ISOTOPE PALEOHYDROLOGY AT THE NORTHERN BOREAL TREELINE, CANADA AND RUSSIA

by

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ABSTRACT

To improve our understanding of the relationship between the northern treeline region and climate change, a Canadian-Russian research project (*Paleoecological Analysis of Circumpolar Treeline*) was established in 1993. Research strategies primarily include analysis of lake sediment cores using a wide variety of sedimentological, biological and geochemical techniques. Oxygen and carbon isotope analysis on fine-grained lake sediment cellulose comprises an integral part of these multidisciplinary investigations, and have provided novel insight into Holocene paleohydrology and watershed carbon cycling in arctic Canada and Russia.

Separation of oxygen isotope effects caused by changes in lake water balance from the oxygen isotope composition of precipitation ($\delta^{18}O_P$) in the lake sediment cellulose $\delta^{18}O$ records indicates that periods of treeline advance and climate warming in central Canada ($\approx$ 5000 - 3000 ^{14}C years BP) and central and eastern Russia ($\approx$ 8000 - 4000 ^{14}C years BP) were characterized by distinct changes in moisture conditions. During these intervals, summer relative humidity increased by about 10 to 15 % in central Canada; central Russia also became wetter whereas a drier climate is associated with treeline advance in eastern Russia. Reconstruction of $\delta^{18}O_P$ in central Canada displays a straightforward relationship with expected temperature change during the mid- to late Holocene. However, high $\delta^{18}O_P$ values during the early Holocene, when mean annual temperature was probably similar to present, may instead reflect a small reduction in distillation of moisture in Pacific air masses traversing the Cordillera, perhaps associated with a higher summer:winter precipitation ratio.

Carbon isotope records in lake sediment cellulose suggest that lake carbon reservoirs at boreal treeline were strongly regulated by catchment hydrology as well as soil and vegetation development. During the moist periods of forest expansion in central Canada and Russia, terrestrial input of dissolved inorganic carbon to downstream aquatic ecosystems was an important process, supplying phytoplankton with non-limiting quantities of carbon. Exploratory investigations suggested that the

nitrogen isotope composition of lacustrine bulk organic matter may also be useful for reconstructing nutrient dynamics in these watersheds.

Overall, these results confirm that lake sediment organic isotope tracers are sensitive to changing hydrologic conditions and are an effective approach for paleoenvironmental reconstruction. Notably, new information acquired from these studies concerning the response of watershed hydrology and carbon balance to natural climate variation provides a fundamental baseline for evaluating the impact of future climate change in northern regions.

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CHAPTER 1: INTRODUCTION

The Northern Boreal Treeline and Climate Change

General circulation model (GCM) scenarios suggest that high northern latitudes may be particularly sensitive to anthropogenically driven climate change (Maxwell 1992; Houghton *et al.* 1996). Scenarios generated by four different GCMs estimate that doubling present atmospheric CO_2 will likely result in an average temperature increase between 3 and 9 °C, whereas precipitation may be elevated by about 15-25 % in the North American arctic (Maxwell 1992). Winter surface warming may be especially pronounced as estimated values are 2-2.4 times greater than the predicted global annual average. In addition to significant climate change, the average rate of warming will likely be greater than any during the past 10,000 years (Houghton *et al.* 1996).

Although computer modelling is a powerful approach to predicting the climatic effects of atmospheric CO_2 loading, paleoenvironmental reconstruction of past warm climate episodes preserved in the geological record provide a rich source of information that is fundamental to this research. Paleoclimate data is critical for (1) testing climate models (e.g. Wright *et al.* 1993), (2) providing a foundation upon which hypotheses regarding the causes of climate change may be tested, and (3) understanding the natural variability of climate in the absence of anthropogenic influences (Bradley 1985; Crowley 1991). "Systematic collection of long-term instrumental and proxy observations of climate system variables" has been targetted as a priority research topic by the Intergovernmental Panel on Climate Change (Houghton *et al.* 1996: 7).

The arctic treeline zone is especially important to examine in the context of future climate change because of potential climate feedbacks that may arise as a result of changes in the distribution of forest and tundra vegetation. For example, important positive feedbacks may be generated by a decrease in snow-covered land surface albedo (Bonan *et al.* 1992; Foley *et al.* 1994; Otto-Bliesner & Upchurch 1997), and an increase in greenhouse gas release due to rapid decomposition of soil organic

matter and peatlands (BOREAS Science Steering Committee 1990) and increased occurrence of forest fires (Wein 1990). In northern Alaska, there already appears to be evidence for tundra soils becoming a source of CO_2 to the atmosphere during the warming of the past century (Oechel *et al.* 1993). Over longer time-scales (centuries to millennia) however, northern ecosystems may act as a small carbon sink in a warmer climate (Marion & Oechel 1993) as a result of elevated rates of productivity, development of new plant communities, and increased carbon storage in plant biomass (Oechel & Billings 1992). The capacity for both positive and negative responses highlights the importance of understanding interactions between the treeline region and the climate system.

