>43.72062</td>
<td>121.20393</td>
<td>0.086455959</td>
</tr>
<tr>
<td>EL7_2 I</td>
<td>7/2/15</td>
<td>43.72063</td>
<td>121.19903</td>
<td>0.268051828</td>
</tr>
<tr>
<td>EL7_2 J</td>
<td>7/2/15</td>
<td>43.72589</td>
<td>121.20336</td>
<td>0.166320292</td>
</tr>
<tr>
<td>EL7_2 K</td>
<td>7/2/15</td>
<td>43.72111</td>
<td>121.20331</td>
<td>0.100629361</td>
</tr>
<tr>
<td>EL7_2 L</td>
<td>7/2/15</td>
<td>43.72091</td>
<td>121.20147</td>
<td>0.45618793</td>
</tr>
<tr>
<td>EL7_2 M</td>
<td>7/2/15</td>
<td>43.72075</td>
<td>121.20146</td>
<td>0.426928526</td>
</tr>
<tr>
<td>EL7_2 N</td>
<td>7/2/15</td>
<td>43.72037</td>
<td>121.20558</td>
<td>0.197302652</td>
</tr>
<tr>
<td>EL7_2 O</td>
<td>7/2/15</td>
<td>43.72062</td>
<td>121.20393</td>
<td>0.086455959</td>
</tr>
</tbody>
</table>

Table 5.4.1.1: Original flux measurements collected during the summer of 2015 at various sites at East Lake.
5.4.2 $\delta^{13}C$ of Lake Gas and Ambient Air Samples

Lake gas and ambient air samples collected at East Lake have relative light $\delta^{13}C$ (CO$_2$) values. Lake gas samples extracted from the accumulation chamber are fairly uniform and range from -10 to -11.4‰. These samples are mixtures of ambient air and lake gas since the chamber is filled with air prior to flux measurement.

Ambient air samples from various sites around East Lake show a wider range of $\delta^{13}C$ (CO$_2$) ranging from -9.8 to -17.4‰. Each of these samples were also analyzed for the concentration of CO$_2$ in the gas sample, however the measurements taken for these samples assumed that the containers were equilibrated at exactly 1 atm, which was not the case. The local pressure at East Lake is ~0.78 atm and as a result, there is some uncertainty in the CO$_2$ concentrations. Pure ambient air should have a $\delta^{13}C$ (CO$_2$) value of ~0‰ (NOAA) and the analytical data show that the lake CO$_2$ is isotopically lighter than the ambient air CO$_2$. It is likely that the ambient air at East Lake is already a mixture of atmospheric CO$_2$ and lake CO$_2$ and no “pure” atmospheric air was ever sampled.

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>$\delta^{13}C$ (%)</th>
<th>CO$_2$ (ppm)</th>
<th>Sample Type</th>
<th>$\delta^{13}C$ (%)</th>
<th>CO$_2$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmosphere</td>
<td>-10.38</td>
<td>410</td>
<td>Gas Chamber</td>
<td>-11.28</td>
<td>405</td>
</tr>
<tr>
<td>Fall 2015</td>
<td>-10.37</td>
<td>408</td>
<td>Summer 2015</td>
<td>-11.03</td>
<td>410</td>
</tr>
<tr>
<td></td>
<td>-9.80</td>
<td>407</td>
<td></td>
<td>-10.81</td>
<td>416</td>
</tr>
<tr>
<td></td>
<td>-11.63</td>
<td>696</td>
<td></td>
<td>-11.40</td>
<td>423</td>
</tr>
<tr>
<td></td>
<td>-17.40</td>
<td>698</td>
<td></td>
<td>-11.08</td>
<td>414</td>
</tr>
<tr>
<td></td>
<td>-14.72</td>
<td>513</td>
<td></td>
<td>-10.13</td>
<td>437</td>
</tr>
<tr>
<td></td>
<td>-10.25</td>
<td>388</td>
<td></td>
<td>-10.25</td>
<td>388</td>
</tr>
<tr>
<td></td>
<td>-10.01</td>
<td>443</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5.4.2.1: $\delta^{13}C$ values of air and gas samples obtained at East Lake.
5.5 Sediment Cores and their Chemical Composition

5.5.1 General Description

Cores that were collected from East Lake were dark in color when wet and rich in organic matter. The majority of the sediment was fine-grained and typically a shade of light grey-brown when dry. Larger bits and pieces of plant organic matter were present. We observed red hair-like strands of organic matter while extruding cores KCEL5 and KCEL2, presumably pieces of bottom vegetation.

5.5.2 Bulk Dry Density (BDD)

![Graph showing depth profile of bulk dry density of cores KCEL5 and KCEL2.]

Figure 5.5.2.1: Depth profile of bulk dry density of cores KCEL5 and KCEL2.
The bulk dry density (BDD) of core samples from KCEL5 varies between 0.2 and 0.4 gr/cm$^3$ with core depth. Samples from core KCEL2 have very high BDD between 10 and 20cm suggesting that the presence of an ash layer, devoid of light organic matter.

5.5.3 Major and Trace Elements

The bulk chemical composition of core samples represents the various components that make the sediment: components such as biogenic silica, organic matter, volcanic ash material, and aeolian dust. Some hydrothermal precipitates may be present as well. Major element analyses by XRF show high silica values (87-94%), very low iron (1.1 to 2.7% Fe$_2$O$_3$) and Al$_2$O$_3$ in the range of 3-7%.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Na$_2$O</th>
<th>MgO</th>
<th>Al$_2$O$_3$</th>
<th>SiO$_2$$^*$</th>
<th>P$_2$O$_5$</th>
<th>K$_2$O</th>
<th>CaO</th>
<th>Fe$_2$O$_3$</th>
<th>MnO</th>
<th>TiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCEL5-7</td>
<td>BD</td>
<td>0.45</td>
<td>2.98</td>
<td>93.67</td>
<td>0.1</td>
<td>0.25</td>
<td>0.74</td>
<td>1.59</td>
<td>0.1</td>
<td>0.12</td>
</tr>
<tr>
<td>KCEL5-13</td>
<td>1.39</td>
<td>0.53</td>
<td>6.56</td>
<td>86.65</td>
<td>0.12</td>
<td>0.73</td>
<td>1.5</td>
<td>2.19</td>
<td>0.09</td>
<td>0.24</td>
</tr>
<tr>
<td>KCEL5-17</td>
<td>0.42</td>
<td>0.37</td>
<td>3.57</td>
<td>92.32</td>
<td>0.1</td>
<td>0.37</td>
<td>0.82</td>
<td>1.81</td>
<td>0.08</td>
<td>0.14</td>
</tr>
<tr>
<td>KCEL5-21</td>
<td>BD</td>
<td>0.65</td>
<td>3.36</td>
<td>92.68</td>
<td>0.08</td>
<td>0.34</td>
<td>0.82</td>
<td>1.83</td>
<td>0.09</td>
<td>0.15</td>
</tr>
<tr>
<td>KCEL5-33</td>
<td>0.06</td>
<td>0.51</td>
<td>4.47</td>
<td>92.46</td>
<td>0.09</td>
<td>0.46</td>
<td>0.6</td>
<td>1.07</td>
<td>0.04</td>
<td>0.24</td>
</tr>
<tr>
<td>KCEL5-37</td>
<td>BD</td>
<td>0.49</td>
<td>5</td>
<td>91.71</td>
<td>0.07</td>
<td>0.57</td>
<td>0.64</td>
<td>1.25</td>
<td>0.04</td>
<td>0.23</td>
</tr>
<tr>
<td>CLE 12-7</td>
<td>1.84</td>
<td>0.35</td>
<td>3.77</td>
<td>89.19</td>
<td>0.24</td>
<td>0.49</td>
<td>0.97</td>
<td>2.68</td>
<td>0.32</td>
<td>0.15</td>
</tr>
<tr>
<td>CLPA5 7</td>
<td>7.12</td>
<td>1.45</td>
<td>3.38</td>
<td>69.56</td>
<td>1.68</td>
<td>0.69</td>
<td>1.5</td>
<td>13.75</td>
<td>0.73</td>
<td>0.16</td>
</tr>
<tr>
<td>CLPA5 18</td>
<td>5.14</td>
<td>0.74</td>
<td>3.10</td>
<td>81.37</td>
<td>1.02</td>
<td>0.59</td>
<td>0.94</td>
<td>6.67</td>
<td>0.33</td>
<td>0.13</td>
</tr>
</tbody>
</table>

Table 5.5.3.1: Major element concentrations from sediment cores by XRF. Seven samples are from East Lake (KCEL5 and CLE12) and two are from Paulina Lake (CLPA5).

For comparison, two sediment core samples for Paulina Lake are provided showing similar high silica, but much higher iron contents (7-14% Fe$_2$O$_3$) Note that
all XRF analyses are based on a carbon and volatile free rock power, so bulk samples with ~10% organic carbon will have lower concentrations.

