Geochemical signatures of parent materials and lake sediments in northern Minnesota

by

EMILY MELLICANT

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Approved by:

Major Professor
Kendra K. McLauchlan

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Abstract

The importance of local parent material has been recognized as a fundamental control on the geochemistry of lake sediments, but there have been relatively few broad-scale surveys of catchment sources of terrigenous lake sediments.

In this paper, I present a geochemical study of catchment parent materials and lake sediments from four lakes in Northern Minnesota. Similar climate and vegetation conditions are present at all four lakes, which vary mainly in catchment parent material and lake morphometry. Geochemical data including major, trace and rare earth elements (REEs) from catchment parent material samples was compared with lake sediment geochemical data using PCA, linear regression, geological indices and elemental ratios.

In homogenous till-dominated catchments, patterns of elemental variation in the catchment till could be extended to predict elemental concentrations in the lake sediments. Simple ratios, which are commonly used to analyze lake sediment geochemical data, were not good predictors of lake sediment composition, however. Catchments with mixed bedrock and till were compositionally heterogeneous, and comparison with lake sediments was difficult. Lack of grain size control and biogenic silica measurements further confounded analysis. However, $\Sigma REE/Y$ ratio was found to be diagnostic of the catchment parent materials and present within the lake sediments.

This study makes a contribution to an improved understanding of lacustrine sedimentary archives by analyzing the spatial linkages among catchment, water and sedimentary geochemistry.

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Chapter 1 - Introduction

Lakes are widespread, complex natural environments that interact with both their terrestrial catchments and the atmosphere (See Figure 1-1) (Cohen, 2002; Bleckner, 2005). On Earth, there are over 117 million lakes found in almost every environment imaginable, from desert playas to high Arctic tundra (Verpoorter et al., 2014). In addition to being ubiquitous features on the Earth's surface, lakes also serve as natural repositories, collecting sediments derived from the area around the lake, in addition to in-lake processes (Gorham et al., 1983; Smol et al., 2002; Melles et al., 2012; Kylander et al.; 2013; Schreiber et al., 2014). Over time, high rates of deposition can provide continuous, high resolution record of past climate change as well as terrestrial changes on local and regional scales (Canham et al., 2012; Brahney et al., 2014; Berntsson et al., 2015). Lacustrine sediments contain a wealth of information, including elemental, molecular, isotopic, magnetic, fossil, pollen and charcoal records which serve as proxies for various in-lake, local and regional processes (Smol et al., 2001; Cohen, 2002). In the absence of long-term monitoring, lake sedimentary records are especially important for documenting past environmental change.

This abundance of potential data is both a blessing and a curse, and lake sediments are often studied in isolation, compared only with other lake proxies due to budget or time constraints (Engstrom and Swain, 1986). The importance of local parent material has been recognized as a fundamental control on the geochemistry of lake sediments, but few studies incorporate analyses of catchment sources of sediment (D'Arcy and Carignan, 1997; Das et al., 2003/2006; Rubensdotter et al., 2003; Jin et al., 2006; Brahney et al., 2014; Schreiber et al., 2014). To accurately interpret lacustrine sediment archives, a good understanding of local parent

material geochemistry is essential, including more extensive surveys of local geology and possible sediment supplies.
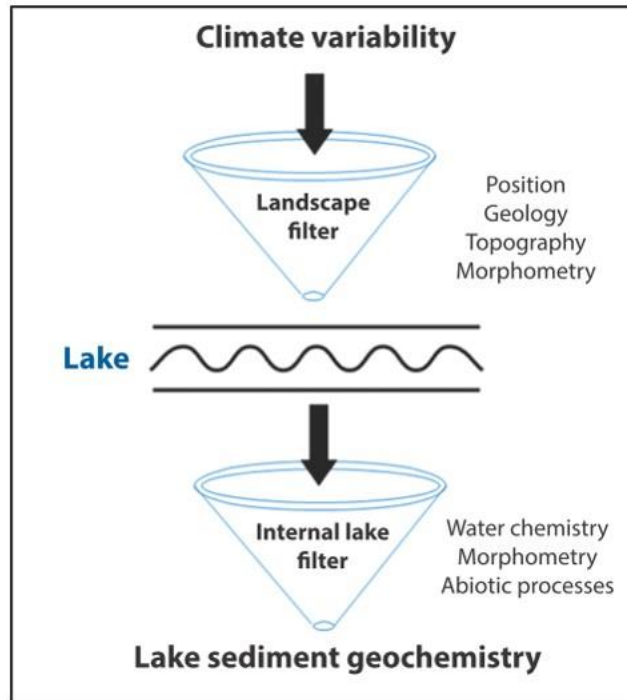
Figure 1-1: Conceptual figure detailing various controls on lake sediment geochemistry based on Bleckner, 2005.

Lake sediments are derived from two sources: allogenic materials transported into the lake from the atmosphere or catchment, and authigenic materials that form due to in-lake mechanisms in the water or sediment column (Smol, 2002). The chemical composition of these sediments is controlled by the processes that take place during weathering, transport and later diagenesis (Nesbitt and Young, 1996; Smol, 2002; Kylander et al., 2011). Therefore, geochemical information can answer a variety of questions concerning these processes, as well as providing a record of source rock composition (Das et al., 2003/2006; Giralt et al., 2008; Bertrand et al., 2010/2012; Kylander et al., 2011; Brahney et al., 2014).

Three factors have been identified as important controls on the sedimentary geochemistry of a lake: catchment parent material, topographic relief and lake structure (See "Landscape filter"

in Figure 1-1). This study will focus on the effects of variations in catchment parent material and lake structure. The geology and topography of the catchment control the nature of transported material as well as its deposition rate; both processes are important contributors to rate of sedimentation (Smol, 2002; Rubensdotter and Rosqvist, 2003).

Specific elements have been shown to serve as proxies for geology and topography of the catchment. Silica (SiO_2) often makes up a large percentage of inorganic lake sediments, though it may be biogenic in origin (Conley et al., 1993; Peinerud, 2000; Cohen, 2003). Because concentrations of silica in lake sediments include both biogenic and minerogenic silica, it can either be an indicator of increased productivity related to diatoms (Brown et al., 2007; Melles et al., 2012) or increased sediment transport related to erosion or wind (Schreiber et al., 2014; Bonk et al., 2016). Aluminum oxide (Al_2O_3) content in lake sediments is primarily controlled by detrital, minerogenic inputs into the lake and is commonly used as a grain size proxy, as it is associated with clay-sized material (Lopez et al., 2006; Clift et al., 2014). Titanium (Ti) is another detrital, minerogenic element which can serve as a useful grain size indicator (Cuven et al., 2010). Other, less common elements such as the rare-earth elements (REEs) and yttrium (Y) are useful indicators of source rock due to relative immobility during weathering and erosion processes (Das et al., 2006; Piper and Bau, 2013; Hu et al., 2014; Vasquez-Ortega, 2015).

Certain elements, such as iron (Fe) and phosphate (P_2O_5) are more strongly controlled by in-lake processes such as alkalinity, pH and redox conditions (Williams et al., 1971; Conley et al., 1993; Davison et al., 1993; Meyers et al., 1993; Morford et al., 1999; Loizeau et al., 2001; Lopez et al., 2006; Maranger et al; 2006). However, these water chemistry conditions are often influenced by the parent material of the catchment (Gorham et al., 1983; Pienitz et al, 1997). Gorham et al. (1983) showed that regional shifts in lake water chemistry of lakes in the upper

Midwest are controlled by both climate and compositional changes in parent material. These compositional changes lead to deposition of Ca-rich marls in the westernmost lakes. Lake morphometry also acts as a control on water chemistry (Rubensdotter and Rosqvist, 2003). Small, deep lakes are less likely to experience mixing, which in turn leads to anoxia in the bottom waters (Shaw et al., 2004).

Thus, although lacustrine sediments are complicated mixtures of components, it is possible to conduct a series of analyses that can identify their geochemical origins (Smol, 2002). The essential question is: what is the origin of each sediment component? By considering the geochemistry of the catchment in addition to the lake sediments, we may begin to identify the source components of the lake sediments, and ultimately better understand the proxy records recorded in the sedimentary archive.

Objectives

This study makes a contribution to an improved understanding of lacustrine sedimentary archives by analyzing the spatial linkages among catchment, water and sedimentary geochemistry. In this paper, I present a geochemical study of catchment parent materials and lake sediments from four lakes in Northern Minnesota. Similar climate and vegetation conditions are present at all four lakes, which vary mainly in catchment parent material and lake morphometry. I had two primary aims:

1. Determine the effect of catchment parent material (bedrock/soil) composition on elemental composition of lake sediments.

2. Interpret the effects of present day lake water composition as an intermediate step between the catchment and lake sedimentation processes.

Chapter 2 - Geographical and Geological Setting

Northern Minnesota

Four small lakes in northeastern Minnesota were chosen for this study, for several reasons. First, this setting provides adequate contrasts in bedrock lithology to accomplish objective #1. Second, this setting provides a relatively unpolluted study area to accomplish objective #2. Lakes in northeast Minnesota can be shallow to deep (up to 64m), with crystalline bedrock basins and small catchments (Dean et al. 1976). This leads to a single basin corresponding with a single type of parent material, which is ideal for this study. Finally, northeastern Minnesota contains several wilderness areas including Superior National Forest, Boundary Waters Canoe Area and Voyageurs National Park.

Parent materials in the area are a combination of crystalline bedrock and tills deposited by glaciers during the Wisconsin glaciation ~11,000-75,000 years ago. Bedrock is often exposed and soils tend to be thin or non-existent (See Figure 2-1). Where sediments do overly the bedrock, they are often made up of thin (<1 m) rocky tills. Tills are poorly sorted glacial sedimentary deposits that tend to be chemically unweathered (Young and Nesbitt, 1998). Tills in this area were deposited by the Des Moines, Rainy or Superior glacial lobes and specific deposition ages tend to be difficult to obtain (Thorleifson et al., 2007; Ojakangas, 2009). The Des Moines till has been sourced to a northern source area in Canada known as the Winnipeg Provenance, and is rich in a mix of basalt-gabbro-diabase clasts as well as limestone and dolomite (Thorleifson et al., 2007). The Rainy till lacks limestone and dolomite clasts, and rich in locally-derived North Shore rock types (Thorleifson et al., 2007). However, till composition is difficult to generalize and can be locally heterogeneous (Hobbs, 1998). Provenance studies are complicated by small-scale reworking of older tills and exposed bedrocks, which is especially an

issue in the Rainy till where a variety of localized bedrocks are exposed and the till is often thin (Hobbs, 1998).

Bedrock geology in this area is complex, but is commonly Precambrian in age with a few Cretaceous rocks exposed in the Mesabi Iron Range (Heinselman, 1996). The Precambrian bedrocks are igneous composed of and metamorphosed basalt, gabbro, diabase and granite (Gorham et al., 1983, Ojakangas, 2009).
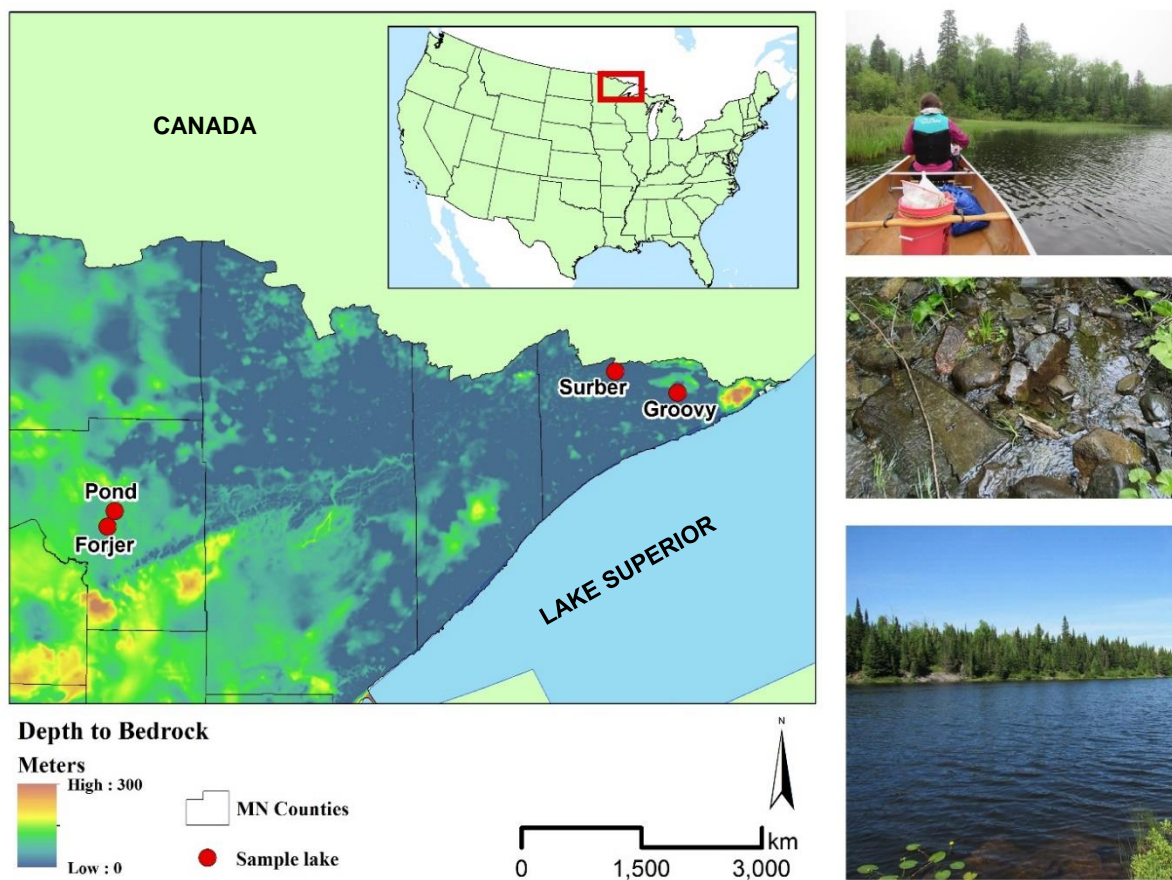
Figure 2-1: Regional map with locations of Forjer, Pond, Groovy and Surber Lakes sampled for purpose of this study. Site photos illustrate conditions common at all sample sites, including dense vegetation and rocky tills.

The Minnesota Department of Natural Resources (DNR) defines this area ecologically as the Laurentian Mixed Forest Province, which is characterized by forests of mixed conifer and hardwoods. These forests were once dominated by white (*Pinus strobus*) and red pine (*Pinus resinosa*), but extensive logging in the 19th century reduced the number of pines outside of a few protected areas. Now these forests are characterized by a mix of aspen (*Populus tremuloides*), paper birch (*Betula papyrifera*) and small numbers of white pine and red pine. The historic fire regime was likely a combination of infrequent high-intensity crown fires and more frequent low-intensity ground fires, and fire is an important factor in these forests (Heinselman, 1996).

The Minnesota Pollution Control Agency (MPCA) defines this ecoregion as "Northern Lakes and Forests" and notes that lakes are typically deep and clear, but extremely sensitive to deposition of pollutants from the atmosphere and storm water runoff (MPCA). Annual precipitation is up to 10-cm higher than evaporation in this region and lakes are mainly derived from rapid surface runoff (Gorham et al. 1983). These extremely dilute lakes have been termed seepage or perched lakes that are isolated above the groundwater table, and tend not to have permanent outlets (Gorham et al. 1983). Groundwater interaction is likely negligible in the northern areas of exposed bedrocks, as groundwater is only locally available along faults and fractures within the bedrock, however groundwater may interact with lakes in the southern part of the region where tills are thicker (MNDNR), but groundwater interactions are beyond the purview of this study.

Compared to southern and central Minnesota, the lakes in the Arrowhead region are relatively unaffected by anthropogenic influence. Limited mining and more widespread logging have taken place beginning in the 19th century, but there is very little agricultural development

due to the cold climate and poor soils. Climate throughout the region is relatively consistent averaging 1ºC mean annual temperature and 81cm mean annual precipitation (MDNR).

Chapter 3 - Methods

Site Selection

To evaluate the effects of a variety of bedrock types on lake sediment geochemistry, four lakes with their catchments lying solely in one bedrock type were sampled in northern Minnesota. In comparing sediments from the same region that have undergone similar processes in their catchments, previously unidentified controls on deposition can be identified, especially bedrock and topographical controls (Dypvik & Harris, 2001).

A large number of lakes were initially identified that met the initial criteria of size (<20 acres surface area of water) and location in a single bedrock and single till type using a Minnesota DNR lake dataset (2015). Many possible sample lakes were identified and their catchments mapped using ArcGIS. One meter Digital Elevation Models (DEMs) derived from LiDAR were obtained from the Minnesota DNR (2011). Slope layers were created for each lake and from these a flow direction layer was created using the ArcHydro toolbox in ArcGIS. Using these flow direction layers, catchments were mapped. These catchments show the furthest extent of local overland flow into the lake (See Figure 2-2). Lakes with permanent stream inflows were excluded. Lakes far from access points such as roads or hiking trails were also excluded.

Sampling sites

Final sampling site lakes were chosen due to accessibility and the presence of similar tills and varied bedrocks within their catchments. Sample size was limited by time and accessibility constraints. Four lakes were sampled, named Surber (48º03'58.6"N, 90º33'30.1"W), Groovy

(47º58'14.9" N, 90º10'57.7"W), Pond (47º31'07.3" N, 93º36'59.6" W) and Forjer lakes

(47º27'14.8" N, 93º29'26.1" W). For the purpose study, lakes were defined by the parent

materials which dominated their catchments and were available to contribute clastic material to

the lake sediments. Forjer and Pond Lake were designated "till lakes" as their catchments were

dominated by glacial till. Surber and Groovy Lake were designated "bedrock lakes" as their

catchments were a mix of exposed bedrock and thin (< 1m) glacial till.

