

**PALEOLIMNOLOGY OF
KLUANE LAKE**

by

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B.Sc., Simon Fraser University, 2004

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ABSTRACT

Causes and consequences of late Holocene fluctuations of Kluane Lake in Yukon Territory have been reconstructed from several sediment cores. In the last 5000 years the level of Kluane Lake has varied from ~27 m below its present level to 12 m above, primarily due to changes in inputs of water from Slims and Duke rivers. Discharge from the Slims River catchment into Kluane Lake is associated with glacial advances. During periods when neither Duke nor Slims rivers flowed into Kluane Lake, the level of the lake fell and stable thermal stratification developed with anoxic conditions in the hypolimnion. Climate related changes in catchment permafrost affected nutrient mineralization and the quality of runoff. Recent Kluane Lake fluctuations have caused corresponding shifts in the local groundwater table, which has affected adjacent small lakes causing an alternation of open and closed basin conditions and reversals in local groundwater flow.

DEDICATION

I dedicate my Masters thesis to my family (even though they wouldn't understand a word). To my mother for instilling in me a sense of wonder and curiosity for the world and for her endless support and encouragement, to my father for bringing me into this world and being a shining example of humanity, to my step-father for giving me my first lessons on the environment and for fostering my love of lakes, to my sister for always being happy, to my brother for always being funny, and to my nieces for being.

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CHAPTER 1 INTRODUCTION

Geochemical signatures and fossils preserved in lake sediments are valuable indicators of environmental change. External processes operating at the regional scale, such as atmospheric circulation, and internal processes operating within the sediments, such as bacterial mineralization, can be reconstructed using proxy evidence (Edwards et al. 1996, Yu et al. 1997, Vigliotti 1999, Talbot 2001).

Kluane Lake is the largest lake in the Yukon Territory with an area of 409 km² (Figure 1.1; Natural Resources Canada 2003). Geomorphic evidence suggests the lake has undergone rapid and large fluctuations in level throughout the late Holocene. Kluane Lake is situated in Shakwak Trench, a broad, northwest-trending valley adjacent to the Kluane Ranges of the St. Elias Mountains and the Ruby Range of the Yukon Plateau (Figure 1.1). The lake is sensitive to climate change due, in part, to the presence of glaciers in the catchment. Its largest source of water is Slims River, which flows from the toe of Kaskawulsh Glacier, 20 km south of the lake.

Temperature and precipitation in the Kluane Lake watershed are strongly controlled by the Aleutian Low, a semi-permanent atmospheric system in the North Pacific. The Aleutian Low shifts from a westerly to an easterly position on annual, decadal, and millennial timescales; these shifts influence the direction and source of atmospheric moisture reaching southwest Yukon (Moore et al. 2002, Spooner et al. 2003, Anderson et al. 2005). At times, atmospheric flow is from the south and moisture-laden air masses are intercepted by the St. Elias Mountains, creating a strong rain shadow

in the Kluane Lake area. At other times, air flow is from the southeast allowing moist air to reach Kluane Lake.

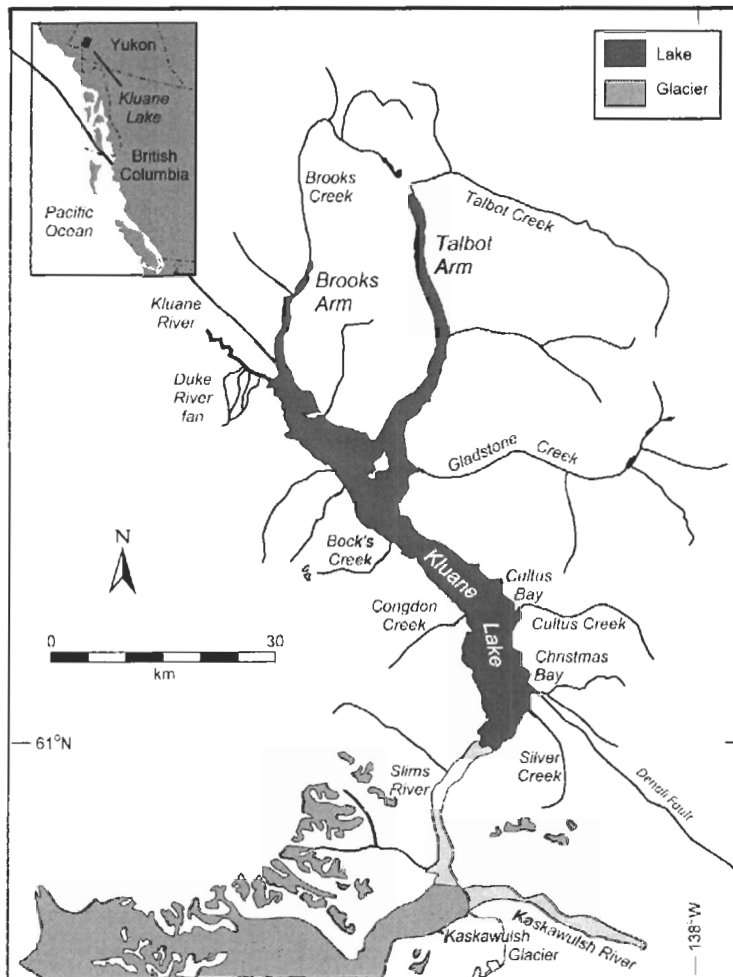


Figure-1-1 Map of Kluane Lake and surrounding region. Modified from Clague et al. (2006) with permission from Elsevier.

Changes in meltwater discharge, climate, and catchment processes are archived in Kluane Lake sediments. A variety of proxy indicators, such as elemental and isotopic geochemistry, lithology, and organic geochemistry, were used in this study to provide information on the local and regional environment. Sediment cores were collected from Kluane Lake and nearby Grayling Lake and Cultus Bay to reconstruct climate, drainage,

and lake-level fluctuations over the past 5000 years. Data acquired from analysis of the cores were interpreted in light of previously published, reconstructed lake-level changes for the past several hundred years (Bostock 1969, Rampton and Shearer 1978a, b, Clague 1981, Clague et al. 2006).

This thesis is organized into three autonomous papers that are intended for publication. Chapter 2 presents elemental geochemistry of Kluane Lake sediment cores to identify sediment sources over the past 5000 years. Changes in inflow from Slims and Duke rivers are inferred from the data. Complexed and co-precipitated trace elements associated with sediment organic constituents, and Fe and Mn oxide and oxyhydroxides are used to infer mixing conditions in the lake and the extent of permafrost conditions in the watershed. Radiocarbon ages and a marker tephra (White River ash, 1150 years BP) provide chronological control.

Chapter 3 uses organic geochemistry, lithology, and magnetic susceptibility of cores from Kluane Lake, Cultus Bay, and Grayling Lake to reconstruct Kluane Lake level fluctuations over the past 5000 years. Isotopes and elemental ratios are also used to infer nutrient cycling in the lake and its watershed.

The modern and late Holocene hydroclimatology of the Kluane Lake watershed is inferred from isotopes of water in Chapter 4. Samples of precipitation and lake and river waters were collected over the spring and summer of 2005 to construct a modern hydrological framework for the Kluane Lake area. Isotopic analysis of sedimentary cellulose was used to reconstruct paleo- $\delta^{18}\text{O}$ of Kluane Lake waters. Results are compared to the $\delta^{18}\text{O}$ record of an ice core from Mt. Logan in the St. Elias Mountains (D.

Fisher, unpublished data) and from carbonates in sediments recovered from Jellybean Lake, 200 km east of Kluane Lake (Anderson et al. 2005).

The final chapter in the thesis is a short conclusion. All geochemical, isotopic, and other data are included in appendices, which are provided in a CD-ROM attached to the thesis.

CHAPTER 2 GEOCHEMICAL RECONSTRUCTION OF LATE HOLOCENE DRAINAGE AND MIXING IN KLUANE LAKE, YUKON TERRITORY

2.1 Abstract

The level of Kluane Lake in southwest Yukon Territory has fluctuated tens of metres during the late Holocene. Contributions of sediment from different watersheds in the basin over the past 5000 years were inferred from the elemental geochemistry of Kluane Lake sediment core. Elements associated with organic material and oxides and oxyhydroxides were used to reconstruct redox fluctuations in the hypolimnion of the lake. The data reveal complex relationships between climate and river discharge during the late Holocene. A period of influx of Duke River sediment coincides with a relatively warm climate around 1300 yr BP. Discharge of Slims River into Kluane Lake occurred when Kaskawulsh Glacier advanced to the present drainage divide separating flow to the Pacific Ocean via Kaskawulsh and Alsek rivers from flow to Bering Sea via tributaries of Yukon River. During periods when neither Duke nor Slims river discharged into Kluane Lake, the level of the lake fell and stable thermal stratification developed, with anoxic and euxinic conditions in the hypolimnion.

2.2 Introduction

Kluane Lake is the largest lake in Yukon Territory, with an area of 409 km² (Figure 2.1; Natural Resources Canada 2003). Geological evidence indicates that the size and level of Kluane Lake have fluctuated markedly throughout the Holocene. Drowned

trees and submerged beaches indicate lake levels up to 30 m below present (Bostock 1969, Rampton and Shearer 1978a, Clague et al. 2006), and raised shorelines and beach deposits occur up to 12 m above present lake level (Bostock 1969, Clague 1981, Clague et al. 2006).

The most recent rise in the level of Kluane Lake to its +12 m high stand occurred in the seventeenth century, during the Little Ice Age advance of Kaskawulsh Glacier. Dendrochronological evidence has constrained the time of this rise to a 50-year period beginning in AD 1650 and ending between AD 1680 and 1700 (Clague et al. 2006). Bostock (1969) hypothesized that, prior to the Little Ice Age, Kluane Lake drained southward through the Kaskawulsh River valley (Figure 2.1). The advance of Kaskawulsh Glacier blocked the southerly outlet and forced glacial meltwater directly to Kluane Lake via Slims River. Kluane Lake rose 12 m above its present level and overtopped the Duke River fan at the north end of the basin, establishing the current drainage route. The outflow incised the fan, lowering the lake to its present level.

The influence of Kaskawulsh Glacier on Kluane Lake prior to the 17th century is presently unknown. The glacier advanced several times before the Little Ice Age (Borns and Goldthwait 1966, Denton and Stuiver 1966, Denton and Karlén 1977) and may have contributed meltwater to the lake at those times.

Duke River presently bypasses Kluane Lake, joining Kluane River 4 km north of the lake outlet (Figure 2.1). Aerial photographs and satellite images, however, reveal abandoned Duke River channels extending to the northwest shore of Kluane Lake near Burwash Landing, but it is not known when the channels were last active.

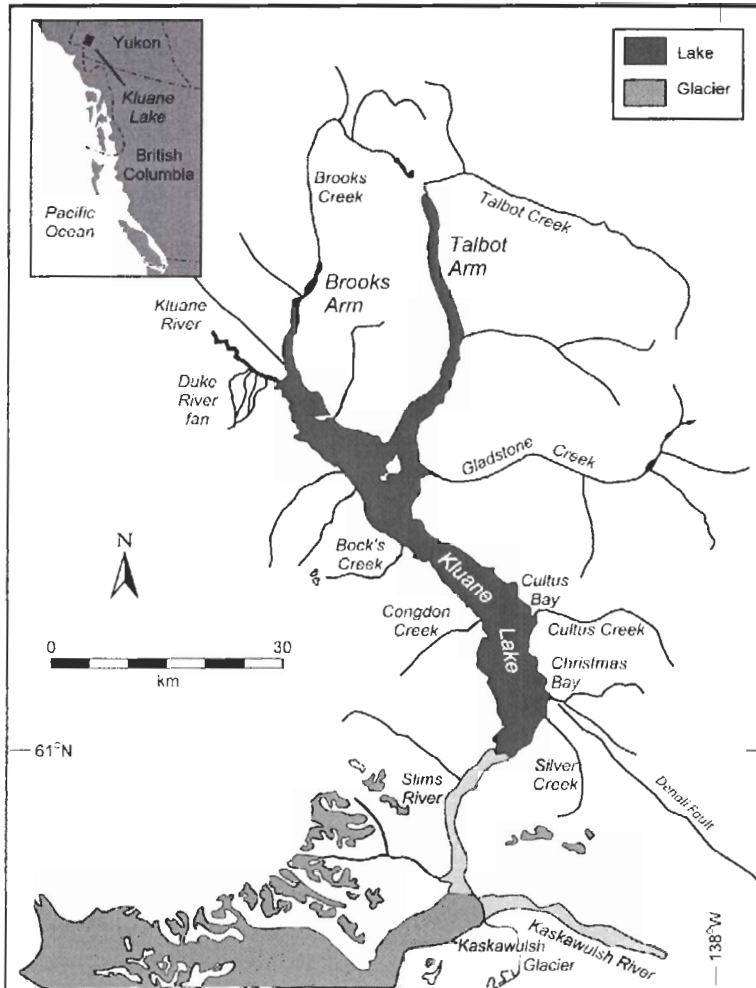


Figure 2-1 Kluane Lake, southwest Yukon Territory. Modified from Clague et al. (2006) with permission from Elsevier.

Geochemistry of lake sediments is a complex function of processes occurring within the lake and the surrounding catchment. Dissolved solutes and sediment originating from the watershed are modified during transport, deposition, and early diagenesis. The elemental chemistry of lake sediments can record details about weathering, runoff, lake productivity, pH, and redox conditions (Engstrom and Wright 1984, Boyle 2001). Climate change and associated watershed drainage processes can influence the types of sediments that enter the lake, as well as limnological characteristics such as lake temperature, depth, and redox conditions. Sediment geochemistry can also

be used to fingerprint sediment sources in the watershed (e.g., Mosser 1991, Collins et al. 1997, 1998).

I used sediment geochemistry to provide insights into the relationship between historical climate change and drainage in the Kluane Lake basin. In addition, I inferred changes in mixing depths, coincident with fluctuations in lake level.

2.2.1 Study area

Kluane Lake is located within Shakwak Trench in southwest Yukon Territory (Figure 2.1). The Kluane Ranges to the west are the easternmost range of the St. Elias Mountains. The Ruby Range to the east is part of the Yukon Plateau. The St. Elias Mountains support the largest ice fields and glaciers in North America, including Kaskawulsh and Donjek glaciers, which terminate, respectively, 20 km south and 40 km west of Kluane Lake.

The Denali fault extends in a northwest direction along the west side of Kluane Lake. It separates sedimentary and volcanic rocks of the Alexander terrane in the Kluane Ranges on the west side of the lake from high-grade metamorphic rocks of the Yukon-Tanana terrane in the Ruby Ranges to the east (Campbell and Dodds, 1982). Thick glaciofluvial and glaciolacustrine sediments dating to the last glaciation (Kluane Glaciation) and one or more earlier glaciations underlie Kluane Lake and border it to the east.

During summer, when Slims River discharge is greatest due to melt of snow and ice, Kluane Lake typically rises 1-2 m above its winter level. Slims River is the dominant source of sediment to the southern portion of the lake. A sediment plume derived from

Slims River, covers much of the southern part of the lake during ice-free periods. Turbid water from Slims River is denser than the lake water and sinks as it flows outward (Bryan 1972). Bottom waters are thus well aerated and the lake mixes throughout the summer. Silt in overflow and interflow plumes derived from Slims River rains out onto the floor of the southern half of the lake during summer and fall. The silt is restricted to water depths greater than 5 m, and most of it occurs at depths greater than 10 m. Currents are too high at shallower depths for silt to accumulate there. Large amounts of silt and sand are carried from the slope of the Slims delta into deeper parts of the southern half of the lake by turbidity currents. Other sediment sources include Gladstone Creek at the northeast corner of the lake, Silver Creek at the south end of the lake, and several ephemeral streams that flow across large fans into the lake along its west side.

2.3 Methods

2.3.1 Core collection and analysis

Thirteen percussion cores, 11 from Kluane Lake, one from Cultus Bay, and one from Grayling Lake, were collected in July 2004; nine of the 13 cores were used in this study (Figure 2.2). Six or more suspended sediment and floodplain samples were collected from Slims River, Silver Creek, Bock's Creek, and Duke River. In addition, a representative sample of glacial drift was collected from the east side of the lake. All cores were split and analyzed at a high resolution for bulk physical properties (details in Chapter 3). Three Kluane Lake cores (08, 10, and 36) and the Cultus Bay core (26) were selected for geochemical analysis. Samples were taken from each core at intervals of 6-10 cm, depending on the stratigraphy.

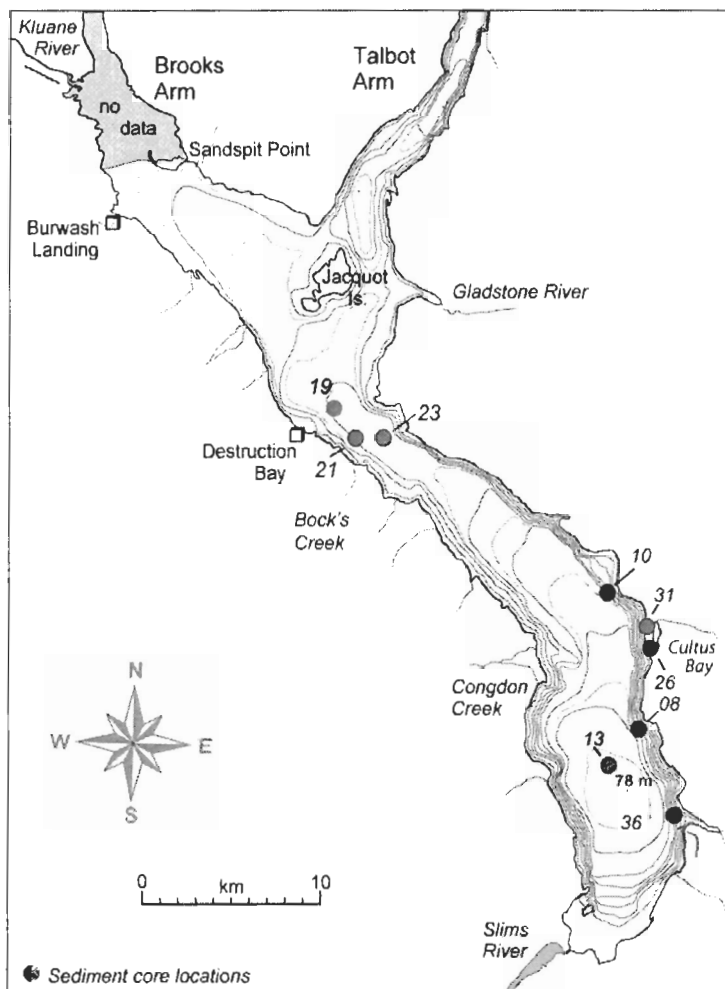


Figure 2-2 Kluane Lake bathymetry and core locations. Cores described in this paper are designated by black dots. Modified from Clague et al. (2006) with permission from Elsevier.

A test was conducted to determine if bulk elemental geochemistry is affected by elements in the organic or oxide fraction of the sediments. Samples from core 10 were treated first with tetra-sodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7$) to remove metals associated with organic matter. Pyrophosphate does not attack sulfides and it does not dissolve amorphous iron oxides (Ross and Wang 1993). Sodium-citrate/dithionite ($(\text{Na}_3\text{C}_6\text{H}_5\text{O}_7) \cdot (\text{Na}_2\text{S}_2\text{O}_4)$) was used as a reducing agent to remove oxides and oxyhydroxides. Magnetite and crystalline silicates are not dissolved by this treatment (Ross and Wang 1993). The residual sediments were washed with distilled water and

aspirated until neutral before the next digestion and final analysis. Major and trace elements in the extractants, residual sediment, and bulk untreated sediment were analyzed using an inductively coupled plasma-mass spectrometer (ICP-MS) and an inductively coupled plasma-atomic emission spectrometer (ICP-AES) at the Ontario Geological Survey Geosciences Laboratory. Trends of some elements in the bulk sediment samples and the treated residual sediment differ, thus the procedure outlined above was used to analyze the remaining lake and stream samples.

The residual fraction contains elements bound in detrital and authigenic minerals. It is a common practice to normalize all elements to Al or Ti to determine those that are not bound in detrital phases (sulfides, oxides, and oxyhydroxides) and those that are associated with the organic fraction (Calvert and Pederson 1993, Boyle 2001, Algeo and Maynard 2004). In this case, however, elements in the oxide and oxyhydroxide fraction are accounted for by the citrate extraction, and elements associated with the organic fraction are accounted for by the pyrophosphate extraction. Normalization is unnecessary for the sulfide fraction because Al and Ti do not vary from the base of core 36 to 97 cm and thus do not affect the trends of the redox-sensitive elements discussed below.

Plant macrofossils were submitted for AMS radiocarbon dating at Beta Analytic and IsoTrace laboratories. All dates are reported as calibrated ages. Additional dating control is provided by the White River tephra, which is about 1150 years old (Clague et al. 1995). The tephra, ^{14}C ages, and the tree-ring ages for the recent rise of Kluane Lake, rising above present level at 1650 AD, were used to estimate sedimentation rates and dates of major events recorded in the cores.

2.3.2 Data analysis

A variety of statistical techniques were used to determine if different mathematical manipulations would provide similar results. Principal component analysis, cluster analysis, discriminant analysis, Euclidean distance metrics, and sediment unmixing models were used to cluster sediment intervals and ascribe them to a particular sediment source. Principal component analysis was performed in R using singular value decomposition on the scaled covariance matrix. The analysis was used on the residual stream sediment data to determine if individual streams had unique principal factors, and on core data to determine whether elemental associations in principal components are related to particular stream sources. The non-hierarchical K-means cluster method was used on the residual data to group sediment samples. Cluster centres were iteratively defined and calculated using the Euclidean distance metric. To assign each sediment interval to a dominant sediment source, I used both multi-group discriminant analysis and unweighted Euclidean distances, E:

$$E = \sqrt{\sum (S_i - C_i)^2}$$

where S_i is the stream source concentration of element i , and C_i is the core interval concentration of element i . Finally, constrained least squares analysis was performed to determine the relative contribution of each stream to specific core intervals. Calculations are similar to those of Bryan et al. (1969). Composite element concentrations were used to minimize the error of proportional stream contributions to each core sediment interval. Constraints are such that each stream source proportion must be:

$$0 \leq S_i \leq 1$$

$$\sum_{i=1}^n S_i = 1$$

2.4 Results

2.4.1 Core descriptions

Core 36 was collected near the southeast end of Kluane Lake at a depth of 36 m depth (Figure 2.2). The core is 240 cm long and comprises three units (Figure 2.3). Unit 1 (240-97 cm) consists of light grey silt (Munsell colours 5Y6/1 and 5Y5/1) with black laminae up to 1 mm thick. Black laminae are most common between 120 and 97 cm depth. Light grey laminae from 120 to 97 cm are coarser grained than those lower in the core. A piece of wood at 219 cm depth yielded a radiocarbon age of 3910 ± 80 ^{14}C yr BP (4570-4090 cal yr BP; Table 2.1). The contact between units 1 and 2 is interfingering. Unit 2 (96-65 cm) consists of massive brown silt (7.5YR4/1 - 7.5YR4/2) with several fine sand laminae. The White River tephra occurs at 88 cm. The contact with unit 3 is abrupt. Unit 3 is mainly light olive-grey clayey silt (5Y6/1-2). Darker laminations (5Y4/1) from 1 to 5 mm thick occur throughout the unit. Sedimentation rates in units 1 and 2 are 0.04 and 0.03 cm yr^{-1} , respectively, and increase to 0.2 cm yr^{-1} in unit 3.

Core 08 was collected at a depth of 25 m near the east shore of Kluane Lake between Christmas and Cultus bays (Figure 2.3). It is 63 cm long and comprises four units. The base of the core and the material found in the core catcher are coarse sand. Unit 2 (63-34 cm) consists of laminated fine to medium grey sand (10Y2.5/1) with a

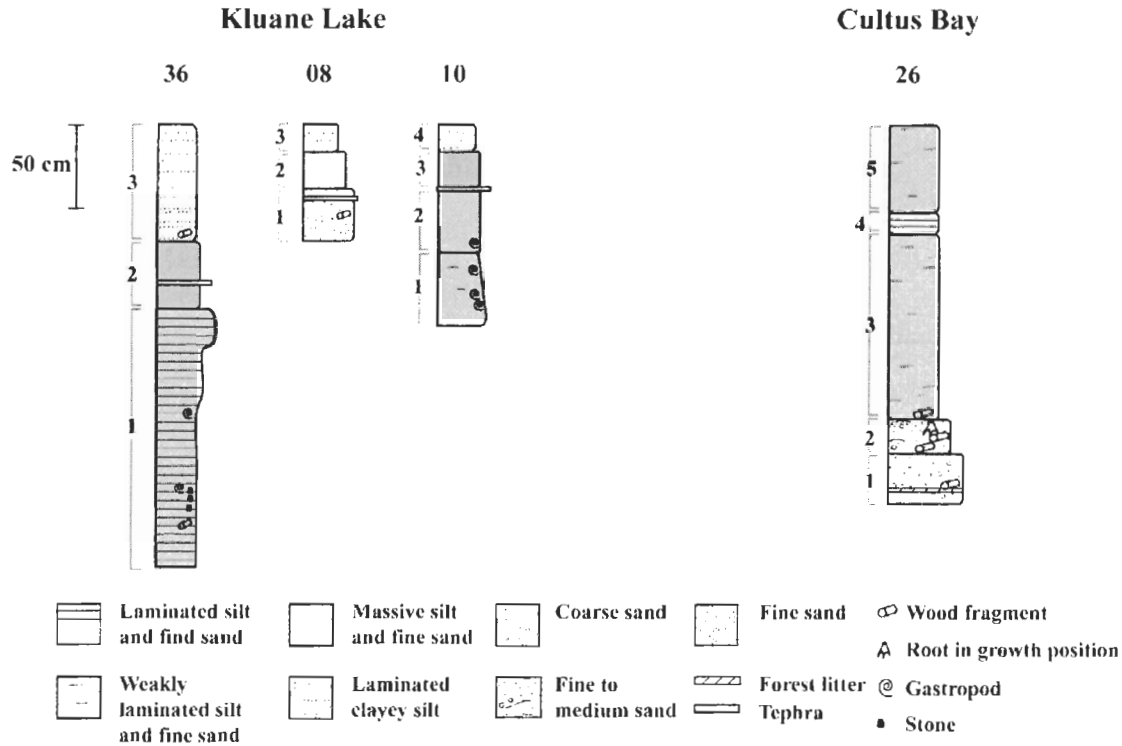


Figure 2-3 Lithostratigraphy of Kluane Lake and Cultus Bay cores.

Table 2-1 Radiocarbon ages from Kluane Lake cores.

Radiocarbon ages used in this study					
¹⁴ C age (yr BP) ¹	Laboratory no	Core no. and sample depth	Material	Calendar age ²	(cal yr BP)
1660 ± 40 BP	Beta - 200708	08 50.5 cm	wood	1690-1660 and 1630-1500	
1180 ± 40 BP	Beta - 200709	26 177 cm	wood	1180-980	
1310 ± 40 BP	Beta - 200710	31 103 cm	wood	1300-1170	
1180 ± 40 BP	Beta - 213014	26 139 cm	wood	1180-980	
3910 ± 80 BP	TO - 12468	36 219 cm	spruce needle and twig	4570-4090	

¹ Radiocarbon laboratory: Beta-Beta Analytic Inc.; TO-IsoTrace Radiocarbon Laboratory (University of Toronto).

² Determined from the calibration data set IntCal98 (Stuiver et al. 1998); calibrated age ranges are reported as ± 2σ.

silty section between 61 and 54 cm depth. The White River tephra occurs at 39 cm, and additional chronological control is provided by a radiocarbon age of 1660 ± 40 ¹⁴C yr BP (1690-1660, 1630-1500 cal yr BP) at 50.5 cm. The contact between units 2 and 3 is gradational and interlayered. Unit 3 (33-17 cm) is laminated brown silt and very fine sand

(2.5Y5/2 and 2.5Y3/3) with distinct bright orange layers (10YR5/6). The contact between units 2 and 3 is sharp. Unit 4 (16-0 cm) is composed of laminated light olive-grey clayey silt (5Y5/2-3) with pale yellow beds (5Y5/2) 1-1.5 cm thick. Sedimentation rates increase from 0.02 cm yr⁻¹ in units 2 and 3 to 0.05 cm yr⁻¹ in unit 4.

Core 10 was collected in 33 m of water on the east side of the lake, north of Cultus Bay. The core is 108 cm long and consists of four units (Figure 2.3). Unit 1 (108-69 cm) and unit 2 (68-36 cm) are upward-fining, light grey laminated silts (5Y4/1). The contact between the two units is gradational. Unit 3 (35-19 cm) is brown silt with several orange laminae (2.5YR4/6). Unit 3 and 4 are separated by a 2-cm-thick layer of White River tephra. Unit 4 (18-0 cm) comprises light olive-grey clayey silt (5Y4/2) with diffuse orange laminae.

Core 26 was collected in Cultus Bay in 14 m of water. Cultus Bay is separated from Kluane Lake by a spit that is breached at its south end. The core is 180 cm long and consists of five units (Figure 2.3). Unit 1, from the base of the core to 156 cm depth, is coarse sand with forest litter at 177 cm. Its contact with unit 2 is sharp. Unit 2 (155-140 cm) consists of fine to medium sand and scattered plant detritus. Unit 3 (139- 53 cm) marks the transition to lacustrine sedimentation and is composed of organic grey silt (5Y2.5/1- 5Y3/1) with fine sand laminae. Several black streaks and laminations, roots in growth position, and plant detritus occur near the base of this unit. A piece of wood at 139 cm and another at 177 cm returned identical radiocarbon ages of 1180 ± 40 ¹⁴C yr BP (1180-980 cal yr BP). Unit 4 (52-42 cm) consists of rhythmically laminated light grey silt (5Y5/1) with 22-25 couplets. Unit 5 (41-0 cm) is weakly laminated light grey silt

(5Y2.5/1 – 5Y4/1) with scattered black spots and streaks. A sharply bounded bed with low organic content occurs at 37-39 cm depth.

2.4.2 Elemental abundances

2.4.2.1 Residual

In core 36, major changes in element abundances occur at 153, 97, and 65 cm (selected analytical data are shown in Figures 2.4 and 2.5). Phosphorus, Ca, and Na increase from 65 cm to the surface; high values of these elements were also obtained in samples at 159 and 203 cm. Calcium and Sr co-vary in units 1 and 2 ($r^2 = 0.82$), likely reflecting the presence of calcite.