Identifying the response of northern ecosystems to past changes in climate may help to evaluate the potential importance of these various feedback mechanisms. Key issues that need to be addressed include the extent to which terrestrial, peatland, and aquatic species have been able to adapt to past episodes of climate amelioration. Or, is there evidence to suggest that rates of climate change have outpaced the response of biota? The latter is a genuine concern given the expected brisk pace of future global warming (Svoboda & Henry 1987; Davis 1989).

A collaborative team of Canadian and Russian scientists has been formed to address these and related issues in a 5-year international research project called the *Paleoecological Analysis of Circumpolar Treeline* (PACT). Terrestrial, peat, and lacustrine paleoecology, as well as paleolimnology and paleohydrology along the northern Canadian and Russian treeline are major themes currently being studied by PACT researchers. The past 10,000 years is the temporal framework for this project, which includes the Mid-Holocene Climatic Optimum or Hypsithermal - a distinct and widespread interval of climate warming. To examine the Holocene record of paleoenvironmental change, PACT researchers employ a multi-proxy approach to the analysis of lake sediments (grain size, elemental geochemistry, loss-on-ignition, pollen, stomates, diatoms, chrysophyte cysts, chironomids, stable isotopes), peat deposits (loss-on-ignition, pollen, macrofossils, chrysophyte cysts, stable isotopes) and fossil wood (dendroclimatology, stable isotopes) obtained near treeline. The geographic

scope of this project represents a significant contribution to international global change research.

This thesis is a contribution to the PACT project and focuses primarily on the Holocene reconstruction of treeline paleohydrology based on the study of several lake sediment cores obtained from central Canada and central and eastern Russia (Figure 1-1). The main tools that are used for this investigation include evaluation of $\delta^{18}O$ (footnote[1]) in sediment cellulose ($\delta^{18}O_{cell}$), $\delta^{13}C$ in bulk organic sediment ($\delta^{13}C_{org}$), and $\delta^{13}C$ in sediment cellulose ($\delta^{13}C_{cell}$). These data are supplemented by determinations of carbon/nitrogen (C/N) ratios in bulk organic sediment.

Research Objectives

The modern hydrologic regime in the arctic is characterized by strongly differing processes occurring during distinct periods: winter, snowmelt, and summer (Kane *et al.* 1992). Important processes during the winter include snowfall and accumulation, redistribution of snow by wind, and freezing of the active layer. The short snowmelt interval is dominated by runoff. During the summer, large rainfall events can also generate significant amounts of runoff, although loss of water via evapotranspiration is a major flux. How these factors may have varied in the past on both local and regional scales, however, has not been investigated systematically. The lack of detailed paleohydrological studies in the arctic and the need for this information was recently highlighted by Kane *et al.* (1992: 36):

> Quantifying the magnitude of hydrologic change due directly to climate change in the Arctic is going to be difficult because of the limited existing data base. From a quick examination of arctic hydrologic literature, one finds that most studies are of limited duration; many field studies start after the snowmelt; most studies concentrate only on one or two hydrologic processes; and the quality of some of the data is compromised because of harsh environmental conditions. Many of the

[1] δ-values represent deviation in per mil (‰) from the international V-SMOW standard (for δ^2H and $\delta^{18}O$) and PDB standard (for $\delta^{13}C$) such that $\delta = ((R_{sample}/R_{std})-1)1000$, where R is the $^2H/^1H$, $^{18}O/^{16}O$, or $^{13}C/^{12}C$ ratio.