Forjer and Pond Lakes (Figure 2-2A and B) are located in eastern Itasca County in the

Chippewa National Forest. The catchments contained no exposed bedrock but were rather

dominated by thick till (50-55m) deposited by the St. Louis Sublobe of the Des Moines Lobe

which reached its maximum extent of Des Moines, Iowa about 14,000 years ago (Ojakangas,

2009). Hereafter the till surrounding these two lakes will be referred to as the St. Louis till.
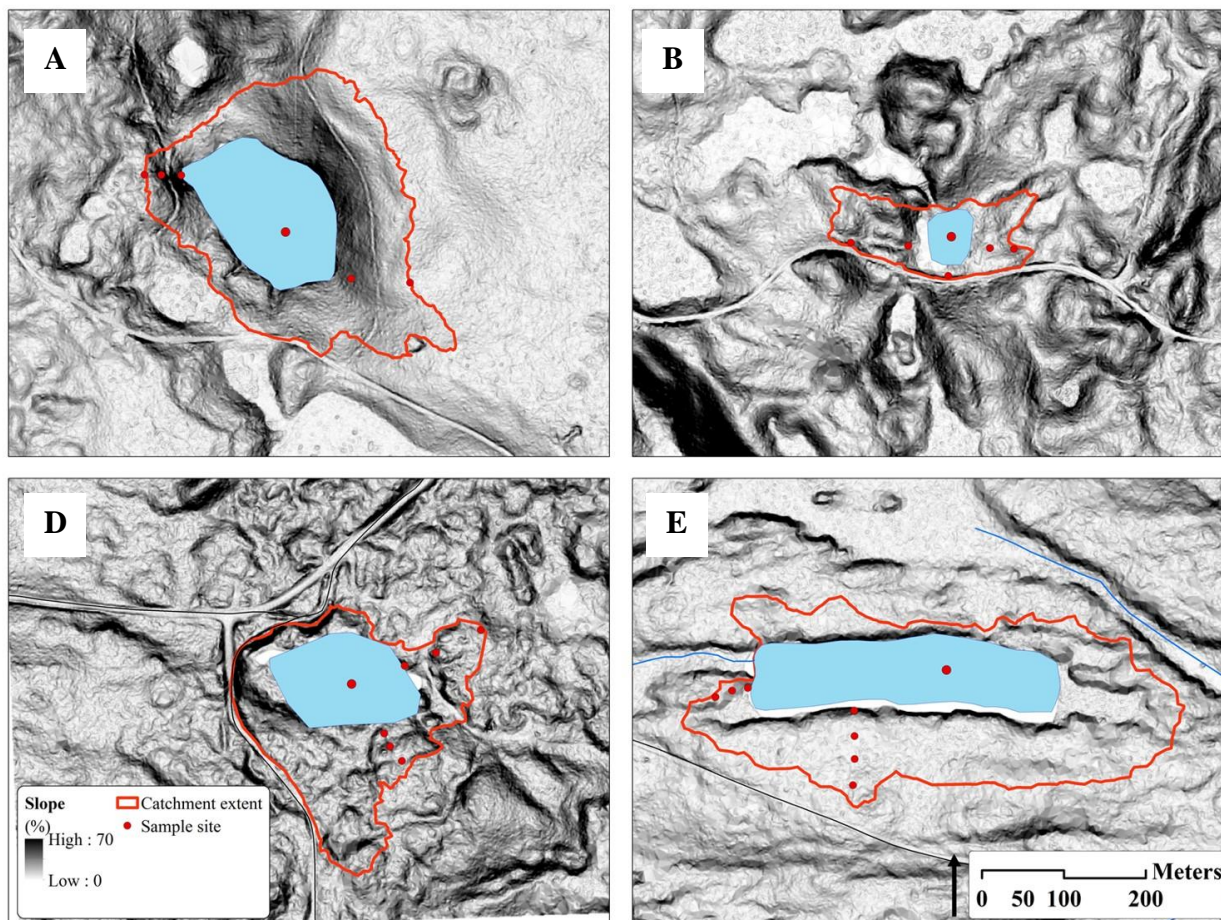
Figure 3-1 Site map of sample lake, their drainage basins and sample locations. A. Forjer Lake; B. Pond Lake*; C. Groovy Lake*; D. Surber Lake. *Named by author

Surber and Groovy Lakes (Figure 2-2C and D) were located in the northern part of Cook County in the Superior National Forest. Their catchments contained large areas of exposed bedrock and thin glacial till. The till present within the catchments of these two lakes was deposited by the Rainy Lobe and will hereafter be referred to as the Rainy till (Ojankangas, 2009).

Surber Lake lies within the Poplar Lake intrusion, a body of gabbroic cumulates mapped by Nathan (1977, 1978) (Miller et al., 2001). The Poplar Lake intrusion is part of an early mafic

phase of the Duluth Complex and has been dated to 1107±0.3 ma (Miller et al., 2001). It is interlayered by minor troctolite and anorthositic cumulates, and the Surber Lake catchment falls nearby one of these anorthositic layers (Miller et al. 2001). In the catchment, bedrock outcrops are common and average exposure of solid rock in the catchment is 45%. Gabbro is an igneous rock is mainly composed of plagioclase feldspar, olivine, pyroxenes and amphibole (Frost and Frost, 2013). Anorthosite is also an igneous rock, and is commonly composed of higher percentages of plagioclase feldspar and minimal amounts of olivine and pyroxene (Frost and Frost, 2013).

Groovy Lake falls within the Hovland lavas, a mixed suite of basalts, basaltic andesite and rhyolite that dates to 1107.7±1.9Ma (Miller et al. 2001; Davis and Green, 1997). The catchment contained large amounts of disturbed area due to pine logging within the catchment by the Forest Service (Wilfahrt, A., personal communication, November, 2016) and outcrops of rock were often boulder-sized material. Average rock exposure within the catchment is 20%. Basalts are commonly composed of feldspars, olivine, amphibole and pyroxenes (Frost and Frost, 2013).

Basalt and gabbro are similar rock types geochemically, and are distinguishable mainly by crystal size. Basalts are extrusive, and aphanitic- meaning they are fine-grained. Gabbros are intrusive and phaneritic- meaning their crystals are visible (Frost and Frost, 2013).

Parent materials and lake sediments

Parent material samples including rock and till were collected using two transects that started at the edge of each lake and ended at the edge of the catchment extent, one 50m transect and one 100m transect. The goal of these transects was to obtain a set of representative samples of the catchment by finding average geochemical values as well as the variability of these

signatures within the catchment. Lakes ranged in catchment size from $0.02km^2$ to $0.1km^2$. Five mixed grain-size till samples were collected around each till lake with a total of ten samples from the St. Louis till. Five to six samples of till were collected around each bedrock lake for a total of eleven samples from the Rainy till. Seven rock samples were collected from the Groovy Lake catchment and five rock samples were collected from the Surber Lake catchment. In addition, one lake sediment sample was collected from the deepest part of lake using an Ekman dredge (Jin et al, 2006).

Major element concentrations were obtained by X-Ray fluorescence spectrometer (ThermoARL X-Ray Fluorescence Spectrometer) at the Washington State University (WSU) GeoAnalytical Laboratory. Samples were ground into a fine powder, mixed with di-lithium tetraborate ($Li_2B_4O_7$), and fused into glass beads at $1000^{\circ}C$. The concentrations of 27 elements in the unknown samples are measured by comparing the X-ray intensity for each element with the intensity for two beads each of nine USGS standard samples (PCC-1, BCR-1, BIR-1, DNC-1, W-2, AGV-1, GSP-1, G-2, and STM -1, using the values recommended by Govindaraju, 1994) and two beads of pure vein quartz used as blanks for all elements except Si.

Trace elements, including rare earth elements (REEs) were measured following di-lithium tetraborate fusion using inductively coupled plasma mass spectrometry (ICP-MS) with an Agilent model 4500 ICP-MS at the WSU GeoAnalytical Laboratory.

Smear slides were created for each of the lake sediment samples and visually analyzed using a petrographic microscope for amorphous silica in the form of diatoms and sponge spicules.

Water chemistry

Two water samples were collected from the surface and near the bottom at the center of the lake, from the pelagic region using a 1 L polyethylene tube triggered by a weight at a specified depth (Brahney et al., 2014). Samples were analyzed at the Kansas State University Soil Testing Laboratory for analyses of chloride, sulfate, nitrogen, cations, phosphorus and total suspended solids. Water sample chemistry was averaged from a surface and deep sample to account for any stratification of lakes due to temperature and depth. Surface water data was verified using in-situ water chemistry data collected using an YSI Professional Plus Quatro.

Analytical methods

To understand large elemental datasets, multivariate statistics are an important tool for grouping elements per similar characteristics and properties (Schrieber et al. 2014, Koinig et al., 2003). Selection of specific elements for final analyses were based on the importance of these elements within initial large-scale principal components analyses (PCAs) of the full suite of 40 elements. Elemental concentrations in lakes sediments were initially compared to elemental concentrations within their catchments (Figures 4-1, 4-4 and 4-5). These concentrations were normalized to Upper Continental Crust (UCC) values from Rudnick & Gao (2004), to better visualize vastly different concentration values. Because of the varied sources, including igneous rocks, high-organic lake sediments and mixed composition tills, Pearson correlation coefficients (r) were calculated for the selected elements in each catchment-lake system to better understand the grouping of elements that defined each system (Tables 4-2 and 4-3). Linear relationships between elements were plotted to visualize the how the ratios between elements were changing from catchment into the lake (Figures 4-3 and 4-6) Finally, PCAs were performed on each catchment-lake system (till and each separate bedrock lake and catchment) on a selection of 15

elements to provide and understanding of the associations between elements and the patterns present in the two different systems (Schreiber et al. 2014, Koinig et al., 2003) (Figures 4-2 and 4-5).

The characteristics of rare earth elements and yttrium are useful indicators of sedimentary environment and provenance (Hu et al. 2014; Aide and Aide, 2012; Das et al. 2005; Taylor and McLennan, 1998). REEs are commonly associated with certain primary heavy minerals such as zircon and apatite, but also undergo adsorption reactions with phyllosilicate or oxyhydroxide clay minerals during weathering (Aide and Aide, 2012). In addition, organic acid complexation may aid REE transport (Aide and Aide, 2012). Rare earth elements and yttrium (REYs) are usually analyzed by normalizing to a standard such as Upper Continental Crust (UCC), chondrites or Post-Archean Average Shale (PAAS) (Piper and Bau, 2013). In this case, the UCC standard was chosen as samples were a mixture of igneous rocks, organic-rich lake sediments and glacial tills. UCC is derived by averaging large numbers of glacial loess and sedimentary rock samples and is commonly used to standardize sedimentary rock values. PAAS is commonly used to analyze shales, while chondrites is commonly used to analyze igneous rocks (Piper and Bau, 2013; Rudnick and Gao, 2004). REYs have also been normalized to assumed source in order to understand concentration variations caused by physical and chemical weathering in Critical Zone Observatories (Vazquez-Ortega et al, 2015). REYs in this study have been normalized to UCC due to the lithologic variation in sample types including igneous/metamorphic rocks and high-organic lake sediments.

In addition to these statistical analyses, a number of geochemical indices were calculated to characterize the processes that have affected clastic material as it had moved through the catchment and the lake.

Chemical Index of Alteration (CIA) is defined by Nesbitt and Young (1982) as:

$$CIA = [Al_2O_3 / (Al_2O_3 + CaO^* + Na_2O + K_2O)] \times 100;$$

where CaO* is the amount of CaO in the silicate fraction of the rock. This index measures the proportion of Al_2O_3 compared to more easily altered oxides and reflects the relative amount of feldspars and clay minerals in a sample. CIA has been used to estimate chemical alteration caused by climate in various environments including lacustrine sediments. CIA values for average shales often fall between 70 and 75 (Young and Nesbitt, 1998).

Chemical Index of Weathering (CIW) is defined by Harnois (1988) as:

$$CIW = [Al_2O_3 / (Al_2O_3 + CaO + Na_2O)] \times 100;$$

where Al_2O_3 is the viewed as an immobile oxide while CaO and Na_2O are mobile oxides. K_2O is not included as it may be leached or re-precipitated in residual weathering products.

Chapter 4 - Results

Water Chemistry

Water chemistry was variable among lakes because of variations in depth, size and position of the lakes within the landscape (Table 4-1). However, all lakes fell within the average water quality indicators measured by the Minnesota Pollution Control Agency (MPCA) except for a few notable exceptions.

Lake waters were generally close to neutral pH, with Pond Lake showing slightly more acidic water at 6.55. Lake water temperatures were close to atmospheric temperatures at the time of sampling (June). Lake water maximum depth was highly variable across the landscape. Forjer was the deepest lake with 7.9m of water, while Pond was extremely shallow with 1.2m of water. Dissolved oxygen levels were relatively high, averaging 6.50 mg/L, except those in Pond Lake which were only 3.30 mg/L. Total suspended solids, dissolved solids, nitrogen and phosphorus were also relatively constant among lakes except for orthophosphate measurements from Pond Lake, which were higher than the other three lakes.

Overall, these lakes are extremely dilute, with low levels of all major cations and anions. Of the major cations and anions measured, only iron shows much variability in concentration among the four sampled lakes, with much higher concentrations in Pond and Surber Lakes than Forjer and Groovy Lakes.

Table 4-1 Water chemistry data from four study lakes. Till lakes are noted in blue and bedrock lakes are noted in orange. Red numbers indicate values that fall outside MPCA water quality indicators for region. Surface and bottom water measurements are included in Appendix B-1.

	Forjer	Pond	Groovy	Surber
pH	7.72	**6.55**	7.57	7.10
Temp (ºC)	24.10	17.60	22.40	20.90
Depth (m)	7.90	1.20	2.30	5.10
DO (mg/L)	7.00	**3.30**	7.90	7.60
TSS (mg/L) average	1.0	2.0	0.90	0.80
TDS (mg/L) average	22.0	13.5	17.0	19.0
Total N (ppm) average	0.38	1.40	0.43	0.48
Total P (mg/L) average	0.00	**0.06**	0.00	0.00
NH_4-N (ppm) average	0.09	0.30	0.08	0.23
NO_3-N (ppm) average	0.00	0.00	0.00	0.02
Ortho P (ppb) average	1.39	31.70	3.08	6.09
Ca (ppm) average	4.27	2.15	1.92	3.49
Mg (ppm) average	1.23	0.63	2.43	1.41
Zn (ppm) average	0.02	0.03	0.01	0.02
Fe (ppm) average	0.05	0.54	0.01	0.52
SO_4 (ppm) average	0.45	0.05	0.69	0.15

Elemental Concentrations

There are both positive and negative correlations among the elemental concentrations of major elements in the catchment samples, which are often reflected in the lake sediment present within these catchments (Table 4-2, 4-3). Distinct correlation strengths are found between lake sediments and their catchment samples on each of the two types of study sites- till lakes and bedrock lakes- through PCAs (Figure 4-2, 4-5). Linear regressions also show strong differences in the relationships of the lake sediments to their varied catchment parent materials (Figure 4-3, 4-6).

Till-dominated lakes
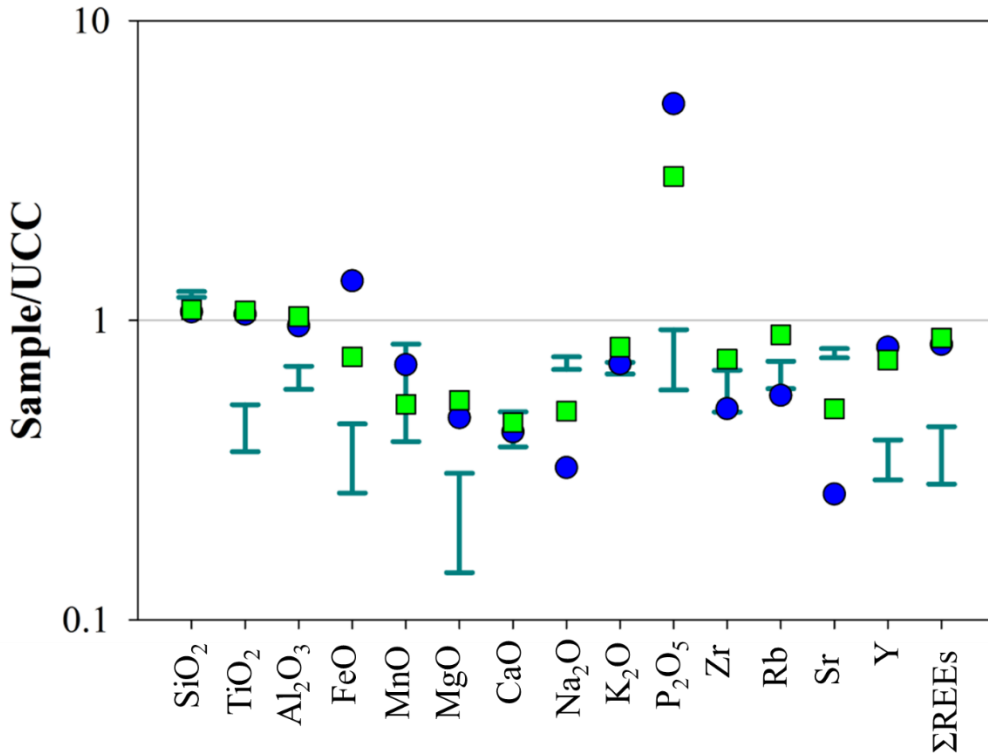
Figure 4-1 Major and trace elements of samples from till-dominated lakes and catchments normalized to Upper Continental Crust (Rudnick & Gao, 2004). Teal error bars show the variation of St. Louis till samples; blue circles are Pond Lake sediment and green squares are Forjer Lake sediment.