<table>
<thead>
<tr>
<th>Core</th>
<th>Depth (cm)</th>
<th>TiO$_2$ (%)</th>
<th>MnO (%)</th>
<th>Fe$_2$O$_3$ (%)</th>
<th>V (ppm)</th>
<th>Cr (ppm)</th>
<th>Co (ppm)</th>
<th>Ni (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCEL5-1</td>
<td>1</td>
<td>0.15</td>
<td>0.11</td>
<td>1.14</td>
<td>73</td>
<td>8</td>
<td>7.0</td>
<td>7.0</td>
</tr>
<tr>
<td>KCEL5-3</td>
<td>5</td>
<td>0.13</td>
<td>0.11</td>
<td>1.04</td>
<td>71</td>
<td>7</td>
<td>4.7</td>
<td>7.0</td>
</tr>
<tr>
<td>KCEL5-5</td>
<td>9</td>
<td>0.13</td>
<td>0.11</td>
<td>1.15</td>
<td>89</td>
<td>15</td>
<td>5.9</td>
<td>5.8</td>
</tr>
<tr>
<td>KCEL5-7</td>
<td>13</td>
<td>0.13</td>
<td>0.11</td>
<td>1.11</td>
<td>66</td>
<td>10</td>
<td>5.9</td>
<td>7.0</td>
</tr>
<tr>
<td>KCEL5-10</td>
<td>19</td>
<td>0.13</td>
<td>0.11</td>
<td>1.23</td>
<td>77</td>
<td>7</td>
<td>3.5</td>
<td>5.8</td>
</tr>
<tr>
<td>KCEL5-13</td>
<td>25</td>
<td>0.22</td>
<td>0.09</td>
<td>1.58</td>
<td>70</td>
<td>10</td>
<td>5.9</td>
<td>9.3</td>
</tr>
<tr>
<td>KCEL5-14</td>
<td>27</td>
<td>0.13</td>
<td>0.10</td>
<td>1.02</td>
<td>77</td>
<td>11</td>
<td>4.7</td>
<td>7.0</td>
</tr>
<tr>
<td>KCEL5-16</td>
<td>31</td>
<td>0.20</td>
<td>0.09</td>
<td>1.47</td>
<td>85</td>
<td>8</td>
<td>4.7</td>
<td>8.1</td>
</tr>
<tr>
<td>KCEL5-17</td>
<td>33</td>
<td>0.15</td>
<td>0.08</td>
<td>1.25</td>
<td>84</td>
<td>12</td>
<td>5.9</td>
<td>7.0</td>
</tr>
<tr>
<td>KCEL5-19</td>
<td>37</td>
<td>0.16</td>
<td>0.11</td>
<td>1.13</td>
<td>104</td>
<td>4</td>
<td>4.7</td>
<td>7.0</td>
</tr>
<tr>
<td>KCEL5-21</td>
<td>41</td>
<td>0.16</td>
<td>0.09</td>
<td>1.20</td>
<td>105</td>
<td>14</td>
<td>5.9</td>
<td>8.1</td>
</tr>
<tr>
<td>KCEL5-24</td>
<td>47</td>
<td>0.17</td>
<td>0.07</td>
<td>1.13</td>
<td>153</td>
<td>19</td>
<td>8.2</td>
<td>9.3</td>
</tr>
<tr>
<td>KCEL5-27</td>
<td>53</td>
<td>0.15</td>
<td>0.06</td>
<td>0.87</td>
<td>160</td>
<td>23</td>
<td>4.7</td>
<td>8.1</td>
</tr>
<tr>
<td>KCEL5-29</td>
<td>57</td>
<td>0.19</td>
<td>0.05</td>
<td>0.83</td>
<td>131</td>
<td>23</td>
<td>5.9</td>
<td>4.6</td>
</tr>
<tr>
<td>KCEL5-30</td>
<td>59</td>
<td>0.20</td>
<td>0.04</td>
<td>1.03</td>
<td>130</td>
<td>17</td>
<td>7.0</td>
<td>7.0</td>
</tr>
<tr>
<td>KCEL5-33</td>
<td>65</td>
<td>0.26</td>
<td>0.04</td>
<td>0.79</td>
<td>129</td>
<td>26</td>
<td>4.7</td>
<td>9.3</td>
</tr>
<tr>
<td>KCEL5-37</td>
<td>73</td>
<td>0.25</td>
<td>0.04</td>
<td>0.91</td>
<td>168</td>
<td>23</td>
<td>5.9</td>
<td>8.1</td>
</tr>
<tr>
<td>KCEL5-38</td>
<td>75</td>
<td>0.22</td>
<td>0.03</td>
<td>0.74</td>
<td>168</td>
<td>24</td>
<td>7.0</td>
<td>8.1</td>
</tr>
<tr>
<td>KCEL5-43</td>
<td>85</td>
<td>0.20</td>
<td>0.07</td>
<td>1.23</td>
<td>149</td>
<td>21</td>
<td>8.2</td>
<td>8.1</td>
</tr>
<tr>
<td>CLE12-2</td>
<td>3</td>
<td>0.28</td>
<td>0.47</td>
<td>2.47</td>
<td>84</td>
<td>12</td>
<td>6.0</td>
<td>6.0</td>
</tr>
<tr>
<td>CLE12-5</td>
<td>9</td>
<td>0.18</td>
<td>0.38</td>
<td>1.88</td>
<td>88</td>
<td>14</td>
<td>6.0</td>
<td>6.0</td>
</tr>
<tr>
<td>CLE12-12</td>
<td>23</td>
<td>0.20</td>
<td>0.26</td>
<td>1.48</td>
<td>62</td>
<td>6</td>
<td>4.0</td>
<td>4.0</td>
</tr>
<tr>
<td>CLE12-16</td>
<td>31</td>
<td>0.18</td>
<td>0.21</td>
<td>1.25</td>
<td>62</td>
<td>13</td>
<td>4.0</td>
<td>5.0</td>
</tr>
<tr>
<td>CLE12-18</td>
<td>35</td>
<td>0.19</td>
<td>0.20</td>
<td>1.53</td>
<td>74</td>
<td>12</td>
<td>4.0</td>
<td>6.0</td>
</tr>
<tr>
<td>CLE12-19</td>
<td>37</td>
<td>0.15</td>
<td>0.27</td>
<td>1.33</td>
<td>69</td>
<td>9</td>
<td>5.0</td>
<td>4.0</td>
</tr>
<tr>
<td>CLE12-22</td>
<td>43</td>
<td>0.20</td>
<td>0.27</td>
<td>1.53</td>
<td>87</td>
<td>12</td>
<td>4.0</td>
<td>6.0</td>
</tr>
<tr>
<td>CLE12-27</td>
<td>53</td>
<td>0.19</td>
<td>0.22</td>
<td>1.44</td>
<td>62</td>
<td>10</td>
<td>4.0</td>
<td>6.0</td>
</tr>
</tbody>
</table>
Table 5.5.3.2: Trace element concentrations by XRF from sediment cores from East Lake.

<table>
<thead>
<tr>
<th>Cu (ppm)</th>
<th>Zn (ppm)</th>
<th>As (ppm)</th>
<th>Rb (ppm)</th>
<th>Sr (ppm)</th>
<th>Y (ppm)</th>
<th>Zr (ppm)</th>
<th>Nb (ppm)</th>
<th>Ba (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.2</td>
<td>16.1</td>
<td>17.6</td>
<td>8.2</td>
<td>51</td>
<td>7.0</td>
<td>41</td>
<td>4.1</td>
<td>133</td>
</tr>
<tr>
<td>6.1</td>
<td>15.0</td>
<td>18.6</td>
<td>7.2</td>
<td>41</td>
<td>7.0</td>
<td>35</td>
<td>4.1</td>
<td>114</td>
</tr>
<tr>
<td>4.0</td>
<td>13.9</td>
<td>19.6</td>
<td>6.2</td>
<td>40</td>
<td>8.0</td>
<td>36</td>
<td>4.1</td>
<td>107</td>
</tr>
<tr>
<td>5.1</td>
<td>12.8</td>
<td>18.6</td>
<td>5.2</td>
<td>37</td>
<td>7.0</td>
<td>35</td>
<td>3.1</td>
<td>96</td>
</tr>
<tr>
<td>7.1</td>
<td>13.9</td>
<td>19.6</td>
<td>7.2</td>
<td>43</td>
<td>7.0</td>
<td>37</td>
<td>4.1</td>
<td>120</td>
</tr>
<tr>
<td>9.1</td>
<td>19.3</td>
<td>15.7</td>
<td>14.4</td>
<td>107</td>
<td>9.0</td>
<td>61</td>
<td>4.1</td>
<td>183</td>
</tr>
<tr>
<td>4.0</td>
<td>11.8</td>
<td>17.6</td>
<td>6.2</td>
<td>38</td>
<td>7.0</td>
<td>35</td>
<td>3.1</td>
<td>108</td>
</tr>
<tr>
<td>11.1</td>
<td>21.4</td>
<td>15.7</td>
<td>13.4</td>
<td>97</td>
<td>9.0</td>
<td>59</td>
<td>4.1</td>
<td>178</td>
</tr>
<tr>
<td>4.0</td>
<td>13.9</td>
<td>24.5</td>
<td>7.2</td>
<td>41</td>
<td>8.0</td>
<td>43</td>
<td>4.1</td>
<td>109</td>
</tr>
<tr>
<td>4.0</td>
<td>16.1</td>
<td>30.4</td>
<td>10.3</td>
<td>43</td>
<td>9.0</td>
<td>47</td>
<td>4.1</td>
<td>154</td>
</tr>
<tr>
<td>5.1</td>
<td>15.0</td>
<td>30.4</td>
<td>10.3</td>
<td>44</td>
<td>9.0</td>
<td>50</td>
<td>4.1</td>
<td>162</td>
</tr>
<tr>
<td>8.1</td>
<td>13.9</td>
<td>40.2</td>
<td>13.4</td>
<td>47</td>
<td>10.0</td>
<td>60</td>
<td>6.2</td>
<td>193</td>
</tr>
<tr>
<td>9.1</td>
<td>9.6</td>
<td>39.2</td>
<td>10.3</td>
<td>38</td>
<td>10.0</td>
<td>43</td>
<td>4.1</td>
<td>155</td>
</tr>
<tr>
<td>10.1</td>
<td>12.8</td>
<td>29.4</td>
<td>12.4</td>
<td>41</td>
<td>11.0</td>
<td>53</td>
<td>4.1</td>
<td>189</td>
</tr>
<tr>
<td>11.1</td>
<td>15.0</td>
<td>28.4</td>
<td>12.4</td>
<td>40</td>
<td>11.0</td>
<td>54</td>
<td>5.2</td>
<td>191</td>
</tr>
<tr>
<td>9.1</td>
<td>16.1</td>
<td>16.7</td>
<td>13.4</td>
<td>42</td>
<td>11.0</td>
<td>60</td>
<td>5.2</td>
<td>228</td>
</tr>
<tr>
<td>12.1</td>
<td>13.9</td>
<td>25.5</td>
<td>18.5</td>
<td>47</td>
<td>11.0</td>
<td>73</td>
<td>6.2</td>
<td>252</td>
</tr>
<tr>
<td>14.1</td>
<td>16.1</td>
<td>27.4</td>
<td>14.4</td>
<td>41</td>
<td>10.0</td>
<td>63</td>
<td>5.2</td>
<td>215</td>
</tr>
<tr>
<td>8.1</td>
<td>15.0</td>
<td>40.2</td>
<td>17.5</td>
<td>50</td>
<td>11.0</td>
<td>67</td>
<td>5.2</td>
<td>225</td>
</tr>
<tr>
<td>15.0</td>
<td>24.0</td>
<td>28.0</td>
<td>21.0</td>
<td>120</td>
<td>13.0</td>
<td>88</td>
<td>6.0</td>
<td>345</td>
</tr>
<tr>
<td>8.0</td>
<td>14.0</td>
<td>34.0</td>
<td>10.0</td>
<td>38</td>
<td>9.0</td>
<td>51</td>
<td>4.0</td>
<td>245</td>
</tr>
<tr>
<td>6.0</td>
<td>15.0</td>
<td>26.0</td>
<td>18.0</td>
<td>43</td>
<td>11.0</td>
<td>70</td>
<td>6.0</td>
<td>269</td>
</tr>
<tr>
<td>5.0</td>
<td>14.0</td>
<td>26.0</td>
<td>16.0</td>
<td>39</td>
<td>11.0</td>
<td>67</td>
<td>6.0</td>
<td>265</td>
</tr>
<tr>
<td>7.0</td>
<td>16.0</td>
<td>28.0</td>
<td>18.0</td>
<td>42</td>
<td>12.0</td>
<td>75</td>
<td>6.0</td>
<td>295</td>
</tr>
<tr>
<td>5.0</td>
<td>11.0</td>
<td>25.0</td>
<td>10.0</td>
<td>35</td>
<td>9.0</td>
<td>47</td>
<td>4.0</td>
<td>225</td>
</tr>
<tr>
<td>8.0</td>
<td>16.0</td>
<td>22.0</td>
<td>14.0</td>
<td>42</td>
<td>10.0</td>
<td>58</td>
<td>5.0</td>
<td>279</td>
</tr>
<tr>
<td>6.0</td>
<td>13.0</td>
<td>24.0</td>
<td>18.0</td>
<td>41</td>
<td>11.0</td>
<td>69</td>
<td>6.0</td>
<td>270</td>
</tr>
</tbody>
</table>
Trace element analyses by XRF independently show the low iron concentration in East Lake muds, similar Ti and Mn contents, and low arsenic compared to Paulina Lake sediment samples (Lefkowitz, 2016). The main base metals Cu and Zn are low while barium reaches up to 345 ppm. Strontium values range from 35 to 51 ppm, with two anomalous samples at 107 and 120 ppm, which may possibly be related to traces of carbonate in the sample. Some depth profiles and details of trends with depth for groups of trace elements are provided below.