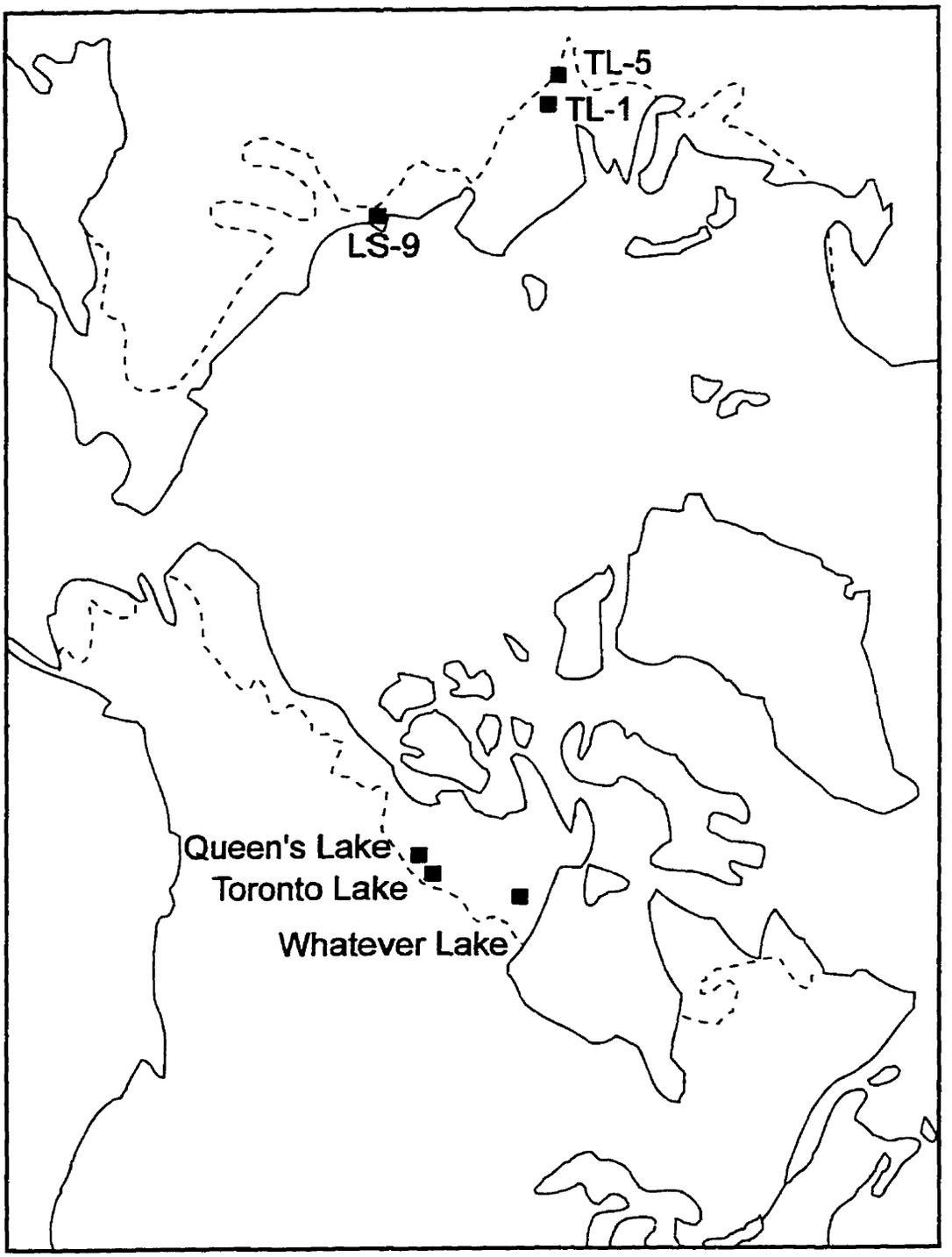


Figure 1-1. Circumpolar map with treeline. Location of lakes discussed in thesis.

publications are in the gray literature, and because of the short duration of record, the stochastic variability of the hydrologic data is unknown. How are we going to separate changes in the hydrology induced by climatic change from natural variation?

Stratigraphic oxygen isotope analysis of fine-grained cellulose in lake sediment cores provides a tool for assessment of the natural amplitude, variability, and rate of past hydrologic change (see Research Approach). The primary research questions that this thesis addresses include:

1. How has the water balance of treeline lakes varied during the Holocene, particularly during periods of terrestrial ecologic change, and are there regional similarities or differences between northern Canada and northern Russia? Have changes been abrupt or lagged behind other changes in the environment? What does the interpreted hydrologic record suggest about moisture conditions during past episodes of climate warming?

2. What do changes in moisture conditions (in association with thermal and vegetation reconstructions) suggest about potentially important climate forcing mechanisms that may have operated in the past?

As previously discussed in the introductory section, "uncertain effects of global change on arctic and boreal forest carbon balance make the study of northern ecosystem response a key to understanding and predicting future global atmospheric CO_2 patterns" (Oechel & Billings 1992: 140). The carbon isotope composition of bulk organic lake sediment and cellulose, which often complement cellulose-derived oxygen isotope profiles (see Research Approach), were performed to address the following secondary inquiries:

3. How has treeline watershed carbon cycling varied during periods of terrestrial ecologic change? Have changes been abrupt or lagged behind other

changes in the environment?