The St. Louis till tends to be relatively consistent geochemically, and is often depleted compared to the UCC. In the St. Louis till, the absolute values of SiO_2 are slightly enriched with an average of 80.3%. All other elemental values are depleted compared to UCC, with FeO (1.8%), MgO (0.6%) and Y (7.4 ppm) being especially notably depleted.

The till lakes show similar absolute values of elements and oxides compared to each other. These lakes mirror concentrations of elements within their catchment parent materials in MnO (0.6%), CaO (1.5%), K_2O (2.1%) and Zr (120 ppm). They are enriched compared to the St. Louis till in TiO_2 (0.65%), Al_2O_3 (14.7%), FeO (5.1%), MgO (1.2%), and P_2O_5 (0.6%). The

lakes sediments are depleted compared to their catchment parent materials in SiO_2 (68.7%), Na_2O (1.3%) and Sr (120 ppm). FeO, Y and Rb show large inter-lake variation.

In till lakes (Table 4-2), variability in the system is defined by the strong negative relationship between SiO_2 and most of the other elements and a positive correlation with Sr and Na_2O. SiO_2 shows strong negative correlations to several of the other elements, including; TiO_2, Al_2O_3, FeO, MgO and P_2O_5 and Y and $\Sigma REEs$. These major and trace elements all show strong positive correlations to each other.

Elements and oxides not positively or negatively correlated with SiO_2 include K_2O, Rb, MgO, CaO and Zr. K_2O and Rb are strongly positively correlated with each other. CaO, MnO and Zr show no strong correlations with any other elements.

Table 4-2 : Pearson (r) correlation coefficients for major and trace elemental analyses from all catchment till and lake sediment samples from till-dominated lakes. The strongest correlations are highlighted in blue.

	SiO_2	TiO_2	Al_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Zr	Rb	Sr	Y	REEs
SiO_2															
TiO_2	-1.0														
Al_2O_3	-1.0	1.0													
FeO	-0.9	0.9	0.8												
MnO	0.2	-0.1	-0.2	-0.2											
MgO	-0.9	0.9	1.0	0.8	-0.3										
CaO	-0.1	0.1	0.2	0.0	0.0	0.4									
Na_2O	0.8	-0.8	-0.7	-0.9	0.0	-0.6	0.3								
K_2O	-0.5	0.5	0.7	0.2	-0.2	0.7	0.4	-0.1							
P_2O_5	-0.9	0.9	0.8	0.9	0.0	0.7	-0.2	-1.0	0.1						
Zr	-0.2	0.3	0.3	0.0	-0.1	0.4	0.4	0.0	0.5	-0.1					
Rb	-0.3	0.4	0.6	0.0	-0.2	0.6	0.4	0.0	0.9	0.0	0.6				
Sr	0.9	-0.8	-0.7	-0.9	0.0	-0.6	0.3	1.0	-0.1	-1.0	0.1	0.1			
Y	-1.0	1.0	1.0	0.9	-0.1	0.9	0.1	-0.9	0.4	0.9	0.2	0.3	-0.9		
REEs	-1.0	1.0	1.0	0.9	-0.2	0.9	0.2	-0.8	0.5	0.9	0.2	0.4	-0.8	1.0	
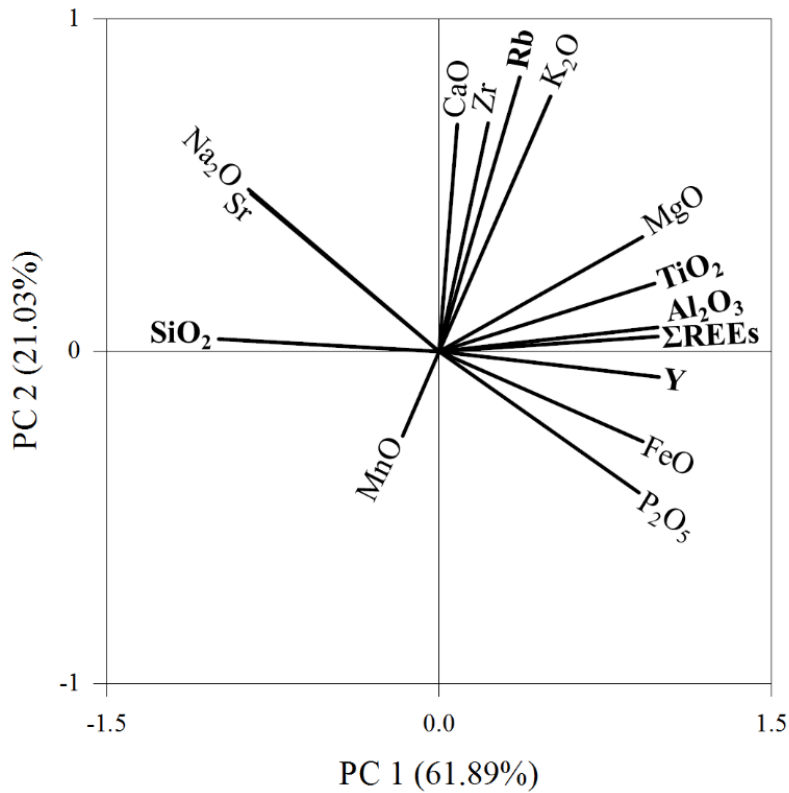
Figure 4-2 Principal component analysis of St Louis till and lake sediments present till lakes. Bold labels show elements with strong correlations to principal components.

In the till-emplaced lakes, multiple elements show strong correlations throughout the system. The first principal component (PC1) explains 61.89% of the total variability and is characterized by a strong negative loading of SiO_2 and a strong positive loading of TiO_2, Al_2O_3, $\Sigma REEs$, and Y. PC2 explains an additional 21.03% of the total variance. PC2 is positively correlated with Rb. Together, PC1 and PC2 explain 82.91% of the variability in the till system.
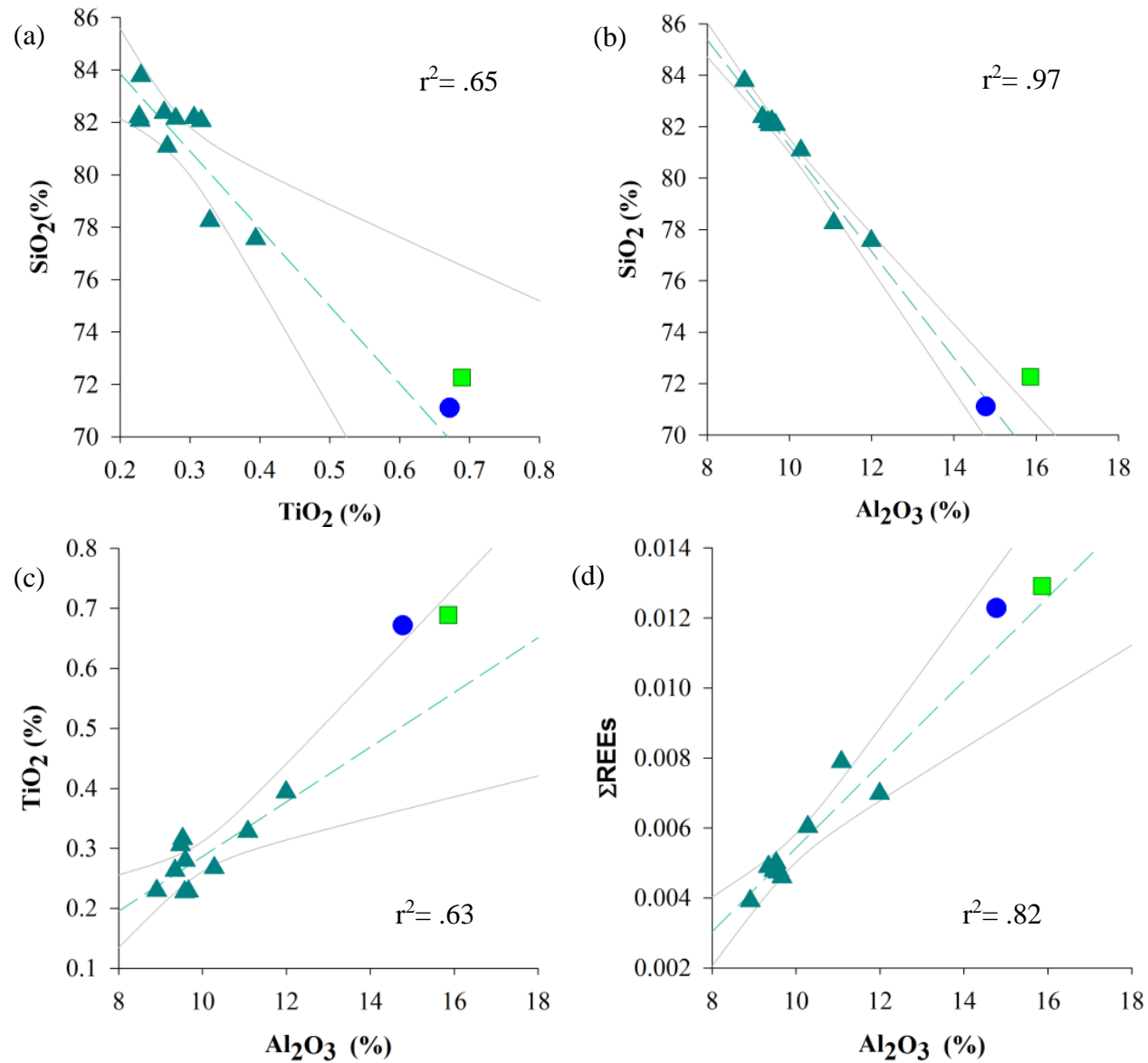
Figure 4-3: Relationships between (a) SiO_2 and TiO_2; (b) SiO_2 and Al_2O_3; (c) TiO_2 and Al_2O_3; (d); (e) $\Sigma REEs$ and Al_2O_3. Teal triangles indicate St. Louis Till samples. Blue circles indicate Forjer Lake sediments and green squares indicate Pond Lake sediments. Teal dashed lines represent a linear regression based on St. Louis Till samples, while the grey lines represent 95% confidence interval. P-values in Table A-8.

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There are strong correlations between the concentrations of major elements in the St.

Louis till and the lake sediments of the lakes found within this till type (Figure 4-2). In the St.

Louis till, SiO_2 shows negative correlations with all other elements (Table 4-2). In the major

oxides, SiO_2 shows a negative relationship with both TiO_2 ($r^2 = 0.65$) and Al_2O_3 ($r^2 = 0.97$). The

St. Louis till has high absolute concentrations of SiO_2 (81.4%) and low concentrations of TiO_2

(0.28%) and Al_2O_3 (9.9%) (See Figure 4-1).

Apart from the major oxides which load positively on PC1, ΣREEs show a strong

positive correlation to Al_2O_3 ($r^2 = 0.99$) and Y ($r^2 = 0.98$). Rb controls the variation in PC2, and

is strongly correlated with K_2O in the catchment till. Commonly compared with Sr in order to

measure chemical alteration, Rb/Sr shows relatively consistent ratios in the catchment sediments.
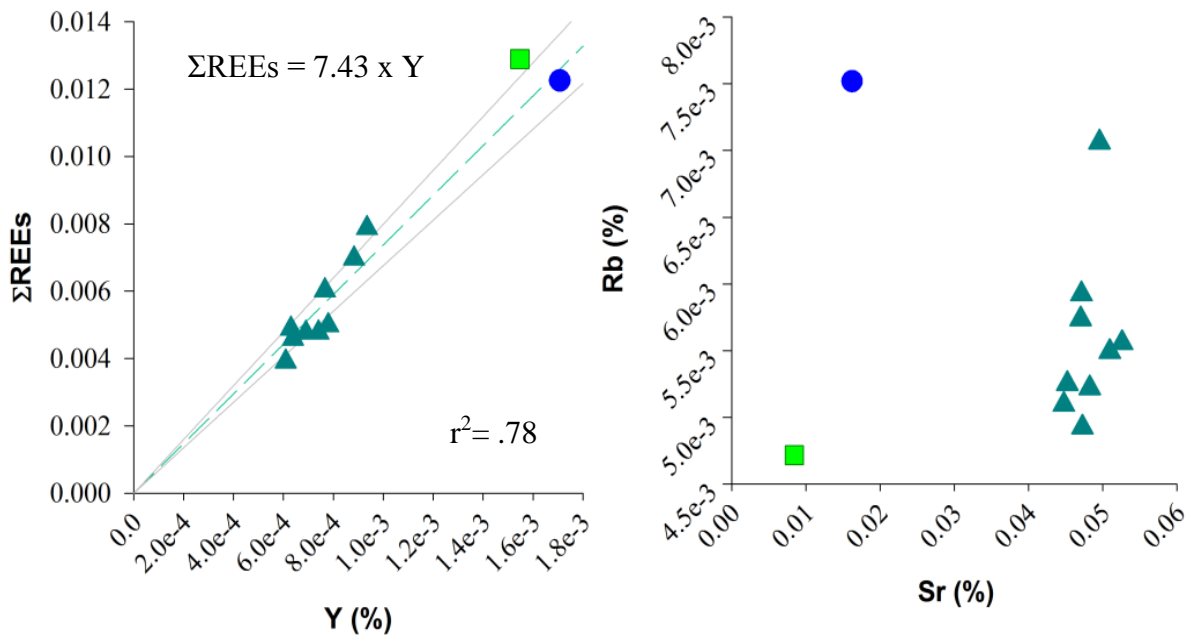
Figure 4-4 Relationships between (a) ΣREEs and Y; (b) Rb and Sr. Teal triangles indicate
St. Louis Till samples. Blue circles indicate Forjer Lake sediments and green squares
indicate Pond Lake sediments. Teal dashed lines represent a linear regression based on St.
Louis Till samples, while the gray lines represent 95% confidence interval. P-values in
Table A-8.

Inorganic lake sediments from the till-emplaced lakes show similar ratios of elemental concentrations to the St. Louis till, with different absolute values. Both Forjer and Pond lake sediments show low SiO_2 (71.7%) compared to their catchments (81.4%). The till lake sediments also show enrichment of TiO_2 (0.68%) and Al_2O_3 (15.3%) compared to their catchments (0.28%, 9.9%). Lake sediments reflect the lower end of the SiO_2/ TiO_2 and SiO_2/ Al_2O_3 ratios. They fall along the upper end of the trendline of TiO_2/ Al_2O_3 with slightly depleted Al_2O_3 concentrations than what could be expected from their catchments. The till lakes also show strong depletion in Sr in comparison with Rb, which falls within the range of concentrations found within the St. Louis till.

Bedrock lakes

In comparison with the St. Louis till, the Rainy till shows a more variability in elemental concentrations, and is often similar to UCC. In addition, bedrock is exposed throughout these catchments, creating an additional complexity in understanding element sources.
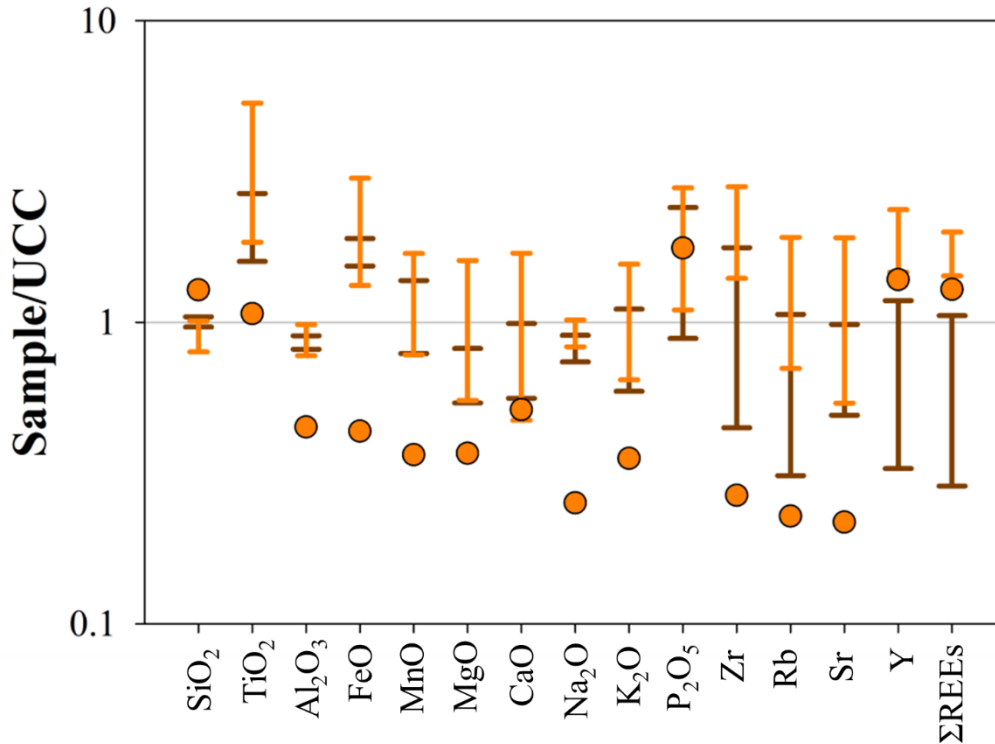
Figure 4-5 Major and trace elements of samples from Groovy Lake and its catchment normalized to Upper Continental Crust (Rudnick & Gao, 2004). Brown error bars show the variation of Rainy till samples; orange error bars show the variation of Groovy rock samples and orange circles are Groovy Lake sediment.

In the Rainy till, the absolute values of SiO_2 are similar to UCC at 64%. MnO (0.10%) and K_2O (2.3%) concentrations are also similar to UCC. TiO_2 (1.3%), FeO (8.3%) and P_2O_5 (0.23%) are enriched. Al_2O_3 (13%), MgO (1.6%), CaO (2.7%), Na_2O (2.6%), Rb (58 ppm), Sr (240 ppm) and Y (16 ppm) concentrations are only slightly depleted compared to UCC. Concentrations of trace elements and phosphate show the greatest amount of variation in the Rainy till.