Figure 5.5.3.1: Iron concentrations in sediment from core KCEL5.
Figure 5.5.3.2: Copper and zinc concentrations against core depth in KCEL5.

Figure 5.5.3.3: Cobalt, nickel and chromium concentrations against core depth in KCEL5.
Copper and zinc concentrations are fairly consistent with depth. Copper concentrations range between ~5 ppm and ~15 ppm, while zinc concentrations range between ~10 ppm and ~20 ppm. There are no extreme excursions in either element with depth. Cobalt and nickel are relatively constant in concentration with core depth. Cobalt concentrations are between ~5 ppm and ~7 ppm and nickel concentrations are ~7 ppm. The chromium concentrations vary with depth. Between 0 and 40 cm the chromium concentrations are ~7-15 ppm, then there is an excursion of chromium concentrations to around ~22 ppm and then from 50-90 cm the concentrations remain between ~17 and ~27 ppm. Clearly the deeper part of the core is enriched in chromium, which could have been brought in by more basaltic material. Strontium concentrations do not vary much with depth. Concentrations are around 50 ppm,
except between 25cm and 35cm where there are peaks around 100 ppm. Vanadium concentrations generally increase with depth from 70 ppm at the core top to around 150 ppm at the bottom of the core, with the strongest increases occurring below 45cm in the core.

5.5.4 Incompatible Elements

Figure 5.5.4.1: Cerium, yttrium, niobium, and rubidium concentrations against core depth in KCEL5.
Figure 5.5.4.2: Zirconium and barium concentrations against core depth in KCEL5.

Cerium and rubidium concentrations are fairly erratic with depth and their concentrations have large ranges. Cerium ranges between ~3 ppm and ~18 ppm and rubidium ranges between ~6 and ~15 ppm. Niobium concentrations stay around 4 ppm and yttrium slightly increases with depth from ~7 ppm to ~11 ppm. Zirconium concentrations remain around 50-60 ppm with core depth. Barium concentrations are high compared to other incompatible elements in East Lake and slightly increase with depth from around 120 to 220 ppm.
5.5.5 Mercury

Mercury concentrations in East Lake sediment cores are particularly high as already shown by Lefkwitz (2012). The concentrations range from 300 to around 3000 ppb Hg, with lower values at the bottom of the two cores (50-90cm) and several peaks in the upper half of the cores. Core KCEL2 shows a strong negative excursion between 10 and 20 cm depth, an interval with a high BDD. Bulk mercury in water was measured by Prentiss Balcom at University of Connecticut. Two deep samples had 0.95pM and 3.33pM Hg(O), and a shallow samples had 1.82pM Hg(O).

Figure 5.5.5.1: Mercury concentrations from KCEL5 and KCEL2 against core depth.
5.5.6 Biogenic Silica

A large portion of sediment is composed of biogenic silica. Biogenic silica concentrations are around 60% in KCEL5, while in KCEL2 concentrations are around 40%. In KCEL2 there is a negative excursion to ~12% between 10cm and 20cm depth.

Figure 5.5.6.1: Biogenic silica concentrations against core depth in KCEL5 and KCEL2.
5.5.7 Carbon and Nitrogen Content

Organic carbon concentrations in East Lake sediment are relatively high ranging from 2-12% with an average of ~8%. The lowest values are found in KCEL2 between 10 and 20cm.

Figure 5.5.7.1: Vertical profile of carbon in cores KCEL5 and KCEL2.
Figure 5.5.7.2: Vertical profile of nitrogen in cores KCEL5 and KCEL2.

The two cores have relatively low concentrations of nitrogen that fall between 0.4% and 0.8%. The negative excursion at ~20cm in KCEL2 is also observed in the carbon concentration profile and many other parameters.
Figure 5.5.7.3: Vertical profile of C/N values in cores KCEL5 and KCEL2.

The C/N values for the core profiles range from ~10 to ~12 with one excursion at 80cm to 16. The low values are typical for phytoplankton matter in lakes and the higher values may represent larger contributions of vascular plants (Meyers and Ishiwatari, 1993).
Table 5.5.7.1: C/N ratios of organic matter samples collected from East Lake (EL) and Paulina Lake (PL) during the summer of 2015. Also included are C/N values acquired from the literature (Meyers and Ishiwatari, 1993).

<table>
<thead>
<tr>
<th>Sample</th>
<th>C/N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Collected</td>
<td>Mass</td>
</tr>
<tr>
<td>EL Plant 1 (Phytoberg)</td>
<td>14</td>
</tr>
<tr>
<td>EL Plant 2 (Phytoberg)</td>
<td>16</td>
</tr>
<tr>
<td>EL Plant 3 (Phytoberg)</td>
<td>13</td>
</tr>
<tr>
<td>EL Cyanobacteria 1</td>
<td>4</td>
</tr>
<tr>
<td>EL Cyanobacteria 2</td>
<td>5</td>
</tr>
<tr>
<td>PL Cyanobacteria 3</td>
<td>13</td>
</tr>
<tr>
<td>Meyers and Ishiwatari (1993)</td>
<td>Atomic</td>
</tr>
<tr>
<td>Diatom (Asterionella formosa)</td>
<td>9</td>
</tr>
<tr>
<td>Walker Lake (plankton)</td>
<td>8</td>
</tr>
<tr>
<td>Pinyon pine, modern</td>
<td>42</td>
</tr>
<tr>
<td>White spruce, modern</td>
<td>46</td>
</tr>
<tr>
<td>White oak, modern</td>
<td>276</td>
</tr>
</tbody>
</table>

Table 5.5.8.1: δ¹³C and δ¹⁵N values from organic matter collected from East Lake and Paulina Lake during the summer of 2015. Also included are δ¹³C values of mixed plankton species from the literature (Meyers and Ishiwatari, 1993).