Concentrations of K, Rb, Ba, Al, Be, Cs, Li, Ga, W, U, Sn, Th, and Tl increase from 97 cm to the top of the core. Zirconium, Ti, Y, Ag, Hf, Nb, Sb, and the lanthanide elements have relatively low concentrations in unit 3, and higher, non-varying concentrations through the remainder of the core. Iron, Mg, Mn, Co, Zn, Cr, Ni, Sc, and V co-vary, with generally low values in unit 3 and in single samples at 159 cm and 203 cm. Molybdenum, S, and organic carbon co-vary in unit 1 and increase from 130 to 97 cm.

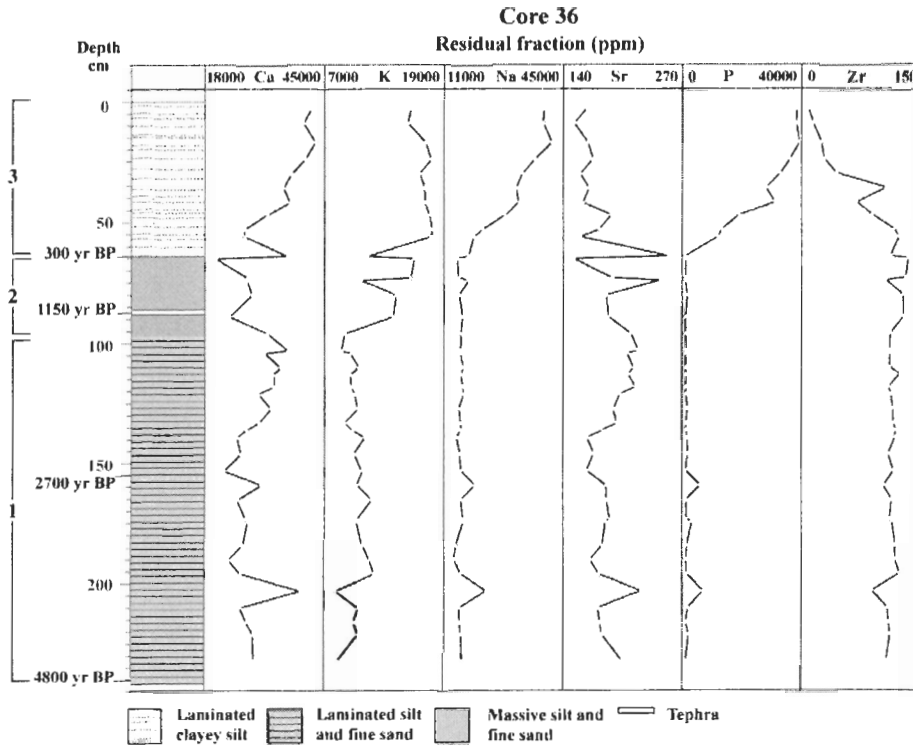


Figure 2-4 Representative concentrations of elements in the residual sediment fraction of core 36

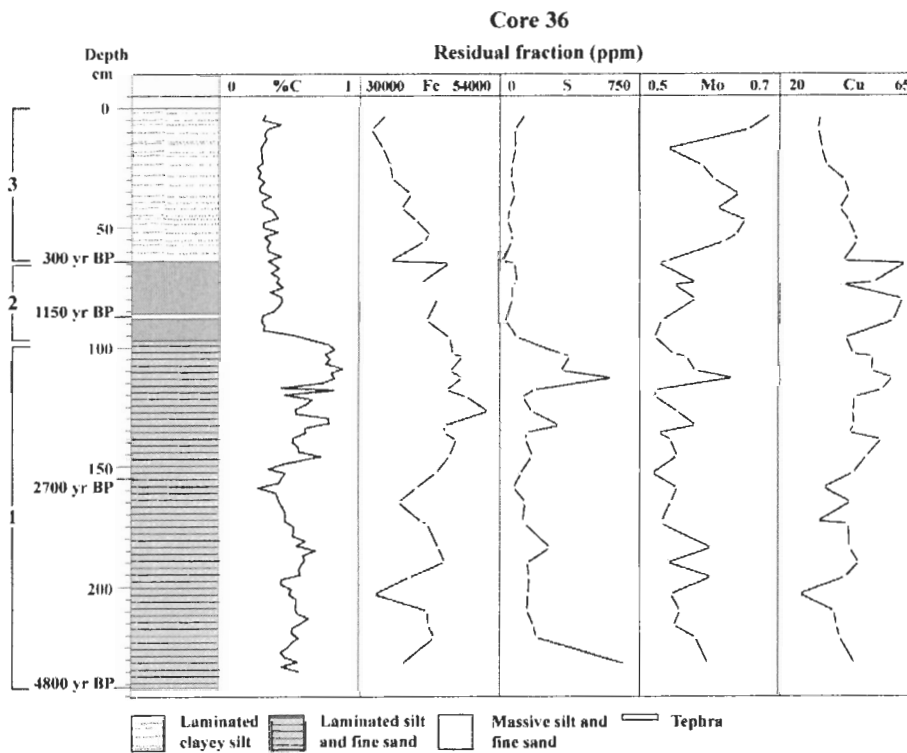


Figure 2-5 Representative concentrations of elements in the residual fraction of core 36.

Cores 10 and 08 show similar trends to core 36 (selected analytical data are shown in Figure 2.6 and 2.7). Elements associated with clay minerals (K, Rb, Al, and Ba) increase upward in these cores, whereas Mn, Ti, and Y decrease upward. Calcium and Sr co-vary from the base of the cores to units 3 and 4 in cores 08 and 10, respectively. Sulfur increases from 80 to 60 cm in core 10, and phosphorus concentrations are higher in units 4 and 3 in core 10 and 08, respectively.

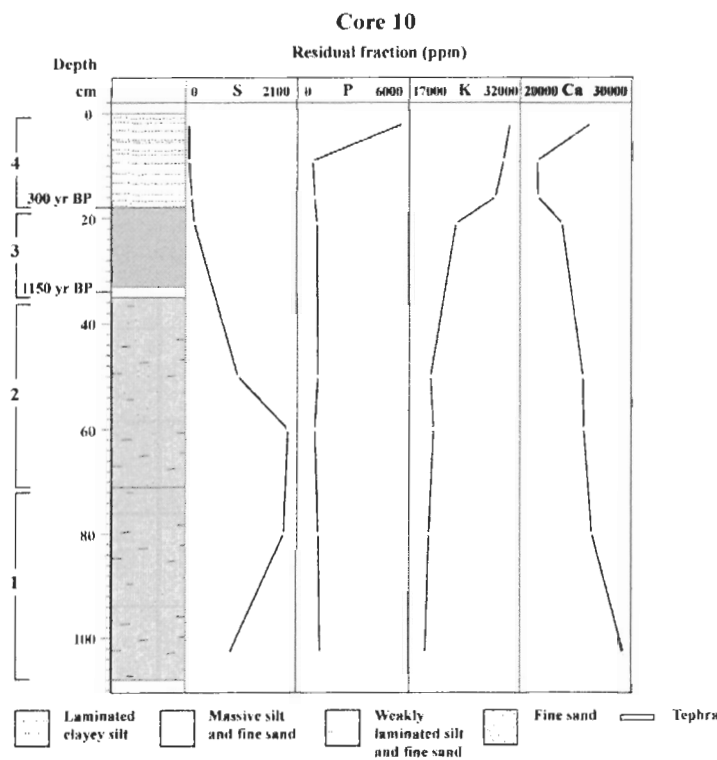


Figure 2-6 Representative concentrations of elements in the residual fraction of core 10.

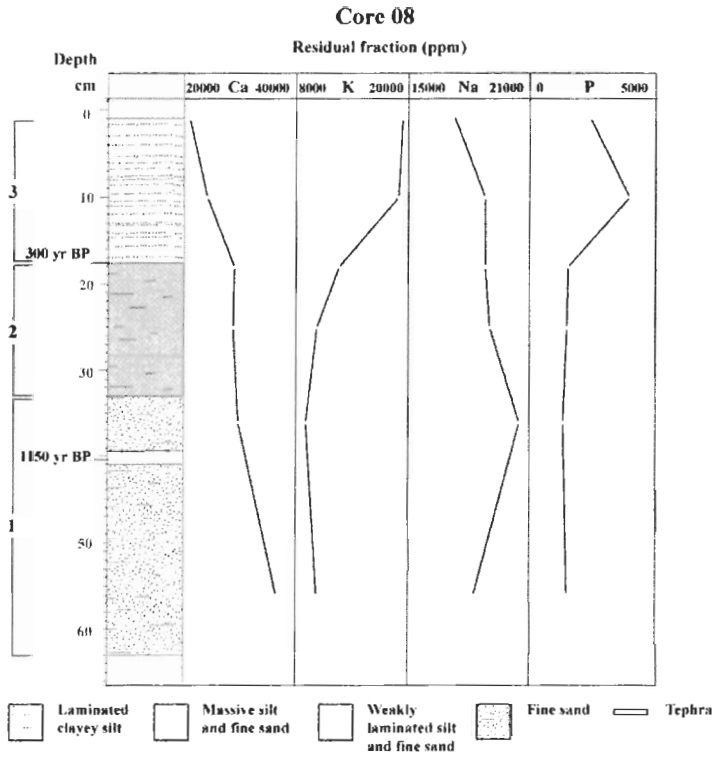


Figure 2-7 Representative concentrations of elements in the residual fraction of core 08.

Concentrations of Ca, Na, Sr, and Y increase from 50 to 40 cm in core 26 and are also relatively high at 70 and 25 cm (Figure 2.8). Manganese, Al, Fe, Mg, and Sc peak at 70 and 37 cm, and P is high through much of the core. Concentrations of S are high near the base of the core and, along with Mo, have single-sample peaks at 130 cm.

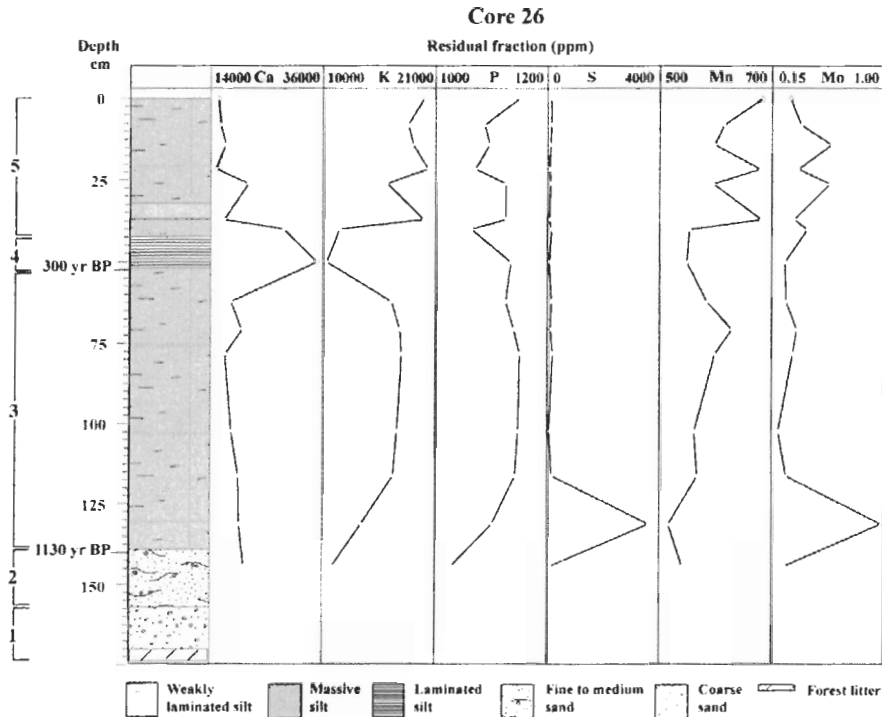


Figure 2-8 Representative concentrations of elements in the residual fraction of core 26.

2.4.2.2 Citrate/dithionite extracts

Oxide concentrations of many elements in core 36 are lowest from 120 to 97 cm depth (Figure 2.9). Above 97 cm, Fe and Mn increase by 29% and 23%, respectively. Cobalt, Zn, Ba, Zr, As, Ti, Ni, V, and U also increase above 97 cm. Oxide concentrations of Cu, Sr, Ti, Rb, Sn, and Au increase from 18 cm to the top of core 10, and other oxides increase upward above 60 cm in this core (Figure 2.10). Oxide values increase from 35 cm to the top of core 08. Oxide peaks at about 18 cm in cores 10 and 08 correspond to orange laminae (Figure 2.10). Phosphorus, Ca, Sr, Ti, U, V, and Sc peak at 70 and 36 cm in core 26; Mn is highest at 40 cm (Figure 2.11). Iron, Co, Ba, Zn, Cr, Rb, Zr, and Y increase upward in this core.

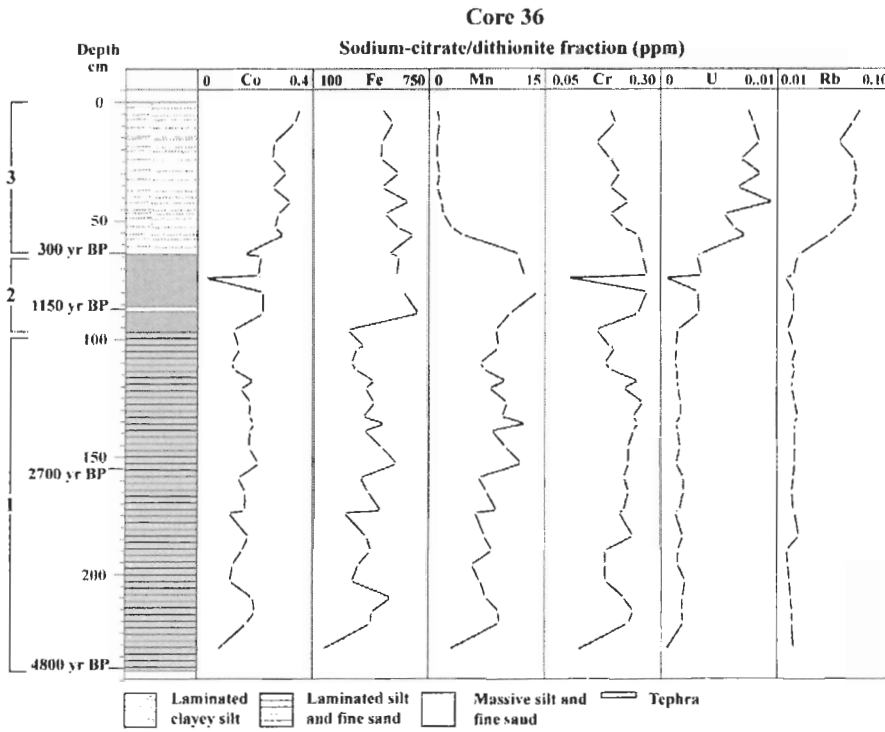


Figure 2-9 Representative concentrations of elements in the citrate/dithionite extracts from core 36.

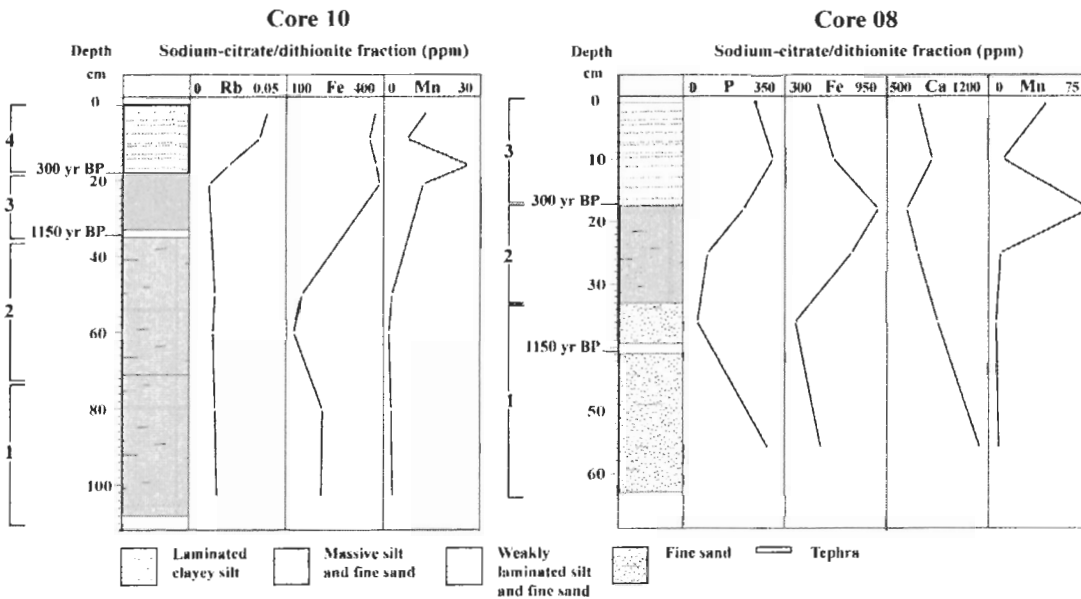


Figure 2-10 Representative concentrations of elements in the citrate/dithionite extracts from cores 08 and 10.

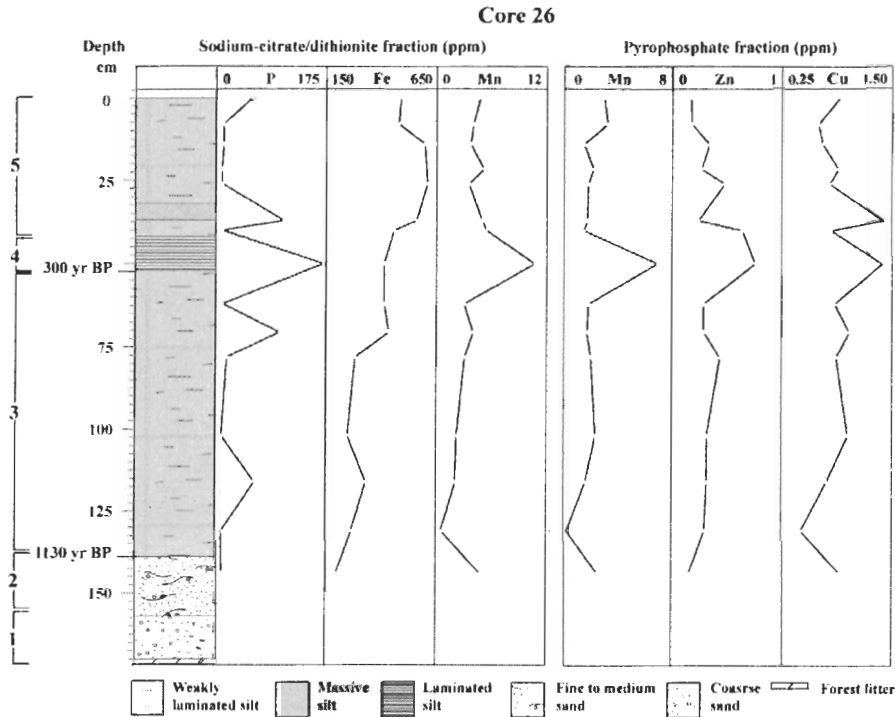


Figure 2-11 Representative concentrations of elements in the citrate/dithionite and pyrophosphate extracts from core 26.

2.4.2.3 Pyrophosphate extracts

Organic-bound metals and %C decrease from 97 cm to the top of core 36 (Figures 2.12 and 2.13). Cobalt, Zn, S, Mn, Fe, V, Cr, Ni, Ti, Cd, and U co-vary with %C.

Pyrophosphate-extractable S was detected only from the base of the core to 97 cm.

Magnesium, Ca, and Sc decrease upward in core 36. Uranium and V increase from 120 to 97 cm; their peaks are, respectively, slightly below and above the peaks in Mo and S in the residual fraction. Sodium and Mn are high from the base of the core to 65 cm and Ba and As concentrations are highest from 97 to 65 cm. Zinc, Fe, and Ni peak above 65 cm, and K, Rb, Sr, and U increase from 65 cm to the top of the core. Most metals in core 10, as in core 36, co-vary with %C (Figure 2.14). Manganese, Ni, Cu, Zn, Co, and Pb peak at 50 cm, whereas Ti, V, Sr, Cr, As, Y, Zr, Ba, Ca, and Mg peak at 60 cm. Copper, Cr, Ni,

U, Au, Ti, Y, Zr, Cd, Sn, S, Zn, and V generally decrease upward in core 08; Sr, K, and Rb increase upward in this core (Figure 2.14). Cobalt, Mg, Mn, Ni, U, and Cd peak at 18 cm in core 08, and Ca, Mn, As, Ba, and Cd are generally high from 18 to 10 cm. Manganese, Cu, and Zn peak at 50-40 cm in core 26; no trends are evident in other metals in this core (Figure 2.11).

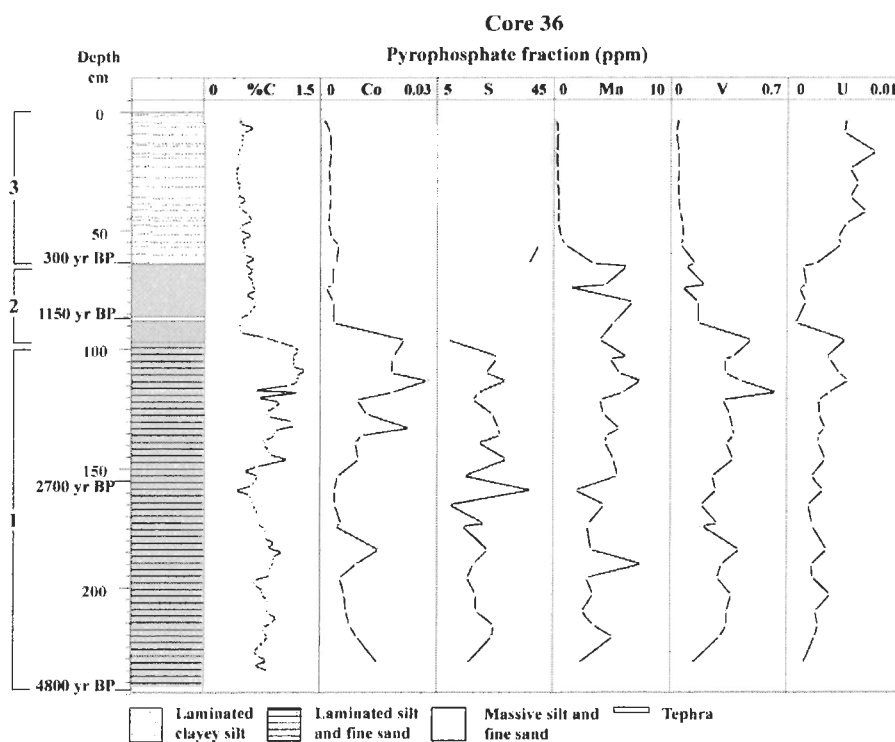


Figure 2-12 Concentrations of elements in the pyrophosphate extracts from core 36.

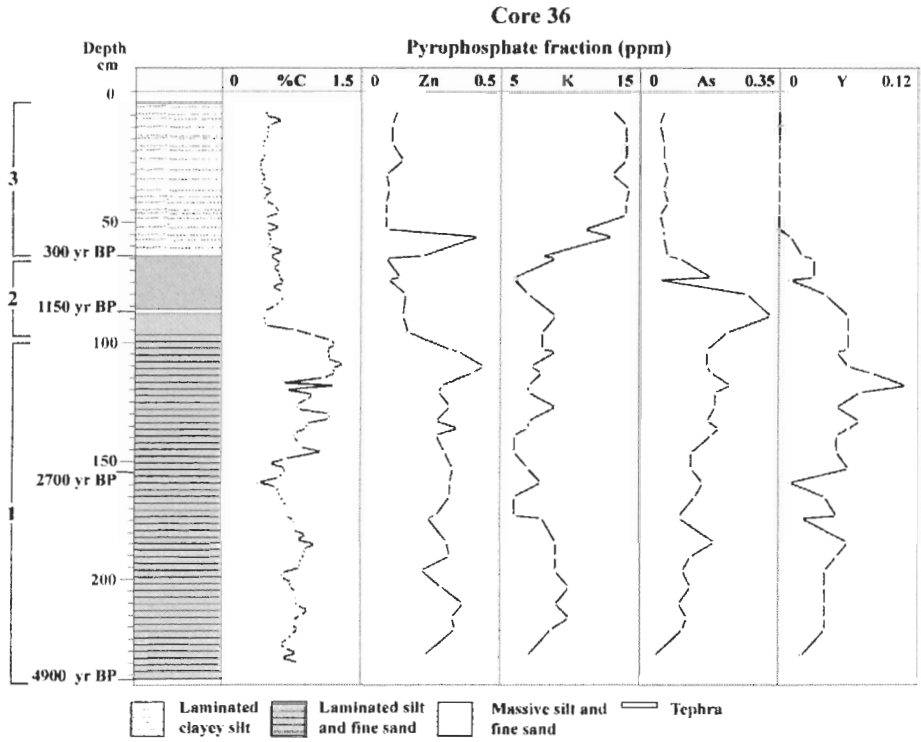


Figure 2-13 Concentrations of elements in the pyrophosphate extracts from core 36.

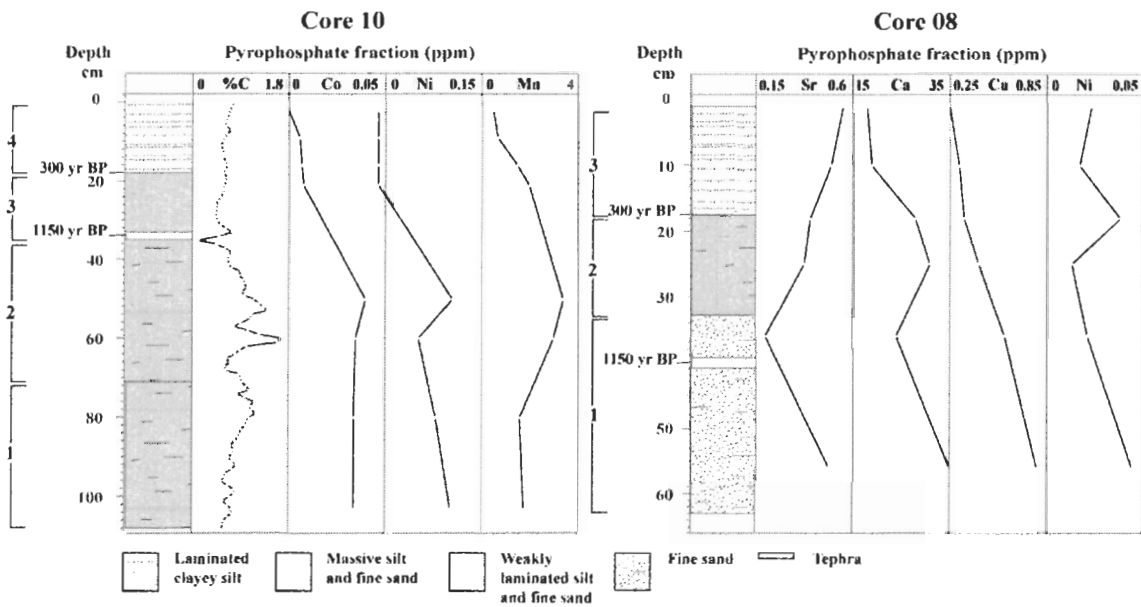


Figure 2-14 Concentrations of elements in the pyrophosphate extracts from cores 08 and 10.

2.4.3 Data analysis

Principal component analysis successfully grouped samples from the same stream, indicating that the sediment transported by each stream is different in composition and that source reconstructions using sediment geochemistry are possible. The first three principal components, which distinguish the four streams, explain 87% of the variance (Figure 2.15).

Principal Components Analysis
Suspended stream and floodplain sediment

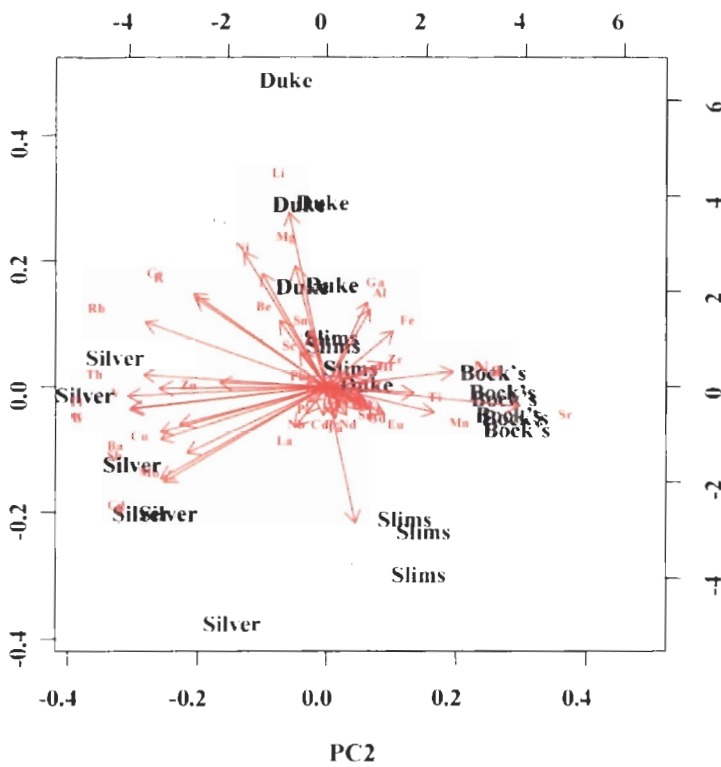
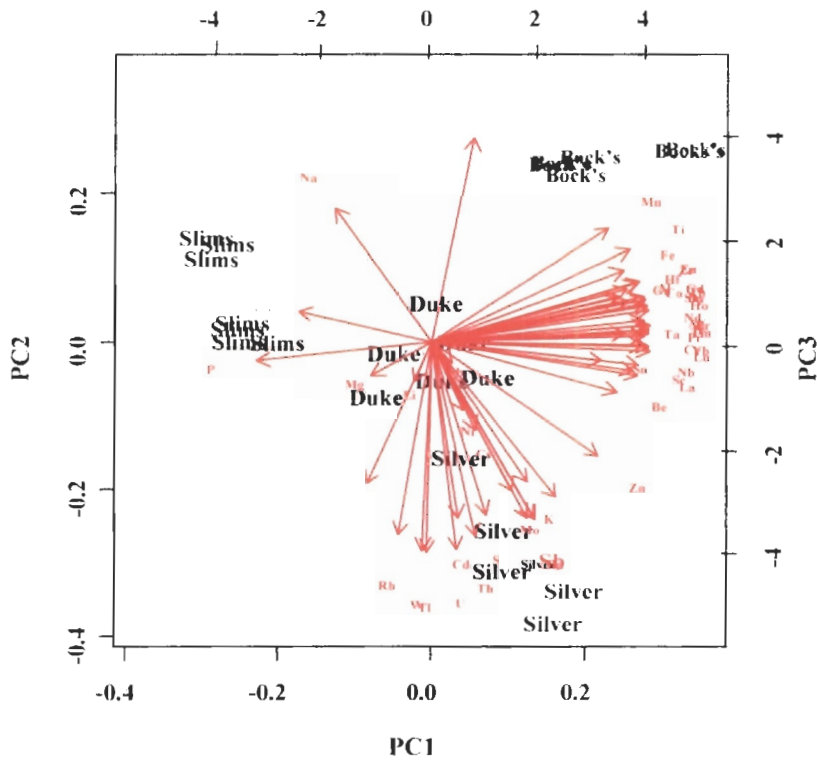


Figure 2-15 Principal component bi-plots showing separation of sediment sources.