The rock samples collected from the Groovy Lake catchment are often enriched compared to UCC. TiO_2 (2.6%), FeO (12.1%), P_2O_5 (0.33%) and Zr (9.6 ppm) are all enriched. SiO_2 (57%), Al_2O_3 (14%) and Na_2O (3.0%) are very slightly depleted compared to UCC and show little variation.
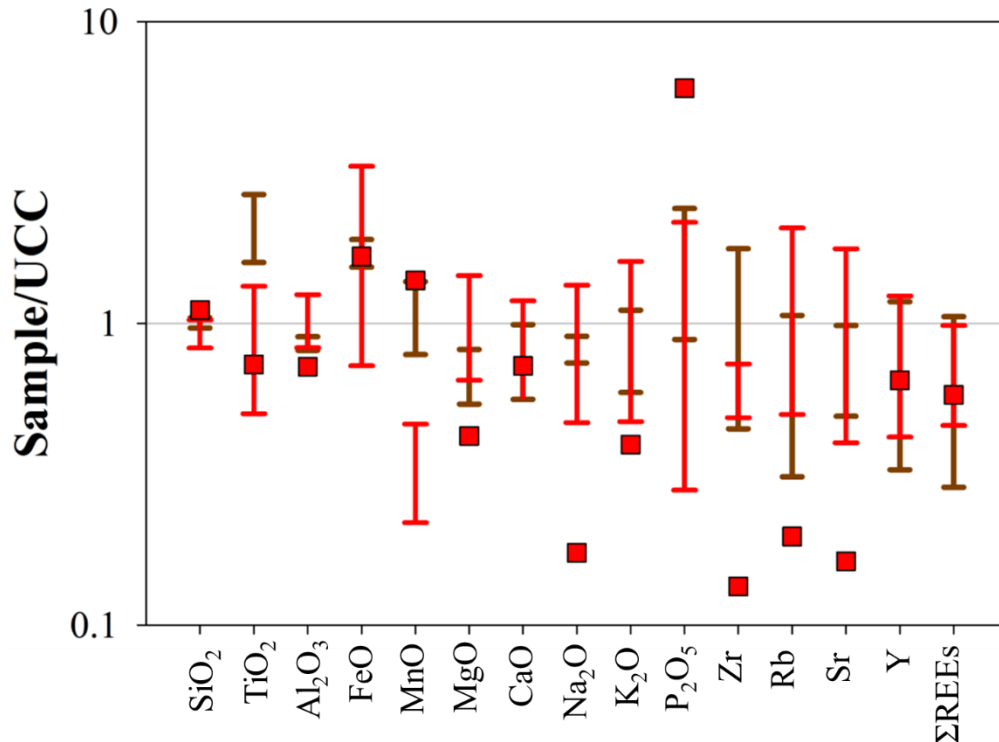
Figure 4-6 Major and trace elements of samples from Surber Lake and its catchment normalized to Upper Continental Crust (Rudnick & Gao, 2004). Brown error bars show the variation of Rainy till samples; red error bars show the variation of Surber rock samples and red squares are Surber Lake sediment.

The rock samples collected from the Surber Lake catchment show a large amount of geochemical variability. Extreme variation in TiO_2 (0.25-0.96%), FeO (2.4-18%), Na_2O (1.0-5.2%) and Sr (84-680 ppm) are most notable. The mean concentrations of SiO_2 (64.5%), TiO_2 (0.58%), Al_2O_3 (16.8%), MgO (2.2%), and K_2O (3.4%) are similar to UCC. MnO (0.34%), CaO (1.0%), P_2O_5 (0.11%)), Zr (112 ppm) and Y (14.2 ppm) are depleted. Only the average concentrations of FeO (8.4) and Rb (124 ppm) show enrichment compared to UCC.

Unlike the till lakes, the bedrock lakes often show different absolute values of elemental and oxide concentrations compared to each other. Surber Lake sediments contain similar SiO_2, FeO, MnO CaO and Y concentrations to the parent materials present in its catchment. All other elemental concentrations in Surber Lake sediments are depleted except TiO_2 and P_2O_5, which are enriched compared to the Rainy till and catchment rocks.

Groovy Lake sediments contain similar P_2O_5 concentrations to the parent materials present in its catchment. All other elemental concentrations in Groovy Lake sediments are depleted compared to the Rainy till and catchment rocks, except SiO_2, which is enriched in the lake sediments.

In bedrock lakes (Table 4-2), SiO_2 shows negative correlations to several of the other major elements, including; TiO_2, FeO and MgO. SiO_2 is not positively correlated with any of the other elements.

TiO_2 shows a strong positive correlation to CaO and weaker positive correlations with MnO, MgO, Zr, Y and ΣREEs. ΣREEs and Y show a strong positive correlation with Zr. One of the strongest positve correlations in the bedrock catchments and lakes sediments is between the ΣREEs and Y. Another strong positive correlation is between K_2O and Rb.

Table 4-3 : Pearson (r) correlation coefficients for major and trace elemental analyses from all catchment rock, till and lake sediment samples from bedrock-dominated lakes. The strongest correlations are highlighted in orange.

	SiO_2	TiO_2	Al_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Zr	Rb	Sr	Y	REEs
SiO_2															
TiO_2	-0.7														
Al_2O_3	-0.3	0.0													
FeO	-0.7	0.5	-0.1												
MnO	-0.5	0.7	-0.3	0.4											
MgO	-0.6	0.7	0.5	0.5	0.3										
CaO	- 0.6	**0.8**	-0.2	0.4	**0.8**	0.5									
Na_2O	-0.3	0.2	0.3	0.0	0.2	0.3	0.4								
K_2O	-0.3	0.0	0.7	0.1	-0.3	0.2	-0.4	0.0							
P_2O_5	-0.3	0.3	-0.4	0.2	0.5	0.0	0.5	-0.3	-0.4						
Zr	-0.3	0.6	0.1	0.3	0.5	0.3	0.3	0.3	0.4	-0.1					
Rb	-0.2	0.1	0.7	0.2	-0.2	0.4	-0.4	0.0	**0.9**	-0.4	0.5				
Sr	-0.4	0.5	0.2	0.3	0.4	0.5	0.7	0.7	-0.2	0.0	0.3	0.0			
Y	-0.3	0.7	0.0	0.3	0.4	0.5	0.4	-0.1	0.3	0.2	0.7	0.3	0.3		
REEs	-0.3	0.6	0.1	0.3	0.4	0.5	0.4	0.1	0.3	0.1	**0.8**	0.4	0.4	**0.9**	

The bedrock lake sediments and catchment parent materials overall show fewer strong correlations and more elements which show little to no correlation to other elements within the system.
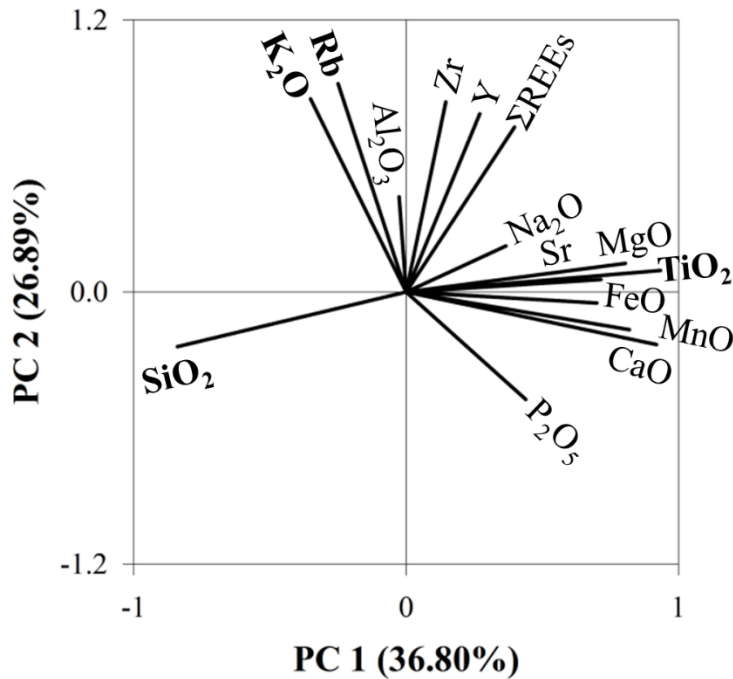
Figure 4-5 Principal component analysis of Rainy till, rocks and lake sediments present in bedrock lakes. Bold labels show elements with strong correlations to principal components.

In contrast to the till lakes, the bedrock-emplaced lakes show weaker correlations among elemental concentrations. PC1 explains only 36.8% of the total variability. It is also characterized by a strong negative loading of SiO_2 and a positive loading of TiO_2. PC2 explains 26.9% of the variability and is characterized by strong negative loadings of Rb and K_2O. Together PC1 and PC2 explain only 63.7% of the variability in the bedrock system.

The sedimentary geochemistry of lakes with mixed bedrock and till in the catchment are more complex than the geochemistry of lakes with till dominated catchments. For Groovy and Surber Lakes, twenty to forty-five percent of their catchments are made up of exposed bedrock in various states of weathering and alteration. In addition, the Rainy till present in this area was more variable geochemically than St. Louis till.
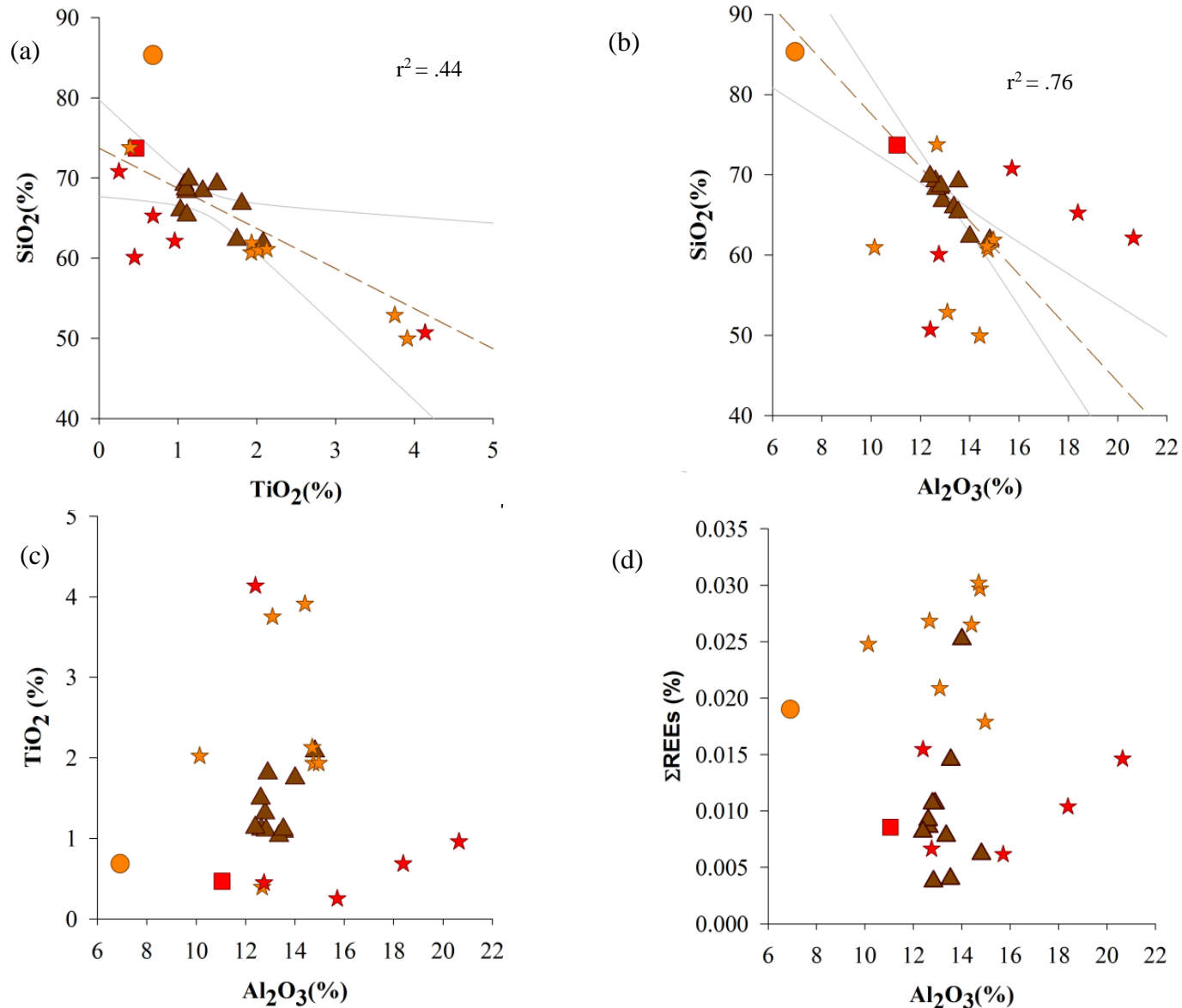
Figure 4-7: Relationships of (a) SiO_2 and TiO_2; (b) SiO_2 and Al_2O_3; (c) TiO_2 and Al_2O_3; (c) ΣREEs vs Al_2O_3. Brown triangles indicate Rainy Till samples. Orange circles indicate Groovy Lake sediments while orange stars represent Groovy catchment rock samples. Red squares indicate Surber Lake sediments while red stars represent Surber catchment rock samples. Brown dashed lines represent a linear regression based on Rainy Till samples, while the grey lines represent 95% confidence interval. P-values found in Table A-8.

In the bedrock catchments and lake sediments, SiO_2 shows negative correlations with nearly all other elements (see Table 4-2 and Figure 4-5). However, the Rainy till itself shows weak correlations between elements. SiO_2 shows little correlation with TiO_2 ($r^2 = 0.44$) and a stronger negative correlation with Al_2O_3 ($r^2 = 0.76$) (Figure 4-8A and B). There is no correlation between TiO_2 and Al_2O_3 (Figure 4-8C). Iron and manganese oxides in the Rainy till are not correlated ($r^2 = 0.08$).
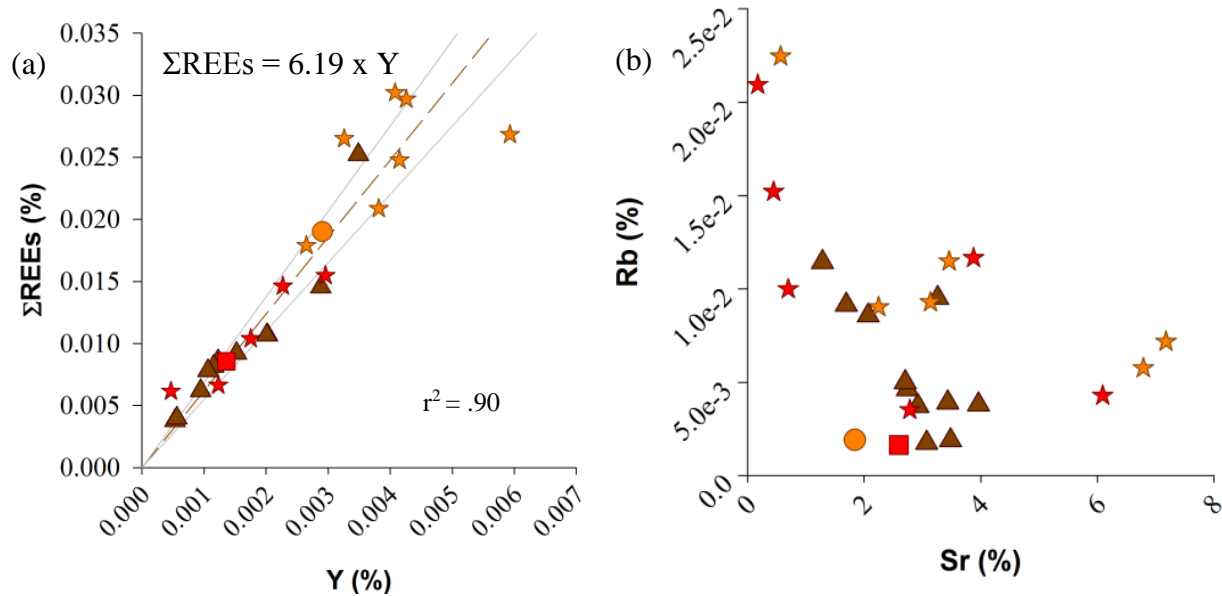
Figure 4-8 Relationships between (a) ΣREEs and Y; (b) Rb and Sr. Teal triangles indicate St. Louis Till samples. Brown triangles indicate Rainy Till samples. Orange circles indicate Groovy Lake sediments while orange stars represent Groovy catchment rock samples. Red squares indicate Surber Lake sediments while red stars represent Surber catchment rock samples. Brown dashed lines represent a linear regression based on Rainy Till samples, while the grey lines represent 95% confidence interval. P-values found in Table A-8.

Because elements within the catchment rocks and Rainy till do not strongly vary in relation to each other, it is difficult to discern patterns that lake sediments would reflect. Lake sediments from Surber show similar ratios of elemental concentrations to the Rainy till, with more similar absolute values. However, Groovy Lake sediments show more variation compared to the till present in the catchment. Both Surber and Groovy lakes show high SiO_2 (73.7 and

85.3% respectively) compared to their catchments (66.9%). Surber Lake sediments are similar to SiO_2/ TiO_2 and SiO_2/ Al_2O_3 ratios but are slightly too depleted in TiO_2 and Al_2O_3. Groovy falls well outside SiO_2/ TiO_2 and SiO_2/ Al_2O_3 ratios, showing a strong enrichment of SiO_2.

$\Sigma REEs$ are not correlated with Al_2O_3 in the Rainy till and with strongly correlated with Y throughout all the samples. These correlations provide one of the few patterns that can be compared to concentrations in the lake sediments. Because both lake sediments are depleted in Al_2O_3 compared to their catchment parent materials, they do not reflect the ratios of $\Sigma REEs/Al_2O_3$ present in the catchment. However, both lakes reflect the $\Sigma REEs/Y$ present within their catchment parent materials.