<table>
<thead>
<tr>
<th>Sample</th>
<th>δ¹³C</th>
<th>δ¹⁵N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Collected</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EL Plant 1 (Phytoberg)</td>
<td>-16.09</td>
<td>2.16</td>
</tr>
<tr>
<td>EL Plant 2 (Phytoberg)</td>
<td>-17.08</td>
<td>2.77</td>
</tr>
<tr>
<td>EL Plant 3 (Phytoberg)</td>
<td>-14.20</td>
<td>2.16</td>
</tr>
<tr>
<td>EL Cyanobacteria 1</td>
<td>-8.64</td>
<td>0.20</td>
</tr>
<tr>
<td>EL Cyanobacteria 2</td>
<td>-14.00</td>
<td>-0.83</td>
</tr>
<tr>
<td>PL Cyanobacteria 3</td>
<td>-27.44</td>
<td>0.52</td>
</tr>
<tr>
<td>Meyers and Ishiwatari (1993)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Walker Lake (plankton)</td>
<td>-28.8</td>
<td></td>
</tr>
<tr>
<td>Lake Biwa (plankton)</td>
<td>-25 to -28</td>
<td></td>
</tr>
<tr>
<td>Pinyon pine needles</td>
<td>-24.8</td>
<td></td>
</tr>
<tr>
<td>White spruce needles</td>
<td>-25.1</td>
<td></td>
</tr>
<tr>
<td>Popular leaves</td>
<td>-27.9</td>
<td></td>
</tr>
</tbody>
</table>
Figure 5.5.8.1: Profile of $\delta^{13}C$ values of sediment samples versus core depth in KCEL5.

The $\delta^{13}C$ values of KCEL5 fall between -18‰ and -25‰. The most negative values are found at the core top while the least negative values occur in the mid-core.
Figure 5.5.8.2: Profile of $\delta^{15}N$ of sediment samples versus core depth of KCEL5.

The $\delta^{15}N$ values of KCEL5 samples vary strongly with depth in the core. More positive values (>3‰) occur in the core top, while mid-core values fall between 1.5‰ and 3‰. At ~80cm there is a strong decrease in $\delta^{15}N$ to <0.5‰, but at ~90cm values reach 3‰ again.
6. Discussion

6.1 Physical Characteristics of East Lake Waters

6.1.1 General

Field data collected at East Lake during the summer of 2015 provide evidence of thermal stratification. There is a well-defined epilimnion (Figure 5.1.1.1) within the upper 5-10m and a thermocline between 10-20m, where the temperature rapidly decreases. The hypolimnion exists below the thermocline with temperatures of about 4-5°C. During the winter East Lake typically freezes over. Spring warming increases the ambient temperature allowing ice to thaw. Spring turnover and mixing then occurs around May. Summer is marked by thermal stratification, which weakens with the approach of winter. The decrease in ambient temperature may lead to a fall turnover (Wetzel 2001). Although East Lake waters experience summer stratification there is no evidence of a chemocline. Chloride concentrations in the water column are low and sulfate concentrations are high, but do not exhibit any trend with depth (Figure 5.2.1.2). The major cations and Si have their highest concentrations within the first 10-15m of East Lake (Figure 5.2.3.1, Figure 5.2.3.2).

The existence of cold deep waters suggests limited mixing between the warmer surface waters and bottom waters, because deep-water temperatures are likely the result of spring turnover. Physical mixing models of East Lake also suggest that deep mixing is not occurring and that East Lake mixing is shallow (Lefkowitz et al., 2016). Therefore, it is possible that the increase in cation concentration in the upper water layer is related to evaporation. However, the surface water increase in
concentrations are on the scale of 5-16%, with the highest increase in silica, which suggests that the evaporative effect cannot be the only process acting. A more complex and local epilimnic mixing, in addition to evaporation is probably occurring (Lefkowitz et al., 2016)

Evidence for surface evaporation is also substantiated by water stable isotope data. Both δ¹⁸O and δ²H in East Lake show enrichment in the surface waters. The values of δ¹⁸O and δ²H provide insight into the water mixing and evaporation process. Less negative δ¹⁸O and δ²H values are most likely associated with an evaporation effect.

Figure 6.1.1.1: Local meteoric water line based on river and surface water data from central Oregon and stable isotope ratios of East Lake waters and its hot springs.
The local meteoric water line is given by stable isotope ratios of several rivers in Oregon (Kendall and Coplen, 2001). East Lake samples from 2011, 2012, 2014 and 2015 plot on a line that passes through a local meteoric water endmember. The dashed line (Figure 6.1.1.1) is likely an evaporation line (Gat, 1996). The evaporation line represents the heavier residual lake water, because lighter isotopes of O and H are more easily evaporated (Kendal and Coplen, 2001). East Lake hot springs gather around the local meteoric water endmember while actual lake samples cluster higher on the evaporation line. The 2011 samples plot the farthest on the evaporation line and are close to the limits for steady state (Varekamp, 2016). The most probable source of East Lake water is meteoric input in the form of snow and rain, with possible inputs from watershed run off, although this is limited by the lack of streams or rivers. Water losses are largely evaporative because East Lake is terminal, although there may be a seepage component due to a hydraulic gradient formed by the surface elevation difference between East Lake and Paulina Lake. However, no evidence exists to suggest seepage as proposed by Sammel and Craig (1983), given that the chemical and isotopic compositions of the two lakes are exceedingly different.

6.1.2 $\delta^{13}C$ DIC Time Trends

One of the most striking features of East Lake is the heavy $\delta^{13}C$ DIC in the surface waters as well as a strong gradient towards lighter values with depth. Previous data show similar patterns, and surface waters have consistently been more positive than bottom waters. A summary of these data is shown in Figure 6.1.2.1. The strongest gradient was observed in August 2011 (green) with a surface water value of
~4.2‰ and a bottom water value of ~0.4‰. The gradient observed in October 2015 (light blue) is also relatively strong, with a surface water value of ~5‰ and a bottom water value of ~0.3‰. The June/July 2015 (KELA and EL) values show a less steep gradient with a surface water value of ~3.9‰ and a bottom water value of ~2‰. The June 2014 data have the heaviest δ¹³C DIC surface water values (5.5-5.6‰) but less steep gradients. Paulina Lake has δ¹³C DIC values that show a very weak gradient with depth and over the years of surveying the values have remained almost constant around 0‰ (Figure 6.1.2.1).

Figure 6.1.2.1: Profiles of δ¹³C DIC with depth in East Lake and Paulina Lake (for comparison) including data collected in 2011, 2014 and 2015.

The sign of the slope of the δ¹³C gradient in East Lake has always been negative for the years of sampling. The degree of the slope may change due to
seasonal differences in biological processes or changes in the geothermal CO₂ input at depth. The weakest gradient was observed in early July of 2015. The surface values were ~4‰ and bottom water values were ~2‰. The strongest gradient was observed in October of 2015 with surface values ~5‰ and bottom water values of ~0‰. The 2011 and 2014 surface and bottom water values have similar slopes and gradients (~3-4‰). Despite differences in the gradients over the years, surface waters have always remained heavy relative to bottom waters. Photosynthesis is probably one process that contributes to the ¹³C enriched surface, because producers preferentially use ¹²C in photosynthesis, leaving the residual carbon pool heavier, or ¹²C depleted. Additionally, the diffusive CO₂ escape likely contributes to the ¹³C enriched surface waters. Evidence for this is provided by isotopically light chamber gas samples.

6.1.3 Compositional Trends in East Lake Waters

The potassium concentrations have remained almost the same from 2011 to 2015, where as calcium magnesium, sodium, and silica have shown a slight increase. Calcium and sodium have the highest concentrations, while potassium and silica have the lowest concentrations. The major cation concentrations in East Lake hot springs measured in 2015 (Table 5.2.3.1) are very different from the average concentrations measured in East Lake for that same year.
The calcium, potassium, magnesium, and sodium concentrations measured in the hot spring are 70.5ppm, 9.3ppm, 34.6ppm and 55.4ppm, while the average East Lake concentrations are 28.7ppm, 4.1ppm, 12.6ppm, and 25.8ppm, respectively. The hot spring concentration of silica is 92.2ppm while the lake concentration of silica is 6.7.

If we assume that alkalinity is entirely comprised of $\text{HCO}_3^-$, given that the pH is almost neutral, the concentration of $\text{HCO}_3^-$ in the East Lake water profiles has increased over the years of study. The lowest concentrations were found in 2011 in the WELVA and WELVB profiles while the highest concentrations were found in EL and KELA, which were collected in June/July of 2015. Data collected from October...
2015 show decreased values in alkalinity relative to the June/July values. This could also be the result of photosynthesis and other chemical processes that use components of alkalinity, such as cations like Mg$^+$ or K$^-$. 

![Figure 6.1.3.2: Shows the HCO$_3^-$ alkalinity with depth from water profiles collected in 2011, 2012, 2014 and 2015.](image)

All water profile data from 2015, and a select few from 2011, 2012 and 2014 were used in speciation calculations that were carried out using the online version of the PHREEQ program (Web-phreeq). The results were used to determine the total DIC for East Lake in 2015 and all years of study. The 2015 speciation calculations show an increase in DIC with depth (Figure 6.1.3.3), which makes sense because there is withdrawal of carbon from the surface of the lake due to photosynthesis and diffusive CO$_2$ escape, and a geothermal input of carbon as well as the possibility of
bacterial respiration at the bottom. The carbon appears to be held between 20 and 40m suggesting a possible net return of carbon as a result of bacterial respiration of organic matter as it falls to the bottom.

Figure 6.1.3.3: Vertical profile of the calculated total dissolved inorganic carbon in East Lake.

It is possible that the resident concentrations of total dissolved carbon from 2011 to 2015 have slightly increased. The values shown in Figure 6.1.3.4 were estimated using East Lake profile data from 25m for 2011, 2012, 2014, and 2015. The data show a general increase in total resident carbon from 2011 to 2015 from ~3000 to ~4000 tonnes of C. From 2011 to 2012 there was a decrease in the standing amount of dissolved carbon. From 2012 to 2014 concentrations are still lower than they were in 2011, but there is a slight increase from ~2400 to ~2600 tonnes of C. The lower
values of resident carbon could be due to increased amounts of photosynthesis trapping carbon since during these years the average pH was also higher. The steep increase from 2014 to 2015 may be the result of the lack of ice cover during the winter of 2015. Uncertainty lies with the speciation calculations because the calculated DIC varied highly with the use of different pH values as well as alkalínities.