Factor analysis of geochemical data from core 36 produced three significant factors that explain 83% of the variation. Factor 1 is interpreted to reflect a Slims River sediment source, with positive loadings on elements that are abundant in the Slims watershed, specifically Na, P, and Ca, and negative loadings on elements with low concentrations in the watershed. Factor 2 has positive loadings on Ca and Sr, suggesting that carbonate is present in the sediment. This factor is important above 45 cm and below 97 cm in core 36. Two event laminae at 65 and 74 cm also load strongly on factor 2. Factor 3 has positive loadings on elements with high concentrations in Duke River sediments.

The first three factors explain 93% and 95% of the variance in the geochemical data from cores 08 and 10, respectively. It is difficult to ascribe any of the three factors to a particular sediment source, although two factors for each core appear to be weakly associated with Slims River and Bock's Creek sediments.

The first four factors explain 89% of the variance in the geochemical data from core 26. This core is from Cultus Bay, not the main lake basin, thus the four factors do not correspond to any of the four stream sediment sources.

Results of the cluster analysis, Euclidean distances, discriminant analysis, and sediment unmixing models are generally consistent for core 36. Discriminant analysis suggests that a representative source, or a combination of sources, is missing from the analysis. Theoretically, all sediment intervals should cluster within the range of the possible sediment sources, but some sources may be missing because not all streams were sampled. Nevertheless, factor analysis indicates that all of the important sediment sources were included in the study. Discriminant analysis indicates two major periods of Duke

River influence in core 36, one from the base of the core to 139 cm depth and another from 65 to 47 cm (Figure 2.16). A Bock's Creek influence is evident from 136 to 97 cm and a Silver Creek influence from 89 to 65 cm. Euclidean distances give similar results. Constrained least squares analysis also indicates two periods of Duke River influence, one from the base of the core to 133 cm and another from 89 to 53 cm (Figure 2.17). The influence of Bock's Creek is reduced when Duke River's influence is high, but is evident from 133 to 97 cm and 73 to 36. A Silver Creek signature is evident until Slims River begins to dominate the sediment supply at 47 cm. Constrained least squares analysis and Euclidean distances reveal Slims-type intervals at 203 and 159 cm, but discriminant analysis assigns only the sample at 203 cm to Slims River. Cluster analysis indicates that these intervals are unique but does not associate them with the same sediment source as unit 3. The inclusion of the drift sample in the data set does not significantly alter the results of the constrained least squares analysis. Constrained least squares analysis was also performed on the data after removing S and Mo, which are incorporated in authigenic sulfides, but no differences were evident in the results.

Discriminant analysis indicates that core 08 is dominated by Duke River sediment. Only the surface sample and the sample at 55-56 cm have a Silver Creek source. Likewise, constrained least squares analysis suggests that most samples from core 08 have a Duke River source. A Silver Creek influence is evident at the base of the core, but decreases upward. A Bock's Creek sediment signature is present throughout the core, increasing in the upper two samples.

The results from core 10 are similar to those from core 36. Discriminant analysis indicates a Slims River source for the sample at 103 cm and the uppermost 10 cm of

sediments. Samples from 80 to 50 cm have a Duke River source. The sample at 21 cm has a Bock's Creek source, and the sample at 16 cm has a Silver Creek source.

Constrained least squares analysis assigned the entire core to a Bock's Creek source. The differences between the analyses may reflect the paucity of major elements analyzed, rather than source differences.

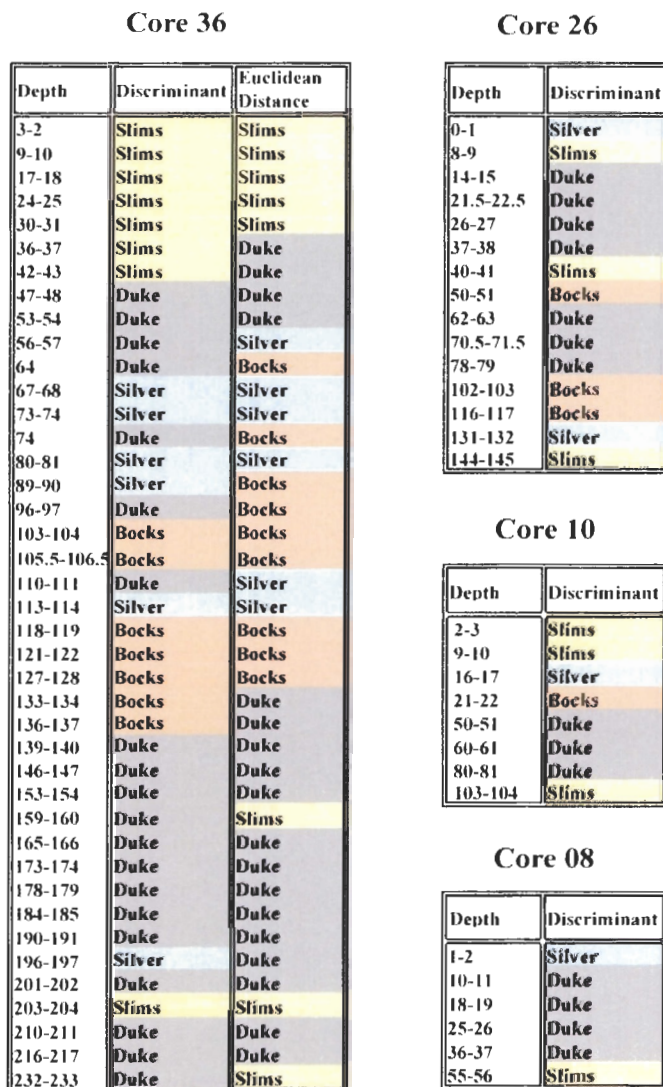


Figure 2-16 Sediment sources for samples from cores 08, 10, and 36 based on discriminant analysis and Euclidian distances.

Core 36 Constrained Least Squares

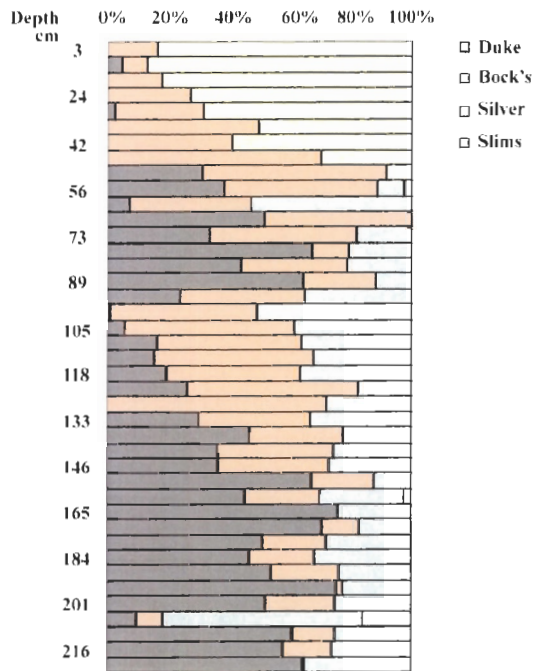


Figure 2-17 Constrained least squares results for core 36. Note the two major periods of Duke River influence. The Slims River source dominates the sediment from 42 cm to the surface.

Core 26 is unique in that none of the four sediment sources are likely to be recorded in Cultus Bay sediments, except during the Kluane Lake high stand when the bay and the lake were united. Discriminant analysis and Euclidean distances assigned the high-stand sediments to the Slims River source, whereas constrained least squares analysis ascribed them to Silver Creek.

2.5 Discussion

2.5.1 Sediment sources

Residual element abundances in core 36 change at 153, 97, and 65 cm depth. Based on average sedimentation rates, these changes date to 2750, 1300, and 300 cal yr BP. The most recent change is marked by a gradual increase in P, Ca, and Na from 65 cm

to the top of the core. These elements are characteristic of the Slims River source, which is consistent with the inception of meltwater inputs from Kaskawulsh Glacier about 300 cal yr BP. Elevated Na and P suggest an influx of unweathered glacial rock flour. Phosphorus, as a limiting nutrient, is transformed within a few thousand years into bioavailable forms through soil development (Filippelli et al 2006). Similarly, sodium is easily leached during weathering, but is not readily sedimented through authigenic reactions, adsorption, or by biological uptake (Engstrom and Wright 1984). The upward increase in P, Ca, and Na reflects the rapid progradation of the Slims River delta from the present Kaskawulsh-Slims drainage divide to its present location. The advance of the delta in historic time was rapid, averaging about 42 m yr^{-1} from 1899 to 1970 (Rampton and Shearer 1978b).

Constrained least squares analysis and Euclidean distances assign the samples at 203 and 159 cm to a Slims River source, largely based on their elevated P, Ca, and Na concentrations. Discriminant analysis also flags the sample at 203 cm as Slims-type sediment. These results suggest that Kaskawulsh Glacier meltwater flowed into Kluane Lake at least twice before 300 cal yr BP. Based on average sedimentation rates, the earlier meltwater inputs date to about 4000 and 2800 cal yr BP. Glaciers in the Purcell, Coast, Rocky, and Selkirk Mountains advanced around 4000 cal yr BP (Gardner and Jones 1985, Osborn and Karlstrom 1989, Wood and Smith 2004), and Kaskawulsh Glacier and other glaciers in the St. Elias Mountains advanced about 2800 cal yr BP (Borns and Goldthwait 1966, Denton and Stuiver 1966, Denton and Karlén 1977).

The gradient of Kaskawulsh River directly downstream of Kaskawulsh Glacier is steeper than that of Slims River. Slims River is thus vulnerable to being pirated by

Kaskawulsh River. Only the presence of glacier ice and drift in the divide area prevents this piracy (Figure 2.1). Any pre-Little Ice Age advance of Kaskawulsh Glacier that brought the toe of the glacier close to the present divide would probably route meltwater away from Kaskawulsh River and into Kluane Lake. The weakness of the Slims sediment signal at 203 and 159 cm is likely due to the distance (25 km) of core site 36 from the point of meltwater inflow to Kluane Lake. Peaks in these elements occur in sediments with low organic carbon contents, suggesting rapid sedimentation, which is consistent with a meltwater source.

The Little Ice Age sediment flux from Slims River is poorly registered in the surface sediments of cores 10 and 08. Phosphorus increases near the top of both cores, but Ca and Na do not increase in tandem with P. The two cores were collected 16 and 20 km north of the current front of the Slims delta, and it is likely that local sediment sources overprint the Slims signal at these sites. Constrained least squares analysis reveals a Slims influence near the base of core 10. Discriminant analysis also assigns the base of cores 08 and 10 to the Slims source. These zones, however, do not have elevated concentrations of P, Ca, and Na.

Constrained least squares analysis indicates two major periods of Duke River influence on Kluane Lake sediments. When Kluane Lake was 10 m or more lower than today, Duke River may have flowed into the lake south of Brooks Arm, strengthening the Duke River signal in cores 36 and 08. A possible stream channel extends southeast along the axis of Brooks Arm and may have carried Duke River during one or more periods of low lake level (Robert Gilbert, personal communication, 2004). In addition, imbrication

in the Duke River fan sediments indicate that flow was to the south-east some time between 2000 and 600 cal yr BP (Clague et al. 2006).

At times, Duke River either flowed north away from Kluane Lake, as it does today, and did not affect the lake or discharged into an isolated basin near Talbot Arm. Dating of core 36 indicates that the river flowed into Kluane Lake from about 4850 to 2400 cal yr BP, when its influence began to decline. Input of Duke River sediment is limited or nil between about 2100 and 1300 cal yr BP. A Duke River influence again becomes evident about 1300 cal yr BP and continues to about 300 cal yr BP (Figure 2.18).

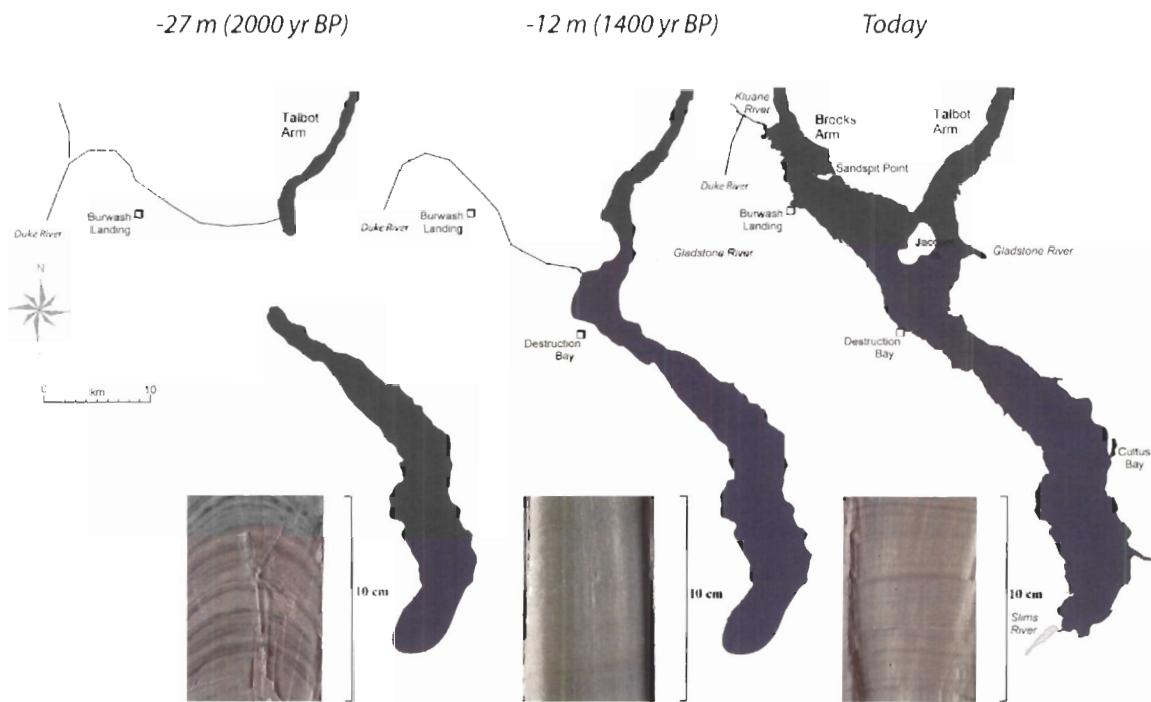


Figure 2-18 Reconstructions of Kluane Lake at three times, showing inferred flow directions of Duke River. The photographs show representative sediment deposited at each time.

The beginning of the most recent period of Duke River discharge into Kluane Lake coincides with a major change in the climate of southern Yukon. Anderson et al. (2005) documented shifts in the North Pacific Index (NPI) at about 2800 and 1300 cal yr BP. The NPI is a measure of sea-level pressure over the North Pacific. North Pacific pressure anomalies are strongly tied to climate in southwest Yukon. Analysis of modern historical climate data from Burwash Landing reveals a strong negative correlation of the NPI ($r^2 = 0.65$) with annual temperature and a positive correlation ($r^2 = 0.59$) with winter precipitation.

Potassium and Ca are negatively correlated through units 1 and 2 of core 36 ($r^2 = 0.77$), which may indicate a change in catchment weathering. Potassium, Al, Rb, and Ba co-vary through these units, suggesting that they are derived from clay minerals. Clay minerals are deposited in greater abundances during wet periods, thus a decrease in these elements or in the K/Na ratio may indicate a change to drier conditions. The K/Na ratio decreases from 139 to 97 cm, but then increases from 97 to 65 cm, suggesting a change in watershed conditions around 1300 cal yr BP.

Warming, inferred from the paleo-climate data (Anderson et al. 2005), may have thawed permafrost in soils in the watershed, increasing the flux of clay minerals and their weathering products to Kluane Lake. Mildly reducing conditions in the catchment may have resulted from melted stagnant water. In a mildly reducing environment, manganese exhibits greater solubility than iron; an increase in Mn relative to Fe is observed from 97-65 cm in all geochemical fractions.

Constrained least squares analysis indicates an upward decrease in sediment of Silver Creek provenance above 97 cm. This trend is consistent with Rampton and

Shearer's (1978b) interpretation of the stratigraphy of Kluane Lake sediments off the Slims River delta. Their subbottom acoustic survey revealed two sharply bounded sediment units: an upper unit derived from Slims River and a lower unit deposited by Silver Creek and other local streams.

2.5.2 Anoxia in Kluane Lake

Constrained least squares analysis of geochemical data from core 36 suggests that Duke River either did not discharge into Kluane Lake from about 2100 to 1300 cal yr BP, or that its flow was reduced. Because Slims River did not exist at this time, the level of Kluane Lake was considerably lower than today and the basin may have been closed. Sediments deposited at this time contain black laminae, consistent with deposition under reducing conditions. Reducing conditions could develop from permanent or near-permanent stratification (meromixis) in the lake. Meromictic and anoxic conditions are not commonly associated with low stands of oligotrophic lakes, but semi-permanent stratification could develop in Kluane Lake under some conditions. Groundwater entering the lake from the south and west is rich in dissolved solutes (150-3000 mg L⁻¹; Harris 1990). Density stratification could develop in the low-level lake in the absence of mixing and influx of fresh Slims and Duke River waters. A concentration of total dissolved solids of roughly 340 mg L⁻¹ is enough to cause a greater density difference in water masses than that created by temperature differences. Pienitz et al. (2000) reported anoxic conditions in a shallow Yukon lake due to high Mg²⁺ and SO₄²⁻ concentrations, similar to concentrations of these ions in groundwater flowing into Kluane Lake.

Under low oxygen conditions, redox-sensitive elements can complex with organic acids or precipitate as insoluble oxyhydroxides or insoluble metal sulfides. Elements

involved in reactions catalyzed by free H_2S or deposited as organic complexes include Cr, U, and V (Calvert and Pedersen 1993, Algeo and Maynard 2004). Elements that can form insoluble sulfides include Mo, Pb, Cd, Co, Ni, and Zn (Calvert and Pedersen 1993, Algeo and Maynard 2004). The presence or absence of these elements in sediments can provide information on paleo-redox conditions in Kluane Lake.

2.5.2.1 Molybdenum

Molybdenum and S concentrations co-vary ($r^2 = 0.91$) from 153 to 97 cm in core 36, suggesting uptake of Mo in pyrite. The associated increase in organic carbon is not likely due to increased productivity, but rather to preservation of organic matter in a low-oxygen environment. Molybdenum can be concentrated in anoxic bottom waters through redox cycling in the water column. MoO_4^{2-} is easily scavenged by manganese oxides and oxyhydroxides (Berrang and Grill 1974, Adelson et al. 2001) in oxygenated waters. Subsequent dissolution of manganese oxides and oxyhydroxides in low-oxygen environments releases MoO_4^{2-} into solution. Sedimentation of Mo seems to require the formation of an intermediary species, thio-oxymolybdate ($\text{MoO}_x\text{S}_{4-x}^{2-}$) (Helz et al. 1996). Molybdenum can then be sedimented by scavenging on iron sulfides or by forming bonds with sulfurized organic matter (Helz et al. 1996, Adelson et al. 2001, Tribovillard et al. 2004). Free $\text{H}_2\text{S}/\text{HS}^-$ is necessary for thiomolybdate to form, thus euxinic conditions are required in the water column, rather than simply reducing conditions in the sediments. Although conversion to thiomolybdates is catalyzed by mineral surfaces (Helz et al. 1996), Crusius et al. (1996) noted that Mo does not seem to accumulate in modern marine environments that are suboxic or anoxic, but rather only in marine environments that are euxinic. Thus, molybdenum fixation probably occurs more rapidly at the sediment-water

interface than at depth in the sediment. It is unlikely that Kluane Lake is productive enough to produce strong reducing conditions within sediments after burial.

MoO_4^{2-} behaves conservatively under oxygenated conditions, although it can be scavenged by manganese oxides and oxyhydroxides. Because Mn decreases in the Slims section of the core (65-0 cm), the increase in Mo above 65 cm is not due to adsorption on manganese oxides, but rather to a change in sediment source.

2.5.2.2 Copper

Copper can be precipitated in anoxic or euxinic environments as an independent sulfide phase, in solid solution with iron sulfides, or as an organic complex (Morse and Luther 1999). Copper co-varies with sulfur from 130 to 97 cm in core 36, perhaps due to authigenic precipitation. The increase in Cu from 97 to 65 cm in the same core probably records a change in sediment source.

2.5.2.3 Vanadium and uranium

Pyrophosphate-extractable V and U increase from 130 to 97 cm in core 36. Pyrophosphate-extractable U also increases from 65 cm to the top of the core. The latter increase may be the result of a change in sediment source because U also increases in the residual fraction. Citrate/dithionite-extractable V and U decrease from 130 to 97 cm. Vanadium and U are known to concentrate in organic sediments under mildly reducing and euxinic conditions (Emerson and Husted 1991, Klinkhammer and Palmer 1991, Algeo and Maynard 2004). Vanadium, like Mo, can be concentrated in anoxic bottom waters (Wehrli and Stumm 1989).

Vanadium occurs as the vanadyl ion (VO^{2+}) under mildly reducing conditions. It can be precipitated as insoluble oxides or hydroxides under strongly reducing conditions (Wanty and Goldhaber 1992). The reduced form of U is the uranyl ion UO^{2+} . No enrichment of either element as authigenic phases is evident in Kluane Lake sediments. Residual V is highly correlated with Zn throughout core 36 ($r^2 = 0.80$). Vanadium correlates with Ti in the Slims interval (65-0 cm; $r^2 = 0.97$) and from 159 cm to the base of the core ($r^2 = 0.88$). It has a lower correlation with Ti from 153 to 97 cm ($r^2 = 0.62$), but is highly correlated with Fe over this section of the core ($r^2 = 0.92$). Residual U correlates with K and Al over the length of the core ($r^2 = 0.86$ and 0.84 , respectively), and U correlates with Fe in unit 1 ($r^2 = 0.83$). These strong correlations suggest that, through much of the core, residual V and U are associated with non-authigenic fractions and thus are likely controlled by sediment provenance. The absence of enrichment in the authigenic phase may be due to competitive complexation of the dissolved species with organic matter. Vanadyl and uranyl ions commonly form organic ligands (Templeton and Chasteen 1980, Lewan and Maynard 1982, Emerson and Husted 1991, Klinkhammer and Palmer 1991, Algeo and Maynard 2004), and complexation of U and V with organic material under suboxic and anoxic conditions may leave the dissolved species unavailable for precipitation in sediments under reducing conditions. The requirement that conditions be only mildly reducing may explain peaks in V and U prior to peaks in Mo and S.

2.5.2.4 Nickel, chromium, zinc, and cobalt

Nickel, Cr, Zn, and Co co-vary in all of the Kluane Lake cores. In core 36, Ni, Cr, and Co in the residual phase correlate strongly with Mg in unit 3 ($r^2 = 0.9$, 0.86 , and 0.92 ,

respectively), and in units 1 and 2 ($r^2 = 0.89, 0.87, \text{ and } 0.91$, respectively). From the base of the core to 97 cm, Zn is strongly correlated with Fe ($r^2 = 0.91$), V ($r^2 = 0.96$), and Al ($r^2 = 0.62$). These strong correlations suggest that the elements in the residual phase reflect sediment provenance.

Zinc, Ni, and Co can be precipitated as independent sulfide phases in anoxic environments, but the process is kinetically slow for Ni and Co (Morse and Luther 1999). Nickel and Co can be incorporated into pyrite, but structural and thermodynamic properties may restrict Zn and prevent Cr from co-precipitating altogether (Huerta-Diaz and Morse 1992, Morse and Luther 1999). Huerta-Diaz and Morse (1992) noted that Mo is more rapidly incorporated into pyrite than Ni and Co. Concentrations of Mo and Cu in Kluane Lake waters are greater than concentrations of Ni, Co, and Cr (J. Bunbury and K. Gajewski, unpublished data), which may account for the elevated values of authigenic Mo and Cu in Kluane Lake sediments.

Nickel, Cr, Zn, and Co correlate with %C in the pyrophosphate extractable fraction in core 36 ($r^2 = 0.76, 0.52, 0.55, \text{ and } 0.68$, respectively) and in the citrate/dithionite fractions below 97 cm. The association of Ni with the organic fraction suggests deposition under reducing conditions in the hypolimnion. In the reduced state, dissolved Ni is preferentially incorporated into organic tetrapyrrole complexes (Lewan and Maynard 1982). Tetrapyrrole complexes degrade faster than other types of organic matter, thus preservation requires deposition in a low-oxygen environment. An association of Ni and Cr with the organic fraction is consistent with the observation of Algeo and Maynard (2004) that these elements are associated with organic matter in non-

sulfide anoxic and euxinic waters. The presence of Co and Zn in the organic fraction suggests that both elements can complex with organic matter under reducing conditions.

Zinc can complex with humic and fulvic acids in anoxic environments (Achterberg et al. 1997). The brief increase in Zn pyrophosphate at 65 cm in core 36 may record in-wash of terrestrial organic matter as Kluane Lake rose during the Little Ice Age. Calcium, Fe, and Ni also increase at this depth, possibly for the same reason.

2.5.2.5 Iron and manganese

Iron and Mn co-vary in core 36. The residual phases probably represent both detrital and authigenic minerals; both elements can form through diagenetic precipitation. Iron and Mn oxides and oxyhydroxides are soluble in their reduced states and are insoluble under oxic conditions (Engstrom and Wright 1984). Thus concentrations of both elements should be low during periods of anoxia.

The presence of Fe and Mn oxides from 120 to 97 cm in core 36 does not necessarily argue against euxinic conditions. The normal sequence of redox reactions is O_2 , NO_3^- , MnO_x , $Fe(OH)_3$, and SO_4^{2-} . The next electron acceptor must be completely used up before the reaction moves on to the next oxidation stage (Schlesinger 1997, and references therein). This sequence, however, may not always occur in natural environments due spatial heterogeneity and variable concentrations of available electron receptors. Kelly et al. (1982) observed some sequential reduction in seasonally stratified lakes, where O_2 and NO_3^- reduction ceased before the lakes overturned but all other reactions proceeded simultaneously. Sulfate concentrations in Kluane Lake and in the lakes that surround it are up to four orders of magnitude greater than dissolved Fe and Mn concentrations, and nitrates are only present in trace amounts.

Complete dissolution of oxides on the floor of Kluane Lake during periods of bottom water anoxia may require lengthy exposure to reducing conditions. Oxides could still be deposited at such times because Kluane Lake is relatively shallow. Dissolution would surely occur, but oxides would have a comparatively short transit through anoxic or euxinic bottom waters. The presence of Fe and Mn oxides may also be an artifact of sampling. Sediments were sampled with a 1-cm diameter plug, and most samples contained both dark and light laminae.

Iron and Mn can be strongly complexed by organic matter (Engstrom and Wright 1984). Iron and Mn pyrophosphate increase with organic carbon from 153 to 97 cm in core 36. Reduction of oxides and oxyhydroxides may have liberated Fe and Mn, which were subsequently complexed with organic matter.

Core 10 is only slightly shallower than core 36 (33 m vs. 36 m), thus its sediments probably would have experienced bottom water anoxia too. Core 10 sulfur concentrations are elevated from 80 to 50 cm, and redox-sensitive elements (Ni, Cu, Zn, Co, and Pb) peak at 50 cm. Citrate extractions of Fe, Mn, Co, Ni, As, U, Ba, V, Zn, Y, and Zr are relatively low in this section of the core.

Core 08 is shallower than cores 36 and 10 and does not show the same associations with redox-sensitive elements. Pyrophosphate extractable metals decrease upward from near the base of the core. Secondary peaks of Co, Ni, and U occur at 17 cm. The trends may reflect higher concentrations of organic matter near the base of the core, associated with shallower water. The peak at 17 cm marks the base of the upper unit in core 08 and possibly records in-wash of terrestrial organic matter during the Kluane Lake high stand.

Core 26 also provides evidence of anoxia. Molybdenum and S peak at 130 cm in black sediments near the base of the core. These sediments may have been deposited in stagnant waters just after the permafrost melted in the area. Alternatively, groundwater levels may have risen at this time, driven by the rise in Kluane Lake.

2.5.3 A return to mixing in the basin

A return to oxygenated conditions in Kluane Lake about 1300 cal yr BP is suggested by a rapid increase in Fe and Mn oxides and oxyhydroxides and associated trace elements at 97 cm in core 36. Citrate/dithionite extractable Fe and Mn increase 29% and 23 %, respectively, at this level. Cobalt, Zn, Ba, Zr, As, Ti, Ni, V, and U increase from 29% to 260%, probably because they were scavenged by oxides and oxyhydroxides. Similarly, Fe and Mn oxide and oxyhydroxide concentrations in the citrate/dithionite extracts of cores 10 and 08 increase above, respectively, 35 cm and 25 cm. Oxide and oxyhydroxide concentrations in core 08 citrate extracts decrease at 36 cm, but increase from 25 cm to the top of the core. The spike at 18 cm is associated with orange laminae.

Constrained least squares analysis suggests that Duke River began to flow into Kluane Lake at this time. Increased input of fresh cold water may have initiated mixing in the lake and re-oxygenation of its bottom waters.

Increases in citrate-extractable P, Al, Mg, and Rb and a decrease in citrate-extractable Mn at 65 cm in core 36 are likely due to a change in sediment source. A change in oxidation state is ruled out by concomitant increases of P, Al, and Rb in the residual fraction. Citrate-extractable P increases slightly during periods of inferred anoxia. Phosphorus sedimentation and retention in sediments are influenced by Fe and

Mn oxides (Engstrom and Wright 1984). Phosphorus does not correlate with either element throughout core 36, suggesting that its sedimentation may not be controlled by Fe or Mn for much of Kluane Lake's history. Phosphorus concentrations in Kluane Lake sediments appear to be related to supply rather than redox state. Citrate-extractable P increases above 108 cm and again above 65 cm. Phosphorus citrate co-varies with Sr citrate and Ca citrate, thus carbonates may be controlling their concentrations.