4. What is the relationship between past hydrologic change and the carbon cycle in treeline lakes of northern Canada and Russia?

Answers to these questions, integrated with information gathered from other proxy records, will provide important baseline data for parameterization and validation of GCMs and ecological models.

Research Approach

Stratigraphic oxygen and carbon stable isotope analysis of organic lake sediments can provide a quantitative record of former paleohydrologic conditions and a qualitative guide to the carbon balance history at the site of investigation. These paleoenvironmental data are frequently a direct reflection of the prevailing climatic and ecologic setting. Isotope-based reconstructions may be sufficiently robust to stand alone and can often place constraints on the interpretation of other proxy data. Below are concise reviews of the fundamental processes and factors that influence the oxygen and carbon isotope composition of lacustrine organic matter, commonly held assumptions, and examples of isotope paleolimnology studies that, together, outline the research approach used in this investigation.

Oxygen Isotopes in Lacustrine Organic Matter

Widespread occurrence of organic matter in treeline lake sediments provides an alternative substrate to the limited distribution of lacustrine biogenic and inorganic carbonates in this region, the more traditional archives of isotope-derived hydrologic information in temperate and tropical environments. The organic-isotope approach to paleohydrologic reconstruction is primarily based on stratigraphic analysis of $\delta^{18}O_{cell}$, first utilized by Edwards & McAndrews (1989), which frequently serves as a proxy for the oxygen isotope history of lake water ($\delta^{18}O_{lw}$). Direct inference of $\delta^{18}O_{lw}$ from $\delta^{18}O_{cell}$ is strongly supported by independent evidence showing that the isotopic

separation between cellulose and water is relatively constant ($\varepsilon_{cell\text{-}lw} \approx 28$ ‰), unaffected by changes in temperature or plant species (see reviews by Sternberg 1989 and Yakir 1992).

Aquatic cellulose is found in the cell walls of many algae, forming about 10 % by weight (De Leeuw & Largeau 1993), and is likely preserved in lake sediments within zooplankton fecal pellets (Edwards 1993). Incorporation of terrestrial cellulose in fine-grained offshore lake sediment often appears to be minimal in boreal treeline lakes (see manuscripts in this document) as well as in many other hydrologic and ecologic settings (Edwards & McAndrews 1989; Duthie *et al.* 1996; Padden 1996; Buhay & Betcher in press). In some arctic lakes where primary productivity is very low, however, bulk sediment cellulose may be predominantly terrestrial in origin and cellulose extracted from aquatic mosses may provide a better record of $\delta^{18}O_{lw}$ (Sauer *et al.* 1997).

Source interpretation of $\delta^{18}O_{cell}$ is best constrained, however, when coupled with bulk organic C/N ratio analyses as well as $\delta^{13}C_{org}$ and $\delta^{13}C_{cell}$ determinations (see following section for further discussion of carbon isotopes in lakes). These data can yield ancillary information on the origin of the organic matter. For instance, low C/N ratios (<10) are commonly indicative of aquatic organic matter (Meyers 1994; Meyers & Ishiwatari 1995). Even in organic-rich sediments with slightly higher values (10-15) however, oxygen isotope analyses of the cellulose fraction appear to predominantly reflect lake water $\delta^{18}O$ (Duthie *et al.* 1996; MacDonald *et al.* in prep.), perhaps due to preferential preservation of aquatic cellulose (Edwards 1993). Parallel time-series trends between $\delta^{13}C_{org}$ and $\delta^{13}C_{cell}$ indicate CO_2 uptake from the same carbon source and can provide further support for the aquatic origin of cellulose especially when combined with low C/N ratios. Conversely, stratigraphic variation in the isotopic difference between $\delta^{13}C_{org}$ and $\delta^{13}C_{cell}$ may signal increased terrestrial contamination in bulk organic matter (Wolfe *et al.* 1996) and also cellulose if the organic content is extremely low (MacDonald *et al.* in prep.). Changes in bulk organic matter sensitivity to fluctuations in dissolved inorganic carbon (DIC) $\delta^{13}C$ (Edwards 1993) and bulk organic matter preservation, however, can complicate these empirical relationships.