Figure 6.1.3.4: Change in the total amount of dissolved carbon in East Lake from 2011 to 2015.
6.1.4 Comparison to Paulina Lake

In order to completely understand the chemical characteristics of East Lake it is crucial to compare it to the chemical characteristics of Paulina Lake. Both lakes can be classified as neutral bicarbonate low activity lakes. Both lakes have alkalinites that differ from the norm of freshwater lakes. However, Paulina Lake has almost 4x more bicarbonate in its waters than East Lake. East Lake has about 130 ppm of bicarbonate while Paulina Lake has around 400 ppm of bicarbonate. In general the differences between the chemical characteristics in the waters of East Lake and Paulina Lake are due to dissimilarities in the processes affecting the main geothermal inputs into the lake system (Lefkowitz et al., 2016). Most rock forming elements (Mg, Ca, K, Al, Na and Fe) are produced from water-rock interactions; however, they can also be brought into the system from volcanic gases or concentrated brines (Varekamp and Pasternack, 2000).

In general, higher average major cation concentrations are found in Paulina Lake (Figure 6.1.4.1). East Lake has similar calcium and potassium concentrations compared to Paulina Lake, but its average magnesium, sodium and silica concentrations are lower. East Lake and Paulina Lake springs have very different cation concentrations. Calcium, magnesium, sodium, and silica concentrations in the springs are far greater than in the lakes suggesting the occurrence of strong dilution of thermal inputs in each the lake. Water dilution alone cannot account for compositional differences, because Paulina Lake is much larger (Johnson, 1985) than East Lake and would likely experience more dilution. However, the higher concentrations of cations found in Paulina Lake correlate with the higher pH (~8).
compared to East Lake waters, which have a pH range of 6.5 to 7, allowing for less
dilution. The pH difference is likely the result of different geothermal fluids. In the
more acidic East Lake waters, a pure CO\textsubscript{2} input is probable, while in Paulina Lake,
rich in bicarbonate and cations, a geothermal input of carbonate and other dissolved
components is likely.

Figure 6.1.4.1: Average major cation and silica concentrations in East Lake and
Paulina Lake and the concentrations in their respective hot springs from the years

Anion concentrations also differ between East Lake and Paulina Lake (Figure
6.1.4.2). East Lake has sulfate-rich waters while Paulina has sulfate-poor waters.
Chloride concentrations are somewhat higher in Paulina Lake than in East Lake, but
are still low in both lakes. Interestingly, East Lake hot springs are low in sulfate
concentrations, suggesting that the source for the hot spring fluids is not the same as
the source for the lake. It is likely that gaseous H$_2$S, a common geothermal gas (Arnorrsón, 2007) enters East Lake and then oxidizes to become SO$_4^{2-}$ in the water column. Sulfur isotopes are being studied in order to clarify and enhance the current understanding of the mechanisms for these compositional differences. Paulina Lake and its hot springs have similar sulfate concentrations, but the springs have higher chloride concentrations. In general, the presence of low Cl, SO$_4^{2-}$ and humble cation concentrations is common in CO$_2$ rich volcanic lakes where pH is neutral (Varekamp and Pasternack, 2000), so the observed values are not surprising. However, the disparity between the chemical compositions of the lakes is curious.

Figure 6.1.4.2: Chloride and sulfate concentrations in East Lake and Paulina Lake as well as concentrations in their respective hot springs.
6.2 Carbon Dioxide Degassing

6.2.1 Analysis of SGS Calculated Flux Data

The estimated CO$_2$ flux off the surface of the lake, as acquired from the SGS algorithm is 44 tonnes of CO$_2$/day. A map (Figure 6.2.1.1) of the SGS calculated flux data (moles CO$_2$ m$^{-2}$ day$^{-1}$) shows yellow-pink colors in areas of high CO$_2$ flux and blue colors in areas of lower CO$_2$ fluxes. The higher CO$_2$ fluxes are aligned on a potential NW-SE fissure trend crossing East Lake near the scoria vent located at its NW side. The scoria vent is shown in Figure 6.2.1.2 and the possible fissure trend is depicted in Figure 6.2.1.1. High fluxes are also associated with a drowned crater area that is outlined in Figure 6.2.1.1. Slightly elevated areas of degassing are observed near the hot springs, which are located close to the SE shore of East Lake. The frequency distribution of fluxes in East Lake is shown in Figure 6.2.1.3. The majority of CO$_2$ fluxes over the lake are below 0.3 moles CO$_2$ m$^{-2}$ day$^{-1}$.

![Figure 6.2.1.1: A map of SGS generated CO$_2$ flux data points in moles of CO$_2$ m$^{-2}$ day$^{-1}$.](image-url)
The estimated CO$_2$ flux average from SGS does not account for disruption or modulation of a daily flux that is modulated by wind speed, water temperature or water viscosity. Furthermore since field measurements were carried out over only a few days during the summer of 2015, the estimated average CO$_2$ flux through SGS is not a true annual average. Seasonal differences, as mentioned before, are evident in East Lake with ice cover during the winter and thawing in May. During ice cover a diffusive loss off CO$_2$ would be improbable and it is likely that CO$_2$ accumulates.
below the ice. When the ice thaws, it is possible that the CO₂ loss is substantially larger than the average daily measured flux in June/July. This catastrophic release of CO₂ could occur as there is already a significant difference between atmospheric and lake partial pressures of CO₂ without ice cover. However, the constraints on ice melt and CO₂ release are not known.

The flux of a gas is driven by the difference in gas pressure within the lake and the atmosphere. Since Newberry caldera is about 2km above sea level, the P<sub>CO₂</sub> is less than what it would be at sea level, due to the atmospheric pressure difference. Aqueous CO₂ values were calculated in Web-phreeq as a function of pH, alkalinity and water temperature. The calculated values were then corrected for temperature dependence of CO₂ dissolution using a Henry’s Law expression (Sander, 2015) and P<sub>CO₂</sub> values for East Lake waters were established. The ΔP<sub>CO₂</sub> was then determined in order to apply the equation below to determine a theoretical flux of CO₂. As mentioned before, the variation in CO₂ flux is also dependent upon seasonal wind speed, temperature, and the viscosity of water. The equation:

\[ F = k (P_{CO₂W} - P_{CO₂A}) \]  (Wanninkhof, 1992)

provides a simple theoretical expression for the diffusive gas loss where F is the flux of CO₂ per unit of time per area, k is the gas transfer coefficient, P<sub>CO₂W</sub> is the partial pressure of CO₂ in the water, and P<sub>CO₂A</sub> is the partial pressure of CO₂ in the atmosphere. The gas transfer velocity is a unique constant that accounts for wind speed variation and water viscosity, as they apply to the diffusion of CO₂ from a body of water. Also it should be noted that this k is not the same as the K factor used in section 4.2.9. Wanninkhof provides significantly different equations for different
wind speeds above and below 3.5m/s. These equations are scaled using the Schmidt number (Sc), which considers the differences between the vertical and horizontal diffusive properties of a particular substance. For freshwater temperatures that fall between 0°C and 30°C the equation:

\[ \text{Sc} = A - Bt + Ct^2 - Dt^3 \]

where \( t \) is in degrees Celsius, is used to calculate the correct Sc. The constants for the A, B, C, and D terms are given by Wanninkhof (1992). Using weather data from the Lapine weather station (Weather Underground), the city at the base of the Newberry volcano, average and maximum wind speeds were obtained for the period over which flux data were measured in the summer of 2015. The average wind speed during the summer of 2015 was 1.9m/s while the maximum wind speed was 6.2m/s. Two Sc numbers were calculated because of the temperature difference between samples. Some samples were taken at the surface of the lake while others were taken 5m below the surface. Samples at the surface were at 19.8°C and their Sc number was 606.37 and those 5m below were at 18.8°C and their Sc number was 636.39. The equation to calculate the gas transfer coefficient at the wind speed of 1.9m/s (below 3.5m/s) was:

\[ k = [ 2.5 (0.5246 + 1.6256 \times 10^{-2} T + 4.9946 \times 10^{-4} T^2 ) + 0.3u^2 ] ( \text{Sc} / 600)^{-1/2} \]

where \( u \) was wind speed and \( T \) was in degrees Celsius. The equation to calculate the gas transfer coefficient at the wind speed of 6.2m/s (above 3.5m/s) was:

\[ k = 0.39 \ u^2 \ (\text{Sc}/600)^{-1/2} \]

where \( u \) is wind speed and the effect of temperature is incorporated in the Sc number.
Table 6.2.1.1: Theoretical CO2 fluxes for East Lake with variations in $\Delta P_{CO2}$ and atmospheric parameters over the years 2011, 2012, 2014 and 2015.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Delta P_{CO2}$</th>
<th>K mean</th>
<th>K max</th>
<th>Flux max</th>
<th>Flux mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>EL7 3.5m</td>
<td>0.032</td>
<td>2.751</td>
<td>14.366</td>
<td>0.463</td>
<td>0.089</td>
</tr>
<tr>
<td>KELA-1</td>
<td>0.037</td>
<td>2.751</td>
<td>14.366</td>
<td>0.534</td>
<td>0.102</td>
</tr>
<tr>
<td>Average 2015</td>
<td></td>
<td></td>
<td></td>
<td>0.498</td>
<td>0.095</td>
</tr>
<tr>
<td>EL 2011</td>
<td>0.044</td>
<td>1.492</td>
<td>10.138</td>
<td>0.444</td>
<td>0.065</td>
</tr>
<tr>
<td>EL 2012</td>
<td>0.007</td>
<td>1.492</td>
<td>10.138</td>
<td>0.067</td>
<td>0.010</td>
</tr>
<tr>
<td>EL 2014</td>
<td>0.008</td>
<td>1.492</td>
<td>10.138</td>
<td>0.079</td>
<td>0.012</td>
</tr>
<tr>
<td>EL 2015</td>
<td>0.075</td>
<td>1.492</td>
<td>10.138</td>
<td>0.757</td>
<td>0.111</td>
</tr>
<tr>
<td>Average All Years</td>
<td></td>
<td></td>
<td></td>
<td>0.337</td>
<td>0.050</td>
</tr>
</tbody>
</table>

The measured CO$_2$ fluxes fall in the range of the average and maximum theoretical fluxes for maximum wind speeds and average wind speeds in 2015. Both the average SGS calculated fluxes and field-measured fluxes had flux values $\sim$0.2 moles of CO$_2$ m$^{-2}$ day$^{-1}$, which suggests that wind speeds might have been higher at East Lake than they were at La Pine. In short, theoretical fluxes can provide insight into the potential variability of fluxes, as well as the agreement between measured and predicted fluxes.