Rb controls the variation in PC2, and is strongly correlated with K_2O in all the samples. Rb/Sr shows relatively consistent ratios in the catchment samples. The bedrock lake sediments show similar concentrations of Rb to some of the Rainy till samples, but are overall depleted compared to most of the catchment parent material samples. The sediments from the two bedrock lakes, overall, are depleted in Sr compared to the catchment parent materials as well.

Geochemical Indices

Chemical Index of Alteration
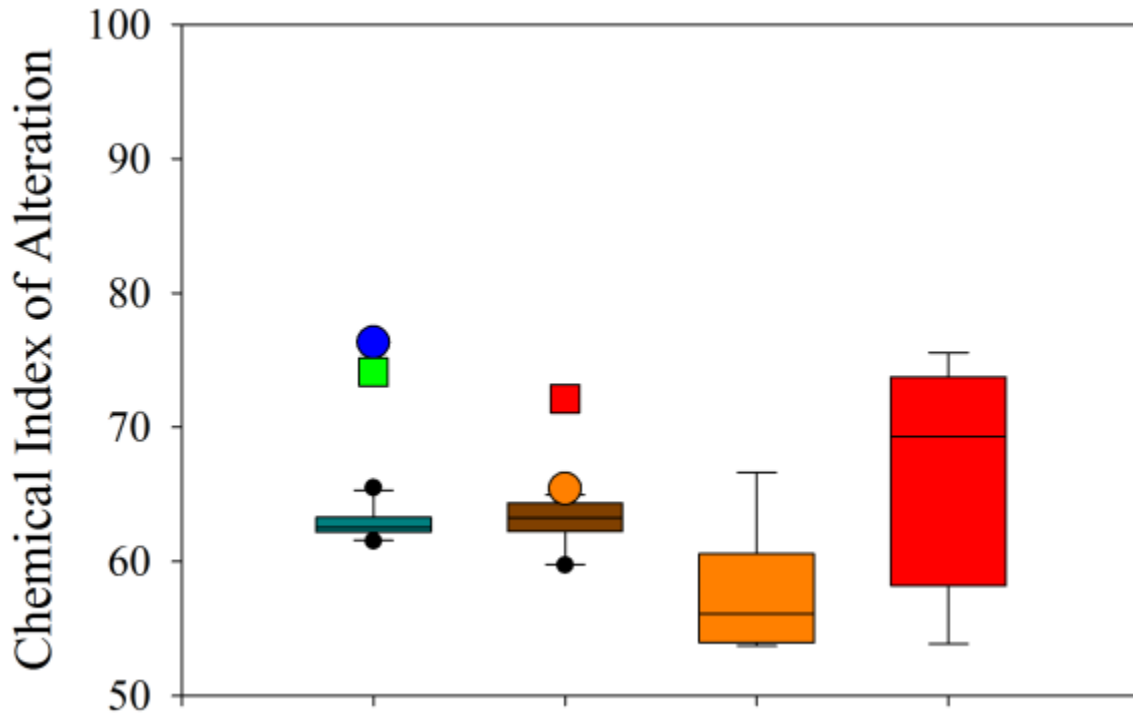
Figure 4-9 Chemical Index of Alteration for each different group of samples. Teal is the St. Louis till; brown is the Rainy till; orange is the Groovy catchment rock samples and red is the Surber catchment rock samples. The lake sediment CIA values are plotted above their respective tills. Forjer Lake is a blue circle; Pond Lake is a green square. Groovy Lake is an orange circle; Surber Lake is a red square.

In the four sets of lake sediments, CIA varies from 65.4 (Groovy Lake) to 76.3 (Forjer Lake). Till lakes show higher CIA than bedrock lakes on average. The St Louis till has a mean CIA of 62.9 while the Rainy till has a mean of 62.8. Rainy till shows more variability, with a range of 59.7-64.8. The two rock types present in the bedrock catchments have noticeably different patterns of alteration. The rock present in the Groovy Lake catchment show relatively low alteration with a mean of 57.5. The rock in the Surber Lake catchment has a distinctly higher mean CIA of 66.7.

Chemical Index of Weathering
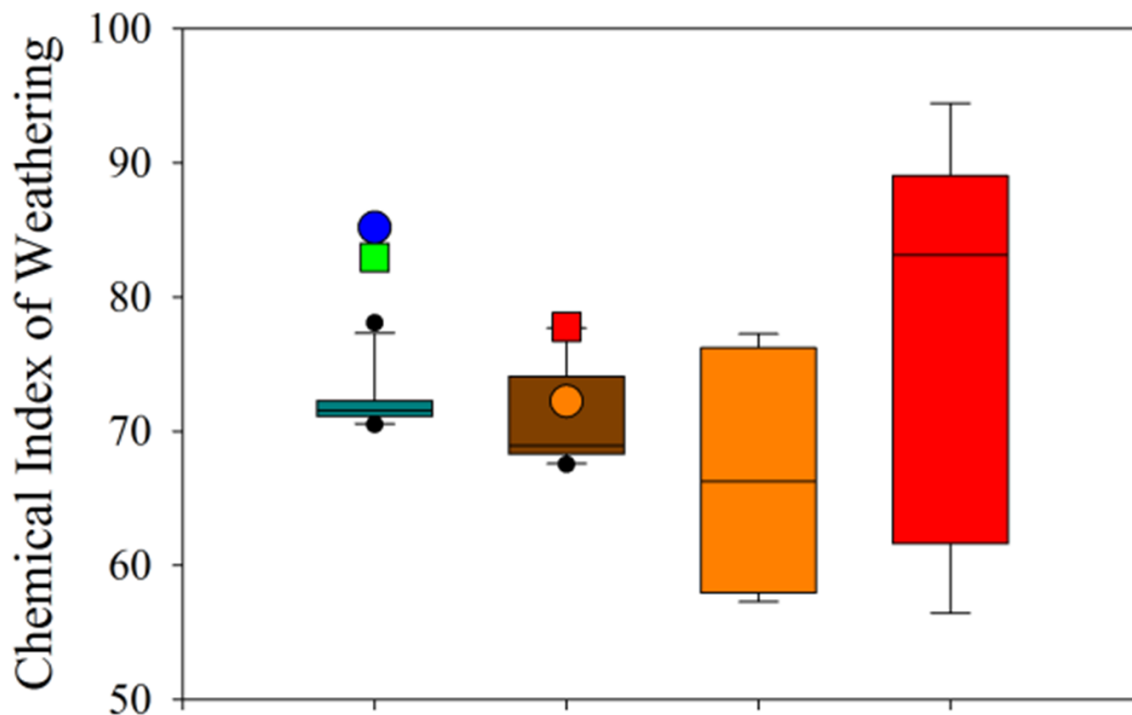
Figure 4-10 Chemical Index of Weathering for each different group of samples. Teal is the St. Louis till; brown is the Rainy till; orange is the Groovy catchment rock samples and red is the Surber catchment rock samples. The lake sediment CIA values are plotted above their respective tills. Forjer Lake is a blue circle; Pond Lake is a green square. Groovy Lake is an orange circle; Surber Lake is a red square.

In the four sets of lake sediments, CIW varies from 72.2 (Groovy Lake) to 85.1 (Forjer Lake). The till lakes are on average have higher CIW values than the bedrock lakes. The St Louis till has a mean CIW of 71.7 while the Rainy till has a mean of 70.9. However, Rainy till shows a greater range of weathering index values (67.5-76.1) whereas St. Louis till shows less variability (70.9-74.2).

The rock present in the Groovy Lake catchment shows relatively low weathering with a mean of 66.8 while the rock in the Surber Lake catchment shows extremely variable amounts of weathering, ranging between 56.4-94.4.

Rare Earth Elements and Yttrium
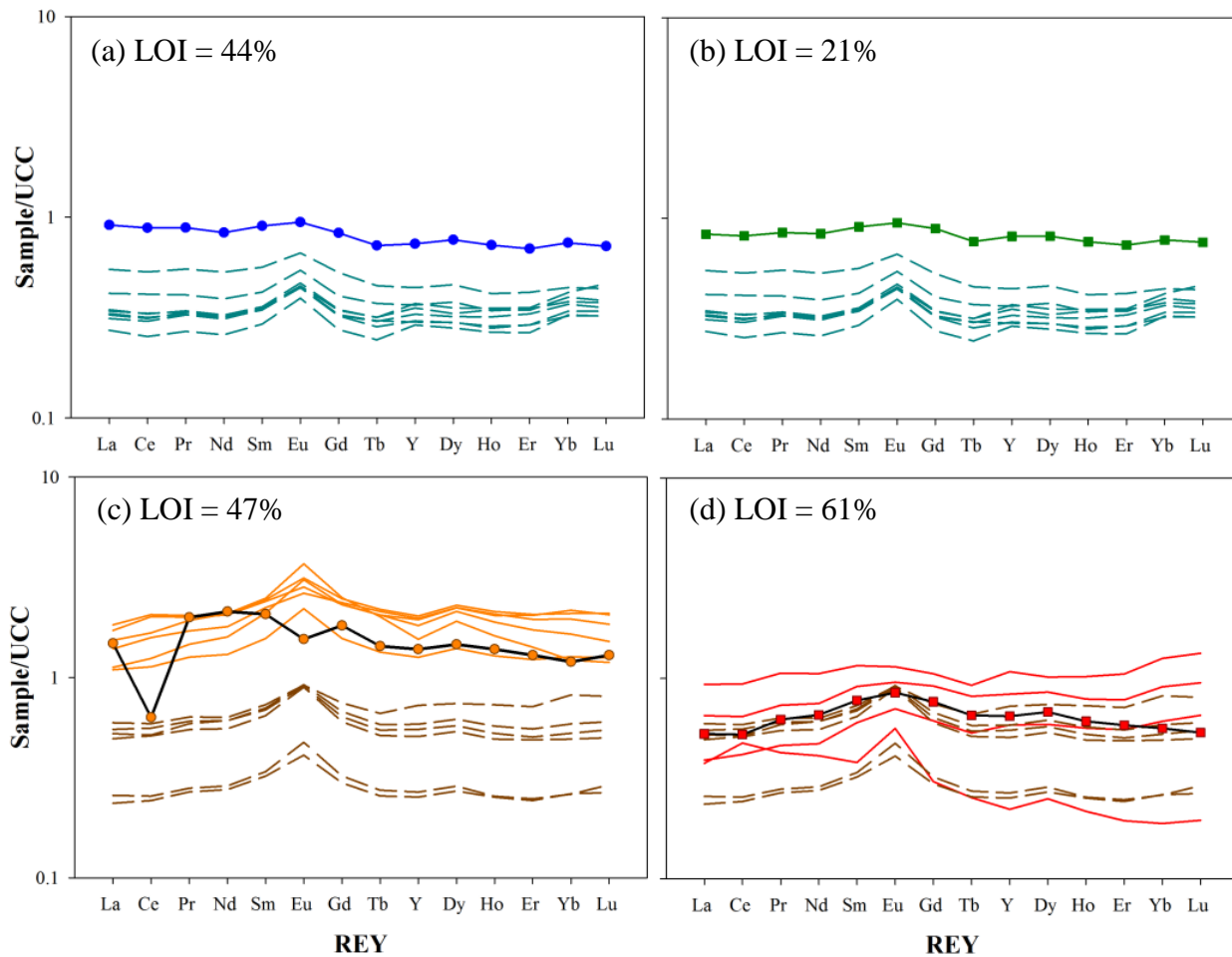
Figure 4-11: Upper continental crust normalized rare earth elements and yttrium of lake sediments, catchment rock and till samples; (a) Blue circles represent Forjer Lake sediments, green squares represent Pond Lake sediments, and teal dashed lines represent St. Louis Till samples; (b) Orange circles represent Groovy Lake sediments, orange solid lines represent Groovy Lake catchment rock samples, and brown dashed lines represent Rainy Till samples; (c) Red squares represent Surber Lake sediments, red solid lines represent Surber Lake catchment rock samples, and brown dashed lines represent Rainy Till samples.

The REY patterns for lake sediments are similar to the REY patterns of their catchment sources with the notable exception of Groovy Lake. In general, lake sediments and catchment

samples both had low concentrations of REYs. Variability in the other lakes was due mostly to variations in magnitude rather than pattern. The two till-dominated lakes showed very little inter-lake variation in REYs, but were strongly enriched compared to their source, the St. Louis till (2-5x). The strong correlation with of REEs with Al_2O_3 suggests that the enrichment of REEs in the lake sediments is due to adsorption onto clay minerals during weathering processes (Aide and Aide, 2012).

The two mixed catchments showed variable REY signatures. Rocks present within the Groovy Lake catchment show a positive Eu-anomaly of 1.0. The samples of Rainy till within the Groovy catchment show more variation in magnitude, but a similar signature with a positive Eu-anomaly of 1.1. Groovy Lake sediments show a strong enrichment (2-5x) compared to the Rainy till and fall closer to the rock REYs present within the catchment, suggesting that the rocks provide an additional source of REYs. When normalized to UCC, the lake sediments show strong negative Ce-anomaly and a strong negative Eu-anomaly.

Rocks within the Surber Lake catchment show more variable patterns in their REYs that are not translated into the lake sediments. Rainy till shows similar REY patterns amongst different samples, but variable magnitude in these patterns. Surber Lake sediments show fairly similar patterns and magnitude of REYs to the Rainy till. Lake sediments show a weaker Eu-anomaly than their source in the catchment, and show small negative Ce and Eu anomalies when normalized by their sources.

There is no correlation between REEs and Al_2O_3 in the Rainy till, suggesting that REEs are not associated with clay minerals.

In-Lake Processes
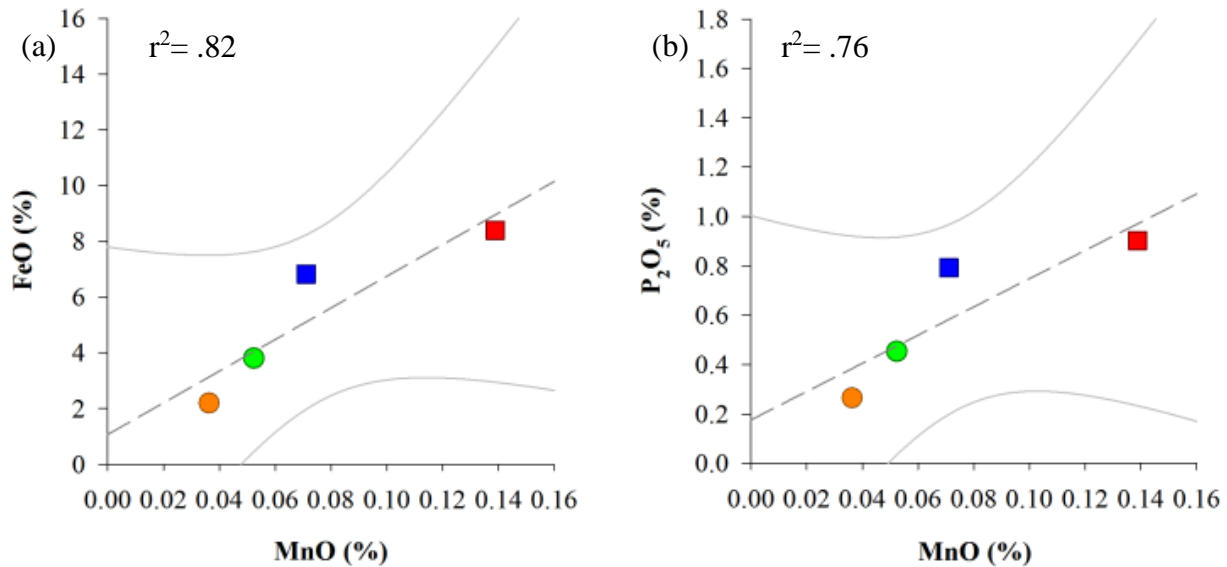
Figure 4-12: Relationships of (a) FeO and MnO; (b) P_2O_5 and MnO. Orange circles indicate Groovy Lake sediments; green circles indicate Pond Lake sediments; blue squares indicate Forjer Lake sediments; and red squares indicate Surber Lake sediments.

Iron and manganese concentrations in lake sediments are typically associated with redox conditions in the lake, as both are sensitive to pH and dissolved oxygen in the lake waters. MnO concentrations in the till lake sediments are similar to those of the St. Louis till. FeO and P_2O_5 are highly enriched in the till lake sediments compared to the parent material present in the catchments.

In the bedrock lakes, MnO concentrations in Surber Lake sediments are relatively similar to those of the Rainy till, but is highly enriched compared to the bedrock within its catchment. Surber Lake sediments show similar FeO concentration to the Rainy till but the variability in the bedrock disallows comparison. Like the till lake sediments, phosphate in the lake sediments is highly enriched compared to the parent material within the catchment. Groovy Lake sediments

show a strong depletion in MnO and FeO compared to both the Rainy till and the rock present within the catchment. Phosphate levels in these lake sediments fall within the variability shown by both the Rainy till and the rock present within the Groovy Lake catchment.

Chapter 5 - Discussion

Geochemical characteristics of lacustrine sediments depend on multiple factors as noted in Figure 1.1; including the (1) chemical composition of the local parent materials; (2) chemical composition of aeolian sediments; (3) physical and chemical processes in the catchment; and (4) in-lake diagenetic changes (Bleckner et al. 2006; Minyuk et al. 2014). Here, I discuss patterns of variation between catchment and sediment samples across the two catchment parent materials in this study that can be used to identify (1) and (3). There are two distinguishable types of variation among these samples in the first two principal components. PC1 is driven by the relationships between SiO_2 and a combination of TiO_2, Al_2O_3 and the REYs in the till lakes, and SiO_2 and Al_2O_3 in the bedrock lakes, which is generally interpreted as a grain size indicator (Lopez et al., 2006; Cuven et al., 2010; Clift et al., 2014). PC2 is driven by concentrations of Rb and K_2O, and likely reflects a signature of the complex weathering of K-bearing minerals (Minyuk et al., 2014). Additional information can be found in the elemental ratios in lake sediments, but for correct interpretation, it is important to distinguish between sources and transport modes (Collins, 2004). Ratios of oxides will henceforth be referred to as Si/Al, Al/Ti etc.