For records in which an aquatic origin for sediment cellulose can be inferred, interpretation of reconstructed $\delta^{18}O_{lw}$ histories usually requires identifying isotopic effects caused by shifts in the oxygen isotope composition of source water (i.e. precipitation and inflow) versus those related to hydrological processes. In its simplest form, this essentially involves separating changes in $\delta^{18}O_{lw}$ that occur along a local meteoric water line from those occurring along a local evaporation line (Figure 1-2). In hydrologically-open lake basins that experience little evaporation and receive water directly from precipitation, $\delta^{18}O_{lw}$ histories inferred from sediment cellulose (as well as those more commonly obtained from lacustrine carbonate records) may trace the mean annual oxygen isotope composition of precipitation ($\delta^{18}O_P$). This parameter has frequently been used as a temperature proxy (e.g. Eicher & Siegenthaler 1976; Lister 1988; von Grafenstein *et al.* 1992, 1996; Ahlberg *et al.* 1996; Duthie *et al.* 1996) or less often as evidence for past changes in moisture sources, seasonal distribution of precipitation, and other aspects of air mass circulation (e.g. Ruifen *et al.* 1994; Talbot 1994; Edwards *et al.* 1996; Hammarlund & Edwards 1997). In other lakes, the $\delta^{18}O_P$ imprint on $\delta^{18}O_{lw}$ may be modified by secondary isotopic effects, including evaporative enrichment as is generally the case in hydrologically-closed basins, thus providing a record of water balance and moisture conditions (e.g. Edwards & Fritz 1988; Lister *et al.* 1991; Hodell *et al.* 1995; Benson *et al.* 1996; Wolfe *et al.* 1996).

Carbon Isotopes in Lacustrine Organic Matter

In contrast to lake water $\delta^{18}O$, which is largely controlled by physical mechanisms, the $\delta^{13}C$ of lake water DIC may be strongly mediated by in-lake biological processes as well as exchange with atmospheric CO_2 (McKenzie 1985; Quay *et al.* 1986; Herczeg 1987; Herczeg & Fairbanks 1987; Lee *et al.* 1987). During photosynthesis, phytoplankton preferentially consume ^{13}C-depleted $CO_{2(aq)}$ leaving the remaining $CO_{2(aq)}$ relatively enriched in the heavy carbon isotope. Fractionation between total dissolved inorganic carbon and particulate organic matter is typically about -20 ‰ (Meyers *et al.* 1993), but can be substantially less due to low levels of $CO_{2(aq)}$ (Deuser *et al.* 1968; Calder & Parker 1973; Herczeg & Fairbanks 1987;