The diffusive flux of CO$_2$ off the surface of East Lake may be a causative mechanism for the $\delta^{13}$C DIC trend with depth. The $\delta^{13}$C values of gas samples taken in the field are shown in Table 6.2.1.1 and include East Lake ambient air and floating accumulation chamber gas samples. These samples were all lighter than the recognized atmospheric $\delta^{13}$C CO$_2$ in 2015, which is around -8‰ (NOAA), indicating that the escaping gas is lighter than the air value. The theoretical $\delta^{13}$C CO$_2$ values in the lake water were calculated using Web-phreeq and temperature dependent interspecies isotope fractionations from the IAEA Hydrologic Cycle: Principles and Applications publication (Mook, 2001). A simple isotope mass balance equation was
used to calculate the $\delta^{13}C$ DIC using the mixing relationship between dissolved CO$_2$ species and how they are fractionated. These calculations provided a range of $\delta^{13}C$ CO$_2$ values of -3 to -5 ‰, depending on water temperature and pH value. These values are heavier than field-measured values, and we speculate that the diffusional process may impose an extra kinetic fractionation on escaping CO$_2$ gas. Many papers on escaping CO$_2$ from non-volcanic lakes hint at such isotopic fractionations, but conditions in these lakes are different than at East Lake (Doctor et al, 2008; Rinta, 2015).

A plot of 1/CO$_2$ versus $\delta^{13}C$ CO$_2$ (Figure 6.2.1.4) provides a linear array between the two endmembers: ambient atmospheric CO$_2$ at -8.5‰ and the $\delta^{13}C$ CO$_2$ of the lake gas. Our data suggest that the $\delta^{13}C$ CO$_2$ of the gas is about -21‰. That is extremely light CO$_2$, and there is some uncertainty regarding the concentration of CO$_2$ measured in our exetainer sample. However, to achieve the observed $\delta^{13}C$ CO$_2$ values, there still has to be a very light input of CO$_2$. It is possible that local ambient air is strongly mixed with lake CO$_2$ and that there might not be a local air endmember with $\delta^{13}C$ CO$_2$ value of -8.5‰. The frequency of the observed values, shown in Figure 6.2.1.5, range from -9.5 to -17.5 ‰. More precise concentration data will allow for a more accurate estimate of the $\delta^{13}C$ CO$_2$. 
Figure 6.2.1.4: Shows the relationship between isotopic signature of the vapor degassing from the surface of East Lake and the concentration of CO$_2$ in the atmosphere.

Figure 6.2.1.5: Frequency of measured $\delta^{13}$C CO$_2$ samples collected from East Lake in early July, late August, and early October of 2015.
6.3 Chemical Composition of the Sediment

6.3.1 Carbon and Nitrogen

East Lake sediment is composed of three major components: organic carbon, biogenic silica and volcanic ash. The organic carbon portion of the sediments is primarily composed of aqueous macro-vegetation, phytoplankton, and cyanobacteria. Figure 5.5.7.1 shows that organic carbon makes up 8-12% of the sediment. The C/N ratios (Figure 5.5.7.3) are all in the range of 10-13. In general C/N ratios are used to establish a source for organic matter in sediment. One component that determines the C/N ratio or a specific type of organic matter is the presence of cellulose. Cellulose often influences the C/N ratio in plants; because it is primarily formed from carbon, making the ratio higher. Plants that have cellulose, such as grasses or trees, are vascular; those that do not have cellulose, such as algae, are nonvascular plants. This is why aquatic plants typically have lower C/N ratios, between 4 and 10, while land plants have C/N ratios higher than 20 (Meyers and Ishiwatari, 1993). The C/N ratios of core samples suggest that nonvascular and aquatic plants dominate in East Lake, as there is minimal evidence for land plant C/N ratios affecting the sediment.

The isotopic ratios of carbon and nitrogen also serve as indicators for the source of organic matter in sediment. Sediment receiving a large portion of land sourced organic matter will have lighter $\delta^{15}$N values than sediment that receives a higher portion of aquatic organic matter. This pattern is the same for $\delta^{13}$C but more difficult to discern (Meyers and Lallier-Verges, 1998). Core samples show $\delta^{13}$C values around -25‰ with an excursion to -20‰ from 45cm to 75cm. The $\delta^{15}$N values
also indicate the presence of land plants; however the lighter $\delta^{15}N$ could also be the result of the occurrence of microbial activity in the water column before sediment is buried (Meyers and Ishiwatari, 1993).

### 6.3.2 Mixing Model for Organic Matter in Sediment

![Graph showing mixing curves for organic matter in cores from East Lake and for comparison Paulina Lake using $\delta^{13}C$ and $\delta^{15}N$ using three endmembers: cyanobacteria, aqueous vegetation and phytoplankton.](image)

Figure 6.3.2.1: Mixing curves for organic matter in cores from East Lake and for comparison Paulina Lake using $\delta^{13}C$ and $\delta^{15}N$ using three endmembers: cyanobacteria, aqueous vegetation and phytoplankton.

A mixing model (Figure 6.3.2.1) uses the C/N ratios, $\delta^{13}C$ and $\delta^{15}N$ of various aquatic producers in East Lake in order to determine what components the sediment samples are largely composed of. Measured data for aqueous plant vegetation (phytobergs) and cyanobacteria (Nostoc sp.) were applied to the model (Table 5.5.7.1, Table 5.5.8.1, Table 6.3.2.1). Values for phytoplankton (diatoms) in East Lake and
Paulina Lake were estimated based on given lacustrine C/N, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values (Table 5.5.7.1, Table 5.5.8.1, Table 6.3.2.1) from the literature. The model was produced using a method for ratio-ratio mixing in Langmuir et al. (1977). Three mixing curves were established for East Lake: one comparing cyanobacteria-aqueous plant endmembers, the second comparing cyanobacteria-phytoplankton endmembers, and the last comparing phytoplankton-aqueous plant endmembers. The $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ and C/N ratios for individual cyanobacteria, aqueous plant, and phytoplankton endmembers were used to calculate the mixed $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values between the endmembers in each curve (Figure 6.3.2.1).

<table>
<thead>
<tr>
<th>Sample</th>
<th>C</th>
<th>N</th>
<th>C/N (mass)</th>
<th>$\delta^{13}\text{C}$</th>
<th>$\delta^{15}\text{N}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>East Lake</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nostoc EL</td>
<td>43.63</td>
<td>11.71</td>
<td>3.73</td>
<td>-8.64</td>
<td>0.20</td>
</tr>
<tr>
<td>Nostoc EL</td>
<td>34.24</td>
<td>7.13</td>
<td>4.80</td>
<td>-14.00</td>
<td>-0.83</td>
</tr>
<tr>
<td>Nostoc EL Average</td>
<td>38.93</td>
<td>9.42</td>
<td>4.13</td>
<td>-11.32</td>
<td>-0.32</td>
</tr>
<tr>
<td>Diatoms</td>
<td>40.00</td>
<td>6.50</td>
<td>6 to 8</td>
<td>-28.50</td>
<td>4.00</td>
</tr>
<tr>
<td><strong>Paulina Lake</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phytoberg</td>
<td>33.00</td>
<td>2.41</td>
<td>13.66</td>
<td>-16.09</td>
<td>2.16</td>
</tr>
<tr>
<td></td>
<td>33.24</td>
<td>2.48</td>
<td>13.40</td>
<td>-17.08</td>
<td>2.77</td>
</tr>
<tr>
<td></td>
<td>38.58</td>
<td>2.38</td>
<td>16.22</td>
<td>-14.20</td>
<td>2.16</td>
</tr>
<tr>
<td>Phytoberg Average</td>
<td>34.94</td>
<td>2.42</td>
<td>14.41</td>
<td>-15.79</td>
<td>2.36</td>
</tr>
<tr>
<td>Diatoms</td>
<td>55.00</td>
<td>5.50</td>
<td>10.00</td>
<td>-33.00</td>
<td>4.00</td>
</tr>
<tr>
<td>Nostoc PL</td>
<td>47.85</td>
<td>1.74</td>
<td>27.54</td>
<td>-27.44</td>
<td>0.52</td>
</tr>
<tr>
<td>Nostoc PL</td>
<td>20.00</td>
<td>10.00</td>
<td>2.00</td>
<td>-13.07</td>
<td>-0.91</td>
</tr>
</tbody>
</table>

Table 6.3.2.1: Values for the three endmembers used to produce the mixing curves for East Lake and Paulina Lake.

As mentioned before the organic carbon portion of East Lake sediment is composed of aqueous macro-vegetation, phytoplankton, and cyanobacteria. No
macro-vegetation has been observed in Paulina Lake, but phytoplankton and cyanobacteria are observed. The model suggests that East Lake sediment is largely composed of phytoplankton with roughly equal parts aqueous vegetation and cyanobacteria. A more realistic model should be made using actual C/N, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values for phytoplankton in East Lake.