2.5.4 Minor fluctuations in lake level

The geochemistry of core 26 changes markedly at 50-40 cm, which corresponds to the time Cultus Bay merged with Kluane Lake during the high stand of the lake about 300 cal yr BP. Two similar geochemical changes occur prior to and just after the high stand. Based on average sedimentation rates, these intervals date to about 500 to 460 cal yr BP and 140 to 120 cal yr BP.

2.6 Summary

Changes in the flow of Duke and Slims rivers affected the level of Kluane Lake and its redox state during the late Holocene. Duke River at times flowed into the lake and at other times bypassed it to the north. Sediment geochemical data indicate that Duke River flowed into Kluane Lake before 2100 cal yr BP and between about 1300 and 200 cal yr BP. Slims River has flowed into Kluane Lake for the past several centuries and, over this period, has deposited a thick wedge of sediments in the southern part of the basin. Older Slims River sediment, dating to about 4000 and 2800 cal yr BP, is present in one core in the southern part of the lake. Fluctuations in discharge and location of both rivers appear to be associated with climate fluctuations. A shift to warmer conditions

occurred around 1300 cal yr BP, and glacier advances occurred about 4000, 2800, and 300 cal yr BP.

Kluane Lake was low and stratified when Duke River and all meltwater from Kaskawulsh Glacier bypassed the lake. Meromixis led to anoxic and eventually euxinic conditions in the hypolimnion, causing precipitation of Mo and Cu sulfides. The lack of enrichment of many other redox-sensitive elements can be explained by their low availability in the water column or by competitive complexation with humic and fulvic acids.

2.7 Acknowledgements

I thank Melanie Grubb and Robert Gilbert for valuable field and laboratory assistance and Rick Routledge and Carl Swartz for discussion of statistical methods. Research funding was provided by the Natural Science and Engineering Research Council of Canada (Postgraduate Scholarship to Brahney; Discovery Grants to John Clague, Brian Menounos, and Tom Edwards), the Geological Society of America, and Northern Scientific Training Program.

CHAPTER 3 TIMING AND CAUSE OF WATER LEVEL FLUCTUATIONS IN KLUANE LAKE, YUKON TERRITORY, OVER THE PAST 5000 YEARS

3.1 Abstract

Late Holocene fluctuations of Kluane Lake in Yukon Territory have been reconstructed from variations in bulk physical properties and carbon and nitrogen elemental and isotopic abundance in nine sediment cores. A tephra layer and radiocarbon ages provide chronological control for the events inferred from the sediment cores. Kluane Lake fluctuated within a narrow range, at levels more than 25 m below the present datum, from about 5000 to 1300 cal yr BP. Low lake levels during this interval are probably due to southerly drainage of Kluane Lake to the Pacific Ocean, opposite the present northerly drainage to Bering Sea. Slims River, which today is the largest contributor of water to Kluane Lake, only rarely flowed into the lake during this period. The lake rose 5-10 m between 1300 and 900 cal yr BP, reached its present level around AD 1650, and within a few decades had risen an additional 12 m. Shortly thereafter, the lake established a northern outlet and fell to near its present level.

3.2 Introduction

The level of Kluane Lake, the largest lake in Yukon Territory, has varied by several tens of metres during the Holocene. Bostock (1969) and Clague (1981) noted drowned trees at the perimeter of the lake that indicate the lake was lower in the recent past. They also described beaches and mats of driftwood up to 12 m above present lake

level. A lake level more than 50 m below present was proposed by Rampton and Shearer (1978b) based on their discovery of an inferred 2000-year-old soil layer in a sediment core near the south end of the lake.

Clague et al. (2006) dated the most recent rise in Kluane Lake to its +12 m high stand to the late seventeenth century based on dendrochronological analyses. They attributed this rise to the climactic Little Ice Age advance of Kaskawulsh Glacier (Figure 3.1), which blocked the former southerly drainage route of the lake. Blockage of the southerly outlet created Slims River, which flowed into Kluane Lake and raised its level 12 m to the lowest point on Duke River fan at the north end of the basin. The lake then began to overflow to the north across the fan and into the Yukon River watershed, establishing Kluane River (Figure 3.1).

Kaskawulsh Glacier advanced several times during the late Holocene prior to the Little Ice Age (Borns and Goldthwait 1966, Denton and Stuiver 1966, Denton and Karlén 1977). Source-area fingerprinting of Kluane Lake sediments suggests that meltwater from the glacier entered the lake during at least two of these advances (Chapter 2). Duke River, which presently bypasses Kluane Lake, also flowed into the lake at times during the late Holocene. Aerial photographs and satellite images show an abandoned channel of Duke River extending to Kluane Lake near Burwash Landing (Figure 3.1), and source-area fingerprinting (Chapter 2) indicates at least two periods of Duke River sediment input.

Changes in the level of Kluane Lake could alter local ecosystems. Kluane River and some streams flowing into the lake are spawning habitat for Coho and Chinook salmon (von Finster 2005). Continued warming of surface air temperatures could cause Kaskawulsh Glacier to retreat to the point that its meltwater no longer flows into the lake.

Abandonment of Slims River could cause Kluane Lake to fall, possibly below its present outlet, altering local ecosystems and preventing salmon from reaching streams that flow into the lake. Reconstructing past catchment drainage changes is important for understanding the impacts of a possible shut-down of Slims River due to recession of Kaskawulsh Glacier. Here I use physical properties and organic geochemistry of sediment cores to infer paleo-lake depth and possible causes of lake-level change.

3.2.1 Site description

Kluane Lake (409 km²) is located within Shakwak Trench in southwest Yukon Territory (Natural Resources Canada 2003). The lake is bordered by the Ruby Ranges, which are part of Yukon Plateau, on the east and the Kluane Ranges, part of the St. Elias Mountains, on the west. It fluctuates 1-2 m annually, due mainly to changes in the flow of Slims River, which is its principal source of surface water. Lake level rises in summer when Slims River discharge is largest and falls during autumn prior to freeze-up.

Large amounts of clay, silt, and sand are discharged into Kluane Lake by Slims River. A conspicuous turbid overflow plume covers much of the southernmost part of the lake during the summer melt season, and turbidity currents transport fine sediment far from the Slims River delta front. Other significant sediment sources include Gladstone River, Silver Creek, and several ephemeral streams that flow from the Kluane Range west of the lake (Figure 3.1).

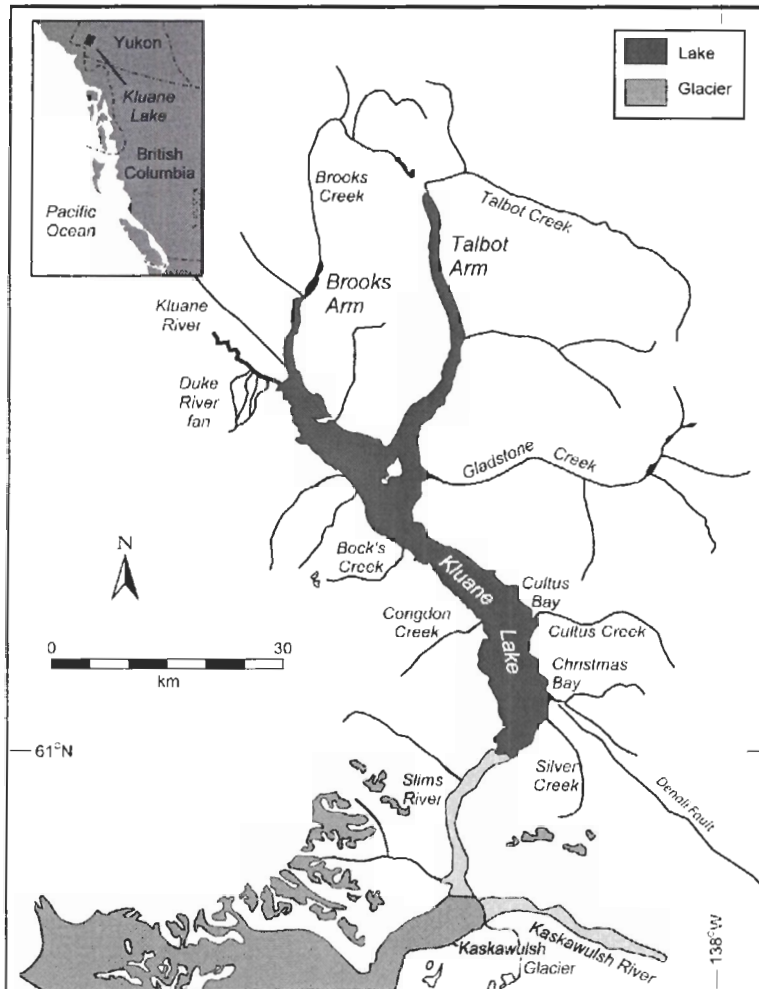


Figure 3-1 Map of Kluane Lake and surrounding region. Modified from Clague et al. (2006) with permission from Elsevier.

3.3 Methods

An acoustic sub-bottom survey of Kluane Lake was conducted with a Datasonics Chirp II system in July 2004 to provide information on bathymetry of the lake and the character and structure of its Holocene sediment fill. About 180 km line of data were collected along thirty oblique transects and one axial transect. Coring locations were chosen on the basis of this survey.

Thirteen percussion cores were collected in July 2004, 11 from Kluane Lake, one from Cultus Bay, and one from Grayling Lake (Figure 3.2). The cores were transported to

the University of Northern British Columbia where they were logged, photographed, and analyzed at a high resolution for water content, bulk density, magnetic susceptibility, and organic content. Samples from cores 26 and 36 were analyzed for grain size using a Malvern 2000G Mastersizer. Magnetic susceptibility was measured with a Bartington MS2B sensor. Water content, bulk density, and loss on ignition were determined by drying in an oven at 105°C and 550°C.

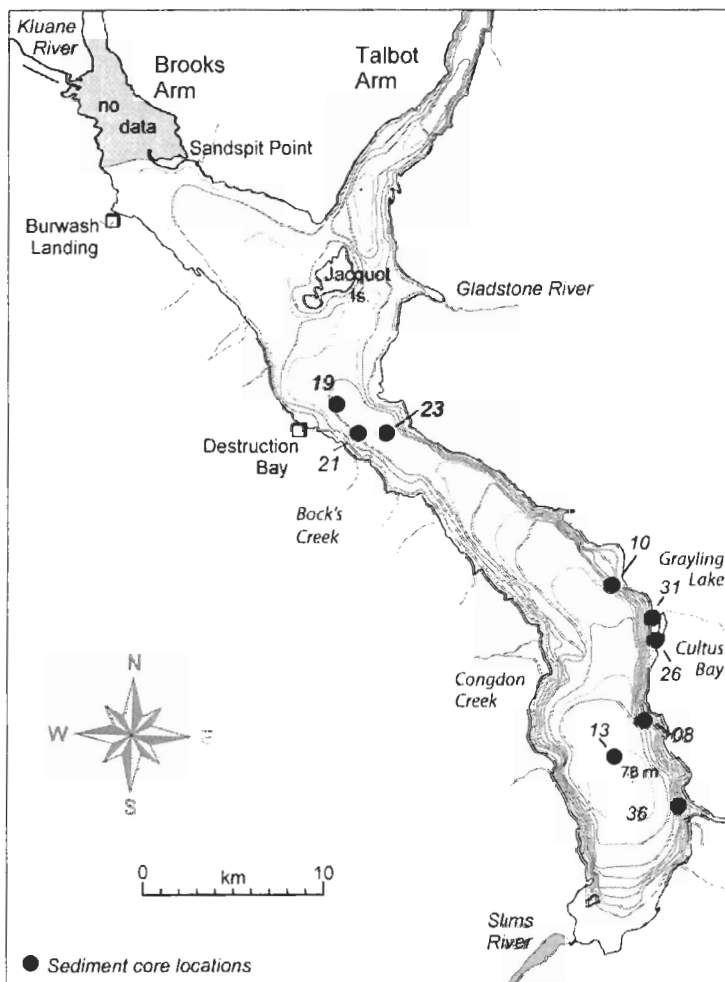


Figure 3-2 Core locations in Kluane Lake, Cultus Bay and Grayling Lake. Modified from Clague et al. (2006) with permission from Elsevier.

Nitrogen and carbon isotope ratios were analyzed on treated sediments from cores 10, 26, and 36 at the University of Waterloo. Sediments were washed in 10% HCl and rinsed with distilled water until neutral. Freeze-dried sediments were then sieved through a 500 μm mesh to remove coarse material and potential terrestrial organic matter. The remaining sediment was analyzed using an Isochrom EA-CFIRMS continuous-flow isotope mass spectrometer and compared to the Vienna Pee-Dee Belemnite (V-PDB) for carbon and the atmospheric standard for nitrogen. Standard deviations for reference materials are $\pm 0.2\text{‰}$ for carbon and $\pm 0.3\text{‰}$ for nitrogen. Scatter plots of elemental C and N were used to detect the presence of elements not bound in organic material that can influence the C/N ratio. Elemental abundances were used to correct C/N values. Loss on ignition was used to determine organic content in cores 13 and 31.

Plant macrofossils were dated by the AMS radiocarbon technique at Beta Analytic and IsoTrace (University of Toronto). Additional dating control is provided by the White River tephra, which is about 1150 years BP (Clague et al. 1995) and is present in most cores. The tephra, ^{14}C ages, and tree-ring ages for the recent rise of Kluane Lake (Clague et al. 2006) were used to estimate sedimentation rates and dates of major events recorded in the cores.

3.4 Results

3.4.1 Core descriptions

Cores are subdivided into lithostratigraphic units based primarily on sediment texture, colour, stratification, and organic content (Figures 3.3 and 3.4). Radiocarbon ages and the White River tephra allow units to be correlated from core to core.

Kluane Lake

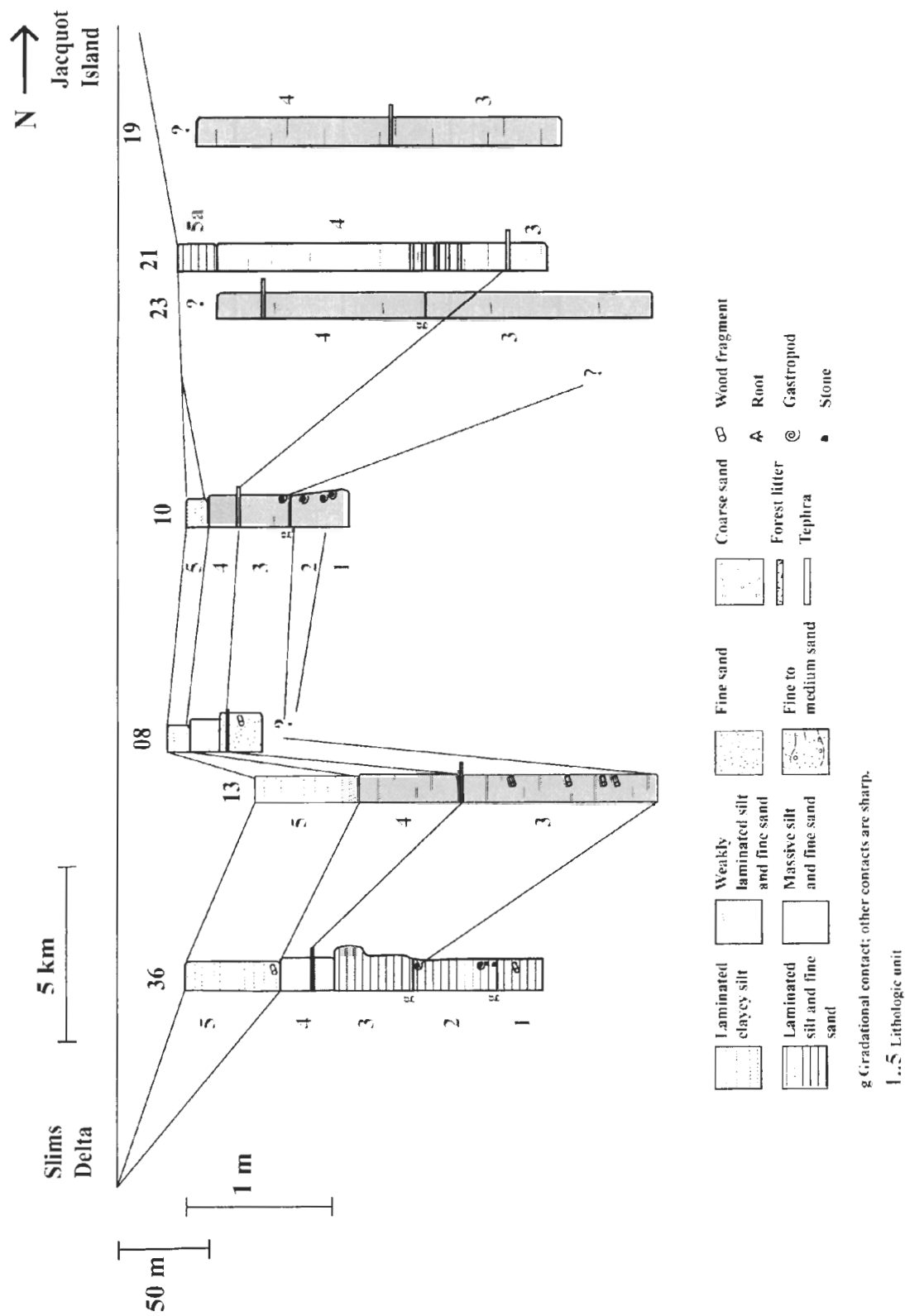


Figure 3-3 Lithostratigraphy and correlation of Kluane Lake cores.

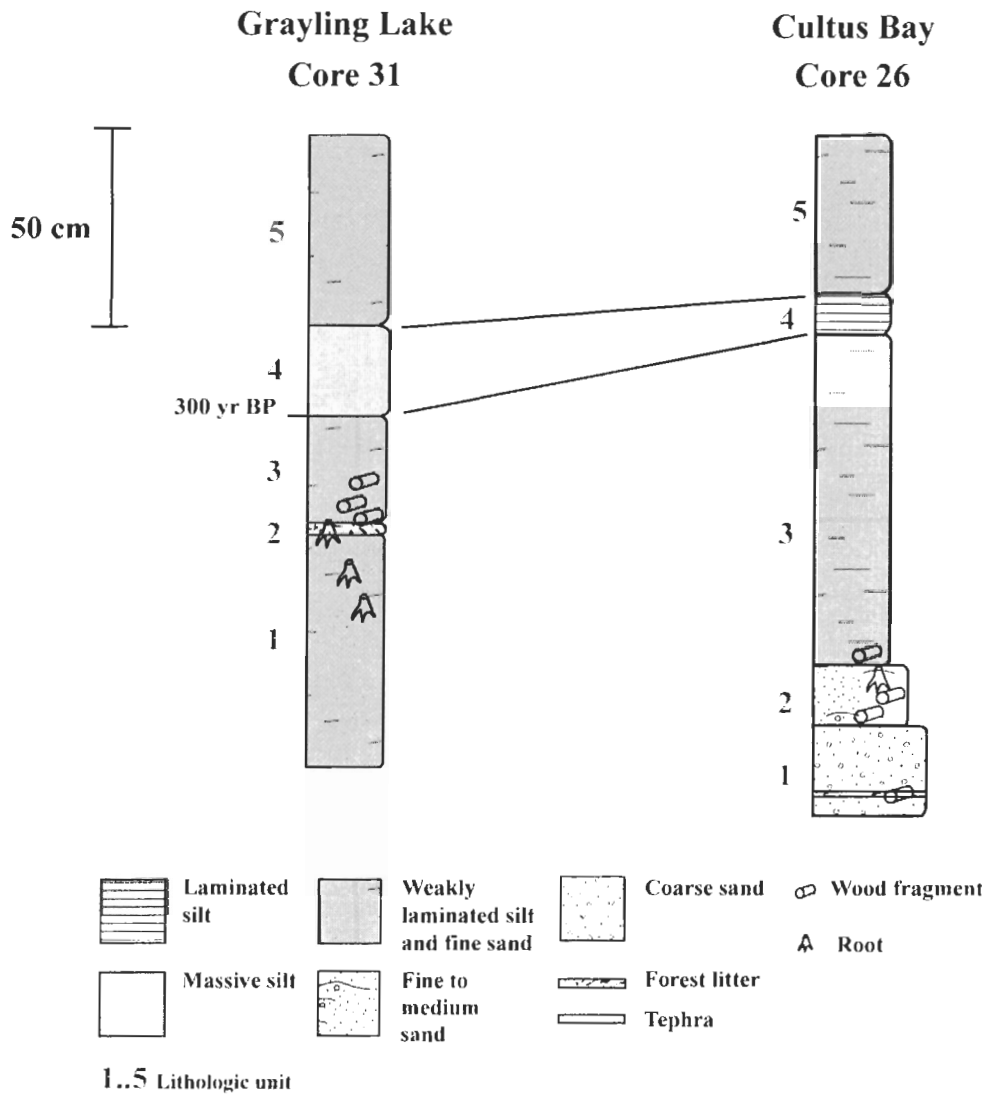


Figure 3-4 Lithostratigraphy of Grayling Lake and Cultus Bay cores.

3.4.1.1 Core 36

Cores 36 was collected in the southeast corner of Kluane Lake in 36 m of water (Figures 3.2 and 3.3). It is 240 cm long and is divisible into five units based on lithology, colour, and abrupt shifts in carbon and nitrogen elemental abundances and isotopic values

(Figure 3.5): unit 1, 240-221 cm; unit 2, 220-154 cm; unit 3, 153-97 cm; unit 4, 96-66 cm; and unit 5, 65-0 cm.

Units 1, 2, and 3 consist mainly of light grey silt and fine to very fine sand (Munsell colour 5Y6/1 – 5Y5/1) (Figure 3.6). The contacts between units 1 and 2, and units 2 and 3 are gradational. All three units contain distinct black laminae up to 1 mm thick, but they are more common in units 1 and 3 than in unit 2. Sandy laminae are especially common between 120 and 97 cm within unit 3. Units 3 and 4 interfinger at about 97 cm. Unit 4 comprises brown fine sand and silt (7.5YR4/1 – 7.5YR4/2). It is massive, with the exception of a few fine- to medium-grained sand laminae. White River tephra occurs within unit 4 at 88 cm. Unit 5 consists of laminated light olive-grey clayey silt (5Y6/1 – 5Y6/2), with laminae 1-5 mm thick. It sharply overlies unit 4.

Carbon-nitrogen plots indicate that the five units have different organic matter compositions (Figure 3.7). Differences in the slopes of the best-fit lines in Figure 3.7 suggest different organic matter types. The intercepts of the lines indicate the presence of inorganic-bound elements. For example, an excess of nitrogen indicates the presence of inorganic-bound nitrogen, probably resulting from organic matter degradation and release of NH_4^+ . This positive ion can bind to clay in the sediments, potentially decreasing the C/N ratio (Talbot 2001). The line that best fits the data from unit 1 has an r^2 of 0.70; its intercept indicates minimal excess C. The carbon-nitrogen plot separates unit 2 into two sections, 219-195 cm and 193-157 cm, with r^2 values of 0.78 and 0.92, respectively. The intercept indicates minimal excess N. The best-fit line for unit 3 has an r^2 of 0.96; its intercept is zero, indicating no elemental excess. The best-fit line for unit 4 has an r^2 of

0.85; its intercept indicates slight excess C. The lowest correlation between C and N is for unit 5 data ($r^2 = 0.66$); the intercept of the best-fit line suggests no elemental excess.

Units 1 and 3 have C/N ratios of 17-18, whereas the other three units have C/N ratios of 10-12. The C/N ratio and %C in units 1 through 4 are negatively correlated to $\delta^{13}\text{C}$ ($r^2 = 0.58$ and 0.65 , respectively). $\delta^{13}\text{C}$ shows small step shifts through the core. $\delta^{13}\text{C}$ and the C/N ratio are positively correlated in unit 5 ($r^2 = 0.81$).

Magnetic susceptibility is relatively constant from the base of the core to 130 cm, where it increases (Figure 3.5). The spike at 88 cm corresponds to the White River tephra, and peaks at 74 and 64 cm correspond to sandy laminae. Unit 5 has low magnetic susceptibility.

The gastropod *Valvata sincera sincera* is present from the base of the core to 150 cm, and pebbles are present from the base of the core to 197 cm. Wood fragments were noted at 219 and 63 cm; the former yielded an age of 3910 ± 80 ^{14}C yr BP (4570-4090 cal yr BP; Table 3.1). Average sedimentation rates are 0.04 cm yr^{-1} for units 1, 2, and 3, 0.03 cm yr^{-1} for unit 4, and 0.2 cm yr^{-1} for unit 5 (Table 3.2).

3.4.1.2 Core 10

Core 10 was retrieved from a depth of 33 m on the east side of the lake, north of Cultus Bay (Figure 3.2). It is 108 cm long and comprises five units (Figures 3.3, 3.6, and 3.8). Unit 1 (108-92 cm), unit 2 (91-69 cm), and unit 3 (68-36 cm) consist of laminated light grey silt (5Y4/1). Each of these three units coarsen downward, but contacts between the units are gradational. Unit 4 (33-19 cm) comprises brown silt with several orange laminae (2.5Y4/2). It is separated from unit 3 by a 2-cm-thick layer of White River

tephra. Unit 5 (18-0 cm) consists of light olive-grey clayey silt (5Y4/2) with diffuse orange laminae.

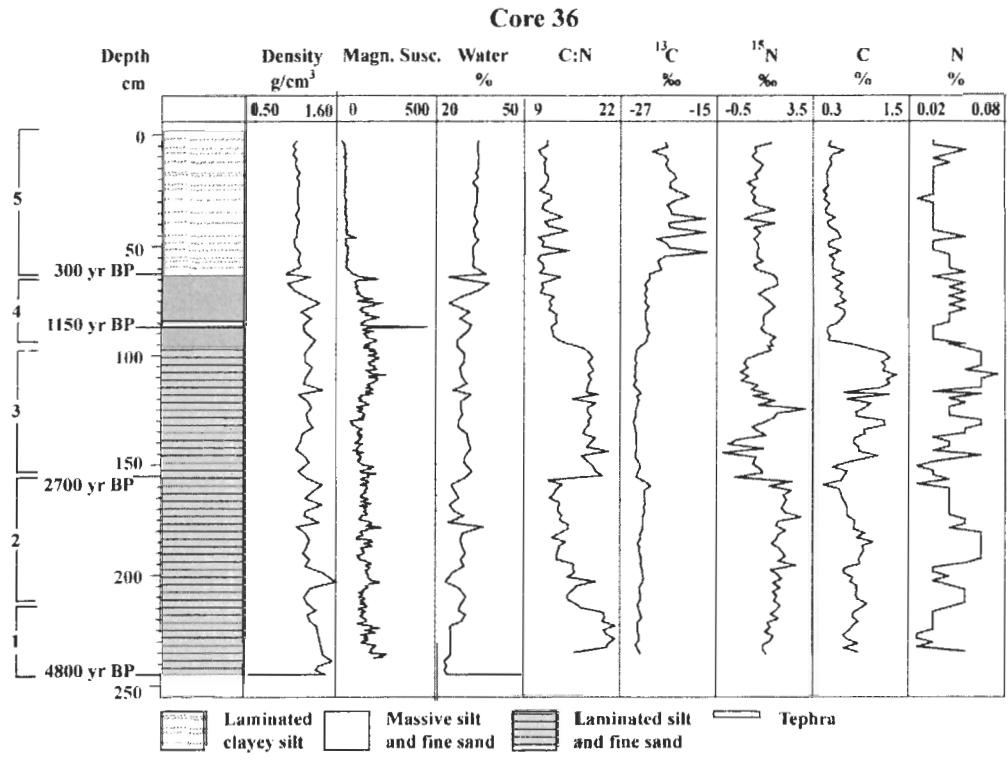


Figure 3-5 Bulk physical and organic properties and stratigraphy of core 36.

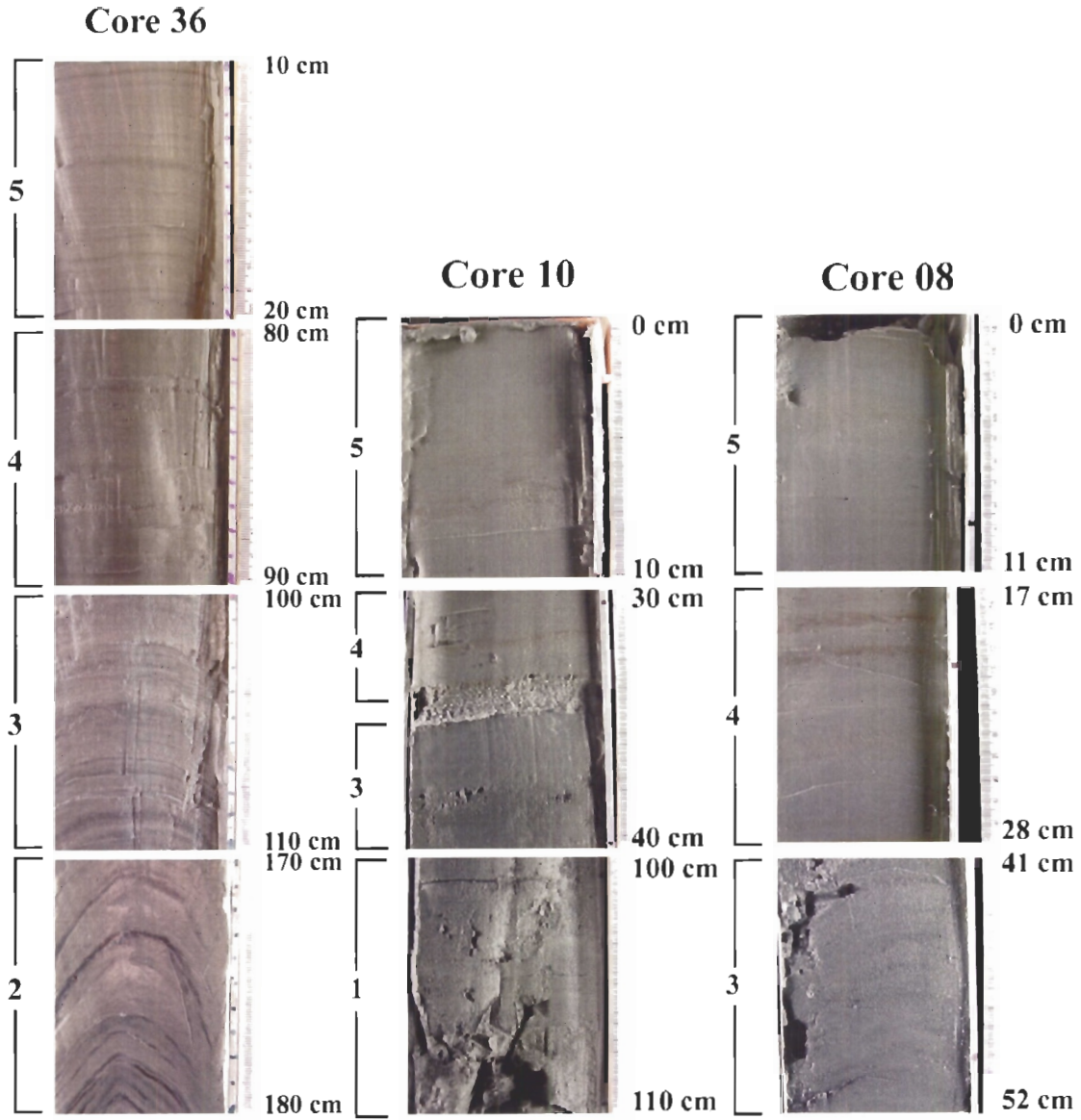


Figure 3-6 Representative photographs of sediment units in cores 36, 10, and 08.