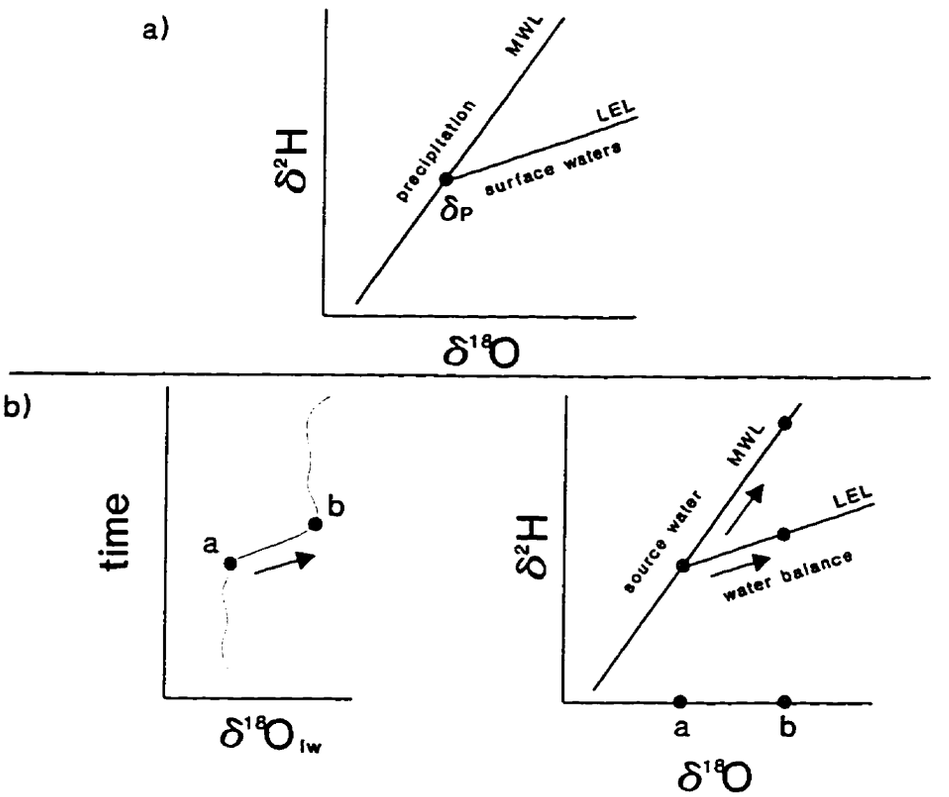


Figure 1-2. a) The oxygen and hydrogen isotope composition of precipitation and surface waters typically define two linear trends in δ^2H and $\delta^{18}O$ space. Precipitation plots on a meteoric water line (MWL) having a slope of near 8 (Craig 1961). Distribution along the MWL mainly reflects variation in temperature-dependent fractionation during condensation of atmospheric vapour and rain-out effects related to the air mass history (Dansgaard 1964; Rozanski *et al.* 1993). Decreasing temperature at the site of condensation, and increasing latitude, altitude, and distance from the moisture source (continentality) will generally result in progressively decreasing δ^2H and $\delta^{18}O$ values in precipitation. Lakes that have undergone evaporation display enrichment in δ^2H and $\delta^{18}O$ and plot on local evaporation lines (LEL) having slopes usually between 4 and 6 (Craig & Gordon 1965; Gonfiantini 1986). Displacement along a LEL varies between lakes in response to varying water balance. Increasing evaporation relative to inflow normally corresponds to increasingly positive values of δ^2H and $\delta^{18}O$ along a LEL trajectory. In regions characterized by a common moisture source, intersection of the LEL and MWL can provide an estimate of the mean annual isotopic composition of precipitation (δ_P).

b) Stratigraphic interpretation of cellulose-inferred lake water $\delta^{18}O$ ($\delta^{18}O_{lw}$) generally involves separating isotopic shifts related to changes in source water isotopic composition, reflected by displacement along a MWL, from shifts in water balance reflected by displacement along a LEL.

Hollander & McKenzie 1991) and HCO_3^- assimilation (Hollander & McKenzie 1991; Talbot & Johannessen 1992; Aravena *et al.* 1992). Diffusive influx of atmospheric CO_2, however, may replenish $CO_{2(aq)}$ withdrawn by phytoplankton. This process usually provides a relatively ^{13}C-enriched source to the DIC pool although recent work suggests that lakes are generally sources rather than sinks of atmospheric CO_2 (Cole *et al.* 1994). Decaying plant material that sinks below the photic zone, in turn, releases ^{13}C-depleted CO_2 (with a negligible fractionation effect). Thus, lakes typically display ^{13}C-enriched DIC values in the epilimnion and ^{13}C-depleted DIC values in the hypolimnion during summer stratification. Hypolimnion DIC may be reincorporated by phytoplankton upon circulation and mixing of lake waters.

In lakes where the carbon isotope effects of photosynthesis and respiration may not be as pronounced, river and groundwater input of DIC may exert a greater influence on lake water $\delta^{13}C_{DIC}$ (Rau 1978). Catchment-derived $\delta^{13}C_{DIC}$ may potentially span a wide range of values ($\approx$ -30 to 0 ‰) reflecting influx of dissolved CO_2 from the decomposition of ^{13}C-depleted soil organic matter (in areas devoid of carbonate) and the chemical weathering of ^{13}C-enriched carbonate terrane (Boutton 1991).

Since the pioneering work of Oana & Deevey (1960), carbon isotopes in organic lake sediments have frequently been used to acquire paleolimnologic information (see reviews by Stuiver 1975, Hakansson 1985, and McKenzie 1985). As in studies of modern lake water $\delta^{13}C_{DIC}$, the balance between photosynthesis and respiration often appears to be the dominant signal recorded in $\delta^{13}C_{org}$ profiles with positive excursions frequently interpreted as increased lake productivity (Schelske & Hodell 1991, 1995; Meyers *et al.* 1993; Dean & Stuiver 1993; Duthie *et al.* 1996). These internal lake processes may, however, be overprinted by changes in hydrology and influx of ^{13}C-depleted $CO_{2(aq)}$ produced in soils (Wolfe *et al.* 1996, in review; Hammarlund 1993). Other studies suggest that $\delta^{13}C_{org}$ may also record changes in atmospheric pCO_2 (Meyers & Horie 1993), early diagenetic processes in lake sediments (Nissenbaum 1984; Herczeg 1988), deposition of organic matter derived from different plant communities (Talbot & Livingstone 1989), and paleotemperature (Ariztegui & McKenzie 1995).