Till-dominated lakes

SiO$_2$

In lake sediments, total silica concentration is controlled by both biogenic and inorganic silica (Cohen, 2003). In the catchment sediments, silica is solely inorganic and lithogenic. Lithogenic silica is found in silicate minerals, which includes a diverse set of minerals making up 90% of the Earth's crust (Nesse, 2011). While silica may be sourced to minerals containing aluminum and titanium, it can also be found in quartz (SiO$_2$) which commonly has a larger grain size than alumino- and titanium-bearing silicates. Quartz is fairly stable in lake water conditions and not subject to dissolution (Siever, 1962).

In the St. Louis till, silica values are high, and lake sediments are depleted in comparison (see Figure 4-1). Silica can be compared to other lithogenic elements such as aluminum and titanium to semi-quantitatively understand grain size changes, as an excess of lithogenic silica is commonly associated with sand-sized and silt-sized quartz while titanium and aluminum are commonly found in finer grainer particles (von Eynatten, 2012; Cuven, 2010; Nesbitt and Young, 1998). The Si/Al ratio has been related to grain size (von Eynatten, 2012, Werne et al. 2002) or increasing textural maturity (Weltje and von Eynatten, 2004) where increasing Si in relation to Al suggests either larger particle size due to excess quartz and/or increasing weathering as finer clays and silts are removed from a parent material. In the St Louis till, SiO$_2$ has an extremely strong negative correlation with Al$_2$O$_3$ and a weaker negative correlation with TiO$_2$. For the catchment till, Si/Al is likely best indicator of grain size variation. There is a simple linear relationship between Si and Al concentrations in the till (Figure 4-3b) which can be expressed as:

$$(1) \; SiO_2 = 100 - 2 * Al_2O_3;$$

There is also a simple linear relationship between Si and Ti concentrations in the till (Figure 4-3a) which can be expressed as:

$$(2) \ SiO_2 = 90 - 30 * TiO_2;$$

where all oxides are present as weight percent.

In lake sediments, Si concentrations can potentially be used as a proxy for primary productivity under conditions when silica concentrations are controlled by diatom inputs. The Si/Ti ratio is commonly used to estimate the amount of biogenic silica in lakes with diatoms present (Minyuk et al. 2014).

Biogenic silica (BSi) may also dilute the concentrations of other elements (Minyuk et al. 2014). However, Si in lake sediments can also be detrital, derived from mineral material from the catchment (Peinerud, 1997; Peinerud, 2000). It is important to distinguish detrital silica from diatomaceous silica to be able to distinguish between climatic and biologic changes affecting the lake. Peinerud (2000) used the Si/Al ratio of catchment sediments to estimate the amount of diatom silica using the equation:

$$(3) \ Si_{nondetitral} = Si_{meas} - (Si/Al)_{detr} * Al_{meas}$$

Pond Lake sediments fall along the linear regression lines for both Si/Al and Si/Ti of the St Louis till, suggesting that despite having very different ratios of these elements, sediments in this lake are derived from these catchment parent materials. Forjer Lake falls below the linear regression of Si/Al, suggesting either depletion in Si or depletion in Al. This may reflect the fact that Forjer is much deeper and larger than Pond, and therefore transport of larger grains of quartz to the center of the lake directly from the catchment is less likely. Or, it may reflect the dilution of Al by biogenic silica (BSi) which is likely to be present in this lake (Minyuk, 2014).

In trying to source SiO_2 using ratios in this study, it can be assumed that catchment sources contain no biogenic silica. In lake sediments, biogenic and lithogenic silica are not easily differentiated using only geochemical data. The equation from Peinerud (2000) consistently overestimates the amount of detrital silica due in part to the fact that the Si is depleted in the lakes in comparison with the catchment.

If, however, we use the linear regressions calculated from the Si/Ti and Si/Al comparisons of the St. Louis till, we can estimate the amount of detrital silica present in the lake sediments as a function of the true weathering process of the detrital sediments. If calculated using detrital Al, predicted detrital silica suggests that only 1% of the Si in Forjer Lake sediment is BSi, while around 4% of the Si in Pond Lake sediment is BSi. However, if calculated using detrital Ti, predicted detrital silica suggests that 21% of Si in Forjer Lake sediment is BSi and 3% of the Si in Pond Lake sediments is BSi. Differences in lake and catchment size could explain this inconsistency in the predicted BSi of Forjer Lake sediments, especially since larger Ti-bearing minerals require more energy to transport.

Smear slides were analyzed for percent biogenic silica in the form of diatoms and sponge spicules to support BSi estimates based on geochemical data. Both Forjer and Pond lake sediments contain ~1% biogenic silica in the form of diatoms, suggesting that use of the linear regression of SiO_2 and Al_2O_3 to estimate BSi would be best.

Al_2O_3, TiO_2

Unlike silica, titanium and aluminum are solely lithogenic elements and are often considered to be immobile during weathering processes (Young and Nesbitt, 1998). Compared to their parent material, the lakes in this study with till-emplaced catchments are enriched in TiO_2 and Al_2O_3 (Figure 4-1). Aluminum is attributed to clay-sized aluminosilicates, while titanium is

derived from both aluminosilicates and silt-sized heavy minerals (von Eynatten et al. 2012; Murphy et al. 2000; Bertrand et al. 1996). Von Eynatten et al. (2012) found that Al_2O_3 was concentrated in the clay-sized fraction while TiO_2 was more concentrated in the silt-sized fraction of sediments in several lakes in Germany. Increasing TiO_2 in relation to Al_2O_3 (hereafter referred to as Ti/Al) has been suggested as a function of increasing grain-size (Murphy et al. 2000) whether due to increased aeolian deposition (Bertrand et al. 1996) or increased fluvial input (Murphy et al. 2000), both of which would result in higher energy deposition. However, sediments in these lakes are unlikely to represent higher energy deposition either from fluvial or aeolian sources, as neither lake has inflows and both are relatively small to be able to collect large amounts of aeolian input. (Brahney et al., 2014).

Ti/Al ratio has also been used as an indicator of sediment provenance and degree of sediment alteration (Minyuk et al. 2014; Young and Nesbitt, 1998). Young and Nesbitt (1998) suggest that sediments derived from slightly to moderately altered source material (CIA <80) should reflect the Ti/Al ratio of its source. Here, strong chemical alteration may mobilize aluminum into lower sections of a source material profile, causing the Ti/Al ratio to increase in altered sediments. However, the Ti/Al ratio in the lake sediments (0.044) does not reflect that of the catchment parent material (0.030) despite the fact that the CIA of the St. Louis till is around 53. The different ratio may be explained by the fact that the chemical alteration of the lake sediments in the till lakes is high compared to the St. Louis till (CIA = 68) and Rb/Sr values are much lower than the catchment parent material. This evidence suggests that sediments have been affected by chemical alteration during transport into the lake, thus aluminum may be mobilized into lower depths of the till and its concentrations reduced in the lake sediments (Young and Nesbitt, 1998).

Both aluminum and titanium concentrations in the lakes are strongly correlated with the rare earth elements and yttrium, suggesting that the REYs are concentrated in the silt and clay-sized fraction of the sediments in both the lake sediments and the parent materials (see Table 4-2 and Figure 4-2). The strong negative correlation with SiO_2 supports this interpretation. Strong correlation with MgO and FeO suggests that the mafic minerals and authigenic FeO present in these sediments are present in the silt and clay-sized fraction.

Rb, K$_2$O, Sr

The second type of variation among all samples is determined by the variation in Rb and K_2O concentrations (PC2, Figure 4-2). These elements are strongly correlated, which suggests that K-feldspars or micas are the source of the Rb (Wennrich et al. 2013). K_2O is derived from potassium silicate minerals, which can be formed from two sources: (1) feldspars and primary micas in igneous rocks or (2) weathering of these minerals into clay minerals (Manning, 2010). Feldspars tend to weather slowly at earth surface conditions and tend to dissolve at acidic (<5.7) conditions (Manning, 2010). Rb and K_2O have similar concentrations in both the lake sediments and the catchment parent material, with some slight enrichment in Pond Lake. Smear slides of Pond Lake sediments revealed feldspar clasts, suggesting that feldspars are the likely source of K_2O in this lake.

Rb/Sr may be a useful indicator of chemical weathering in addition to the CIA, as Sr is a mobile element during chemical weathering and is soluble in water while Rb tends to remain relatively immobile (Minyuk et al. 2014). Increasing Rb/Sr values suggest increasing chemical weathering, and this is reflected in the lake sediments when compared to the catchment till (See Figure 4-2). Rb/Sr ratios are strongly positively correlated to CIA (r^2 = .98, p < 0.001) and CIW

(r^2 = .97, p < 0.001) in the till lake sediments and catchment samples, suggesting that this may be a useful indicator of weathering and alteration in these lakes.

CIA and CIW

Till lake sediments show a high degree of alteration and weathering as compared to the till present in the catchment. The CIA summarizes the weathering of feldspar minerals such as Na_2O, CaO and K_2O. CIW removes K_2O, because of the effects of leaching and precipitation that can affect concentrations of this oxide. However, the CIW is confounded by K_2O-rich rocks and sediments, showing fresh granite and anorthosites as having unusually high degrees of weathering. CIA values below 80 are considered to be moderately to slightly weathered (Nesbitt and Young, 1996). The St. Louis till shows slightly weathered CIA values and the till lake sediments show moderate CIA values, suggesting that the lake sediments have experienced alteration during their transport to the lake.

Strong alteration and weathering due to exposure to the atmosphere and water during transport from the catchment to lake sediments may explain the increase in CIA and CIW values from the catchments to the lake. Alternatively, these indices may also be affected by grain size. Von Eynattern et al. (2012) show that CIA may be 57-61 for clays and 45-50 for sands when both grain sizes are produced from physical sorting of the same source material. Samples from the St. Louis till represent a variety of grain sizes as till is often poorly sorted, but it is likely that the till lake sediments represent a subset of finer-grained material than the till parent material. Finer grained material removed from the till would likely show higher CIA even if it had undergone little chemical alteration during transport into the lake.

Increasing Al_2O and TiO_2 as compared to SiO_2 in lake sediments would seem to support the interpretation that differences between the lake sediments and catchment till CIA and CIW

values may simply represent different grain sizes of material drawn from the same source. However, increasing Rb/Sr would suggest that some chemical alteration has taken place in the lake sediments, but without strict grain size control, it is difficult to quantify the extent of this alteration.

REYs

Rare earth elements (La-Lu) and yttrium (Y) are useful for identifying source-area composition for lake sediments because different rock types have characteristic REY signatures (Vasquez-Ortega, 2015; Piper and Bau, 2013; Das, 2006; Hu et al, 2014). These elements normally have a 3+ charge and are relatively unaffected by chemical processes within the catchment and transferred rapidly into the sedimentary record (Das, 2006). Y is often grouped with the REEs as it has similar properties, and this study will do the same unless ΣREEs are compared to Y.

However, certain of the REYs are sensitive to conditions at the Earth's surface, resulting in anomalous signatures compared to the rest of the series. Europium (II) is more common in magmatic systems and substitutes into plagioclase in source rocks, where it replaces Ca^{2+}, Na^{2+} and K^+ (Vasquez-Ortega et al. 2014). Preferential dissolution and alteration of feldspars compared to other REE-bearing minerals may result in positive Eu anomalies. (Vasquez-Ortega, 2015). Cerium may oxidize to a highly insoluble Ce (IV) state in oxic aqueous conditions, which tends to quickly remove it from solution, trapping in in soils and creating a positive Ce anomaly in soils and river sediments (Vasquez-Ortega, 2015; Piper and Bau, 2013). Variable redox conditions may also mobilize colloids that are enriched in REEs, and influence their movement through the system (Vazquez-Ortega et al. 2015).

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In the St. Louis till, concentrations of ΣREEs are relatively low, with a mean of 54.2 ppm. This is depleted compared to the UCC (147.8 ppm). Low ΣREE concentration is often found in sandy soils, and high SiO_2 content and low Al_2O_3 and TiO_2 suggest that the St. Louis till depleted in clays and silts which retain REYs (Vasquez-Ortega, 2015; Hu et al. 2006). REY patterns in the St. Louis till are relatively flat, with a slight positive Eu anomaly which is common in soils (Vasquez-Ortega, 2015). Consistent REY patterns are observed throughout the St. Louis till, and only slight variation in magnitude was observed between different samples over a large spatial scale. This suggests that the REY pattern observed in this study can serve as a fingerprint for sediments derived from the St. Louis till. A slight positive Eu anomaly suggests slight preferential weathering of feldspar minerals from the source rock of the till.

In the lake sediments, REY concentrations are two to three times higher than those of the St. Louis till with a mean of 125.7 ppm and show little to no variation between lakes. However; the essential pattern in the St. Louis till REYs is present in the lake sediments of both till lakes. This, taken in conjunction with the elevated levels of Al_2O_3 and TiO_2, suggest that the clastic sediment in the lakes is representative of fine-grained material derived from the catchment. The positive Eu anomaly is smaller than the one present in the St. Louis till, which is likely due to the removal of Eu (II) into the water column.

ΣREEs were strongly correlated to Y throughout all the samples and they often show similar relationships in rock and during weathering (Vasquez-Ortega et al., 2015). The relationship between the two is strong in the St. Louis till, and as a simple ratio of 7.4 it is also present in the till lake sediments despite increased concentrations of both.

Bedrock lakes

Variability in the Rainy till is controlled mainly by the variation in incompatible trace elements such as Zr, Rb, Y and the REEs. In comparison with the St. Louis till, the Rainy till shows weak correlations among the major elements.

SiO$_2$

In the Rainy till, silica values are lower than the St. Louis till, and lake sediments are enriched in comparison with the Rainy till (see Figure 4-5 and 4-6). In the Rainy till, SiO$_2$ has a strong negative correlation with Al$_2$O$_3$ and a weak negative correlation with TiO$_2$. For the catchment till, Si/Al is likely best indicator of grain size variation. There is a simple linear relationship between Si and Al concentrations in the till which can be expressed as:

$$(1) \ SiO_2 = 111 - 3.3 * Al_2O_3;$$

There is also a simple linear relationship between Si and Ti concentrations in the till which can be expressed as:

$$(2) \ SiO_2 = 74 - 5 * TiO_2;$$

where all oxides are present as weight percent.

Both sets of catchment rocks show wide variation in geochemistry among the major and trace elements, with inconsistent Si/Al and Si/Ti ratios. Surber Lake catchment rocks show overall lower TiO$_2$ than rocks present in Groovy Lake catchment, but otherwise concentrations are highly variable.

The bedrock lakes show an enrichment in SiO$_2$ concentrations in comparison with their catchments. In Groovy Lake sediments, however, the enrichment is extreme, with 83% of the inorganic sediments being SiO$_2$. In addition, these sediments are depleted in TiO$_2$ and extremely depleted in Al$_2$O$_3$ in comparison with both the Rainy till and the rocks present within the

catchment. An increasing Si/Al ratio, which has been related to increasing grain size (von Eynatten, 2012; Werne et al. 2002) or increasing textural maturity (Weltje and von Eynatten, 2004) appears to show that Groovy Lake has either coarse-grained or extremely mature sediments in comparison with its catchment parent materials. However, on visual inspection, Groovy Lake sediments appeared to be fine-grained and extremely organic-rich which would suggest that coarse-grained sediments are unlikely. In addition, indices of alteration and weathering for the Groovy Lake sediments are relatively similar to those in the Rainy till and catchment rocks, suggesting the interpretation of increased textural maturity would also be incorrect.

Surber Lake shows a similar, though less extreme increase in the Si/Al ratio due to enrichment in SiO_2 and depletion in Al_2O_3 concentrations compared to the Rainy till. Though TiO_2 concentrations in the lake sediments more closely match those in the catchment rock, SiO_2 concentrations more closely match the Rainy till. This leads to the lake sediment showing a more similar ratio to the Rainy till than the catchment rocks.

Surber Lake sediments fall along the linear regression lines for both Si/Al and Si/Ti of the Rainy till, suggesting that despite having very different ratios of these elements, sediments in this lake are derived from these catchment parent materials instead of another source such as aeolian deposition. Groovy Lake falls above the linear regression of Si/Ti, suggesting either enrichment in Si or depletion in Ti. Enrichment in Si from BSi is more likely, as the rock in this catchment shows low concentrations of Ti.

In trying to source SiO_2 using ratios in this study, catchment source concentrations contain no biogenic silica. But biogenic and detrital silica in the lake sediments are not easily differentiated using only geochemical data. The equation from Peinerud (2000) can be used, as

SiO$_2$ in these lake sediments is enriched compared to the catchment parent materials. This calculation estimated that around 50% of the SiO$_2$ in Groovy Lake sediment is BSi. It also estimated that about 17% of the SiO$_2$ in Surber Lake sediment is BSi.

The linear regressions calculated from the Rainy till produce very different concentrations of BSi. If calculated using lake sediment Al$_2$O$_3$ concentrations, predicted detrital silica suggests that there is no BSi present in either lake sediments. However, if calculated using lake sediment TiO$_2$ concentrations, predicted detrital silica suggests that 15% of SiO$_2$ in Groovy Lake sediments is BSi, and only 2% of SiO$_2$ in Surber Lake sediments is BSi.