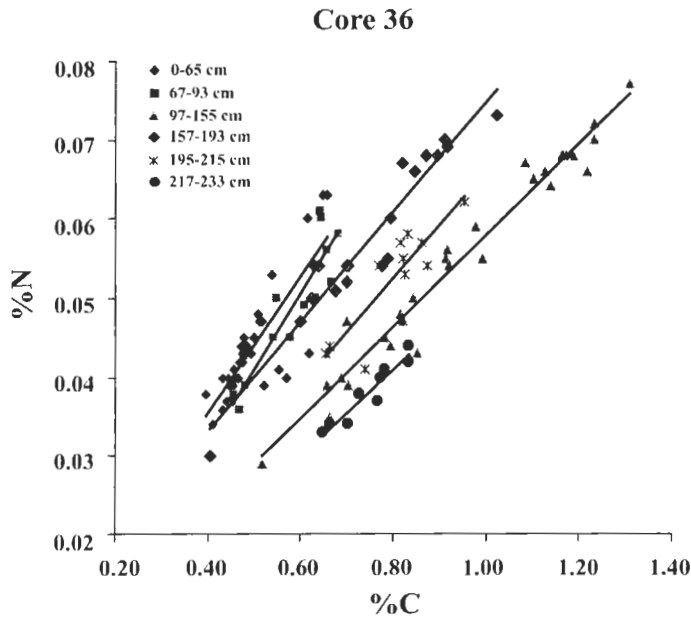


Figure 3-7 Scatter plot of %C vs. %N in core 36.

Table 3-1 Radiocarbon ages from Kluane Lake cores.

Radiocarbon ages used in this study

¹⁴ C age (yr BP) ¹	Laboratory no	Core no. and sample depth	Material	Calendar age ² (cal yr BP)
1660 ± 40	Beta - 200708	08 50.5 cm	wood	1690-1660 and 1630-1500
1180 ± 40	Beta - 200709	26 177 cm	wood	1180-980
1310 ± 40	Beta - 200710	31 103 cm	wood	1300-1170
1180 ± 40	Beta - 213014	26 139 cm	wood	1180 - 980
3910 ± 80	TO - 12468	36 219 cm	spruce needle and twig	4570-4090

¹ Radiocarbon laboratory: Beta-Beta Analytic Inc.; TO - IsoTrace Radiocarbon Laboratory (University of Toronto).

² Determined from the calibration data set IntCal98 (Stuiver et al. 1998); calibrated age ranges are reported as ± 2σ.

Table 3-2 Calculated sedimentation rates (cm/yr).

	Core 08	Core 10	Core 13	Core 36	Core 21	Core 26	Core 31
Unit 5	0.05	0.05	0.27	0.22	0.19		0.23
Unit 4	0.025	0.02	0.07	0.03	0.19	0.25	0.27
Unit 3	0.02	0.02	0.07	0.04	0.19	0.13	0.03
Unit 2		0.02		0.04	0.19		
Unit 1		0.02		0.04	0.19		

Carbon-nitrogen plots allow me to divide core 10 into six intervals, each of which has organic material of a different origin: 108-92, 91-69, 68-58, 57-36, 32-19, and 18-0 cm (Figure 3.9). The interval from 35 to 33 cm is White River tephra and was not analyzed. The best-fit lines for the data from 108 to 92 cm and 91 to 69 cm have r^2 values of 0.70 and 0.83, respectively. The best-fit lines for data from 68 to 58 cm and 57 to 36 cm have r^2 values of 0.98 and 0.93, respectively; they indicate nitrogen excesses of 0.02 and 0.018, respectively. The intervals from 32-19 cm and 18-0 cm plot together and have an r^2 value of 0.86. When corrected for elemental excesses, C/N variations in core 10 are similar to those in core 36. Unit 1 and unit 3 in core 10 have high C/N ratios, ranging from 14 to 19. C/N ratios in the remainder of the core are lower, ranging from 9 to 12.

Carbon-13 increases slightly in unit 4 and then again in unit 5. A peak in $\delta^{13}\text{C}$ in unit 5 correlates with a peak in C/N. As in core 36, $\delta^{13}\text{C}$ negatively correlates with %C ($r^2 = 0.77$) through much of core 10. The peak value of $\delta^{15}\text{N}$ (4.43‰) at 88 cm may represent instrument error. However, a smaller peak occurs at 72-64 cm, and $\delta^{15}\text{N}$ generally increases from 88 cm to the top of the core.

Sedimentation rates average 0.02 cm yr^{-1} in units 1, 2, 3, and 4, and 0.05 cm yr^{-1} in unit 5. The age of the base of the core is approximately 5000 cal yr BP. *Valvata sincera sincera* shells are present from the base of the core to 61 cm depth. Variations in water and organic contents in units 1, 2, 4, and 5 are similar, whereas in unit 3 the trends are opposite. Magnetic susceptibility and density trends are similar throughout the core. Minor peaks in susceptibility coincide with sandy laminae.

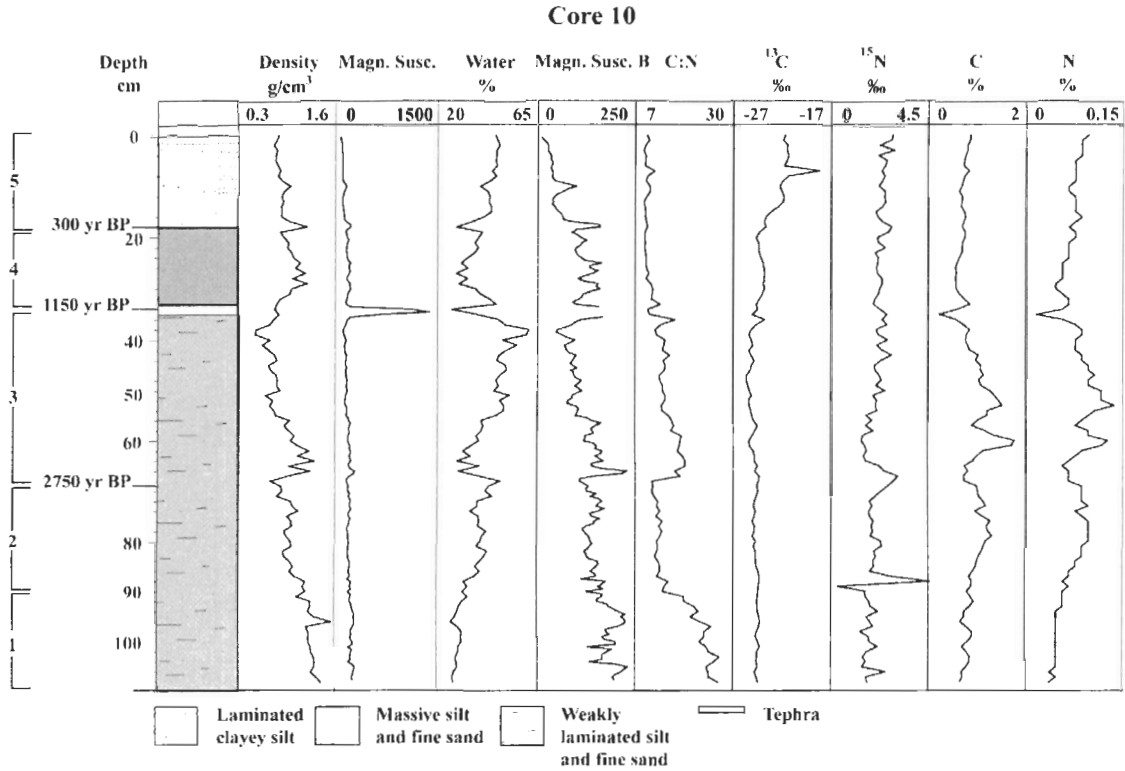


Figure 3-8 Bulk physical and organic properties and stratigraphy of core 10. The high magnetic susceptibility of the White River tephra obscures variations through the rest of the core. For this reason, magnetic susceptibility is displayed on the right with the tephra removed.

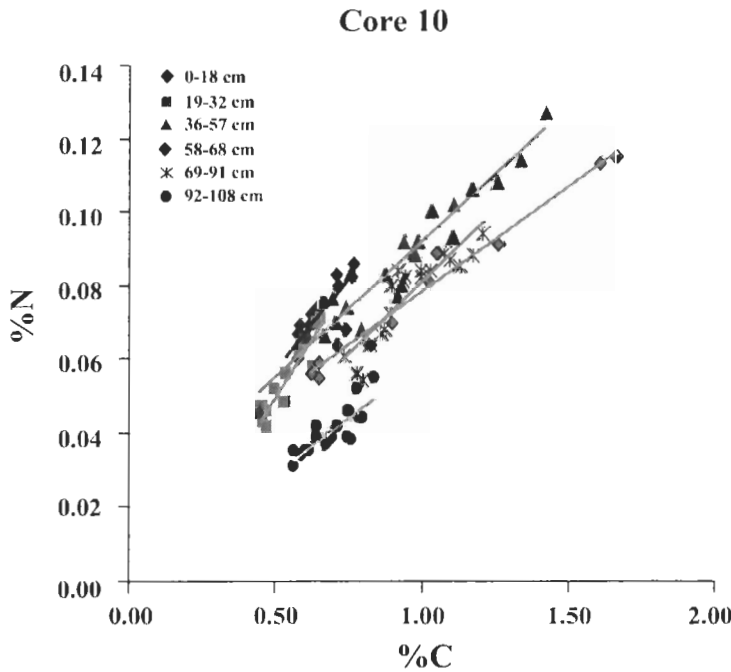


Figure 3-9 Scatter plot of %C vs. %N in core 10.

3.4.1.3 Core 08

Core 08 was collected near the east side of the lake, midway between Christmas and Cultus bays, at a depth of 25 m (Figure 3.2 and 3.3). It is 63 cm long and comprises four units (Figures 3.6 and 3.10). Material in the core catcher (unit 1) is coarse sand. Unit 2, from the base of the core to 34 cm, is laminated grey fine to medium sand (10Y2.5/1). A silty section in this, otherwise sandy unit occurs at 61-54 cm. Unit 3 (33-17 cm) interfingers with unit 3 and consists of brown laminated fine sand (2.5Y5/2 and 2.5Y3/3) with distinct orange laminae (10YR5/6). The contact between units 3 and 4 is sharp. Unit 4 (16-0 cm) comprises light laminated olive-grey silt (5Y5/2 – 5Y5/3) with pale yellow beds (5Y5/2) 1-1.5 cm thick. Density and water content change at 40 and 16 cm; water content increases and density decreases above these depths.

White River tephra occurs at 39 cm in core 08. Additional chronological control is provided by a radiocarbon age of 1660 ± 40 ^{14}C yr BP (1690-1500 cal yr BP; Table 3.1) on a piece of wood at 50.5 cm. Average sedimentation rates for units 3 and 4 are, respectively, 0.02 cm yr^{-1} and 0.03 cm yr^{-1} . The average sedimentation rate for unit 5 is 0.05 cm yr^{-1} . The base of the core is approximately 2500 cal yr BP.

3.4.1.4 Core 13

Core 13 was collected near the centre of the southern part of the lake at a depth of about 78 m (Figure 3.2 and 3.3). The core is 277 cm long and comprises three units (Figure 3.11). Unit 3 (277-140 cm) and unit 4 (139-90 cm) consist of weakly to strongly laminated dark grey silt (2.5Y4/1); these units are distinguished from correlative ages across cores as there is no visual distinction in lithology. The contact between units 4 and

5 is abrupt. Unit 5 (89-0 cm) consists of laminated light grey silt and clay (5Y6/2 – 5Y5/2).

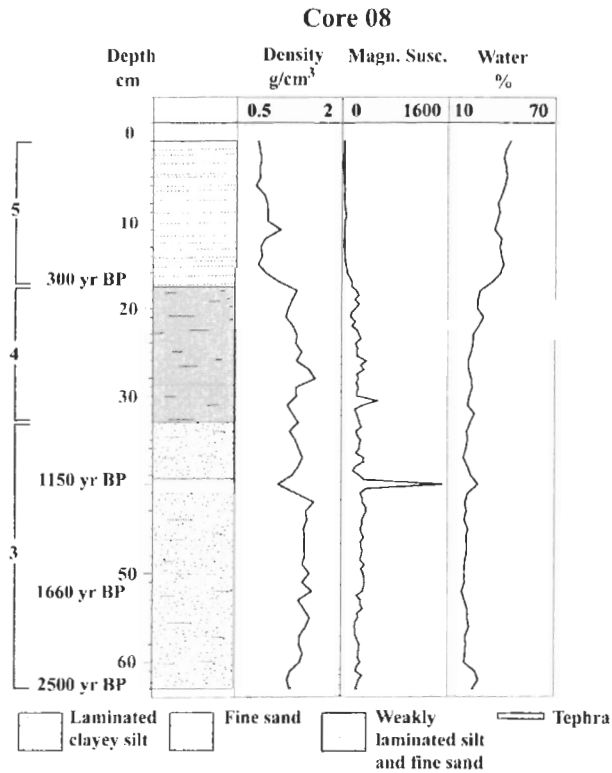


Figure 3-10 Bulk physical properties and stratigraphy of core 08.

Water content and percent carbon decrease upward through unit 1. Fragments of degraded wood were found from the base of the core to 170 cm. White River tephra occurs at 140 cm depth. Sedimentation rates are approximately 0.07 cm y⁻¹ in unit 1 and 0.27 cm y⁻¹ in unit 2. The base of the core is about 2700 cal yr old.

Magnetic susceptibility in core 13 is highest between 218 and 195 cm (ca. 2200-1900 cal yr BP), an interval with several black laminae. This interval is also marked by lower water content and higher density. Peaks in magnetic susceptibility at 111 and 90

cm correspond to two sandy intervals, which probably correlate with the sandy laminae at 74 and 64 cm in core 36.

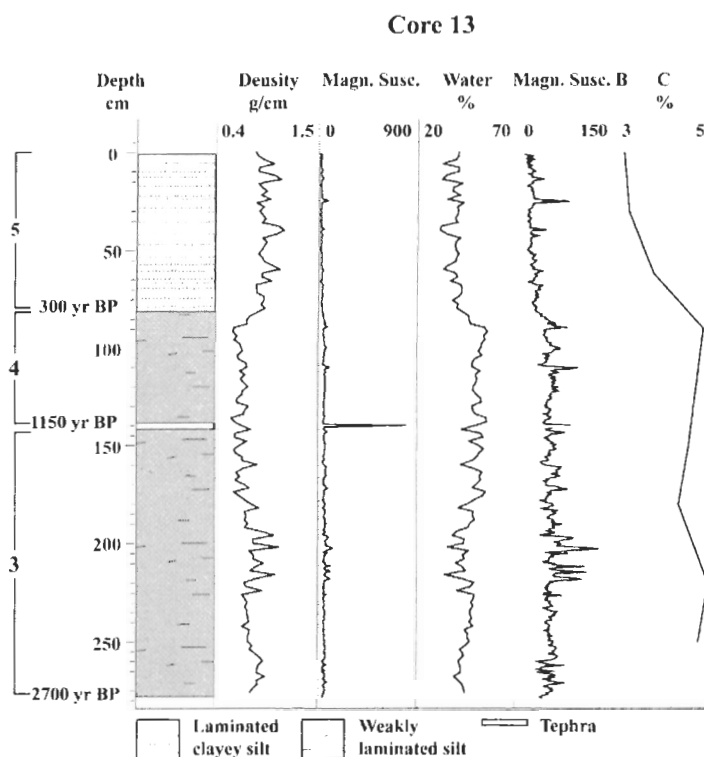


Figure 3-11 Bulk physical properties and stratigraphy of core 13.

3.4.1.5 Core 26

Core 26 was collected in Cultus Bay in about 14 m of water (Figure 3.2). A breached spit separates Cultus Bay from Kluane Lake. The core is 180 cm long and consists of five units (Figures 3.4, 3.12, and 3.13). Unit 1, which extends from the base of the core to 156 cm, is coarse sand with a layer of plant detritus at 177 cm. Its contact with unit 2 is sharp. Unit 2 (155-140 cm) consists of fine and medium sand with scattered plant macrofossils. Unit 3 (139-53 cm) is grey silt (5Y2.5/1 – 5Y3/1) with minor fine sand laminae. Several black streaks and laminae were noted near the base of the unit.

Roots in growth position and plant detritus occur at about 133 cm. Pieces of wood at 177 and 139 yielded identical radiocarbon ages of 1180 ± 40 ^{14}C yr BP. (1180-980 cal yr BP; Table 3.1). Unit 4 (52-42 cm) comprises 22-25 couplets of light grey silt (5Y5/1). Unit 5 (41-0 cm) is weakly laminated light grey silt (5Y2.5/1 – 5Y4/1) with scattered black spots and streaks. A distinctive bed of silt with low organic content and sharp upper and basal contacts occurs at 39-37 cm. Sedimentation rates in units 3 and 4 are, respectively, 0.13 and 0.25 cm yr^{-1} .

Magnetic susceptibility increases in steps from 55 to 43 cm and from 40 to 37 cm due to the presence of reworked tephra. A lesser susceptibility peak also occurs at 73-67 cm. Sediment density and $\delta^{13}\text{C}$ correlate positively with magnetic susceptibility, peaking at 73-67, 55-43, and 40-37 cm. Carbon-13 and %C are negatively correlated, and $\delta^{13}\text{C}$ correlates positively with C/N. C/N ratios are high in unit 4, with peak values of 17. C/N ratios are low and nearly constant in unit 5, ranging from 10 to 11. Percent C and N are highest in unit 5. They are highly correlated from 43 to 0 cm ($r^2 = 0.98$); the intercept of the best-fit line is zero, indicating no elemental excess. They are also highly correlated from 54 to 44 cm ($r^2 = 0.99$). Nitrogen-15 increases steadily from the base of the core to 126 cm, but is relatively constant from there to unit 4. $\delta^{15}\text{N}$ increases steadily in unit 5 to its highest value at the top of the core.

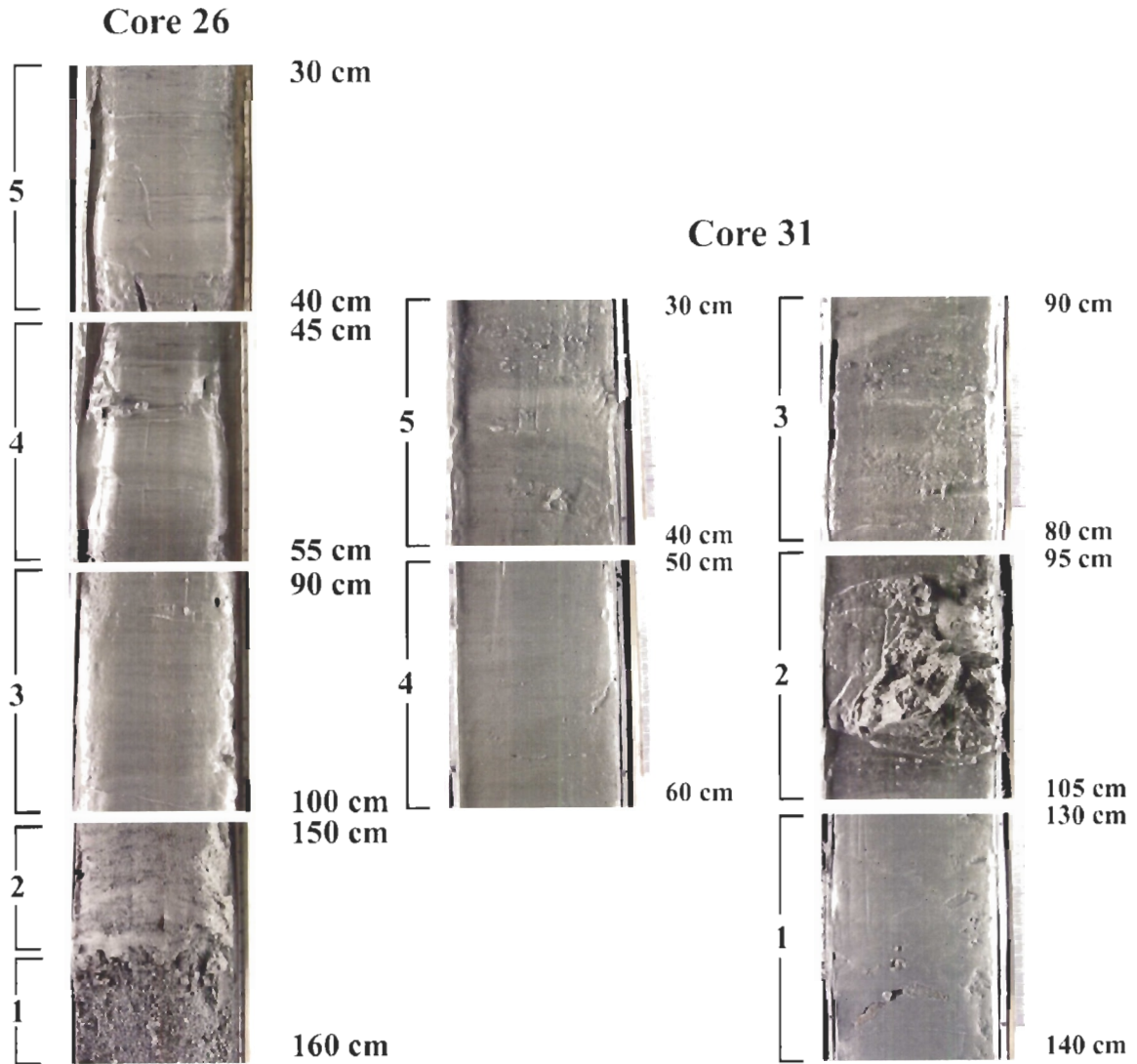


Figure 3-12 Representative photographs of sediment units in cores 26 and 31.

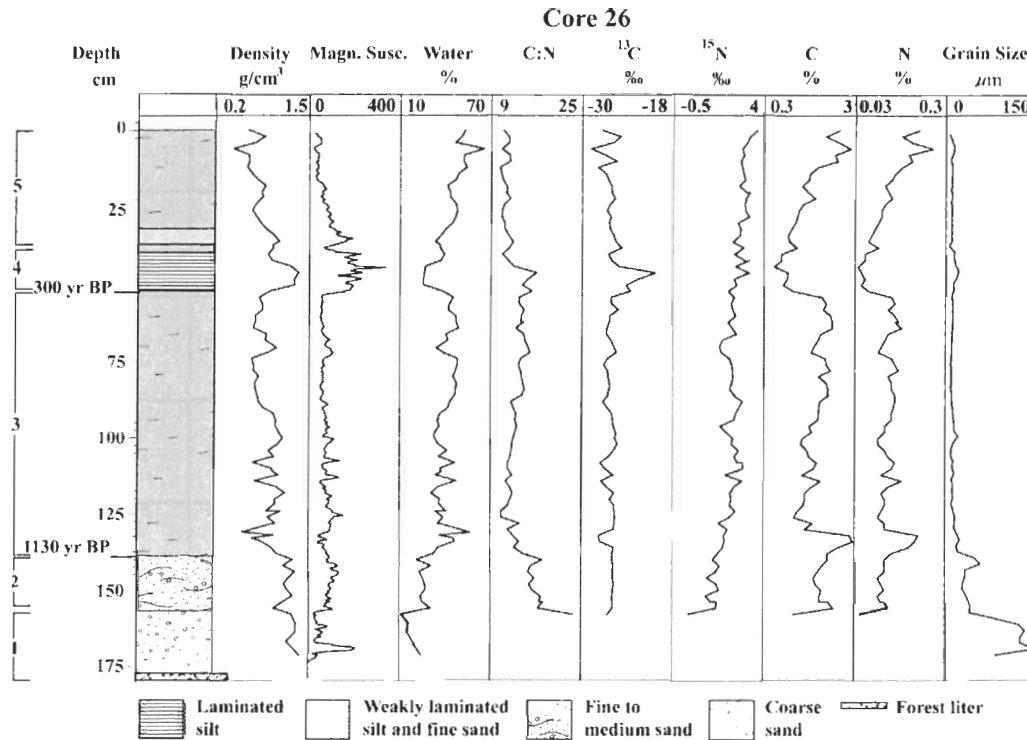


Figure 3-13 Bulk physical and organic properties and stratigraphy of core 26.

3.4.1.6 Core 31

Core 31 was collected in 12 m of water in the deepest part of Grayling Lake (Figure 3.2). Grayling Lake is a small basin adjacent to, but separate from, Kluane Lake and Cultus Bay. The core is 167 cm long and comprises five units (Figure 3.4, 3.12, and 3.14). Unit 1, which extends from the base of the core to 106 cm, is dense laminated light grey silt (5Y4/1). Unit 2 (105-98 cm) is a soil with abundant roots in growth position. The soil contains fungal hyphae, roots casts, and root oxidation rings. An in situ woody root recovered from the soil yielded a radiocarbon age of 1310 ± 40 ¹⁴C yr BP (1300-1170 cal yr BP; Table 3.1). Unit 3 (97-76 cm) is an organic-rich poorly laminated silt containing many wood fragments. The contact with unit 4 is gradational. Unit 4 (75-50 cm) consists of light grey silt. Unit 5 (49-0 cm) is weakly laminated, dark grey silt. The

contact between units 4 and 5 is sharp and undulating. The average sedimentation rate for unit 4 is 0.27 cm yr^{-1} , similar to the average sedimentation rate for the correlative unit in Cultus Bay. Sedimentation rates for units 3 and 5 are, respectively, 0.03 and 0.23 cm yr^{-1} . Magnetic susceptibility peaks at 94-89 cm in unit 3 and at the base of unit 4, the latter due to the presence of reworked tephra in this unit. Small increases in density and a decrease in water content are evident from 96 to 88 cm and at 32 cm.

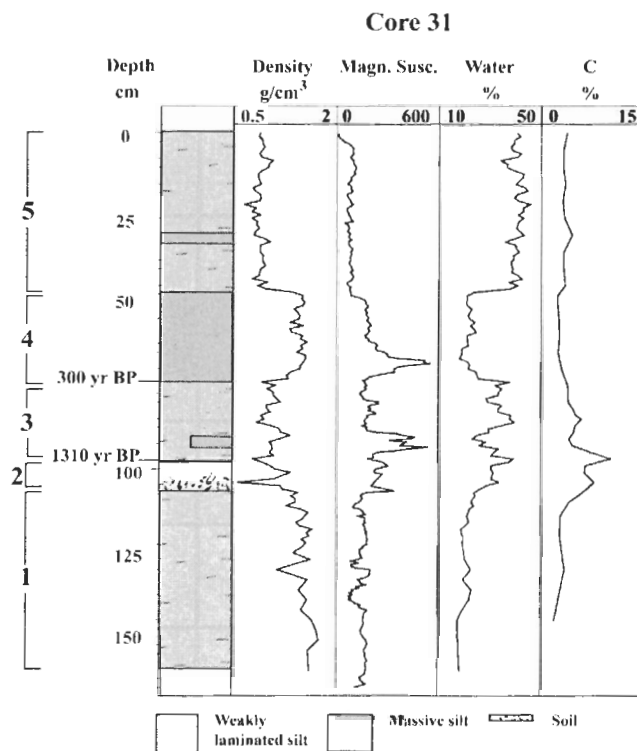


Figure 3-14 Bulk physical properties and stratigraphy of core 31.

3.4.1.7 Core 21

Core 21 is one of three cores collected south of Jacquot Island (Figures 3.2 and 3.3). It was retrieved from 33.5 m of water, is 250 cm long, and consists of two units

(Figure 3.15). The lower unit, which extends from the base of the core to 25 cm is massive to weakly laminated grey silt (5Y3/1) with laminae of fine to very fine sand. Density decreases and water content increases upward through the unit. The upper unit consists of laminated silt ranging in colour from orange to grey (10YR5/4, 10RY3/2, 5Y5/1, 2.5Y5/4). The contact between the two units is gradational. Numerous fine sand event laminae occur from 190 to 155 cm. Density increases and water content decreases upward through this interval. The White River tephra occurs at 223 cm. The average sedimentation rate for the core is 0.2 cm yr^{-1} , giving an extrapolated basal age of about 1200 years. Peaks in magnetic susceptibility occur at 120 and 5 cm without any visible lithologic indicators.

3.4.1.8 Core 19

Core 19 was collected at the north end of the lake at 32 m depth (Figure 3.2 and 3.3). The core is 244 cm long and consists entirely of massive grey silt (2.5Y4/1 – 2.5Y3/1) with scattered plant detritus, some of which appears black and sulfurized (Figure 3.16). White River tephra occurs at 130 cm depth. Peaks in magnetic susceptibility correspond to intervals with sulfurized organic detritus, lower water content, and higher density. In general, water content increases upward. Surface sediments were lost during coring, thus sedimentation rates cannot be calculated.

3.4.1.9 Core 23

Core 23 was collected 2 km northwest of core 21 in 38.5 m of water. The core is 292 cm long and consists of massive to weakly laminated grey silt (5Y4/1 – 5Y3/1) (Figure 3.17). High magnetic susceptibility is associated with black streaks, probably

sulfurized organic matter, in the otherwise grey sediments. Water content is higher, and density lower, in the upper 140 cm of the core. White River tephra occurs at 31 cm. Surface sediment was lost during coring, thus an average sedimentation rate cannot be calculated.