There is a $\sim5\%$ offset in the $\delta^{13}\text{C}$ between Paulina Lake and East Lake sediments, as shown by the mixing curve. This relationship is due to the $\sim5\%$ offset in the $\delta^{13}\text{C}$ DIC between the two lakes.

Biogenic silica was differentiated from volcanic or crystalline forms using timed extraction. These biogenic silica analyses revealed that about 60% of the sediment in East Lake is composed of biogenic silica. Diatoms are a type of phytoplankton whose frustules are composed of opaline silica. The large amount of biogenic silica in East Lake sediment suggests that diatoms are a highly productive component in the ecosystem and serve as an important carbon sink. Silica concentrations are enriched in the surface waters and decrease with depth (Figure 5.2.3.2). In productive lakes systems, where phytoplankton are productive, a decrease in silica concentration occurs in the surface waters. Assuming East Lake diatoms exist in the photic zone, the observed trend in silica is atypical and suggests the possibility of another silica input that is counteracting its depletion by diatoms. It is also possible that diatoms in East Lake live lower in the water column or below 10m (Lefkowitz et al. 2016).
6.3.3 Mass Accumulation Rate (MAR)

Mass accumulation rates can provide insight into the drawdown rates of sedimentary components and how or if they’ve changed over time. The mass accumulation rate for KCEL5 was determined using bulk dry density and the sedimentation rate was determined through dating with $^{210}\text{Pb}$ in 2011 East Lake cores. The linear sedimentation that was determined using the 2011 data is roughly equal to 1.7 mm/yr (Lefkowitz et al. 2016). The product of the bulk dry densities of core samples from KCEL5 and the linear sedimentation rate give the mass accumulation rate, which slightly increases with depth. Around 1600 AD (~70cm) BDD values are high and the resulting increase in MAR is shown (Figure MAR). As biogenic silica makes up the largest proportion of sediment, it has the highest MAR. The volcanic ash component was derived from the difference of the sediment MAR and the other two components (BSi and organic carbon). In this study, the drawdown rate of carbon is a main concern as it plays a significant role in the cycling of carbon in East Lake. The drawdown rate of carbon was determined by taking the average MAR of organic carbon and multiplying by the area of the lake which is $\sim 4.2 \times 10^{-6}$ km$^2$ (Johnson, 1985).
Figure 6.3.3.1: Mass accumulation rate of sediment of KCEL5 in brown. The mass accumulation rates of biogenic silica, organic carbon, and ash are also provided. At depth 0cm time is set at the year 2009. The deepest part of the core is at 85cm and at set at the year 1527.

<table>
<thead>
<tr>
<th>MAR</th>
<th>Average (mg/cm²/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sediment</td>
<td>40.2</td>
</tr>
<tr>
<td>Biogenic Silica</td>
<td>23.8</td>
</tr>
<tr>
<td>Organic Carbon</td>
<td>2.9</td>
</tr>
<tr>
<td>Ash</td>
<td>13.4</td>
</tr>
</tbody>
</table>

Table 6.3.3.1: Mean mass accumulation rates for bulk sediment and its constituents in KCEL5. The ash component was calculated as the difference of the biogenic silica and organic carbon components subtracted from the bulk sediment component.
6.3.4 Mercury

Mercury is a common volcanic gas constituent (Varekamp and Buseck, 1986). Concentrations of mercury in East Lake are high, ranging between 500 ppb to 5000 ppb. The flux of Hg from geothermal sources is reflected through changes in mercury concentration over time (Varekamp and Buseck, 1986). Mercury fluxes, which are often associated with increased volcanic activity, can be identified in sediment cores if they are dated. In core KCEL5, there is an increase or peak in the MAR Hg around 1800 (30-40cm). The increase in Hg may correspond to global trends in Hg accumulation mirrored in East Lake, but more data and further assessment is necessary. The average mass accumulation rate for mercury is .00059 mg cm\(^{-2}\) yr\(^{-1}\) and decreases with core depth. Annually ~3.4kg/yr Hg are buried in the sediment.

Figure 6.3.4.1: Mass accumulation rate of Hg.
Since mercury has a bonding affinity for fine-grained substances, it is often associated with organic matter and iron oxides (Varekamp et al., 2000). Fe-oxide concentrations in East Lake are low (Tables 5.5.3.2) leaving organic matter in the form of organic carbon as a likely host for mercury. Analyses for Hg concentrations in organic matter carried out in the summer of 2015 showed East Lake aqueous plants (phytobersgs) with 218, 241, and 267 ppb of Hg and Nostoc species with 22 and 44 ppm of Hg. These values are low compared to East Lake sediment samples that have 1000s ppb Hg, suggesting that aqueous plants and Nostoc cannot be the main host for Hg.

Still, there is a significantly positive relationship between organic carbon and mercury (Figure 6.3.4.2). Since East Lake sediment is largely composed of the frustules of diatoms (~60% biogenic silica) it is probable that diatomaceous organic
matter provide residence for Hg. Also, diatoms, as primary producers, sit low on the food chain and are consumed by higher trophic level grazers, such as fish (Schindler et al., 1997). This relationship could be the reason why fish samples have as much as 3.5 ppm Hg, which is an extremely high value for lacustrine fish.

6.3.5 Assessment of Volcanic Ash

East Lake sediment is composed of 8-12% organic carbon and 50-60% biogenic silica, leaving 30-40% of sediment to consist of another component. Core samples with low organic carbon contents suggest the presence of volcanic ash layers. The XRF analyses allow some insight into the presence of volcanic ash layers components in the sediment. Trace elements and major elements from known ash layers from the general area of Newberry Volcano (Kuehn, 2002) can be used to estimate the contribution of ash in East Lake sediments.

The silica-rich East Lake sediment samples are well outside the calibration range of the XRF analyses. By assuming that all sample elemental analyses were accurate, silica values, on an organic carbon free basis, could be determined from the difference of the sum of those elemental analyses out of 100%. These values are slightly lower than the measured SiO₂ contents (within 2-3 %). Biogenic silica data fall around 65% SiO₂ on a carbon free basis. Figure 6.3.5.1 shows an imperfect mixing relationship between volcanic ashes from the pumice cone ridge, located between East Lake and Paulina Lake, and core samples suggesting, that ~35% volcanic ash is contributed to the sediment.
Figure 6.3.5.1: Silica and potassium diagram showing the relationship between biogenic silica and volcanic silica components (Kuehn, 2002; MacLeod and Sherrod, 1988).

Incompatible elements like Rb, Zr, Y, Ti and Ba are common components in volcanic ash. Data from cores KCEL5, CLE12 (East Lake) and CLPA5 (Paulina Lake) show clear differences between elemental components such as high concentrations of Fe, Ni, Co, and As in Paulina Lake and high concentrations of Ti and Hg in East Lake. Figure 6.3.5.2 show linear arrays between all three cores. Volcanic ash data from Kuehn (2002) and MacLeod and Sherrod (1988) are also plotted. Linear mixing calculations suggest that East Lake sediment has the following contributions of volcanic ash (based on individual mixing models using the element in parenthesis): 10% (Rb), 16% (Zr), 17% (Y) and 22% (Ba).
Figure 6.3.5.2: Trace element concentrations in core samples from East Lake and Paulina Lake as well as ash data from the lake surroundings (MacLeod and Sherrod, 1988; Kuehn, 2002)
Trace and major elemental data show that evolved rhyolitic ashes may make up ~15-35% of the sediment. Basaltic dust may also be a component in the sediment, derived from the scoria cones and lava fields north of East Lake, which may explain the relatively high Ti concentrations in the sediment Table 5.5.3.2 and the variations in the linear trends in Figure 6.3.5.2. Rhyolitic ash is most likely the main component of volcanic ash in the sediment entering through aeolian processes. The XRF data also substantiate the independent BSi analyses that indicate that more than 50% BSi is present in East Lake sediment and the remaining silica-rich material is volcanic ash.

6. 4 Carbon Cycling

6.4.1 $\delta^{13}C$ Geothermal Carbon

Carbon is present in lacustrine systems in organic and inorganic form through various processes (Cohen, 2003). Inorganic carbon may enter a lake via CO$_2$ dissolution where it combines with water to create various carbonate species or it can enter as the product of the dissolution of mineral bicarbonates (Cohen, 2003). In East Lake a major contributor to dissolved inorganic carbon is geothermal CO$_2$. Cellular respiration may also be a source for DIC in East Lake, but further research needs to be done in order to quantify this input.

The isotopic value of DIC in the water column is determined by processes that fractionate carbon such as photosynthesis, respiration or evaporation, but also by the isotopic values of carbon inputs and outputs themselves.
Figure 6.4.1.1: The relationship between the total amount of carbon (DIC) in East Lake and the product of the $\delta^{13}C$ (DIC) and the DIC for 2015. The slope of the line provides the $\delta^{13}C$ of the geothermal input (Craig, 1953; D’Alessandro et al., 1996).

The geothermal input into East Lake is very light. Accepted values for geothermal inputs are between -6 and -8‰, however in East Lake the linear regression estimates that the geothermal CO$_2$ input is ~10‰ (Craig, 1953; D’Alessandro et al., 1996). The $\delta^{13}C$ values from past years include geothermal input values of -6‰ and -8‰ (Lefkowitz et al. 2016).

### 6.4.2 Carbon Cycle Model

Developing a first order carbon budget allowed for a preliminary examination of carbon cycling in East Lake. In East Lake there are two main fluxes that take carbon out of the system: The evasion of CO$_2$ from the surface of the lake amounts to 4400 tonnes of C per year. Carbon burial takes out an additional 140 tonnes of C per
year. Assuming that carbon in East Lake is at steady state, then the sum of the fluxes that take out the carbon have to equal the flux that is adding carbon into the system which is predominantly geothermal CO₂. Figure 6.4.2.1 shows the relationship between these inputs and outputs that control the standing amount of carbon in East Lake.