Smear slides were analyzed for percent biogenic silica in the form of diatoms and sponge spicules to support BSi estimates based on geochemical data. Groovy Lake sediments contained ~10-15% biogenic silica in the form of diatoms and sponge spicules. Surber Lake sediments contained ~5% biogenic silica in the form of diatoms. This suggests that the use of the linear regression of SiO$_2$ and TiO$_2$ to estimate BSi would be best.

Al$_2$O$_3$, TiO$_2$

Aluminum and titanium oxides are weakly correlated in the Rainy till. Al$_2$O$_3$ correlates with P$_2$O$_5$, but is otherwise unrelated to any other oxide concentrations, except the strong negative relationship with SiO$_2$. TiO$_2$ concentrations are also unrelated with any other elements except for a strong negative relationship with SiO$_2$.

Surber catchment rock tends to show low concentrations of TiO$_2$ while Groovy catchment rock shows high concentrations of TiO$_2$. Neither show consistent Ti/Al ratios.

The Ti/Al ratio in the Groovy Lake sediments (0.1) reflects the average Ti/Al of the Rainy till (0.1) and has similar CIA, suggesting similar levels of alteration. This evidence

suggests that sediments have been unaffected by chemical alteration during transport into the lake, thus Ti/Al values should reflect that of the source material (Young and Nesbitt, 1998).

The Ti/Al ratio of Surber Lake sediments (0.04) is less than half that of the Rainy till, and in some ways better matches some of the catchment rock samples. Low TiO_2 in many of the catchment rocks may explain low TiO_2 in the lake sediments.

Rb, K$_2$O, Sr

The second type of variation among all samples is determined by the variation in Rb and K_2O concentrations (PC2, Figure 4-5). These elements are strongly correlated, which suggests that K-feldspars are the source of the Rb (Wennrich et al. 2013). K_2O and Rb are relatively stable at earth surface conditions in comparison with more easily weathered elements such as CaO, Na_2O and Sr. Ratios of K and Rb to these elements can be used to estimate weathering and alteration of lake sediments in comparison with their catchments. Both bedrock lake sediments are depleted in K_2O and Rb compared to the Rainy till and catchment rocks. Unusually, both bedrock lake sediments have similar CaO concentrations to their catchment parent materials.

Increasing Rb/Sr values suggest increasing chemical weathering, and this is reflected in the lake sediments when compared to the catchment till (See Figure 4-8). Rb/Sr ratios in both bedrock lake sediments (0.29) are similar to those of the Rainy till (0.29), though the Rainy till shows some strong variability in Rb and Sr concentrations.

Unlike the till lakes, the Rb/Sr ratios in the bedrock lake sediments and catchment samples are weakly correlated with CIA (r^2 = .25, p = 0.084). Even with the catchment rock samples excluded, the Rb/Sr ratio does not correlate to CIA.

CIA and CIW

Bedrock lake sediments show a varied degree of alteration and weathering as compared to the till present in the catchment. If CIA < 80, weathering is slight or moderate (Nesbitt and Young, 1996). The Rainy till shows slightly weathered CIA values. Groovy Lake sediments have a CIA value that falls within the upper 25% of CIA values of the Rainy till. This suggests little alteration during transport to the lake. Surber Lake sediment show moderately weathered CIA values which suggests alteration during transport into the lake.

Higher CIA values may indicate chemical weathering during transport into the lake, or simple grain size sorting during transport (von Eynattern et al., 2012). Samples from the Rainy till represent a variety of grain sizes as till is often poorly sorted, but it is likely that the bedrock lake sediments represent a subset of finer-grained material than the till parent material. Finer grained material would likely show higher CIA than its source, even if it has experienced little chemical alteration during transport.

Unchanged CIA and CIW values in Groovy Lake sediments would suggest that little chemical or physical weathering has occurred to these sediments during their transport from the catchment to the lake. Considering how different the lake sediments are geochemically from the catchment parent materials, this interpretation may suggest either a different source for the sediments present in Groovy Lake or some other process that is affecting elemental concentrations within these sediments.

REYs

Rare earth elements (La-Lu) and yttrium (Y) are useful for identifying source-area composition for lake sediments because different rock types have characteristic REY signatures (Vasquez-Ortega, 2015; Piper and Bau, 2013; Das, 2006; Hu et al, 2014).

In the Rainy till, concentrations of ΣREEs are relatively low, with a mean of 99 ppm. This is depleted compared to the UCC (147.8 ppm). While ΣREE concentrations are correlated with clay-sized Al_2O_3 in the St. Louis till, in the Rainy till they only have a strong correlation to Y and Rb. REY patterns in the Rainy till are relatively flat, with a similar pattern to concentrations in the St. Louis till and a slight positive Eu anomaly which is common in soils (Vasquez-Ortega, 2015). Consistent REY patterns are observed throughout the Rainy till, and only variation in magnitude was observed between different samples over a large spatial scale. This suggests that the REY pattern observed in this study can serve as a fingerprint for sediments derived from the Rainy till. A slight positive Eu anomaly suggests slight preferential weathering of feldspar minerals in the till.

The Groovy Lake catchment rock shows consistent REY patterns and magnitudes amongst samples and are enriched compared to the UCC. These catchment rocks show a relatively flat pattern with a positive Eu anomaly, suggesting preferential weathering of feldspar minerals in the rock.

The Surber Lake catchment rock shows highly variable REY signatures, suggesting the rocks in this catchment are heterogeneous in composition and likely from different sources. In this case, the REY pattern in these rocks cannot serve as a fingerprint for sediments derived from the rock.

In the Groovy lake sediments, REY concentrations are two times higher than those of the Rainy till and show a similar average concentration to the rock present within the catchment. However; the essential pattern in the Groovy Lake sediment REYs is different from that of the rock. There is a strong negative Ce anomaly and a negative Eu anomaly. These are likely due to weathering processes, as both Ce and Eu are susceptible to alteration at surface conditions

(Vasquez-Ortega, 2015). The negative Eu anomaly may be due to the removal of Eu (II) into the water column (Vasquez-Ortega, 2015).

The Surber Lake sediment shows a fairly similar signature and magnitude to the Rainy till, with a similarly reduced positive Eu anomaly that would suggest dissolution of Eu (II). The pattern appears to be unaffected by the rock within the catchment, and suggests that the REYs are derived from the Rainy till.

ΣREEs were strongly correlated to Y throughout all the samples and they often show similar relationships in rock and during weathering (Vasquez-Ortega et al., 2015). The relationship between the two is strong in the Rainy till, and as a simple ratio of 6.2 it is also present in the bedrock lake sediments. The ratios of ΣREEs/Y in the catchment rocks are fairly similar to those found in the Rainy till, but variations in absolute concentrations distinguish them from each other. Groovy Lake catchment rocks show high concentrations that are easily differentiated from the Rainy till. Surber Lake catchment rocks show similar concentrations to the Rainy till. It appears that Groovy Lake sediments are being enriched due to the catchment rocks, however, this enrichment may be comparable to that present in the till lakes in comparison with their catchments and rather due to grain size variations. However, as ΣREEs are not associated with Al_2O_3 within the bedrock lakes, so it may be that this enrichment is associated with the catchment rock.

In-Lake Processes

FeO, MnO, P$_2$O$_5$

FeO concentrations are enriched in lake sediments compared to parent material. MnO concentrations in lake sediments fall within the variation shown by parent material. Phosphate, like FeO, shows enrichment in the lake sediments in comparison to the parent material.

FeO and P$_2$O$_5$ show strong correlations with TiO$_2$ and Al$_2$O$_3$, suggesting they are associated with the finer fraction (either clastic or organic material) in both the parent material and lake sediments. MnO shows no correlation to any other elements. These three oxides are often associated with redox conditions in lake sediments and inter-lake comparisons better explain their variation. Ratios of Fe/Mn are often used as an indicator for redox conditions (Minyuk et al. 2012; Melles et al. 2012; Loizeau et al. 2001). Ratios of Fe/P in lake sediments tend to fall in between 5-10 despite variations in catchment parent material (Williams et al. 1971). The lake sediments fit this pattern, with MnO, FeO and P$_2$O$_5$ showing strong correlations (see Figure 5-1), and Fe/P ratios for all lake sediments falling around 8.6 despite strong variability in FeO and P$_2$O$_5$ in their catchment parent materials. The two shallower lakes show lower concentrations of iron and phosphate, suggesting stronger mixing and oxygenation at the lake bottom. The deeper lakes show higher concentrations, suggesting possible anoxia.

Chapter 6 - Conclusion

Lake sediments provide and archive of a variety of processes taking place on multiple spatial scales, including local erosional events, regional climate variation and in-lake biological changes. Lake sediment geochemical data is an important proxy that is often used in conjunction with pollen, grain size and charcoal data to understand past changes in climate and ecology. Geochemical data is relatively easy to collect, but often overwhelming in quantity. For this

reason, lake sediment geochemical data is often analyzed in isolation, compared only to other proxies within the lake. Few lake sediment geochemical studies have included extensive surveys of local sources of clastic sediments.

The essential question is: how does variation in the composition of catchment parent materials affect the geochemistry of lake sediments?

With this study, we can begin to judge what scale of survey is necessary to answer this question and what sort of information can be gathered with only geochemical data. Lake sediments are often highly altered in comparison with catchment parent materials, and may have additions of biological material that can increase concentrations of SiO_2 and/or dilute concentrations of other elements. Grain size of the clastic material entering the lake sediments may also have a confounding effect on concentration data, as fine-grained materials are often enriched in specific elements. The lithological heterogeneity of the catchment is also extremely important. Tills in this study were often relatively homogenous, but rocks within the catchment were geochemically variable and their signatures were not diagnostic.
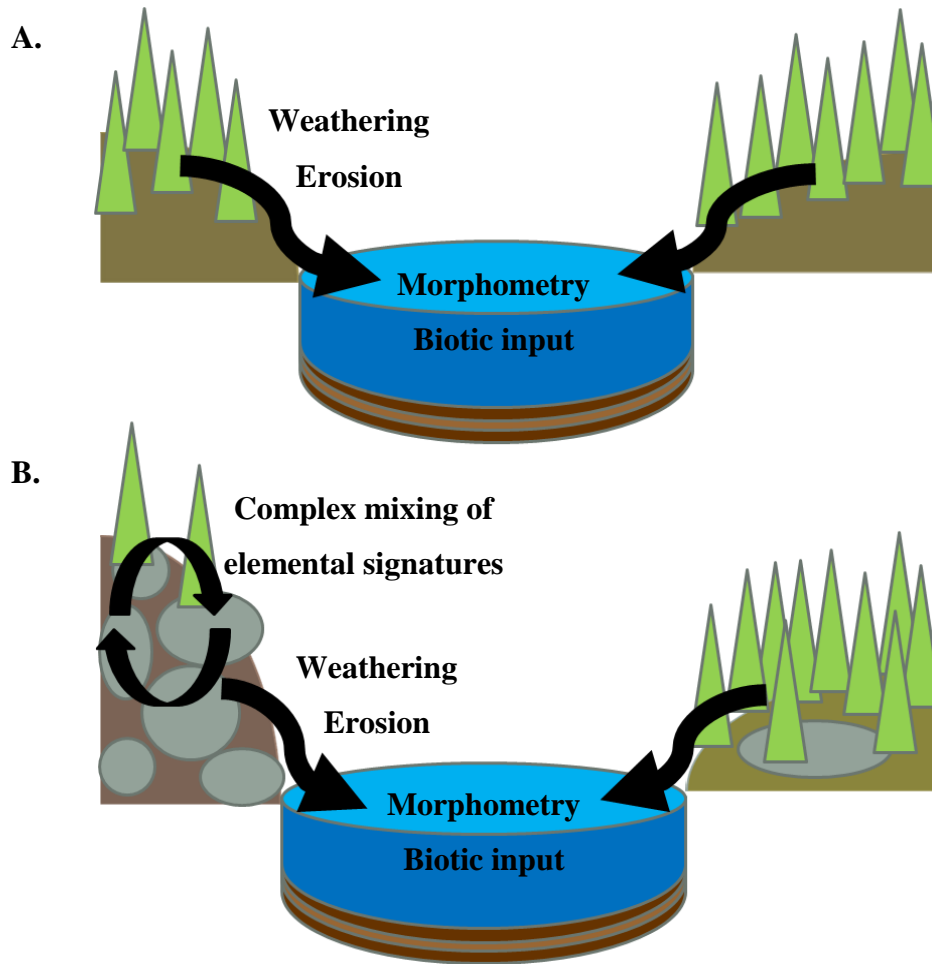
Figure 6-1 A conceptual diagram of the processes affecting the geochemical signatures of lake sediments in (A) till lakes and (B) bedrock lakes.

Overall, the small lakes emplaced in a homogenous till showed close connectivity with their catchment parent materials. Patterns of elemental variation in the catchment till could be extended to predict elemental concentrations in the lake sediments. Simple ratios, which are commonly used to analyze lake sediment geochemical data, were not good predictors of lake sediment composition, however. Certain elements and oxides such as iron, manganese and phosphate were controlled by physical properties of the lake such as depth and size. Strong enrichment of certain elements such as aluminum, titanium and the REYs in conjunction with the

depletion of silica and a lack of biogenic silica, suggests that the clastic sediments in these lakes represent fine-grained material sorted and derived from the till. The ΣREE/Y ratio was the only ratio found to be diagnostic of both the catchment sediments the lake sediments.

The bedrock lakes, on the other hand, were complex and seemingly disconnected from their catchments in many ways. The till and rock present within their catchments showed stronger heterogeneity, which confounded analysis of connections with the lake sediments. Variability in the till was likely due to the presence of varied local bedrocks as well as the thinness of the till itself. Variability of the bedrock was likely due to differences in exposure leading to variations in physical and chemical weathering. Increasing sample size in future studies may account for this variability and better represent the catchment parent materials. Though some patterns were present in the till, they were in some ways not comparable to those present within the lake sediments. Strong enrichment in silica and depletion in aluminum and titanium suggest the dilution of clastic material by biogenic silica, but smear slides showed <15% biogenic silica in both lake sediments. Attempting to distinguish biogenic silica and lithogenic silica using only geochemical data resulted in a variety of possible compositions for the siliceous sediments and is not advisable. Visual identification of biogenic silica with smear slides supported BSi estimations using a linear regression of SiO_2 and TiO_2. However, comparisons of known terrigenous elements with the rock and till were difficult due to low correlation between many of these elements. The lack of correlation of REYs with aluminum was useful in this case, as it was not likely subject to the same dilution effects. The ΣREE/Y ratio was therefore also found to be diagnostic of the catchment parent materials and present within the lake sediments.

By completing this study, I attempted to distinguish the effects of variations in catchment parent material on the geochemistry of lake sediments. With only geochemical data, this is difficult. In future studies, it is necessary to increase the number of samples collected from heterogeneous catchments that include a variety of parent material types. Homogeneous catchments may be analyzed with few samples. Increasing the number of sample lakes and catchments would be advisable to verify conclusions made in this study, as tills are known to be regionally heterogeneous. Grain size control is extremely important, as weathering in the catchment and through the lake influences the geochemistry of clastic material that settles in the lake, essentially a winnowing effect where only fine-grained materials enter the lake sediment record. It may be advisable to analyze a subset of fine-grained material from the catchment. In addition, biogenic silica should be measured using an extraction in order to obtain more accurate and precise values to compare to geochemical estimates in the lake sediments and its dilution effects measured.

These additional measurements could provide more clarity to this and future studies, allowing us to place the lake sediment geochemical data within the context of the local scale of the catchment.

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Appendix A - Elemental Data

Sample ID	St Louis	St Louis	St Louis	St Louis	St Louis	Forjer Lake
Lake Association	Forjer	Forjer	Forjer	Forjer	Forjer	Forjer
Distance	100	25	25	25	43	0
Direction	E	E	E	W	W	-
LOI %	3.195	2.843	3.195	5.095	3.991	44.096
Major oxides (%)						
SiO_2	82.378	82.075	82.221	82.067	82.185	71.110
TiO_2	0.263	0.228	0.227	0.316	0.305	0.672
Al_2O_3	9.341	9.661	9.569	9.524	9.475	14.775
FeO	1.957	1.688	1.648	1.536	1.701	6.828
MnO	0.043	0.042	0.042	0.074	0.060	0.071
MgO	0.448	0.405	0.411	0.598	0.470	1.172
CaO	1.397	1.355	1.343	1.669	1.534	1.523
Na_2O	2.225	2.453	2.459	2.236	2.293	1.054
K_2O	1.831	1.933	1.929	1.875	1.849	2.003
P_2O_5	0.118	0.158	0.150	0.106	0.128	0.793
Trace elements (ppm)						
La	10.54	9.69	9.95	10.71	10.10	25.84
Ce	20.87	19.08	19.75	20.74	19.66	51.51
Pr	2.40	2.31	2.37	2.42	2.38	6.03
Nd	8.58	8.39	8.82	8.78	8.61	22.61
Sm	1.64	1.63	1.70	1.68	1.65	4.26
Eu	0.45	0.44	0.46	0.47	0.45	0.95
Gd	1.30	1.29	1.26	1.38	1.37	3.55
Tb	0.21	0.20	0.19	0.22	0.22	0.54
Dy	1.17	1.16	1.13	1.38	1.29	3.18
Ho	0.23	0.24	0.23	0.29	0.29	0.63
Er	0.67	0.67	0.64	0.81	0.79	1.69
Tm	0.10	0.10	0.09	0.13	0.12	0.26
Yb	0.68	0.64	0.65	0.84	0.80	1.56
Lu	0.11	0.10	0.11	0.14	0.12	0.24
Ba	448	452	451	482	473	325
Th	3.66	2.91	2.89	3.27	3.21	6.20
Nb	3.42	3.76	3.69	4.44	3.94	6.85
Y	6.30	6.39	5.92	7.79	7.40	17.08
Hf	2.51	2.56	2.50	3.70	3.30	2.71
Ta	0.30	0.26	0.27	0.34	0.34	0.49
U	0.67	0.66	0.63	0.84	0.73	1.66
Pb	11.31	10.55	10.68	11.46	11.63	13.23
Rb	51.0	52.5	52.1	52.2	49.3	47.2
Cs	1.17	1.12	1.04	1.25	1.07	2.44
Sr	247	244	247	240	250	84
Sc	3.7	3.4	3.3	3.9	4.0	6.4
Zr	101	99	97	143	131	98

Table A-1 Raw concentration values of all elements collected from Forjer Lake sample site.