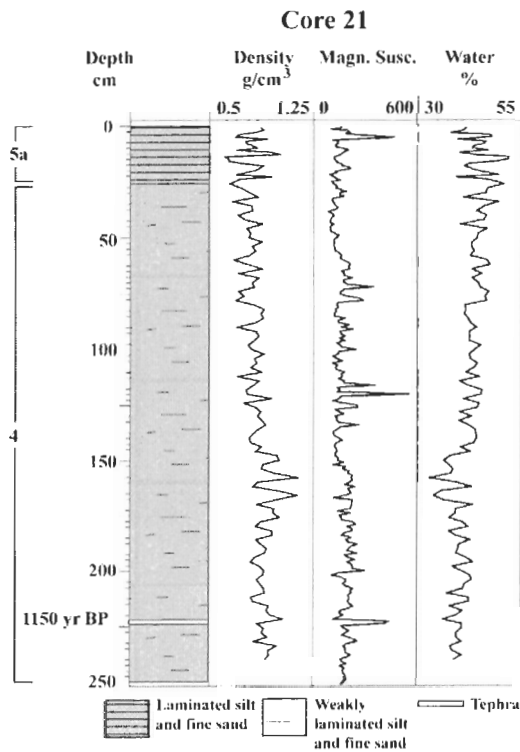


Figure 3-15 Bulk physical and organic properties and stratigraphy of core 21.

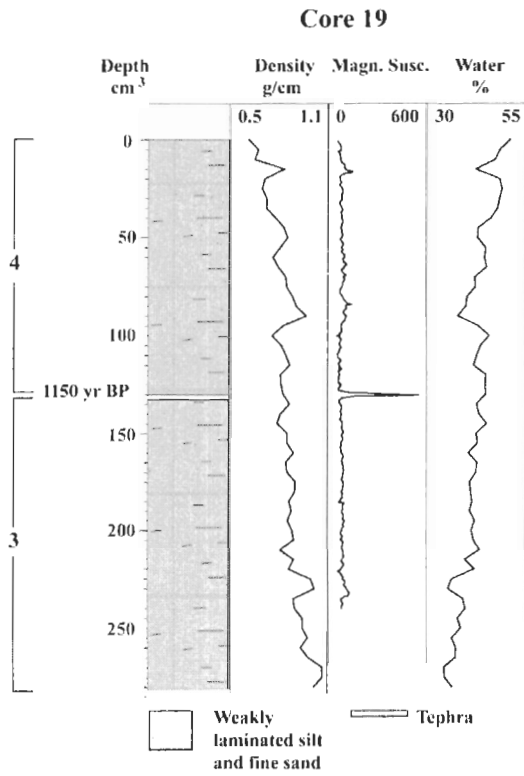


Figure 3-16 Bulk physical and organic properties and stratigraphy of core 19.

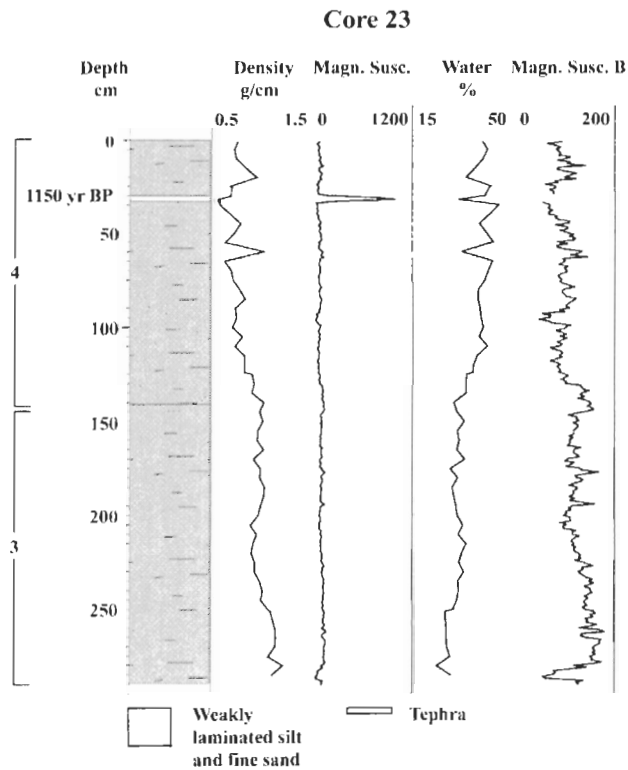


Figure 3-17 Bulk physical and organic properties and stratigraphy of core 23.

3.5 Discussion

Physical, chemical, and biological properties of lake sediments provide information on a variety of environmental parameters. Organic matter provenance, productivity, nutrient availability, and depositional conditions can be inferred from carbon and nitrogen concentrations as well as isotopic and elemental ratios. Organisms living in lakes have specific physical and chemical requirements; their body parts preserved in sediments provide information on environmental conditions.

Paleo-lake depth can be inferred from sediment properties sensitive to proximity to the shore, for example terrestrial organic matter, or to depositional energy, for example grain size. A gradual coarsening of sediment could signal a decrease in water depth. No single environmental proxy is definitive, thus a multi-proxy approach must be employed to reconstruct the history of lake-level fluctuations and other environmental conditions.

3.5.1 5000-2700 cal yr BP

Carbon/nitrogen ratios at the base of cores 10 and 36 range from 16 to 27, indicating the presence of terrestrial organic matter or nitrogen limitation in the lake (Meyers and Eadie 1993, Brahney et al. 2006). This period lasted from about 4800 to 4200 cal yr BP. The high flux of carbon at this time may result from lake-level lowering and re-suspension of sediments from the lake margins, or from higher runoff and in-wash of terrestrial organic matter. The former explanation is unlikely because productivity is low in shallow water at the margins of Kluane Lake. However, at a lower lake level, site 36 may have been closer to shore and thus a depocenter of increased sedimentation of terrestrial organic matter (Tenzer et al. 1997). The C/N ratio may have become elevated, in part, due to the loss of ammonia gas through degradation of the organic matter in the

sediments. A correction based on the carbon excess places the C/N ratio at about 18, higher than in most algal sources but still within the range of terrestrial vegetation. This result suggests that lake level may have been relatively low during this period, rising shortly thereafter. Wood fragments and stones below 219 cm also suggest lower lake levels than today. Similarly, coarser sediment near the base of core 10 suggests a lower lake level about 5000 cal yr BP. By 215 cm depth in core 36 and 91 cm depth in core 10, C/N ratios decrease to values characteristic of aquatic organic matter (6-10), suggesting an increase in lake level. The increase was probably not greater than a few metres, because core 08 does not indicate deep-water sedimentation at this time. In addition, Cultus Bay and Grayling Lake did not exist at this time, suggesting that lake level was below -14 m.

3.5.2 2700 to 1300 cal yr BP

A step-shift increase in C/N ratios, from 12 to 19, occurs in core 36 from at ~2700 and remains high until 1300 cal yr BP; a similar step-shift increase, from 10 to 17, occurs in core 10 at ~3000 and remains high until 1350 cal yr BP. Grain size data from core 36 indicate a shoaling at 2700 cal yr BP (153 cm), followed by further shoaling at 1850 cal yr BP (117 cm). Sediment fingerprinting in Chapter 2 is consistent with these results and indicates a gradual reduction in Duke River sediment in core 36 from 2700 to 1850 cal yr BP (153-117 cm) and little or no contribution of sediment from Slims River at that time. Duke River may have completely bypassed Kluane Lake between 1850 and 1300 cal yr BP (117-97 cm).

As sediment becomes coarser, its water content generally decreases due to a decrease in pore space; this change is also accompanied by an increase in dry density

(Menounos 1997). Increased organic content would also influence these properties by increasing pore space and water content, and decreasing density. If density and water content are taken to reflect subtle changes in grain size, then a shoaling between 2750 to 2000 cal years BP (68-53 cm in core 10).

Core 08 is the shallowest core and thus is likely to be most sensitive to lake level fluctuations. The presence of coarse sand in the core catcher and fine sand layers in unit 3 indicates that the lake may have been close to -20 m about 2500 year ago. At present, sand is deposited mainly in water depths less than 5 m, grading to silt between 5 and 10 m depth.

Paleoclimate data from this region indicate that the period from 2800 to 1300 cal yr BP was colder and wetter than today (Anderson et al. 2005). Reduced or no inflow from Slims and Duke rivers would have kept Kluane Lake low, while increased run-off from small streams could have contributed more terrestrial organic matter to the lake without significantly raising its level. This situation could explain the observed increases in %C and C/N during this period. The high carbon/nitrogen ratios are probably not due to organic degradation because C and N values are at their highest levels in core 36. More likely, anoxia in the basin at this time contributed to the preservation of organic material. Anoxia is supported by the absence of the gastropod *Valvata sincera sincera* above 150 cm in core 36 and above 61 cm in core 10. This species lives at depths from 1 m to >30 m and thus is not a useful direct indicator of lake level. It is, however, limited by food and oxygen availability. Magnetic susceptibility is relatively high between 218 and 195 cm in core 13, coincident with visible black laminae. This interval dates to ~2200 to 1900 cal yr

BP. The black laminae and what appear to be scattered sulfidic organic remains and are likely responsible for the elevated magnetic susceptibility.

Increases in %C and %N from 2700 to 1300 cal yr BP in cores 36 and 10 cannot be explained by heightened productivity because $\delta^{13}\text{C}$ decreases during this period. Heightened productivity would likely enrich $\delta^{13}\text{C}$ through a more intense use of the available carbon pool. Instead, $\delta^{13}\text{C}$ and %C are negatively correlated in units 3, 4, and 5 of core 36 ($r^2 = 0.65$). The two are also negatively correlated in core 10 ($r^2 = 0.77$).

$\delta^{13}\text{C}$ is in the -24 to -25‰ range in units 1, 2, and 4 of core 36, and a small step-shift to more depleted values occurs in unit 3. A shift to more negative $\delta^{13}\text{C}$ in lake sediments is commonly attributed to selective degradation of isotopically heavy proteins and carbohydrates. This explanation, however, is unlikely in the case of Kluane Lake, because %C and %N values during this period are the highest in the core and scatter plots do not indicate any elemental excess. If we assume that the high C/N ratios in unit 3 are derived from terrestrial organic matter and not nitrogen-limited algae, the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values reflect the isotopic composition of terrestrial plants. The aquatic organic matter is then slightly enriched in $\delta^{13}\text{C}$ relative to the terrestrial vegetation. $\delta^{13}\text{C}$ from aquatic organic matter and from plants in the same watershed is generally indistinguishable because the aquatic and terrestrial plants produce organic matter from the same atmospheric CO_2 source. A difference requires a dissolved inorganic carbon source that is not in equilibrium with the atmosphere. Increased productivity may shift the $\delta^{13}\text{C}$ to higher values through intense use of the available carbon pool, but productivity in Kluane Lake probably was never high. Disequilibrium from the atmosphere could stem from

enriched dissolved inorganic carbon supplied from the watershed, leaving the terrestrial and aquatic organic material with different signatures.

A drop in $\delta^{15}\text{N}$ in unit 3 is consistent with a terrestrial organic matter source. Terrestrial plants have an atmospheric nitrogen source of 0‰. In contrast, aquatic organisms use a NO_3^- source that is generally more enriched. The shift to values as high as 3‰ within this interval probably does not reflect terrestrial organic matter. The value is not spurious as duplicates were run for this interval and $\delta^{15}\text{N}$ values increase and decrease gradually. The high $\delta^{15}\text{N}$ values may reflect terrestrial organic matter that has been modified by lacustrine processes. Under mildly reducing conditions, $\delta^{15}\text{N}$ can increase through the release of isotopically light N_2 gases during organic degradation (Talbot 2001). The $\delta^{15}\text{N}$ peak precedes peaks in elements that indicate highly reducing conditions (Chapter 2).

Despite the suggestive evidence of lake-level lowering at this time, the abrupt step shift in C/N is perplexing. Nitrogen limitation can, however, raise the C/N ratio to within the range of terrestrial organic matter. Reduced nitrogen input into the lake may have occurred due to permafrost expansion in the watershed. The area is presently within the zone of discontinuous permafrost. Permafrost was likely more widespread 2700-1300 cal yr ago when climate was colder than today. Under these circumstances, nitrogen may have been less available due to slow nitrogen mineralization (Heilman 1966, Bonan 1990). Permafrost can also contribute dissolved organic carbon to the lake by focusing flow through shallow soil layers.

If we assume that the organic proxies during this period are controlled by nitrogen-limited aquatic organic matter, we must still explain the step-like isotopic shift

in dissolved inorganic carbon in the lake water. Carbon dioxide solubility increases in colder water. With more available CO₂, isotopic discrimination between the inorganic carbon and biotic carbon will decrease as the lighter isotope of carbon is more available. In addition, isotopically light carbon from the watershed may decrease the overall isotopic values of the inorganic carbon in the lake. Respired carbon from organic soils would be isotopically lighter than dissolved inorganic carbon supplied from the atmosphere. The sudden isotopic shift is thus more likely the result of a change in the extent of permafrost in the watershed than a fall in lake level, which would probably take more time. Geochemical evidence in core 36 suggests that permafrost may have expanded at this time (Chapter 2).

3.5.3 1300-300 cal yr BP

Environmental proxies in unit 2 of core 36 are consistent with rising lake level about 1300 yr ago. Specifically, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ increase, and C/N, % organics, and grain size decrease. Scattered fragments of wood were found in core 13 from its base to 160 cm, which dates to about 1450 cal yr BP, suggesting that the lake rose on or after this time. Results in Chapter 2 indicate that Duke River began to flow into the lake at about this time. Sedimentation rates in the northern part of the lake are higher than in the southern part from 1200 to 300 cal yr BP, consistent with an important northerly sediment source.

Sediment in core 08 begins to fine at 34 cm, suggesting a deepening of the lake about 900 cal yr BP, after deposition of the White River tephra. A similar change occurs in core 36, but before deposition of the tephra; the change in core 10 is almost coincident with tephra deposition. The diachronous nature of the contact is due to the different

depths of the cores. The water depth at site 08 is 25 m, which is 10 m less than at sites 36 and 10. Because the transgression was diachronous, silt began to accumulate at site 08 after sites 36 and 10.

Density and water contents change in two steps in core 08. A small shift to lower densities and higher water content occurs at 34 cm. A more substantial shift in the same direction occurs at 16 cm, the contact with unit 5. The data suggest a gradual deepening of the lake, followed by more substantial deepening when the modern Slims River became established.

Grain size in core 23 decreases from 130 cm to the top of the core. This change is accompanied by an increase in water content and a decrease in density. These changes probably reflect deepening of the lake. Unfortunately, surface sediment is missing from this core, thus the timing of the change cannot be precisely determined. The White River tephra, however, lies above 130 cm. Assuming the same sedimentation rate as at nearby core site 21, the 130-cm level dates to 1300 cal yr BP.

3.5.4 300 cal yr BP - present

Grain size decreases in the upper unit of cores 36, 10, and 08, suggesting a further increase in lake level. No decrease in grain size is evident in the upper part of core 13, but it is the deepest core and thus less sensitive to changes in lake level. The upper unit in cores 36, 10, and 08 also shows an increase in water content and, in the case of cores 36 and 10, a decrease in C/N.

$\delta^{13}\text{C}$ and C/N increase in the upper unit of core 36 ($r^2 = 0.82$), perhaps due to the contributions of DIC from carbonate in sediment in the Slims River watershed and

carbon from C₄ plants growing on the Slims River delta. The close correlation between $\delta^{13}\text{C}$ and C/N suggests that peaks in both may be related to terrestrial plant matter. The low correlation between %C and N may, in turn, reflect derivation from a mixture of aquatic and terrestrial plants, which is not surprising given that Slims River was newly established and lake level was rising. Rising waters inundated vegetated land, washing more terrestrial organic detritus into the lake. Wood fragments are abundant at the bottom of the upper unit in both cores 10 and 36. $\delta^{13}\text{C}$ values are high, around -17‰, and are nearer those of C₄ plants than C₃ plants. C₃ plants incorporate carbon into their biomass using the Calvin pathway. Both C₄ and C₃ plants preferentially take in ¹²C, with an isotopic discrimination of -12‰ from the dissolved inorganic carbon source in C₃ plants, giving an average isotopic value of -28‰. Provided both sources of carbon are in equilibrium with atmospheric $\delta^{13}\text{C}$ at -7‰, C₄ plants use the Hatch-Slack pathway, which causes a 7‰ discrimination and gives these plants an average isotopic value of -14‰ (O'Leary 1988). The measured $\delta^{13}\text{C}$ values of about -17‰ could represent a mixture of the two plant types. C₄ plants are rare at this latitude, but several species of halophytes use the C₄ pathway. Some of the plants living on the Slims River delta and floodplain are halophytes and could be the source of the isotopic shift in the upper unit of cores 10 and 36. Unfortunately, no specific metabolic information is available for the species that live on the Slims delta.

3.5.5 Short-term changes in lake level over the past 1000 years

Sediments at the base of core 26 from Cultus Bay record a change from terrestrial to lacustrine conditions. Wood fragments from the base of the core yielded an age of 1180 ± 40 ¹⁴C yr BP (1180-980 cal yr BP). The core was collected in 14 m of water, thus

Kluane Lake rose above -14 m at that time. The high C/N values near the base of core 26 record the transgression of the Cultus Lake basin. Similarly, Grayling Lake sediments were deposited on a buried soil at -12 m after 1310 ± 40 ^{14}C yr BP (1300-1170 cal yr BP).

The brief +12 m high stand of Kluane Lake is clearly visible in unit 2 of both cores. Increases in C/N and magnetic susceptibility reflect in-washing of terrestrial organic matter from the surrounding slopes. An increase in $\delta^{13}\text{C}$ at this time is consistent with the enrichment in the main lake basin after inception of the Slims River.

Similar changes in sediment type are observed at 73-67 cm and 40-37 cm in core 26, and at 96-89 cm and 32 cm in core 31. These intervals are characterized by elevated magnetic susceptibility, density, and $\delta^{13}\text{C}$, and low water content, and may record short-lived rises in water level (see also Chapter 2).

C/N values near the top of core 26 suggest a return to aquatic organic sedimentation after the high stand. %C, %N, and $\delta^{15}\text{N}$ achieve their highest values near the top of core 26, possibly reflecting an increase in productivity from maturation of Cultus Bay. Aquatic organisms will preferentially use the lighter nitrogen isotopes. Thus an increase in $\delta^{15}\text{N}$ could occur through the progressive removal and burial of organic matter in sediments. An increase in both productivity and $\delta^{15}\text{N}$ could also be related to spawning salmon, which first entered the lake about 300 cal yr ago, when the northern outlet was established.

3.5.6 Summary of level changes over the past 5000 years

Fluctuations in the level and areal extent of Kluane Lake during the late Holocene are the result of changes in Slims and Duke River inflow, which in turn are linked to glacier and climate change. To summarize, in sequence (Figure 3.18):

Kluane Lake has been higher than about -27 m for the past 5000 years, because lacustrine conditions have persisted throughout this period at core site 36. Sand occurs on the modern lake floor to a depth of 5 m; below that, it grades into silt at 10 m depth (Rampton and Shearer 1978b). Silty sediments dominate core 36, which was collected from a depth of 37 m, thus I infer that a minimum of 10 m of water continuously covered that site throughout the time span of the core. The presence of fine sand near the base of core 10 suggests that lake level may have been between -27 and -22 m about 5000 cal yr BP. High C/N ratios near the base of cores 10 and 36, and the upcore decrease in grain size in core 10 further suggest that lake level was lower than -20 m and rising around 4000 cal yr BP. The rise probably was no more than a few metres and the lake was no higher than -14 m at that time, a constraint imposed by cores 08, 31, and 26.

A fall in lake level between 2900 and 2700 cal yr BP is suggested by an increase in grain size and C/N ratios in core 36 at this time and by the increase in C/N ratios and dry density in core 10. Again, the change in lake level probably was not more than a few metres. Core 08 indicates that lake level may have been between -20 and -25 m, as sand was deposited at this site 2500 cal yr BP. Data presented in Chapter 2 suggest that this lowering of the lake is related to a reduction or elimination of flow of Duke River into Kluane Lake. Further lake level lowering and the development of anoxia about 2000 cal yr BP are suggested by the increase in grain size in core 36 and disappearance of *Valvata*

sincera sincera in cores 10 and 36. However, the lake did not fall below -27 m 2000 cal yr BP because lacustrine sedimentation continued at core site 36. This result is inconsistent with Rampton and Shearer's (1978b) interpretation of the ca. 2000-year-old peat layer they found at -50 m in a core near the south end of Kluane Lake. It is possible, however, that the peat layer is not terrestrial or, alternatively, that it slumped to the core site from a shallower depth.

Cores 08, 26, 31, 10, 36, 13, and 23 provide evidence for a rise in lake and groundwater levels between 1300 and 900 cal yr BP. Increases in $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$, and decreases in C/N, % organics, and grain size in unit 2 of core 36 are consistent with lake deepening. The Grayling Lake and Cultus Bay cores show that the lake rose above -14 m about 1300 to 1200 cal yr BP. Geochemical data presented in Chapter 2 indicate that Duke River began to flow into Kluane Lake about 1300 cal yr BP and continued for several centuries, causing the lake to rise. Inflow of Duke River water during this period is consistent with sedimentation rates in cores at the time of deposition of White River tephra. Sedimentation rates are higher at core site 21 in the central part of the lake and nearer Duke River than at core sites farther south. The transgression may have been slow because the Duke River sediment signature appears at different times at the core sites, depending on their depths. Rampton and Shearer (1978b) did not find tephra in a core taken at 12 m depth, suggesting that the lake may have been at or below -12 m about 1150 cal yr BP. By AD 1650, however, the lake had risen to its present level due to diversion of Kaskawulsh Glacier meltwater into Kluane Lake (Clague et al. 2006). The influx of meltwater is clearly recorded by sediments of Slims River origin in all cores taken from the southern part of the lake. By about AD 1700, Kluane Lake achieved its

Holocene high stand of +12 m and soon thereafter began to fall as its new, northern outlet was incised. The short-lived nature of the high stand is indicated by the thin, laminated, inorganic silt unit overlying shallow-water organic-rich sediments in the Grayling Lake and Cultus Bay cores.

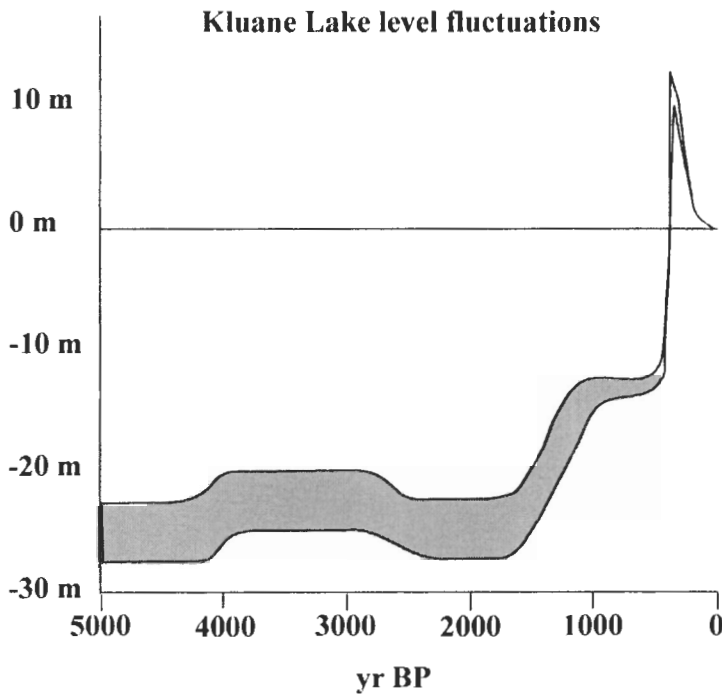


Figure 3-18 Inferred Kluane Lake level fluctuations over the past 5000 years.

3.5.7 Evidence for a pre-5000 yr BP high stand of Kluane Lake

Dense, laminated silt underlies the soil in the Grayling Lake core. The silt must have been deposited in a previous high-stand of Kluane Lake. This early lake is also suggested by the sub-bottom acoustic record from Brooks Arm. The acoustic record shows laminated sediments beneath ~1 m of modern lacustrine sediments (R. Gilbert, personal communication, 2005). A conspicuous acoustic reflector separates the two units and probably represents a prolonged period of non-deposition. Brooks Arm is shallow, 5 to 10 m, and was not flooded until the recent rise in lake level. The sediments above the

reflector were deposited during the past 350 years. The sediments below the reflector must be much older because, except for the past several hundred years, Kluane Lake has been below -5 m for at least the past 4800 years.

3.6 Conclusion

Kluane Lake has experienced complex and rapid fluctuations in its level and areal extent over the past 5000 years, primarily due to changes in input of waters from Slims and Duke rivers. From 5000 to 4200 cal yr BP, Kluane Lake was 22 to 27 m shallower than today. Lake level increased a few metres around 4200 cal yr BP and may have remained at that level until 2700 cal yr BP, when it fell several metres. A further small decrease in water level may have occurred around 1850 cal yr BP. About 1300 cal yr BP, the level of the lake rose from -14 m to -12 m as a result of the diversion or increased flow of Duke River into Kluane Lake. Several lines of evidence suggest thawing of permafrost around 1300 cal yr BP. The level of Kluane Lake level rapidly rose to +12 m about 300 cal yr BP after when Slims River began to flow into the lake. The lake has been within 2 m of its present level over the past 150-200 years. During much of the late Holocene, slow nitrogen mineralization in the watershed may have limited nitrogen in the lake.

3.7 Acknowledgements

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CHAPTER 4 PRESENT AND PAST ISOTOPE HYDROLOGY OF KLUANE LAKE AND SURROUNDING AREA.

4.1 Abstract

I reconstructed modern hydrologic processes in the Kluane Lake watershed in southwest Yukon Territory by analyzing samples of precipitation, lake water, and water from streams for oxygen and hydrogen isotopes. Changes in hydrology in the watershed over the past 1000 years were inferred from cellulose $\delta^{18}\text{O}$, bulk physical properties, and carbon and nitrogen elemental abundances in sediment cores extracted from Kluane Lake. The data indicate that Kluane Lake has been influenced by changes in synoptic climate patterns and by marked changes in the flow patterns of Slims and Duke rivers. Over the past 1000 years, the level of Kluane Lake has fluctuated by about 20 m. Corresponding shifts in the local groundwater table have affected adjacent small lakes, causing an alternation of open and closed basin conditions and localized reversals in groundwater flow.

4.2 Introduction

The level of Kluane Lake, southwest Yukon Territory (Figure 4.1), has fluctuated by several tens of metres during the late Holocene (Bostock 1969, Rampton and Shearer 1978a, b, Clague 1981, Clague et al. 2006; Chapters 2 and 3). Sediment cores retrieved from the lake suggest that its level was about 27 m below present 5000 years ago (Chapter 3). Small-scale changes in lake level occurred over the next 3700 years. Kluane

Lake rose 5-10 m about 1300 years ago when Duke River abandoned a northern channel on its alluvial fan and began to flow into the lake effectively increasing the lake catchment area (Chapter 2). This change coincided with warming in southern Yukon (Anderson et al. 2005). Flow of Kaskawulsh Glacier meltwater into Kluane Lake, beginning in the seventeenth century, raised the lake 12 m above its present level (Clague et al. 2006), whereupon it overflowed to the north across the Duke River fan, creating present-day Kluane River. This high stand lasted less than 50 years. Kluane River incised the fan, lowering the outlet to near its present level by AD 1800. More recent, small-scale fluctuations in lake level are suggested by the stratigraphy and geochemistry of sediments deposited in small lakes adjacent to Kluane Lake (Chapter 2 and 3).

Today, Slims River dominates surface water discharge to Kluane Lake (Figure 4.1). Other significant water sources include Gladstone Creek on the north, Silver Creek on the south, and several small streams sourced in the Kluane Ranges to the west. Inflow is greatest in late spring and summer (Bryan 1972). Kluane Lake and ponds adjacent to it rise during the summer and fall during the winter, primarily in response to changes in the discharge of the Slims River (R. Gilbert, personal communication 2005).

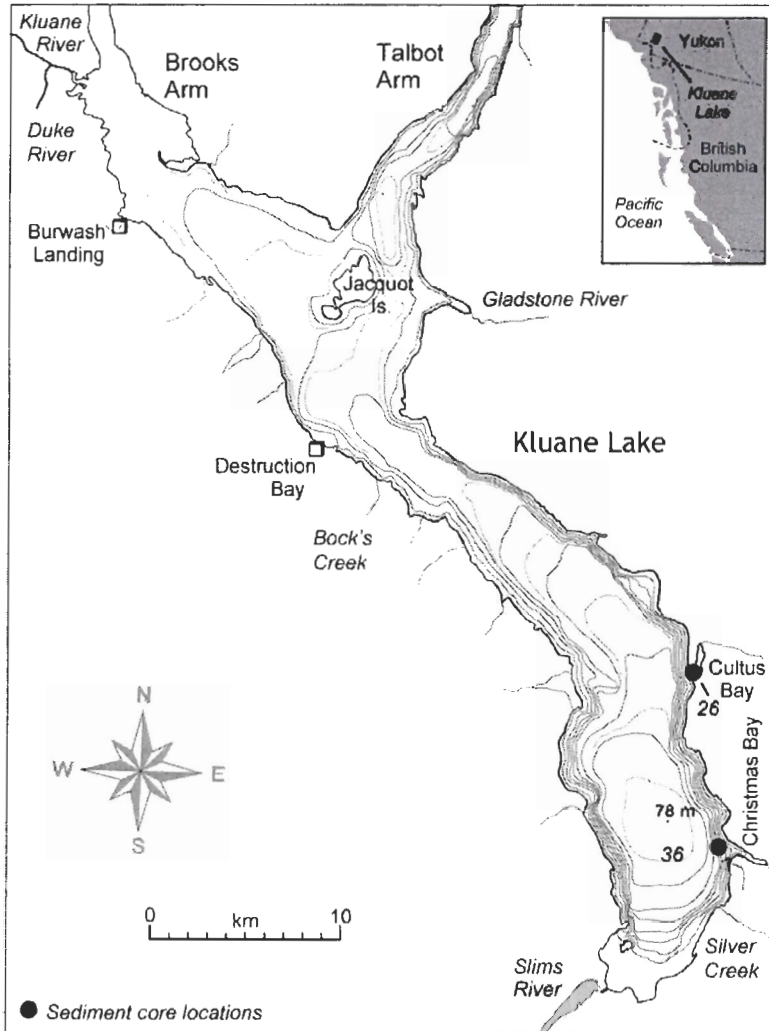


Figure 4-1 Kluane Lake, Yukon Territory, showing location of streams and cores sampled for this study.