Seasonal variation in the carbon inputs and outputs are difficult to constrain. East Lake typically freezes over during the winter meaning that the evasion of CO₂ is unlikely to occur, while in summer the evasion of CO₂ is probably ongoing. In the summer, photosynthesis is also ongoing; however, ice cover could prohibit photosynthetic processes in winter. Also assuming that the geothermal input of CO₂ is constant during the winter months, with no escape, it would accumulate. With the thawing of ice in the spring it is possible that a catastrophic release of CO₂ would occur, as all the accumulated CO₂ would be released at one time. The total resident DIC of 3900 tonnes of C was calculated from DIC values (Web-phreeq). This value gives a residence time for carbon in East Lake of ~.87 year, meaning that carbon is being cycled fairly quickly, especially when compared to water residence time of ~20 years (Lefkowitz, 2012).

A simple mass balance model for the δ¹³C of total DIC can be created by employing the relationship between carbon fluxes described above, and knowing their isotopic values. Analyses of 2015 East Lake data suggest that the mean δ¹³C of the evading CO₂ is at least -15‰, the geothermal CO₂ is -10‰ and the δ¹³C of sediment is -24‰ (Figure 6.4.2.1). We assume all fluxes remain constant when “active” in the model. The goal was to see if the isotopic signature of the total resident DIC,
produced by the interaction of these carbon fluxes, could ever reach a steady state close to the $\delta^{13}C$ DIC values observed in East Lake which vary from $\sim$0.0‰ to $\sim$5‰.

![Box model for East Lake](image)

**Figure 6.4.2.1**: A box model for East Lake that simplifies the relationship between carbon inputs and outputs.

The model is based on interactions that occur in two areas of East Lake: the surface waters and the bottom waters. In theory, a two-box model would better constrain the cycling of carbon however we do not know how the geothermal flux is distributed between the bottom and surface waters. The model divides a 52-week year into two-parts: a summer period (22 weeks) and a winter period (30 weeks). We assume that the initial total DIC in East Lake is 3900 tonnes of C with a $\delta^{13}C$ that is at 0.0‰, and that the geothermal carbon input is 86.65 tonnes of C per week, which
represents the overall mass balance between the escaping CO$_2$ and burial of organic
carbon on an annual basis. The model was run for 4.5 years using weekly steps
keeping the geothermal input consistently at -10‰, the evasive flux at 84 tonnes of C
per week with a $\delta^{13}$C of -15‰ and carbon sequestration in sediment at 6.3 tonnes of
C per week with a $\delta^{13}$C of -24‰. During the summer period it is assumed that carbon
is being lost from the surface of East Lake at the rate of 84 tonnes C per week and
that carbon is being stored in the sediment at a rate of 6.3 tonnes of C per summer
week. At the same time the geothermal input is adding 86.65 tonnes of C per week.
This means there is no net increase or decrease in total resident DIC (Figure 6.4.2.2),
but there is an increase in the $\delta^{13}$C DIC (Figure 6.4.2.3). This occurs because the
carbon taken out of the water column is isotopically lighter than the geothermal
carbon input of carbon, leaving a heavier residual. In winter carbon cannot escape due
to ice cover and carbon burial is not occurring because of the much lower degree of
photosynthesis. The only process that is occurring is the geothermal input, which adds
carbon at a rate of 86.65 tonnes of C each week, strongly increasing the total resident
DIC (Figure 6.4.2.2). During this period there is net decrease in the $\delta^{13}$C since the
$\delta^{13}$C of the geothermal input is -10‰, which is lighter than the DIC (Figure 6.4.2.3).
With the ending of winter in early May, the thawing of ice cover results in a spring
turnover causing catastrophic release of 2520 tonnes of C in the form of CO$_2$. In the
model we assume that all “winter” carbon is released, but this may not be an accurate
representation of what transpires at East Lake.
The shape of the weekly $\delta^{13}$C DIC values produced by the model are evolving (light yellow-blue, in Figure 6.4.2.3) toward steady state and almost reach the maximum $\delta^{13}$C DIC values of surface waters measured in East Lake (~5‰). They are not at steady state by the end of the 4.5 years; however, it is probable that after a few more residence times, they will flatten out, lending some credibility to the modeling effort.

Figure 6.4.2.2: Model output of total resident DIC over 4.5 years.
6.5 Biological Implications

The biological implications of the effects of the volcanic inputs at East Lake have not yet been studied in detail. The literature can provide some insight as to how the organisms living in and around East Lake might respond or interact with their unique environment. Nutrient input has a large effect on productivity in lakes. Sediment analyses suggest that East Lake is dominated by phytoplankton and equal parts cyanobacteria and aqueous vegetation (Figure 6.3.2.1). The only predatory species are fish, which are stocked every year, and heavily fished. As no observed algal blooms have been observed from 2011 to 2015, nutrients are likely not in excess.
in East Lake; however, it is fair to say that the input of geothermal carbon and other volcanic inputs in the lake help producers to survive.

In general primary production in lacustrine systems is regulated by nutrient loading and food web interactions. The depletion in total DIC (Figure 6.1.3.3) in the surface waters suggests biological productivity in the surface waters (Schindler et al., 1997). In East Lake, this depletion could also represent gas escape. The significantly larger portion of biogenic silica (~60%) compared to organic carbon (8-12%) in East Lake sediment indicates that the ecosystem may be largely influenced by phytoplankton such as diatoms. Lakes that are dominated by planktonic species, such as East Lake, have the ability to be more productive than lakes dominated by higher trophic level organisms (Schindler et al., 1997). Phosphorus data (Figure 5.2.5.1) show an increase with depth and a depletion at the surface, suggesting a deep P input and biological activity in surface waters. Small inputs of phosphorus are shown to increase diatom production and sedimentation (Schelske et al., 1986). With an increase in diatom production there should also be an observable depletion in silica concentrations, particularly in the surface waters (Schelske et al., 1986). Although there is decreasing trend in silica (Figure 5.2.3.2) in the upper 20m of East Lake, silica values are maintained at ~6.5 ppm from 20m to 50m, suggesting a constant input of silica.

Cyanobacterial *Nostoc*, which are nitrogen fixing, photosynthetic, gelatinous organisms, play a crucial role in the East Lake system (Møller et al., 2014). They help make nitrogen, another crucial nutrient for photosynthesis, available to the primary producers in East Lake. Under enhanced dissolved inorganic carbon conditions
*Nostoc* species have higher photosynthetic and growth rates (Møller et al., 2014). East Lake is the ideal ecosystem for *Nostoc* as most species are found in oligo-mesotrophic hardwater lakes, and with the addition of CO₂ in East Lake these cyanobacteria have the potential to be highly productive (Møller et al., 2014).

The observed trends in East Lake water and sediment suggest that the volcanic inputs have not had a detrimental effect over the years of surveying. Nevertheless, it may be true that throughout past during periods of higher volcanic activity, that volcanic inputs did have an effect on biological life in East Lake, and that this could be an issue for the future.

### 7. Conclusions

The volcanic inputs at East Lake set the stage for a variety of unique features at temporal and spatial scales. Differences observed between major cation, chloride, sulfate and bicarbonate concentrations between East Lake and Paulina Lake waters, as well differences in sediment chemistries, suggest that the geothermal inputs reaching the two lakes are not the same or are not of the same magnitude (Lefkowitz et al., 2016). A geothermal input of CO₂ likely enters East Lake with H₂S and vaporous Hg through bubbles that dissipate before reaching the surface of the lake (Lefkowitz et al., 2016; Varekamp, 2016).

An interesting trend observed in East Lake waters is the δ¹³C gradient with depth and the unusual isotope enrichment in the surface waters. This feature has been observed in all years of research at East Lake. The δ¹³C gradient with depth is the result of two carbon-loss processes and one additive carbon process. The main carbon
loss process is the escape of carbon dioxide from the surface of East Lake, based on SGS estimates, averages to a total loss of 44 tonnes of CO₂/day. This escaping CO₂ is particularly light in δ¹³C (~15‰) and thus leaves a heavy DIC residue in the surface waters. Photosynthesis also contributes to surface water enrichment in ¹³C. The relationship between total DIC and δ¹³C DIC of water samples suggest that the geothermal input is around -10‰, adding an isotopically light carbon source to the East Lake bottom waters.

East Lake sediment is composed of 50-60% biogenic silica, 8-12% organic carbon, and 15-35% volcanic ash. The biogenic silica and organic carbon measurements in the sediment show that organic productivity also constitutes an important carbon sink for the lake waters. The DIC δ¹³C gradient builds up from spring through fall due to burial of carbon and loss of CO₂ through the evasive flux, but is then reset in the winter. While some geothermal inputs such at the Hg and H₂S may be harmful to aquatic life, the growth and productivity at an observational scale does not seem to be an issue. The constant CO₂ availability aids in productivity in this environment. Life in East Lake is not just predominantly fueled by the geothermal inputs of CO₂; it also is sustained through geothermal Si and P inputs providing photosynthetic reactants. Nitrogen, a main photosynthetic nutrient, enters the lake system and water column through cyanobacterial N₂ fixation from the atmosphere and becomes available for use by other producers.

The carbon cycling at East Lake is dynamic and efficient. Although carbon inputs are governed by the underlying volcanic system, the lake system—biological
and inorganic aspects—works to redistribute, sequester and stabilize carbon resulting in a perfunctory recycling process that takes less than a year to complete.
References


DeMaster, D. J., 1979, The marine budgets of silica and 31Si, PhD Dissertation, 308 pp., Yale University, New Haven.


Varekamp, JC, 2016, Stable isotope–based water budgets of the two Newberry crater lakes, OR. NE GSA meeting, Albany, NY, paper 47-4


***see attached files for Web-phreeq calculations***