Many of these investigations have exclusively focused on the usage of $\delta^{13}C$ in bulk organic matter, which may be hampered for several reasons. Clearly, many different processes can invoke similar shifts in the $^{13}C/^{12}C$ ratio. For example, increased lake productivity, reduced contribution of respired $CO_{2(aq)}$ from bottom waters or sediment to the DIC pool, lake water $CO_{2(aq)}$ equilibration with the atmosphere, and decreased supply of DIC from non-carbonate bedrock catchments can all result in ^{13}C-enrichment trends in profiles of bulk organic lake sediment. Second, delivery of both aquatic and terrestrial material to lake sediment can complicate the $\delta^{13}C_{org}$ record. Consequently, additional analyses such as isotopic measurement of macrofossils of known origin and C/N ratios are often required to ascertain the importance of autochthonous and allochthonous contributions (e.g. Aravena *et al.* 1992; Meyers 1990). Third, major components of plant matter have varying carbon isotope composition (Deines 1980) and a change in the relative proportion of these constituents preserved in lake sediments (e.g. as a result of selective degradation of labile fractions) may cause a shift in $\delta^{13}C_{org}$ that is unrelated to any climate-induced isotopic effect (Epstein *et al.* 1976; Spiker & Hatcher 1984).

Some of these potential difficulties in interpreting $\delta^{13}C_{org}$ profiles can, however, be resolved by additional carbon isotope analysis of the fine-grained cellulose since this component frequently appears to be aquatic in origin and is resistant to degradation. Although interpretation remains qualitative and often speculative, incorporation within a multi-proxy approach (C/N ratios, $\delta^{18}O_{cell}$, diatoms, pollen, etc.) can effectively constrain the number of possible interpretations (Wolfe *et al.* 1996, in prep.; MacDonald *et al.* in prep.).

Thesis Organization

The remainder of this dissertation is composed of four main chapters each comprising one or more self-contained manuscripts followed by a concluding chapter and appendices. Manuscripts that have been previously published (or are in press) have been subject to varying degrees of modification for inclusion into the thesis. Methodologies are described in the individual manuscripts. Revised technical

procedures used in the Environmental Isotope Laboratory, University of Waterloo are provided in APPENDIX 1. Chapters logically progress from a modern isotopic assessment of lake surface sediment calibrations to individual lake paleohydrologic reconstructions to regional compilations. Each manuscript is prefaced by a synopsis which contains supplementary information and highlights important contributions. The following chapter briefs are provided to assist the reader in locating specific investigations.

CHAPTER 2: INTEGRATING MECHANISTIC AND TRANSFER FUNCTION APPROACHES TO PALEOLIMNOLOGY

> Wolfe BB & TWD Edwards, 1997. Hydrologic control on the oxygen-isotope relation between sediment cellulose and lake water, western Taimyr Peninsula, Russia: Implications for the use of surface-sediment calibrations in paleolimnology. *Journal of Paleolimnology* (in press).

This chapter compares mechanistic and transfer function approaches to the interpretation of paired oxygen isotope composition of surface sediment cellulose and lake water for a suite of lakes near treeline in central Russia. Variable deviation from the expected cellulose-water fractionation is used to provide a source of lake-specific hydrologic information and constrain interpretations based on microfossil surface-sediment calibrations.

CHAPTER 3: PALEOHYDROLOGY AT THE NORTHERN BOREAL TREELINE: CENTRAL CANADA

> Wolfe BB, TWD Edwards, R Aravena & GM MacDonald, 1996. Rapid Holocene hydrologic change along boreal treeline revealed by $\delta^{13}C$ and $\delta^{18}O$ in organic lake sediments, Northwest Territories, Canada. *Journal of Paleolimnology* 15: 171-181.

This chapter presents carbon and oxygen isotope results from a tundra lake sediment core in central Canada and complements an earlier pilot study from a nearby site (MacDonald *et al.* 1993). Discussion focuses on the relationship between forest expansion and changes in the lake water and carbon balance, as well as the effect of a hydrologically complex catchment on the isotopic records.

CHAPTER 4: PALEOHYDROLOGY AT THE NORTHERN BOREAL TREELINE: TAIMYR PENINSULA AND LENA RIVER, RUSSIA

Velichko AA, OK Borisova, CV Kremenetski, AA Andreev, KE Duff, TE Laing, BB Wolfe, R Aravena, LC Cwynar, TWD Edwards, JP Smol, RT Riding, GM MacDonald & D Porinchu, in prep. Holocene environmental change at treeline on the western Taimyr Peninsula of Siberia. For submission to *Quaternary Research*.