Water balance in lakes is controlled by climate, mainly precipitation and humidity. Lake and groundwater levels in presently glacierized basins are particularly sensitive to climate, because prolonged warming releases water stored in snow and ice. The modern climate of the Kluane Lake watershed is subarctic continental, slightly tempered by proximity to the Pacific Ocean. Precipitation is low, averaging 280 mm per year (Environment Canada 2002). Climate in the region is strongly influenced by the Aleutian Low, a semi-permanent, migrating, low-pressure system situated over the North

Pacific Ocean (Moore et al. 2002, Spooner et al. 2003, Anderson et al. 2005). The position of the Aleutian Low influences storm tracks and thus temperature and humidity conditions. When the Aleutian Low is located over the eastern North Pacific, air masses move from the south, bringing warm air to the region. Anderson et al. (2005) and Fisher (2005) presented evidence from lake sediment and ice core records showing that southwest Yukon has been influenced by fluctuations in the location of the Aleutian Low over the past several thousand years, causing millennial- and centennial-scale fluctuations in precipitation and hydrology. They documented major shifts in the Aleutian Low about 2700, 1300, 500, and 300 cal yr BP.

Isotopes of water are powerful tracers of hydrologic processes, because they provide direct information on the phase changes of water. On a global scale, water is evaporated at low latitudes and carried poleward. Successive rainouts along atmospheric flow paths partition the different water isotope species due to differences in the mass of individual molecules. Heavy isotope species are precipitated preferentially, leaving a vapour mass that becomes progressively depleted in ^{18}O and ^2H . This process fractionates water predictably on a global scale, creating a linear relationship between $\delta^{18}\text{O}$ and $\delta^2\text{H}$ known as the Global Meteoric Water Line (GMWL).

Local Meteoric Water Lines (LMWL) record seasonal variability in the isotopic composition of local precipitation resulting from temperature-dependent effects during distillation. Evaporative enrichment from a water body causes displacement of its composition from the LMWL along a linear path with a slope that typically ranges from 4 to 6, known as the Local Evaporation Line (LEL). The intersection of the LEL and the LMWL commonly approximates the isotopic signature of local weighted annual

precipitation. Displacement along the LEL represents the isotopic evolution of a basin undergoing net evaporation. The LEL can be determined empirically by sampling waters in a basin over the thaw season. It can also be calculated using δ^* , the maximum potential enrichment for a lake undergoing evaporation, and δ_{SSL} , the steady-state isotopic composition of a lake where evaporation equals inflow. δ^* and δ_{SSL} are calculated using measured local climate and isotopic parameters, and the linear resistance model of Craig and Gordon (1965).

Sedimentary aquatic cellulose is useful for paleo-hydrologic reconstruction of lacustrine systems. Aquatic cellulose reliably records the isotopic composition of the water from which it formed, with a constant positive isotopic offset of 27-28‰ (Edwards and McAndrews 1989, Wolfe and Edwards 1997, Sternberg et al. 2003). Fractionation is not complicated by lake temperature, chemistry, or the photosynthetic mode of the organism (Wolfe et al. 2001, 2007), therefore sedimentary aquatic cellulose provides a direct window into lake water composition. The isotopic composition of lake waters is controlled by the weighted mean isotopic composition of local precipitation and subsequent hydrological processes, mainly evaporation.

This paper provides information on the modern water balance and hydrology of the Kluane Lake watershed and reconstructs the paleohydrology of the lake and one of its bays using oxygen and hydrogen isotopes in water and sediment cellulose. Shallow bay waters should be sensitive to evaporative enrichment and thus may provide a stronger paleo-humidity signal than the waters of Kluane Lake itself. In contrast, Kluane Lake may provide information on regional climate processes, for example, changes in synoptic conditions that influence the isotopic composition of source waters.

A goal of the research is to provide insights into the impact of climate change on Kluane Lake and the ecosystems it supports. Fluctuating lake levels can affect riparian habitat, shoreline property, and, in Kluane Lake, salmonid migration routes. Kluane Lake provides spawning habitat for Coho and Chinook salmon (von Finster 2005). Continued climate warming could cause Kaskawulsh Glacier to recede to a point that its meltwater no longer flows into Kluane Lake. If so, the level Kluane Lake might fall, reducing or ending outflow from the northern outlet and preventing salmon from reaching the lake. Results from Chapter 1 indicate that Kluane Lake was a closed basin in the past, when neither Duke River nor Slims River flowed into the lake.

4.3 Methods

4.3.1 Modern water balance

Samples of modern snow, rain, river water, and lake water were collected for oxygen and hydrogen isotope analyses in 2005. Kluane Lake, Grayling Lake, Emerald Lake, Cultus Bay, Slims River and an informally named groundwater-fed pond on the south shore of the lake (AINA pond) were sampled throughout the spring and summer (Figure 4.2). Samples were collected in high-density polyethylene bottles, filled to the brim and capped tightly. Fresh snow samples were collected in plastic whirl-pack bags and allowed to thaw before being transferred to polyethylene bottles. Samples were analyzed on a VG MM 903 triple Faraday cup collector mass spectrometer at the University of Waterloo and compared with the Vienna Standard Mean Ocean Water (VSMOW). Analytical precision for $\delta^{18}\text{O}$ is $\pm 0.2\text{‰}$ and for $\delta^2\text{H}$, $\pm 2.0\text{‰}$.

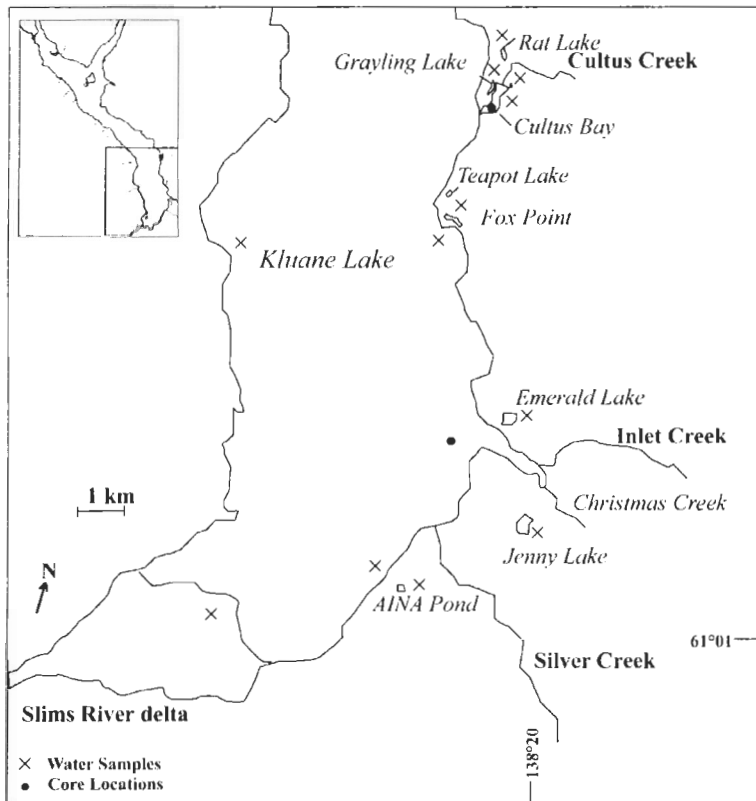


Figure 4-2 Water sample locations.

The isotopic composition of snow and rain samples was used to constrain the LMWL and to establish the local isotope framework for the Kluane Lake area. The data were also used to quantify the evaporation-to-inflow ratio of the Kluane Lake basin using the isotope mass balance equation:

$$E_L / I_L = \delta_I - \delta_L / \delta_E - \delta_L \quad (1)$$

where E_L is evaporation from Kluane Lake, I_L is inflow, and δ_I , δ_L , and δ_E are the isotopic composition of, respectively, the inflow, lake water, and evaporated water.

According to the Craig and Gordon (1965) model:

$$\delta_E = ((\delta_L - \epsilon^*)/\alpha^* - h\delta_A - \epsilon_k)/(1 - h + \epsilon_k)$$

where h is the relative humidity, δ_A is the respective isotopic composition of ambient atmospheric vapour, α^* is the temperature-dependent liquid-vapour fractionation factor for ^{18}O and ^2H (Horita and Wesolowski 1994), $\epsilon^* = (\alpha^* - 1)1000$, and ϵ_k is the humidity-dependent kinetic liquid-vapour separation, calculated by $\epsilon_k = (1 - h)C_k$, where $C_k = 14.2\text{‰}$ and 12.5‰ , respectively, for ^{18}O and ^2H (Gonfiantini 1986).

With respect to ^{18}O , δ_A is calculated using the following equation:

$$\delta_A^{\text{fw}} = \delta P^{\text{fw}} - \epsilon^*(T^{\text{fw}}) / \alpha^*(T^{\text{fw}})$$

This equation assumes equilibrium between atmospheric isotopic composition and the flux-weighted value for precipitation and ignores any contributions from other vapour sources, such as lake evaporation and local evapotranspiration. For this reason, δ_A with respect to deuterium is adjusted based on the principal of conservation of mass and isotopes. Calculated E/I ratios for both $\delta^{18}\text{O}$ and $\delta^2\text{H}$ should theoretically match. Forcing $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values in the Kluane Lake area to match provides an appropriate value for δ_A and distributes calculated δ_E values along the extension of the LEL, to the left of the LMWL, where they should ideally plot.

Evaporation (E) from the lake is calculated using the following equation (Dingman 2002):

$$E = K_E * W * \text{svp}_{(s)} - \text{vp}_{(a)} \quad (2)$$

where E is in m d^{-1} ; K_E is in $\text{m km}^{-1} \text{kPa}^{-1}$ and is the coefficient of vertical transport estimated from $K_E = 1.69 \times 10^{-5} A^{-0.05}$, where A is the area of the lake in km^2 ; W is the wind speed in km day^{-1} ; $\text{svp}_{(s)}$ is the saturation vapour pressure of the surface and is calculated from $\text{svp}_{(s)} = 0.611 * \exp(17.3 * T_s / T_s + 237.3)$, where T_s is the temperature of

the evaporating surface, and $vp_{(a)}$ is the vapour pressure in the air and is equal to $svp_{(a)} * \text{humidity}$.

4.3.2 Paleohydrology

Cores were collected at the south end of Kluane Lake at 36 m depth in the deepest part of Cultus Bay, at 13 m depth. Cultus Bay is separated from the main basin of Kluane Lake by a narrow spit that is breached at one end (Figure 4.3). Both cores were photographed, and analyzed at a high resolution for water content, bulk density, magnetic susceptibility, and percent carbon. Magnetic susceptibility was measured with a Bartington MS2B sensor. Water content, bulk density, and loss on ignition were determined by drying in an oven at 105°C and 550°C, respectively. Carbon percent and isotopic values were measured on samples that were washed in 10% HCl and rinsed with distilled water until neutral. The washed samples were freeze-dried and then sieved through a 500 μm mesh to concentrate the fine fraction. Samples were analyzed by elemental-analyser continuous-flow isotope ratio mass spectrometry at the University of Waterloo.

Plant macrofossils were submitted for AMS radiocarbon dating at Beta Analytic and IsoTrace laboratories. Additional dating control is provided by the White River tephra, which is about 1150 years old (Clague et al. 1995). The tephra, ^{14}C ages, and the tree-ring dates on the recent rise of Kluane Lake (Clague et al. 2006) were used to estimate sedimentation rates and dates of major events recorded in the cores.



Figure 4-3 Oblique aerial photography of Cultus Bay, Grayling Lake, and Rat Lake on the east shore of Kluane Lake. The approximate location of the Cultus Bay core is shown.

Aquatic cellulose was isolated from the lake sediments using a six-step extraction technique. Lake sediments were initially washed in 10% HCl to remove carbonates. Solvents, including resins, tannins, and lipids were then removed using a 2:1 mass ratio of benzene and ethanol. Lignins were removed with a mixture of acetic acid (CH_3COOH) and sodium chlorite (NaClO_2). Xylan, mannan, and other non-glucan polysaccharides were removed using 17% sodium hydroxide. Iron and manganese oxyhydroxides were leached using a mixture of sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$), tri-ammonium citrate ($(\text{NH}_4)_3\text{C}_6\text{H}_5\text{O}_7$), and hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCL}$). Aquatic cellulose was separated from the remaining mineral fraction using sodium polytungstate ($3\text{Na}_2\text{WO}_4\cdot 9\text{WO}_3\cdot \text{H}_2\text{O}$) at a specific density of 2.00. After each digestion, sediments were

rinsed with distilled water and aspirated until the digesting compound was completely displaced. Sediments were allowed to settle for 24-48 hours between each rinse. Lake water $\delta^{18}\text{O}$ was calculated from sediment cellulose using a fractionation factor (α) of 1.028 (Wolfe et al. 2007)

4.4 Results

Water isotope results are presented in Table 4.1. The LMWL calculated from snow and rain samples collected around Kluane Lake is $\delta^2\text{H} = 6.8 \delta^{18}\text{O} - 24$, which is similar to the LMWL for the Global Network of Isotopes in Precipitation (GNIP) station at Whitehorse. The local evaporation line is $\delta^2\text{H} = 4.3 \delta^{18}\text{O} - 76.8$ (Figure 4.4). Slims River, Kluane Lake, and AINA pond plot on the local meteoric water line (LMWL) throughout the sampling season. Slims River isotopic values cluster around -24‰ and -184.5‰ for $\delta^{18}\text{O}$ and $\delta^2\text{H}$, respectively. Kluane Lake samples have a greater range in $\delta^{18}\text{O}$, from -21.13 to -22.96 ‰, although all samples are close to the LMWL. Samples from nearby basins and seepage ponds show different degrees of isotopic enrichment throughout the melt season, with $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values as high as -8.8‰ and -114‰, respectively.

Evaporation-to-inflow (E/I) values are low for Kluane Lake, Cultus Bay, and AINA pond. Grayling Lake and Emerald Lake have E/I ratios of 0.43 and 0.48, respectively. Higher E/I values were obtained for seepage ponds and closed lakes farther from Kluane Lake.

Calculated potential evaporation for the 2005 melt season is 397 mm; the largest potential evaporation values are in the fall (Figure 4.5). Climate normals from 1971-2000

give a long-term average evaporation for the melt season of 365 mm (Environmental Canada, unpublished data).

Table 4-1 Water isotope results.

Date	Sample Site	$\delta^{18}\text{O}(\text{‰})$	$\delta^2\text{H}(\text{‰})$
	Basins		
Jun-14	Groundwater seepage near Rat Lake	-13.92	-130.81
Jun-14	Fen north of Cultus Bay	-8.82	-113.96
Jun-14	Jenny Lake	-12.56	-132.94
Jun-14	Fen near Jenny Lake	-13.55	-133.47
Jun-14	Basin attached to Cultus Bay	-20.99	-165.99
Jun-14	Main basin of Fox Point Lake	-13.46	-136.25
Jun-14	Small basin of Fox Point Lake	-11.81	-127.75
May-10	Kluane Lake, iceoff	-21.13	-168.16
Jun-05	Kluane Lake near AINA	-22.51	-176.67
Jun-05	Kluane Lake, center	-22.94	-180.59
Jun-14	Kluane Lake near Fox Point Lake	-22.86	-179.27
Jul-09	Kluane Lake near AINA	-22.95	-177.54
Jul-30	Kluane Lake near AINA	-22.86	-178.12
Aug-06	Kluane Lake near AINA	-22.58	-177.46
Jun-05	Kluane Lake west shore	-22.81	-177.19
Jul-09	Kluane Lake west shore	-22.79	-178.85
Jul-30	Kluane Lake west shore	-22.84	-178.08
Aug-06	Kluane Lake west shore	-22.52	-179.00
Jun-16	Kluane Lake near Burwash Landing	-22.47	-176.02
Jul-09	Kluane Lake near Burwash Landing	-22.49	-176.56
Jul-30	Kluane Lake near Burwash Landing	-22.54	-174.95
Aug-06	Kluane Lake near Burwash Landing	-22.16	-175.92
May-18	Cultus Bay	-21.13	-164.58
Jul-09	Cultus Bay	-20.92	-165.45
Jul-30	Cultus Bay	-20.80	-164.90
Aug-08	Cultus Bay	-20.63	-165.32
Jun-05	Emerald Lake	-20.96	-166.97
Jul-09	Emerald Lake	-13.72	-136.59
Jul-30	Emerald Lake	-13.64	-134.73
Aug-06	Emerald Lake	-13.13	-135.10

Table 4.1 (Con't)

Date	Sample Site	$\delta^{18}\text{O}(\text{‰})$	$\delta^2\text{H}(\text{‰})$
Jun-16	AINA pond	-21.80	-172.86
Jul-09	AINA pond	-22.31	-174.64
Jul-30	AINA pond	-22.58	-175.69
Aug-06	AINA pond	-22.20	-172.17
May-18	Grayling Lake	-15.19	-140.48
Jun-14	Grayling Lake	-15.95	-145.65
Jul-30	Grayling Lake	-16.11	-146.37
Aug-06	Grayling Lake	-16.12	-146.14
Precipitation			
Apr-16	Snow	-24.43	-182.95
May-05	Rain	-17.55	-142.82
Jun-05	Snow	-30.31	-232.47
Jun-05	Rain	-25.22	-194.34
Jun-15	Rain	-14.20	-113.22
Jun-15	Rain	-15.04	-133.28
Rivers and Creeks			
May-17	Slims River	-23.96	-184.13
Jun-16	Slims River	-23.81	-182.68
Jul-07	Slims River	-24.02	-184.56
Jul-07	Slims River	-24.13	-185.44
Aug-07	Slims River	-23.96	-185.33
Jun-16	Bock's Creek	-22.06	-172.39
May-17	Duke River	-23.15	-180.89
Jun-16	Duke River	-22.57	-174.39
Jun-16	Mines Creek	-22.03	-172.21
Jun-16	Halfbreed Creek	-21.88	-172.84
Jun-16	Silver Creek	-22.12	-170.49
Jun-14	Inlet Creek to Christmas Bay	-21.12	-166.87
Jun-14	Christmas Creek	-21.55	-168.33
Jun-14	Cultus Creek	-21.29	-167.30
Jun-14	No name Creek	-21.70	-171.23

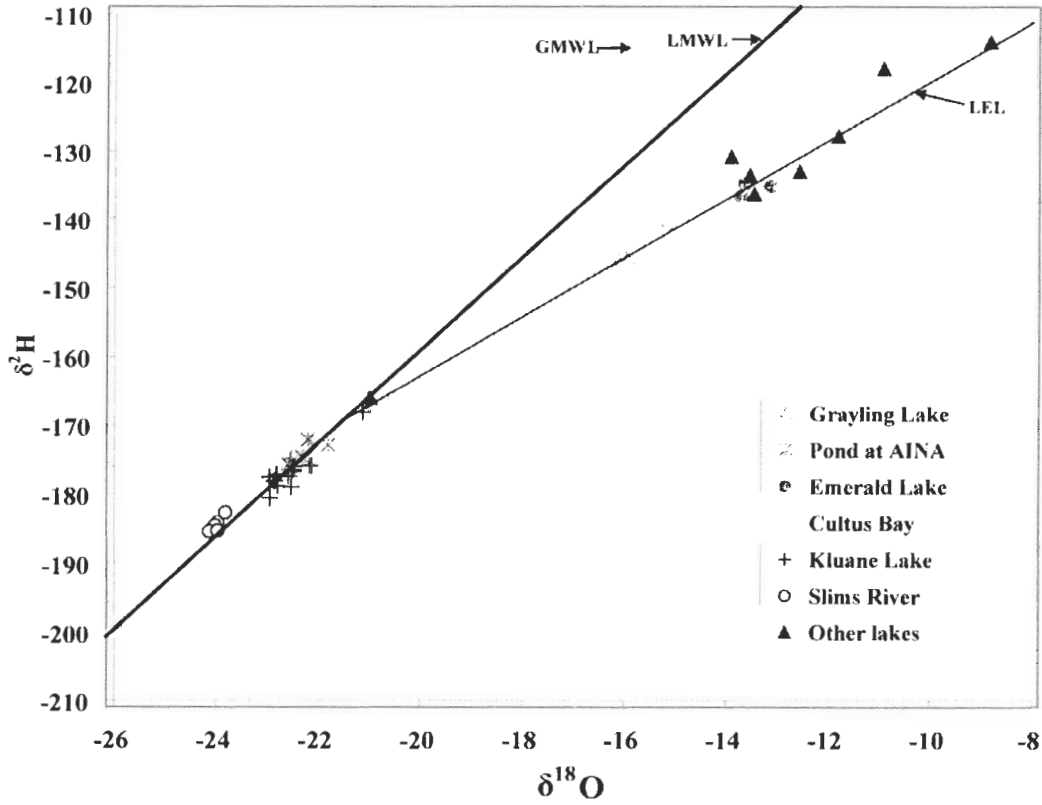


Figure 4-4 Isotopic composition of lake, pond, and river samples. The local meteoric water line, calculated from local snow and precipitation samples is $\delta^2\text{H} = 6.8 \delta^{18}\text{O} - 24$. The LEL is $\delta^2\text{H} = 4.31 \delta^{18}\text{O} - 76.8$.

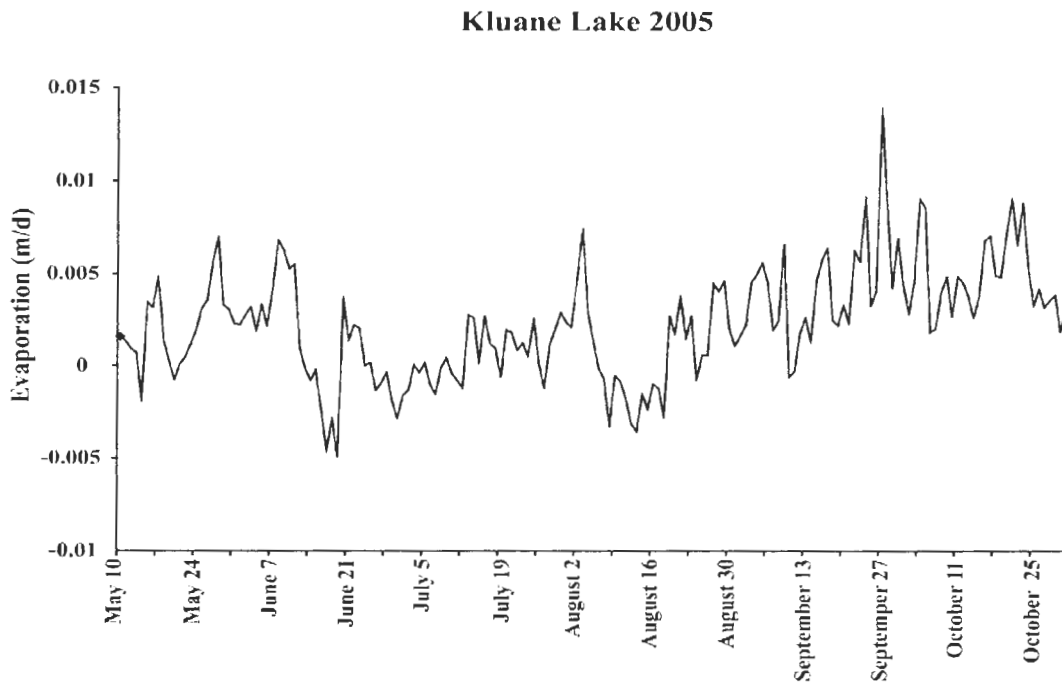


Figure 4-5 Calculated potential daily evaporation from Kluane Lake in 2005.

4.4.1 Cultus Bay core

The Cultus Bay core is 180 cm long and consists of five units (Figure 4.6). Unit 1, from the base of the core to 156 cm depth comprises coarse sand and a forest litter layer at 177 cm. Its contact with unit 2 is sharp. Unit 2 (155-139 cm) consists of fine and medium sand with scattered organic detritus. Fragments of wood at 177 cm and 139 cm yielded identical radiocarbon ages of 1130 ± 50 ^{14}C yr BP (1180-980 cal yr BP; Beta-200709 and 213014). Unit 3 (138- 53 cm) is grey silt (Munsell colour 5Y2.5/1 – 5Y/3/1) with fine sand laminae. Several black streaks and laminae occur near the base of the unit. Roots in growth position and organic detritus were noted at 133 cm. Unit 4 (52-42 cm) is laminated, light grey silt (5Y5/1). It consists of 22-25 couplets. Unit 5 (41-0 cm) is weakly laminated, light grey silt (5Y2.5/1 - 5Y4/1) with scattered black spots and streaks. A distinctive, sharply bounded horizon with low organic content occurs from 39 to 37 cm. The average sedimentation rates for units 2 and 3 are, respectively, 0.25 cm yr^{-1} and 0.1 cm yr^{-1} .

Percent carbon decreases at the base of unit 3 and again at 50 cm. Above 40 cm, organic carbon increases to its highest values in the core. Magnetic susceptibility shows a step-wise increase from 55 to 43 cm, and again from 40 to 37 cm. A smaller peak also occurs at 73-67 cm. Sediment density is positively correlated to magnetic susceptibility and has peaks at the same depths in the core.

Inferred lake water $\delta^{18}\text{O}$ ranges from -10.47 ‰ to -19.63 ‰ through the Cultus Bay core. An interval of isotopic enrichment is evident from 67 to 57 cm, or about 430 to 330 cal yr BP. Isotope depletion is also evident during intervals of high density and low organic carbon.

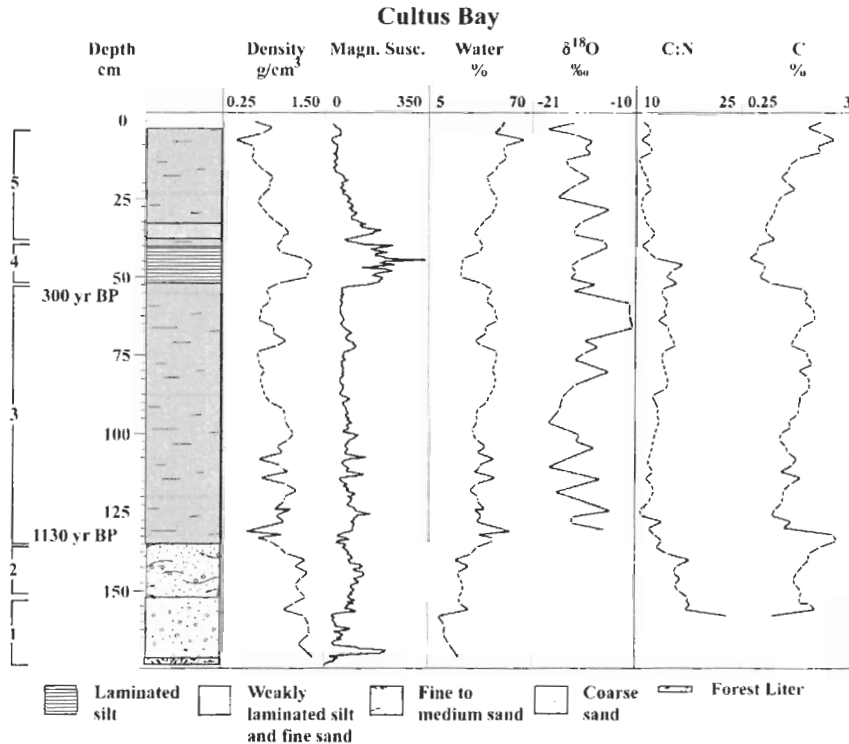


Figure 4-6 Bulk physical properties and trends in $\delta^{18}\text{O}$, C:N, and %C in the Cultus Bay core.

4.4.2 Kluane Lake

The Kluane Lake core is 240 cm long. It was subdivided into five units based on visual inspection and differences in carbon and nitrogen elemental abundances and isotopic values (Figure 4.7). Unit 1 extends from the base of the core to 215 cm; unit 2 from 214 cm to 155 cm; unit 3 from 154 cm to 100 cm; unit 4 from 99 to 64 cm; and unit 5 from 63 cm to the top of the core.

Unit 1, 2, and 3 are similar in lithology; they consist of light grey silt (5Y6/1 – 5Y5/1) with black laminae (5Y2.75/1) up to 1 mm thick. Black laminae are more numerous between 120-100 cm. Unit 1 and unit 3 have higher concentrations of C/N than unit 2. Contacts between units 1 and 2, and 2 and 3 are gradational. Unit 4 is massive brown silt (7.5YR4/1 and 7.5YR4/2) with scattered laminae of fine to medium

sand. The White River tephra occurs at 88 cm within unit 4. Unit 5 sharply overlies unit 4 and is composed of laminated, light olive-grey, clayey silt (5Y6/1-2). The laminae in unit 5 range in thickness from 1 to 5 mm.

Percent carbon increases from 150 to 100 cm. Magnetic susceptibility is relatively constant from the base of the core to 130 cm, whereupon it increases. The peak in magnetic susceptibility at 88 cm marks the White River tephra, and peaks at 74 and 64 cm correspond to sand layers. Unit 1 has uniformly low magnetic susceptibility.

Inferred lake water $\delta^{18}\text{O}$ range from -18.44 to -11.61‰. The lowest value is at 203 cm depth. Peaks occur at 115, 93, and 45 cm.

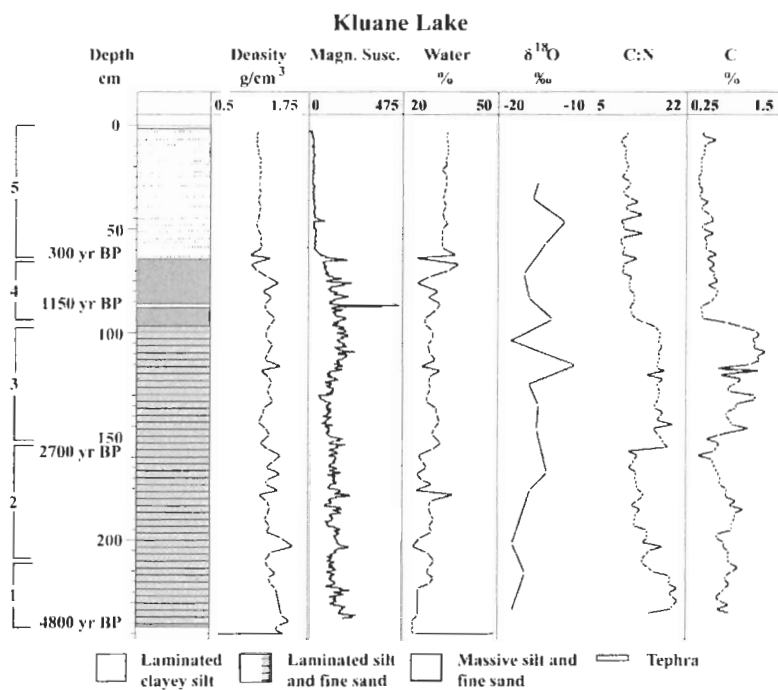


Figure 4-7 Bulk physical properties and trends in $\delta^{18}\text{O}$, C:N, and %C in the Kluane Lake core.