Sample ID	St Louis	St Louis	St Louis	St Louis	St Louis	St Louis	Pond Lake
Lake Association	Pond	Pond	Pond	Pond	Pond	Pond	Pond
Distance	100	13	13	25	25	41	0
Direction	W	S	S	E	W	E	-
LOI %	3.195	2.843	3.195	5.095	3.991	6.662	44.096
Major oxides (%)							
SiO_2	77.561	78.252	78.290	83.783	81.080	82.147	72.265
TiO_2	0.394	0.328	0.326	0.229	0.267	0.279	0.689
Al_2O_3	11.991	11.077	11.028	8.905	10.278	9.589	15.859
FeO	2.689	2.553	2.565	1.031	1.773	1.470	3.802
MnO	0.043	0.052	0.052	0.066	0.076	0.116	0.052
MgO	0.915	0.974	0.966	0.357	0.570	0.461	1.340
CaO	1.735	2.061	2.046	1.395	1.600	1.567	1.636
Na_2O	2.431	2.578	2.606	2.226	2.342	2.304	1.626
K_2O	2.148	2.018	2.018	1.947	1.907	1.962	2.277
P_2O_5	0.095	0.106	0.103	0.062	0.108	0.107	0.453
Trace elements (ppm)							
La	14.37	17.03		8.46	12.93	10.24	28.32
Ce	31.36	33.57		15.99	26.00	19.92	55.71
Pr	3.25	3.92		1.91	2.91	2.33	6.29
Nd	11.81	14.37		7.01	10.57	8.44	22.61
Sm	2.28	2.65		1.38	1.99	1.62	4.25
Eu	0.62	0.66		0.39	0.54	0.45	0.94
Gd	1.76	2.12		1.10	1.62	1.30	3.34
Tb	0.29	0.32		0.17	0.26	0.21	0.51
Dy	1.66	1.79		1.09	1.47	1.25	3.01
Ho	0.32	0.34		0.22	0.28	0.26	0.60
Er	0.94	0.97		0.61	0.80	0.76	1.60
Tm	0.14	0.15		0.10	0.12	0.11	0.23
Yb	0.91	0.89		0.65	0.76	0.74	1.49
Lu	0.14	0.14		0.10	0.12	0.11	0.22
Ba	496	470		510	471	526	490
Th	5.06	4.84		2.45	3.18	2.95	8.09
Nb	5.36	4.40		3.46	3.75	4.11	8.84
Y	8.83	9.35		6.09	7.66	6.90	15.47
Hf	3.82	2.79		2.46	2.54	2.90	3.89
Ta	0.41	0.33		0.26	0.28	0.37	0.64
U	0.93	0.81		0.66	0.79	0.74	1.61
Pb	12.95	13.16		12.47	12.40	14.94	19.92
Rb	70.6	57.4		54.9	59.2	55.6	75.2
Cs	1.84	1.40		1.20	1.36	1.30	3.32
Sr	264	263		234	247	250	162
Sc	6.1	5.6		3.0	4.1	3.6	9.3
Zr	145	110		98	99	112	143

Table A-2 Raw concentration values of all elements collected from Pond Lake sample site.

Sample ID	Groovy rock	Groovy rock	Groovy rock	Groovy rock	Groovy rock	Groovy rock	Groovy rock
Lake Association	Groovy	Groovy	Groovy	Groovy	Groovy	Groovy	Groovy
Distance	15	25	25	35	35	5	85
Direction	SE	NE	SE	SE	SE	NE	NE
LOI %	1.141	2.077	3.168	0.251	0.868	2.264	1.150
Major oxides (%)							
SiO_2	60.682	52.878	61.886	49.946	73.786	60.946	61.106
TiO_2	1.932	3.752	1.933	3.910	0.393	2.023	2.127
Al_2O_3	14.749	13.091	14.963	14.403	12.669	10.139	14.698
FeO	9.357	14.447	10.021	14.531	3.352	16.578	8.127
MnO	0.111	0.183	0.084	0.177	0.044	0.131	0.134
MgO	2.442	3.937	3.385	4.350	0.316	1.500	2.762
CaO	3.457	6.788	2.246	7.177	0.567	3.135	3.876
Na_2O	3.251	2.968	2.520	3.173	3.166	2.634	3.430
K_2O	3.730	1.522	2.721	1.877	5.660	2.589	3.491
P_2O_5	0.290	0.435	0.239	0.456	0.048	0.325	0.249
Trace elements (ppm)							
La	53.29	34.89	33.91	47.55	47.57	43.16	56.85
Ce	127.00	78.50	71.37	105.32	111.40	99.84	129.89
Pr	14.21	10.40	8.98	13.70	12.50	12.13	14.47
Nd	55.43	43.09	35.25	56.40	45.70	48.48	55.45
Sm	11.49	9.86	7.37	11.70	9.89	10.49	11.28
Eu	3.14	3.07	2.21	3.69	1.88	2.64	2.83
Gd	9.89	9.27	6.27	10.01	9.16	9.47	9.24
Tb	1.53	1.44	0.94	1.41	1.72	1.50	1.43
Dy	8.95	8.34	5.45	7.45	11.04	8.71	8.68
Ho	1.77	1.57	1.06	1.34	2.37	1.72	1.69
Er	4.75	3.98	2.83	3.26	6.76	4.49	4.70
Tm	0.70	0.53	0.40	0.43	1.03	0.64	0.70
Yb	4.17	3.29	2.54	2.44	6.35	3.91	4.33
Lu	0.65	0.47	0.39	0.37	0.94	0.57	0.64
Ba	691	547	627	463	817	473	681
Th	11.53	5.14	7.02	5.02	19.14	9.56	13.97
Nb	44.76	29.61	24.12	37.07	64.47	40.31	54.74
Y	42.60	38.17	26.51	32.59	59.31	41.51	40.81
Hf	12.34	7.69	6.40	8.11	18.00	10.12	12.67
Ta	2.87	1.98	1.64	2.51	4.30	2.69	3.78
U	3.34	1.52	3.92	1.14	4.95	2.59	3.22
Pb	8.85	21.10	37.81	6.81	7.24	6.60	23.61
Rb	114.8	57.6	90.3	71.8	224.6	93.0	116.7
Cs	2.89	2.81	2.66	6.63	2.68	3.11	2.34
Sr	394	443	207	793	87	259	557
Sc	15.3	25.2	18.2	20.7	2.6	13.3	12.3
Zr	475	293	239	316	677	381	466

Table A-3 Raw concentration values of all elements collected from Groovy Lake rock samples.

Sample ID	Rainy	Rainy	Rainy	Rainy	Rainy	Groovy Lake
Lake Association	Groovy	Groovy	Groovy	Groovy	Groovy	Groovy
Distance	25	15	35	25	85	0
Direction	NE	SE	SE	SE	NE	-
LOI %	16.127	4.665	60.948	16.447	17.438	47.167
Major oxides (%)						
SiO_2	69.168	62.294	61.879	66.760	68.356	85.339
TiO_2	1.083	1.747	2.081	1.809	1.313	0.684
Al_2O_3	13.542	14.004	14.811	12.897	12.790	6.918
FeO	7.366	9.967	9.235	9.346	8.875	2.193
MnO	0.076	0.123	0.155	0.098	0.152	0.036
MgO	1.122	2.250	1.378	1.572	1.364	0.911
CaO	1.284	3.261	3.960	2.067	1.693	1.841
Na_2O	2.523	3.118	2.769	2.446	2.316	0.823
K_2O	3.688	2.948	3.249	2.838	2.924	0.990
P_2O_5	0.148	0.287	0.484	0.167	0.216	0.264
Trace elements (ppm)						
La	53.29	34.89	33.91	47.55	47.57	43.16
Ce	127.00	78.50	71.37	105.32	111.40	99.84
Pr	14.21	10.40	8.98	13.70	12.50	12.13
Nd	55.43	43.09	35.25	56.40	45.70	48.48
Sm	11.49	9.86	7.37	11.70	9.89	10.49
Eu	3.14	3.07	2.21	3.69	1.88	2.64
Gd	9.89	9.27	6.27	10.01	9.16	9.47
Tb	1.53	1.44	0.94	1.41	1.72	1.50
Dy	8.95	8.34	5.45	7.45	11.04	8.71
Ho	1.77	1.57	1.06	1.34	2.37	1.72
Er	4.75	3.98	2.83	3.26	6.76	4.49
Tm	0.70	0.53	0.40	0.43	1.03	0.64
Yb	4.17	3.29	2.54	2.44	6.35	3.91
Lu	0.65	0.47	0.39	0.37	0.94	0.57
Ba	691	547	627	463	817	473
Th	11.53	5.14	7.02	5.02	19.14	9.56
Nb	44.76	29.61	24.12	37.07	64.47	40.31
Y	42.60	38.17	26.51	32.59	59.31	41.51
Hf	12.34	7.69	6.40	8.11	18.00	10.12
Ta	2.87	1.98	1.64	2.51	4.30	2.69
U	3.34	1.52	3.92	1.14	4.95	2.59
Pb	8.85	21.10	37.81	6.81	7.24	6.60
Rb	114.8	57.6	90.3	71.8	224.6	93.0
Cs	2.89	2.81	2.66	6.63	2.68	3.11
Sr	394	443	207	793	87	259
Sc	15.3	25.2	18.2	20.7	2.6	13.3
Zr	475	293	239	316	677	381

Table A-4 Raw concentration values of all elements collected from Groovy Lake till and lake samples.

Sample ID	Surber rock	Surber rock	Surber rock	Surber rock	Surber rock
Lake Association	Surber	Surber	Surber	Surber	Surber
Distance	100	120	15	5	5
Direction	S	S	W	S	W
LOI %	1.001	5.081	5.837	2.130	3.366
Major oxides (%)					
SiO_2	70.804	60.099	62.136	50.709	65.279
TiO_2	0.251	0.448	0.959	4.136	0.684
Al_2O_3	15.713	12.751	20.645	12.400	18.386
FeO	2.419	18.729	6.799	17.207	5.755
MnO	0.046	0.037	0.014	0.190	0.040
MgO	1.242	2.194	2.641	4.277	2.588
CaO	2.782	0.697	0.174	6.091	0.446
Na_2O	5.206	1.897	1.050	3.477	3.149
K_2O	1.426	3.047	5.449	1.048	3.566
P_2O_5	0.112	0.101	0.132	0.465	0.107
Trace elements (ppm)					
La	11.68	12.11	28.95	23.74	20.20
Ce	29.97	26.27	59.19	55.05	40.61
Pr	3.03	3.28	7.54	7.66	5.22
Nd	11.10	12.75	28.56	33.93	20.24
Sm	1.79	2.83	5.45	8.25	4.29
Eu	0.56	0.71	1.14	3.11	0.96
Gd	1.22	2.46	4.23	7.91	3.67
Tb	0.18	0.37	0.65	1.21	0.57
Dy	0.98	2.30	3.97	6.60	3.33
Ho	0.18	0.47	0.85	1.22	0.65
Er	0.45	1.28	2.42	3.01	1.80
Tm	0.06	0.19	0.39	0.40	0.28
Yb	0.38	1.22	2.52	2.30	1.82
Lu	0.06	0.20	0.41	0.33	0.30
Ba	576	770	838	325	456
Th	2.52	6.17	9.93	4.17	7.34
Nb	1.70	6.85	11.81	24.48	8.82
Y	4.67	12.30	22.70	29.59	17.52
Hf	2.24	2.54	3.92	3.93	3.50
Ta	0.08	0.44	0.86	1.70	0.68
U	0.36	3.94	6.52	2.45	5.22
Pb	6.05	9.89	8.84	6.23	6.97
Rb	35.3	100.0	209.4	42.9	152.1
Cs	0.76	2.88	8.66	1.69	7.53
Sr	685	337	84	477	151
Sc	5.5	11.3	28.0	28.7	19.5
Zr	84	97	144	140	123

Table A-5 Raw concentration values of all elements collected from Surber Lake rock samples.

Sample ID	Rainy	Rainy	Rainy	Rainy	Rainy	Rainy	Surber Lake
Lake Association	Surber	Surber	Surber	Surber	Surber	Surber	Surber
Distance	25	120	25	100	5	5	0
Direction	S	S	W	S	S	W	-
LOI %	16.797	17.225	56.337	26.516	27.581	53.200	61.888
Major oxides (%)							
SiO_2	68.256	69.239	68.604	69.824	65.967	65.355	73.723
TiO_2	1.110	1.496	1.099	1.134	1.030	1.113	0.467
Al_2O_3	12.636	12.611	12.828	12.391	13.356	13.528	11.051
FeO	8.599	7.572	8.309	7.111	9.207	9.567	8.398
MnO	0.103	0.108	0.077	0.093	0.139	0.065	0.139
MgO	1.925	1.995	1.337	1.730	2.125	1.733	1.050
CaO	2.738	2.704	3.071	2.920	3.433	3.482	2.592
Na_2O	2.713	2.219	2.714	2.832	2.889	3.032	0.567
K_2O	1.774	1.867	1.669	1.763	1.715	1.684	1.110
P_2O_5	0.145	0.190	0.292	0.201	0.138	0.442	0.903
Trace elements (ppm)							
La	17.08	18.41	7.30	16.25	15.32	7.99	16.39
Ce	35.20	37.02	15.30	32.46	32.24	16.09	33.06
Pr	4.29	4.51	1.91	4.18	3.90	1.99	4.43
Nd	16.43	17.07	7.44	16.45	14.99	7.76	17.77
Sm	3.31	3.44	1.51	3.24	3.03	1.59	3.65
Eu	0.92	0.92	0.41	0.90	0.90	0.47	0.85
Gd	2.70	2.98	1.19	2.55	2.40	1.29	3.06
Tb	0.41	0.46	0.18	0.38	0.36	0.19	0.46
Dy	2.41	2.89	1.06	2.24	2.10	1.12	2.65
Ho	0.47	0.61	0.21	0.44	0.41	0.21	0.51
Er	1.27	1.64	0.56	1.16	1.12	0.57	1.34
Tm	0.19	0.25	0.08	0.18	0.16	0.08	0.19
Yb	1.17	1.64	0.53	1.05	0.98	0.52	1.13
Lu	0.19	0.25	0.08	0.17	0.16	0.09	0.17
Ba	485	574	287	445	438	282	140
Th	3.37	4.47	1.83	3.10	2.72	1.87	2.99
Nb	8.57	12.39	4.57	7.81	6.79	4.42	2.62
Y	12.27	15.24	5.31	11.56	10.64	5.62	13.59
Hf	4.31	6.35	1.80	3.42	3.05	1.51	0.78
Ta	0.59	0.89	0.33	0.54	0.47	0.29	0.19
U	1.42	1.70	0.66	1.14	1.08	0.65	0.99
Pb	14.92	28.75	21.66	15.15	14.75	19.69	21.84
Rb	46.3	50.0	17.6	37.3	39.2	18.9	16.5
Cs	2.27	2.33	0.83	1.56	2.31	0.76	1.32
Sr	325	230	199	315	309	218	52
Sc	8.9	9.7	3.9	8.2	7.9	4.7	5.9
Zr	166	253	70	136	121	57	26

Table A-6 Raw concentration values of all elements collected from Surber Lake till and lake samples.

St Louis till			
	TiO$_2$	Al$_2$O$_3$	ΣREEs
SiO$_2$	0.005	<0.001	.
Al$_2$O$_3$	0.006	.	<0.001
Y	.	<0.001	<0.001
Rainy till			
	TiO$_2$	Al$_2$O$_3$	ΣREEs
SiO$_2$	0.027	<0.001	.
Al$_2$O$_3$	0.073	.	0.492
Y	.	0.603	<0.001

Table A-7 P-values for linear regressions of elements and oxides shown in Figures 4-3, 4-4, 4-7 and 4-8.

Appendix B - Water Chemistry Data

	Forjer	Pond	Groovy	Surber
TSS (mg/L) surface	0.7	1.2	0.4	0.7
TSS (mg/L) bottom	1.3	2.8	1.5	0.9
TDS (mg/L) surface	19	13	17	18
TDS (mg/L) bottom	24	14	17	21
Total N (ppm) surface	0.17	1.29	0.32	0.31
Total N (ppm) bottom	0.58	1.5	0.53	0.65
Total P (mg/L) surface	0	0.04	0	0
Total P (mg/L) bottom	0	0.07	0	0
NH_4-N (ppm) surface	0.05	0.3	0.07	0.1
NH_4-N (ppm) bottom	0.12	0.3	0.08	0.35
Ca (ppm) surface	3.67	2.03	1.91	3.23
Ca (ppm) bottom	4.88	2.27	1.92	3.75
Mg (ppm) surface	1.13	0.62	2.43	1.40
Mg (ppm) bottom	1.33	0.64	2.43	1.41
Zn (ppm) surface	0.01	0.02	0.01	0.01
Zn (ppm) bottom	0.03	0.05	0.02	0.02
Fe (ppm) surface	0.05	0.54	0.01	0.15
Fe (ppm) bottom	0.05	0.54	0.01	0.90
SO_4 (ppm) surface	0.51	0.03	0.68	0.19
SO_4 (ppm) bottom	0.39	0.06	0.71	0.10

Table B-1 Surface and bottom water chemistry data from four study lakes. Till lakes are noted in blue and bedrock lakes are noted in orange.