4.5 Discussion

4.5.1 Modern isotope hydrology

The slope of the calculated LMWL (6.8), although relatively low, is similar to that at the Whitehorse GNIP station (6.6). The low slope may result from secondary evaporation during rainfall, as southern Yukon is relatively arid. Similarly, the low slope of the LEL (4.3) is a result of stronger kinetic fractionation during evaporative processes, reflecting the dry modern climate.

Slims River $\delta^{18}\text{O}$ and $\delta^2\text{H}$ co-varied through the summer of 2005. Both isotopes became enriched from May to June, followed by a reversal in July, and another small enrichment in August. These variations probably relate to water sources. In May, Slims River is fed largely by snowmelt and groundwater, whereas in July and August ice melt is dominant.

Isotopes in the Kluane Lake water samples do not change significantly throughout the melt season. $\delta^{18}\text{O}$ values remain close to -22.5‰ and within the range of analytical error, with the exception of the earliest sample (-21.13‰), which was collected immediately after ice break-up. Later, lower isotopic values reflect increased discharge of Slims River. A two-part mixing model indicates that approximately 41% of the water in Kluane Lake comes from the Slims River; the remainder is derived from local streams and groundwater.

Isotopic values in Grayling Lake and AINA pond decreased through the summer. Both basins are hydrologically closed at the surface, thus the isotope trends must be due to groundwater flow. AINA pond is situated on a composite fan formed by Silver Creek and an unnamed ephemeral stream. Groundwater reaching the pond may have originated

from mountain slopes to the south; the higher elevation would account for the relatively depleted waters in the pond (-22.2‰) compared to the local water (-21.5‰). Grayling Lake waters are enriched relative to the local groundwater, but became depleted over the sampling season, indicating that the water has a long residence time and has been affected by evaporation. Sampling ended on August 9th, but evaporation calculations for Kluane Lake indicated that the possibility for evaporation is greater later in the season, probably because lake waters are warmer than air temperatures at this time. Cultus Bay samples remained close to the intersection of the LMWL and the LEL throughout the summer, indicating that its waters have a short residence time.

Emerald Lake is the only sampled lake showing evaporative enrichment over the summer; although the sample collected on June 5, 2005, is problematic because evaporation of that magnitude is not likely. Unlike the other sampled lakes, Emerald Lake is elevated above Kluane Lake and is not affected by it. Sampling ended on August 9th, but evaporation calculations indicate that enrichment probably persisted into September.

The isotopic data show that groundwater is flowing into Kluane Lake at some locations, but waters from Kluane Lake, and ultimately Slims River, may be feeding small adjacent ponds and lakes. Kluane Lake typically rises 1 to 2 m during the summer, and this rise is mimicked in the small lakes near its eastern shore. The concomitant rise in water level may be due to a seasonal reversal in local groundwater flow due to the increased head of Kluane Lake. Inflow of groundwater from Kluane Lake has been observed in Teapot Lake (Figure 4.2; J. Bunbury, personal communication, 2006). Local groundwater is high in dissolved solutes, thus inflow of fresher water from Kluane Lake

may be important for some aquatic organisms. Conductivity in Teapot Lake and other nearby lakes is lower ($400 \mu\text{s cm}^{-1}$ on average) than in lakes fed primarily by groundwater farther from Kluane Lake ($700 \mu\text{s cm}^{-1}$) (J. Bunbury, unpublished data).

4.5.2 Paleohydrology

The Kluane Lake isotope record was difficult to obtain due to the low concentrations of organic matter, and hence cellulose, in the sediments. The organic content of several samples was below normally acceptable limits, but only one core sample (115 cm) yielded an anomalous isotopic value. High C/N ratios in unit 3 could potentially obscure the historical isotope record but, nevertheless, the variations in $\delta^{18}\text{O}$ for Kluane Lake waters are similar to those in the paleo-records of nearby lakes, notably Jellybean Lake (Anderson et al. 2005) and Jenny Lake (Johnson et al. 1998), as well as variations in the Mt. Logan ice core (D. Fisher, personal communication. 2006). The Mt. Logan ice core shows a range in $\delta^{18}\text{O}$ values of 7‰, which is similar to the range of 6.83‰ found in Kluane Lake.

Kluane Lake is large and thus is insensitive to seasonal variations in isotopic composition due to evaporation. The paleo-oxygen isotope record thus should reflect variations in source waters, including local precipitation and streams flowing into the lake, especially Slims and Duke rivers. The isotopic values of modern Slims and Duke River waters are more depleted than the isotopic values of local groundwater because the sources of both rivers are at high elevations.

Similarities between the Mt. Logan ice core data and the Kluane Lake data suggest that isotope variations in Kluane Lake in part reflect synoptic climate

fluctuations, as outlined by Anderson et al (2005). Comparisons of both data sets with historical climate data from Burwash Landing (1971-2000) on the west shore of Kluane Lake indicate strong positive correlations between a westerly Aleutian Low and cooler temperatures ($r^2 = 0.65$) and increased precipitation ($r^2 = 0.59$). A westerly Aleutian Low allows more moisture to penetrate inland because air-mass flow paths are parallel to the main northwest-tending valleys, including Shakwak Trench. As a result, reduced rainout of heavy isotopes leaves moisture relatively enriched in $\delta^{18}\text{O}$. In contrast, under an easterly positioned Aleutian Low, moisture-laden air moves in from the south and encounters the coastal mountain barrier, causing uplift and enhanced rainout of heavy isotopes along the coast (Anderson et al. 2005).

The Mt. Logan isotopic record indicates that $\delta^{18}\text{O}$ declined around 4000 cal yr BP, coincident with the lowest $\delta^{18}\text{O}$ values in the Kluane Lake core. Kaskawulsh Glacier may have advanced at this time, introducing meltwater into Kluane Lake. Duke River also contributed isotopically depleted water to the lake about 4000 cal yr BP (Chapter 3).

$\delta^{18}\text{O}$ increases at about 3000 cal yr BP (167 cm in the Kluane Lake core), suggesting a shift of the Aleutian Low to a dominantly westerly location. Neither Duke River nor Slims River flowed into Kluane Lake at this time, which may also account for the slight enrichment of isotopic values in the lake water, because local precipitation would have become a more important water source.

Three subsequent $\delta^{18}\text{O}$ peaks in the Kluane Lake core (115, 93, and 46 cm) date to about 1800, 1200, and 200 cal yr BP. Similarly, enrichments in $\delta^{18}\text{O}$ in the Mt. Logan ice core date to about 2100, 1600-1200, and 200 cal yr BP. A decrease in $\delta^{18}\text{O}$ in unit 4, between 1300 and 1000 cal yr BP, suggests a period of warmer climate, consistent with

inferred melting of permafrost in the region and a diversion of Duke River into Kluane Lake (Chapter 3). The $\delta^{18}\text{O}$ peak at 1800 cal yr BP (-11.6‰) coincides with a time of stratification and low water levels in Kluane Lake (Chapter 2 and 3). It may reflect evaporation of surface waters in a closed, non-mixing lake. The average annual precipitation at Burwash Landing between 1971 and 2000 was 280 mm. Evaporation calculations indicate that the potential evaporation during 2005 was 397 mm, suggesting that the isotopic composition of Kluane Lake can be affected by evaporation on timescales of decades to centuries.

Cultus Bay, in contrast to Kluane Lake, is a small shallow basin. Isotopic data on water samples collected from the bay indicate that it is not currently sensitive to evaporation. However, the range of sediment-derived oxygen isotope values in Cultus Bay suggests that this has not always been the case. Reconstructed Cultus Bay values range from -19.4 to -10.8‰, a larger range than isotopic values in adjacent ponds and lakes (-15.9 to -10.9‰).

The interval from 100 to 70 cm in the Cultus Bay core has relatively low $\delta^{18}\text{O}$ values. This interval dates to about 750 to 500 cal yr BP and was perhaps a time of cooler and wetter climate. A period of strong isotope enrichment occurs from 67 to 58 cm, which is roughly a 100-yr period from about 430 to 330 cal yr BP. This period does not coincide with any known periods of lower humidity; however the bay may have been relatively shallow and closed at this time, allowing for greater evaporation. Percent carbon also is relatively high during this period, perhaps due to the smaller water body or to a reduction in clastic input. Today, Cultus Bay is an open basin, with both a feeder stream and an outlet to Kluane Lake through a breached spit (Figure 4.3). It is likely that

prior to the seventeenth century rise of Kluane Lake, Cultus Bay was an enclosed basin similar to present-day Grayling Lake.

$\delta^{18}\text{O}$ declines in unit 4, which was deposited about 300 cal yr BP during the +12 m high stand of Kluane Lake. Cultus Bay was fully connected to Kluane Lake at this time, and their waters were similar, with $\delta^{18}\text{O}$ values of about -16 ‰. During the eighteenth century, Kluane Lake fell to its present level and $\delta^{18}\text{O}$ decreased towards values indicative of its modern open-basin conditions. Two brief intervals during the past 300 years, characterized by lower $\delta^{18}\text{O}$ and organic matter and higher density, may record short-lived rises of Kluane Lake (Chapter 2 and 3). Kluane Lake typically rises 1 to 2 m in years of particularly high Slims River inflow. At such times, Kluane Lake could overtop the spit that separates the two basins.

4.6 Conclusion

The climate of southwest Yukon is dry, but rapid subsurface water exchanges prevent evaporative enrichment in closed lakes and ponds adjacent to Kluane Lake. Local groundwater levels have been controlled by recent fluctuations in the level of Kluane Lake, which, in turn, have been controlled by the on-off discharge behaviour of Slims and Duke rivers. Changes in Kluane and Duke river flow and in regional atmospheric circulation over the past several thousand years are registered in the Kluane Lake paleo-oxygen isotope record. Lake-level changes have been accompanied by reversals of subsurface flow between Kluane Lake and its small satellite water bodies. At present, Cultus Bay is an open system and isotopic signatures are similar to local precipitation averages. In the past, however, the bay was isolated and an evaporation-sensitive basin.

Changes in the Cultus Bay paleo-oxygen isotope record indicate shifts between open and closed basin conditions.

4.7 Acknowledgements

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CHAPTER 5 CONCLUSIONS

The level of Kluane Lake has differed from a few tens of metres below its present level to 12 m its above present level over the last 5000 years, primarily due to changes in inputs of water from Slims and Duke rivers. From 5000 to 4200 years BP, Kluane Lake was about 22-27 m lower than today. Advances of Kaskawulsh Glacier about 4000 and 2800 cal yr BP introduced meltwater into Kluane Lake, accompanied by a rise in lake level of a few metres. Lake level decreased slightly around 2700 cal yr BP and still further around 1850 cal yr BP. These fluctuations appear to be related to changes in Duke River inflow. Duke River may have completely bypassed Kluane Lake between about 2000 and 1300 cal yr BP. With no inputs of water from Slims and Duke rivers, Kluane Lake stratified during this period. Anoxic and eventually euxinic conditions developed in the hypolimnion.

Sedimentary oxygen isotopes suggest that precipitation and shallow groundwater were the dominant water sources to Kluane Lake at this time. Colder temperatures and permafrost expansion may have led to a reduction in nitrogen mineralization in the watershed and nitrogen limitation in Kluane Lake.

Lake level increased to approximately -12 m about 1300 cal yr BP due to the diversion or increased flow of Duke River into Kluane Lake. The influx of freshwater initiated mixing in the lake and increased oxygen penetration to the hypolimnion. Oxygen isotopes in Kluane Lake and Jellybean Lake suggest warmer temperatures at this time, consistent with sediment geochemistry indicating thawing of permafrost in the watershed.

The climactic Holocene advance of Kaskawulsh Glacier about 350 years ago diverted large volumes of meltwater into Kluane Lake via the newly established Slims River. A rapid rise in the lake to +12 m is indicated by an abrupt change in sediments in all cores collected at the south end of the lake. The Cultus Bay and Grayling Lake cores show that the high stand was brief, consistent with previously published tree-ring based reconstructions of lake-level change over the past several hundred years. The lake dropped to near its present level by about AD 1800 due to downcutting of a new, northern outlet by Kluane River.

Shifts between open and closed basin conditions in Cultus Bay over the past 1000 years are suggested by oxygen isotope variations in the core collected from the bay. The rise to the +12 m high stand is clearly indicated in sediment oxygen isotope values. The lithology, magnetic susceptibility, and geochemistry of sediments in both Grayling Lake and Cultus Bay suggest Kluane Lake waters may have mixed with waters in these basins on at least two other occasions, 500-460 and 140-120 cal yr BP. Reversals in groundwater flow between Kluane Lake and its satellite ponds may occur due to annual fluctuations of 1-2 m in the level of the lake.

The modern hydrology of the Kluane Lake watershed indicates that Slims River contributes approximately 40% of inflow to Kluane Lake. If warming continues, Kaskawulsh Glacier will retreat from the present divide between Slims and Kaskawulsh rivers, and Slims River may then cease to carry Kaskawulsh Glacier meltwater into Kluane Lake. Should this happen, the level of Kluane Lake will fall and the lake might become a closed basin, with potentially damaging ecological effects. The potential loss of the outlet would impact salmon that use Kluane River as spawning grounds or as a

conduit into Kluane Lake and its tributaries. Stratification would impact the whitefish, lake trout, and burbot that inhabit the lake and possibly cause a shift in the plankton structure. The reduction in local groundwater levels would cause many local lakes to decrease in size and possibly desiccate.

REFERENCES

- Achterberg, E.P., van der Berg, C.M.G., Boussemart, M., Davison, W. 1997. Speciation and cycling of trace metals in Esthwaite water: A productive English lake with seasonal deep-water anoxia. *Geochimica et Cosmochimica Acta* 61: 5233-5253.
- Adelson, J.M., Helx, G.R., Miller, C.V. 2001. Reconstructing the rise of recent coastal anoxia; molybdenum in Chesapeake Bay sediments. *Geochimica et Cosmochimica Acta* 65: 237-252.
- Algeo, T.J., Maynard, J.B. 2004. Trace-element behavior and redox facies in core shales of Upper Pennsylvanian Kansas-type cyclotherms. *Chemical Geology* 206: 289-318.
- Anderson, L., Abbott, M.B., Finney, B.P., Burns, S.J. 2005. Regional atmospheric circulation change in the North Pacific during the Holocene inferred from lacustrine carbonate oxygen isotopes, Yukon Territory, Canada. *Quaternary Research* 64: 21-35.
- Berrang, P.G., Grill, E.V. 1974. The effect of manganese oxide scavenging on molybdenum in Saanich Inlet, British Columbia. *Marine Chemistry* 2: 125-148.
- Bonan, G.B. 1990. Carbon and nitrogen cycling in North American boreal forests. I. Litter quality and thermal regime effects in interior Alaska. *Biogeochemistry* 10: 1-28.
- Borns, H.W., Jr., Goldthwait, R.P. 1966. Late-Pleistocene fluctuations of Kaskawulsh Glacier, southwestern Yukon Territory, Canada. *American Journal of Science* 264: 600-619.
- Bostock, H.S. 1969. Kluane Lake, Yukon Territory; its drainage and allied problems. *Geological Survey of Canada Paper* 69-28.
- Boyle, J.F. 2001. Inorganic geochemical methods in palaeolimnology. In Last, W.M., Smol, J.P., eds., *Tracking Environmental Change Using Lake Sediments. Volume 2: Physical and Geochemical Techniques*. Kluwer Academic Publishers, Dordrecht, The Netherlands, pp. 83-141.
- Brahney, J., Bos, D.G., Pellatt, M.G., Edwards, T.W.D., Routledge, R. 2006. The influence of nitrogen limitation on $\delta^{15}\text{N}$ and carbon:nitrogen ratios in sediments from sockeye salmon nursery lakes in British Columbia, Canada. *Limnology and Oceanography* 51: 2333-2340.
- Bryan, M.L. 1972. Variations in quality and quantity of Slims River water, Yukon Territory. *Canadian Journal of Earth Sciences* 9: 1469-1478.

- Bryan, W.B., Finger, L.W., Chayes, F. 1969. Estimating proportions in petrographic mixing equations by least-squares approximation. *Science* 163: 926-927.
- Calvert, S.E., Pedersen, T.F. 1993. Geochemistry of recent oxic and anoxic marine sediments: Implications for the geologic record. *Marine Geology* 113: 67-88.
- Campbell, R.B., Dodds, C.J. 1982. Geology, Kluane Lake map area (115F and G). Geological Survey of Canada Open File 829.
- Clague, J.J. 1981. Landslides at the south end of Kluane Lake, Yukon Territory. *Canadian Journal of Earth Sciences* 18: 959-971.
- Clague, J.J., Evans, S.G., Rampton, V.N., Woodsworth, G.J. 1995. Improved age estimates for the White River and Bridge River tephra, western Canada. *Canadian Journal of Earth Sciences* 32: 1172-1179.
- Clague, J.J., Luckman, B.H., Van Dorp, R.D., Gilbert, R., Froese, D., Jensen, B.J.L., and Reyes, A.V. 2006. Rapid changes in the level of Kluane Lake in Yukon Territory over the last millennium. *Quaternary Research* 66: 342-355.
- Collins, A.L., Walling, D.E., Leeks, G.J.L. 1997. Source type ascription for fluvial suspended sediment based on a quantitative composite fingerprinting technique. *Catena* 29:1-27.
- Collins, A.L., Walling, D.E., Leeks, G.J.L. 1998. Use of composite fingerprints to determine the provenance of the contemporary suspended sediment load transported by rivers. *Earth Surface Processes and Landforms* 23: 31-52.
- Craig H., Gordon L.I., 1965. Deuterium and oxygen-18 variations in the ocean and the marine atmosphere. In E Tongiorgi, ed., *Proceedings of a Conference on Stable Isotopes in Oceanographic Studies and Paleotemperatures*. Spoleto, Italy, pp 9-130.
- Crusius, J., Calvert, S., Pedersen, T., Sage, D. 1996. Rhenium and molybdenum enrichments in sediments as indicators of oxic, suboxic and sulfidic conditions of deposition. *Earth and Planetary Science Letters* 145: 65-78.
- Denton, G.H., Karlén, W. 1977. Holocene glacial and tree-line variations in the White River valley and Skolai Pass, Alaska and Yukon Territory. *Quaternary Research* 7: 63-111.
- Denton, G.H., Stuiver, M. 1966. Neoglacial chronology, northeastern St. Elias Mountains, Canada. *American Journal of Science* 264: 577-599.
- Dingman, L. 2002. *Physical Hydrology* (2nd ed.). Prentice Hall, Upper Saddle River, NJ.
- Edwards, T.W.D., McAndrews, J.H. 1989. Paleohydrology of a Canadian Shield lake inferred from $\delta^{18}\text{O}$ in sediment cellulose. *Canadian Journal of Earth Sciences* 26: 1850-1859.

- Edwards, T.W.D., Wolfe, B.B., Macdonald, G.M. 1996. Influence of changing atmospheric circulation on precipitation $\delta^{18}\text{O}$ temperature relations in Canada during the Holocene. *Quaternary Research* 46: 211-218.
- Emerson, S.R., Husted, S.S. 1991. Ocean anoxia and the concentration of molybdenum and vanadium in seawater. *Marine Chemistry* 34: 177-196.
- Engstrom, D.R. Wright, H.E., Jr. 1984. Chemical stratigraphy of lake sediments as a record of environmental change. In Haworth, E.Y. Lund, J.W.G., eds., *Lake Sediments and Environmental History. Studies in Paleolimnology and Paleoecology*. Leicester University Press 11: 11-67.
- Environment Canada. 2002. Canadian Climate Normals 1971-2000. http://www.climat.meteo.ec.gc.ca/climateData/canada_e.html (accessed June 2005).
- Filippelli, G.M., Souch, C., Menounos, B., Slater-Atwater, S., Jull, T., Slaymaker, O., 2006. Alpine lake records reveal the impact of climate and rapid climate change on the biogeochemical cycling of soil nutrients. *Quaternary Research* 66: 158-166
- Fisher, D. 2005. Stable isotope records from Mount Logan and Eclipse Ice cores and nearby Jellybean Lake; Water cycle of the North Pacific over 2000 years and over 5 vertical kilometers' sudden shifts and tropical connections [abstract]. Abstracts, Rapid Landscape Change and Human Response in the Arctic and Subarctic, Yukon College, Whitehorse, YT, p. 81.
- Gardner, J.S., Jones, N.K. 1985. Evidence for a Neoglacial advance of the Boundary Glacier, Banff National Park, Alberta. *Canadian Journal of Earth Sciences* 22: 1753-1755.
- Gonfiantini, R., 1986. Environmental isotopes in lake studies. In Fritz, P., Fontes, J.C., eds., *Handbook of Environmental Isotope Geochemistry, Volume 3*. Elsevier, New York, pp. 113-168.
- Harris, S.A. 1990. Dynamic and origin of saline soils on the Slim River delta, Kluane National Park, Yukon Territory. *Arctic* 43:159-175.
- Heilman, P.E. 1966. Change in distribution and availability of nitrogen with forest succession on north slopes in interior Alaska. *Ecology* 47: 825- 831.
- Helz, G.R., Miller, C.V., Charnock, J.M., Mosselmans, J.F.W., Patock, R.A.D., Garner, C.D., Vaughan, D.J. 1996. Mechanism of molybdenum removal from the sea and its concentration in black shales: EXAFS evidence. *Geochimica et Cosmochimica Acta* 60: 3631-3642.
- Horita, J., Wesolowski, D.J. 1994. Liquid-vapor fractionation of oxygen and hydrogen isotopes of water from the freezing to the critical temperature. *Geochimica et Cosmochimica Acta*, 58: 3425-3437.
- Huerta-Diaz, M.G., Morse, J.W. 1992. Pyritization of trace metals in anoxic marine sediments. *Geochimica et Cosmochimica Acta* 56: 2681-2702.

- Johnson, P., Gajewski, K., Lacourse, T. 1998. Paleoenvironment reconstruction in the southwest Yukon. Potential for fine resolution studies over the last 1000 years. Proceedings, Wolf Creek Research Basin, Hydrology, Ecology, Environment, Whitehorse, YT, p 109-119.
- Kelly, C.A., Rudd, J.W.M., Cook, R.B., Schindler, D.W. 1982. The potential importance of bacterial processes in regulating rate of lake acidification. *Limnology and Oceanography* 27: 868-882.
- Klinkhammer, G.P., Palmer, M.R. 1991. Uranium in the ocean where it goes and why. *Geochimica et Cosmochimica Acta* 55: 1799-1806.
- Lewan, M.D., Maynard, J.B. 1982. Factors controlling the enrichment of vanadium and nickel in the bitumen of organic sedimentary rocks. *Geochimica et Cosmochimica Acta* 46: 2547-2560.
- MacDonald, G.M. 2005. Variations in the Pacific Decadal Oscillation over the past millennium. *Geophysical Research Letters* 32: L08703, doi:10.1029/2005GL022478.
- Menounos, B. 1997. The water content of lake sediments and its relationship to other physical parameters: An alpine case study. *The Holocene* 7: 207-212.
- Meyers, P.A., Eadie, B.J. 1993. Sources, degradation and recycling of organic matter associated with sinking particles in Lake Michigan. *Organic Geochemistry* 20: 47-56.
- Moore, G.W.K., Holdsworth, G., Alverson, K. 2002. Climate change in the North Pacific region over the past three centuries. *Nature* 420: 401-402.
- Morse, J.W., Luther, G.W. III. 1999. Chemical influence on trace metal-sulfide interaction in anoxic sediments. *Geochimica et Cosmochimica Acta* 63: 3373-3378.
- Mosser, C. 1991. Relationship between sediments and their igneous source rocks using clay mineral multi-element chemistry the Cenozoic lacustrine Anloua Basin (Adamaoua, Cameroon). *Chemical Geology* 90:319-342.
- Natural Resources Canada. 2003. The Atlas of Canada: Facts about Canada: Lakes. <http://atlas.gc.ca/site/english/learningresources/facts/lakes.html#yukon> (accessed January 2005).
- O'Leary, M.H. 1988. Carbon isotopes in photosynthesis. *Bioscience* 38:328-336.
- Osborn G.D., Karlstrom, E.T. 1989. Holocene moraine and paleosol stratigraphy, Bugaboo Glacier, British Columbia. *Boreas* 18: 311-322
- Pienitz, R., Smol, J.P., Last, W.M., Leavitt, P.R., Cumming, B.F. 2000. Multi-proxy Holocene paleoclimatic record from a saline lake in the Canadian Subarctic. *The Holocene* 10: 673-686.

- Rampton, V.N., Shearer, J.M. 1978a. Bottom and sub-bottom conditions at Kluane Lake, Teslin River, and Nisutlin Bay pipe line crossings. Terrain Analysis and Mapping Services Ltd., Stittsville, ON.
- Rampton, V.N., Shearer, J.M. 1978b. The geology and limnology of Kluane Lake, Yukon Territory, I Preliminary assessment. Terrain Analysis and Mapping Services Ltd., Stittsville, ON.
- Ross, G.J., Wang, C. 1993. Extractable Al, Fe, Mn and Si. In Carter, M.R., ed., Soil Sampling and Methods of Analysis for Canadian Society of Soil Science. Lewis Publishers, Boca Raton, FL, pp. 239-246.
- Schlesinger, W.H. 1997. Biogeochemistry: An analysis of global change. Academic Press, London.
- Spooner, I.S., Barnes, S., Baltzer, K.B., Raeseide, R., Osborn, G.D., Mazzucchi, D. 2003. The impact of air mass circulation dynamics on Late Holocene paleoclimate in northwestern North America. Quaternary International 108: 77-83.
- Sternberg, L.S.L., Anderson, W.T., Morrison, K. 2003. Separating soil and leaf water ^{18}O isotopic signals in plant stem cellulose. Geochimica et Cosmochimica Acta 67: 2561-2566.
- Stuiver, M., Reimer, P.J., Bard, E., Beck, J.W., Burr, G.S., Hughen, K.A., Kromer, B., McCormac, G., van der Plicht, J., Spurk, M. 1998. INTCAL98 radiocarbon age calibration, 24,000-0 cal BP. Radiocarbon 40: 1041-1083.
- Talbot, M.R. 2001. Nitrogen isotopes in palaeolimnology. In Last, W.M., Smol, J.P., eds., Tracking Environmental Change Using Lake Sediments. Volume 2: Physical and Geochemical Techniques. Kluwer Academic Publishers, Dordrecht, The Netherlands, pp. 401-439.
- Templeton, G.D., III, Chasteen N.D. 1980. Vanadium fulvic acid chemistry: Conformational and binding studies by electron spin probe techniques. Geochimica et Cosmochimica Acta 44: 741-752.
- Tenzer, G.E., Meyers, P.A., Knoop, P. 1997. Sources and distribution of organic and carbonate carbon in sediments of Pyramid Lake, Nevada. Journal of Sedimentary Research 67: 884-890.
- Tribovillard, N., Riboulleau, A., Lyons, T., Baudin, F. 2004. Enhanced trapping of molybdenum by sulfurized marine organic matter of marine origin in Mesozoic limestones and shales. Chemical Geology 213: 385-401.
- Vigliotti, L. 1999. Magnetic properties of sediments deposited in suboxic-anoxic environments relationship with biological and geochemical processes. In D.H. Tarling, P. Turnery., eds., Paleomagnetism and Diagenesis in Sediments. Geological society of London Special Publication 151. pp 71-83.

- von Finster, A. 2005. Impacts of Kluane Lake drainage reversal on fisheries [abstract]. Abstracts, Rapid Landscape Change and Human Response in the Arctic and Subarctic. Yukon College, Whitehorse, p. 81.
- Wanty, R.B., Goldhaber, M.B. 1992. Thermodynamics and kinetics of reactions involving vanadium in natural systems: Accumulation of vanadium in sedimentary rocks. *Geochimica et Cosmochimica Acta* 56: 1471-1483.
- Wehrli, B., Stumm, W. 1989. Vanadyl in natural waters: Adsorption and hydrolysis promote oxygenation. *Geochimica et Cosmochimica et Acta* 53: 69-77.
- Wolfe, B.B., Edwards, T.W.D. 1997. Hydrologic control on the oxygen-isotope relation between sediment cellulose and lake water, Taimyr Peninsula, Russia: Implications for the use of surface-sediment calibrations in paleolimnology. *Journal of Paleolimnology* 18: 283-291.
- Wolfe, B.B., Edwards, T.W.D., Beuning, K.R.M., Elgood, R.J. 2001. Carbon and oxygen isotope analysis of lake sediment cellulose: Methods and applications. In Last W.M., Smol. J.P., eds., *Tracking Environmental Change Using Lake Sediments: Volume 2: Physical and Chemical Techniques*. Kluwer Academic Publishers, Dordrecht, The Netherlands, pp. 373-400.
- Wolfe, B.B., Falcone, M.D., Clogg-Wright, K.P., Mongeon, C.L., Yi, Y., Mark, W.A., Edwards, T.W.D. 2007. Progress in isotope paleohydrology using lake sediment cellulose. *Journal of Paleolimnology* 37: 221-231.
- Wood, C., Smith, D.J. 2004. Dendroglaciological evidence for a Neoglacial advance of the Saskatchewan Glacier, Banff National Park, Canadian Rocky Mountains. *Tree-Ring Research* 60: 59-65.
- Yu, Z., McAndrews, U., Eicher, U. 1997. Middle Holocene dry climate caused by change in atmospheric circulation patterns: Evidence from lake levels and stable isotopes. *Geology* 25: 251-254.

APPENDICES

The appendices listed below are included on a CD-ROM, attached to this thesis. The files have been created in Excel and can be accessed with that software.

Appendix A: Sediment core locations.

Appendix B: Elemental geochemistry of samples from cores 08, 10, 26, and 36, and stream sediments.

Appendix C: Cellulose $\delta^{18}\text{O}$ values for samples from cores 36 and 26.

Appendix D: Carbon and Nitrogen elemental and isotopic data for core 10, 26 and 36.

Appendix E: Magnetic susceptibility of samples from cores 05, 06, 08, 10, 13, 15, 17, 18, 19, 21, 23, 26, 29, 31, and 36.

Appendix F: Density and water content of samples from cores 05, 06, 08, 10, 13, 15, 17, 18, 19, 21, 23, 26, 29, 31, and 36 and loss on ignition for samples from cores 13 and 31.

Appendix G: Constrained least squares results for cores 08, 26 and 36.

Appendix H: Principal components for samples from cores 08, 10, 26, and 36, and stream sediments.