Wolfe BB, TWD Edwards & R Aravena, in prep. Changes in carbon and nitrogen cycling during treeline retreat recorded in the isotopic content of lacustrine organic matter, western Taimyr Peninsula, Russia. For submission to *The Holocene*.

Contribution to MacDonald GM, AA Velichko, LC Cwynar, M Pisaric, D Porinchu, TE Laing, BB Wolfe, AA Andreev, OK Borisova, TWD Edwards & JP Smol, in prep. A continuous record of Late Quaternary climatic and environmental change from Arctic Siberia. For submission to *Science*.

In Velichko *et al.* (in prep.), a draft manuscript is presented that integrates multi-proxy data collected at a site in north-central Russia. Paleolimnologic and paleohydrologic responses associated with terrestrial vegetation changes are described. This paper is presented in its entirety to clearly illustrate the contribution of stable isotope analysis within the overall multidisciplinary framework of the PACT project. In Wolfe *et al.* (in prep.), additional isotopic and elemental data from this site are reported, including exploratory investigations using nitrogen isotope analysis on organic lake sediments. Also included in this chapter is an excerpt from a manuscript in preparation that describes isotope results from a tundra site on the Lena River delta.

CHAPTER 5: REGIONAL SYNTHESES

Edwards TWD, BB Wolfe & GM MacDonald, 1996. Influence of changing atmospheric circulation on precipitation $\delta^{18}O$-temperature relations in Canada during the Holocene. *Quaternary Research* 46: 211-218.

Wolfe BB, TWD Edwards & R Aravena, 1997. Paleohydrology at treeline, northern Russia: A multi-faceted isotope approach. *Proceedings, International Symposium on Isotope Techniques in the Study of Past and Current Environmental Changes in the Hydrosphere and the Atmosphere.* International Atomic Energy Agency, Vienna, IAEA-SM-349/9.

This chapter contains two manuscripts that integrate lake sediment core $\delta^{18}O_{cell}$ data from northern Canada and northern Russia and provide regional reconstructions

of Holocene paleohydrology. Possible climate forcing mechanisms are discussed.

CHAPTER 6: SUMMARY AND RECOMMENDATIONS

This chapter summarizes important conclusions presented in chapters 2-5 and provides recommendations for future research.

Note on Contributions to Multi-Authored Manuscripts

Due to the strong emphasis on utilizing a multidisciplinary and collaborative research approach, the manuscripts in this dissertation are multi-authored. In the four manuscripts in which I am the lead author, I am largely responsible for the scientific and literary contributions. In Velichko *et al.* (in prep.; see CHAPTER 4), I am responsible for the section entitled "Oxygen Isotope Analysis" and contributed to roughly 50 % of the "Discussion". In Edwards *et al.* (1996; see CHAPTER 5), I collaborated in equal partnership with Edwards on the scientific development and literary presentation.

CHAPTER 2: INTEGRATING MECHANISTIC AND TRANSFER FUNCTION APPROACHES TO PALEOLIMNOLOGY

Wolfe BB & TWD Edwards, 1997. Hydrologic control on the oxygen-isotope relation between sediment cellulose and lake water, western Taimyr Peninsula, Russia: Implications for the use of surface-sediment calibrations in paleolimnology. *Journal of Paleolimnology* (in press).

Synopsis

Perhaps the most significant recent advancement in the science of paleolimnology is the improvement of techniques for quantitatively inferring specific lake properties from biological remains in lake sediments (Charles *et al.* 1994). Transfer functions, based on empirically-defined relations between biological distributions in surface sediment and lake water characteristics, have successfully been developed for lake water pH, salinity, trophic variables, and climatic parameters in widely differing environments (see Smol 1995 and references cited within). Although statistical robustness and ecologic reality of the inference method has been rigorously evaluated (Charles *et al.* 1994; Smol 1995), among the potential sources of variability that may introduce error relates to "the quality, appropriateness, and frequency of measurements of limnological characteristics" (Charles *et al.* 1994: 268-269). Temporal variability in lake water properties may be incorporated into the calibration model by measuring chemical and environmental parameters on several water samples obtained throughout a year from the same lake or from several years in ideal situations (Charles & Smol 1994).

In our field sites in remote northern Canada and Russia, however, multi-episode sampling was not feasible and consequently only one water sample from each lake was obtained in order to develop diatom, chrysophyte, and chironomid-based surface sediment calibrations. Although most paleolimnologists recognize that seasonal variations in water chemistry, for example, must be considered in the development of surface-sample training sets, this uncertainty is often poorly quantified although some attempts have recently been made (e.g. Xia *et al.* 1997). Strong seasonal, climatic variability in the arctic yet strengthens the likelihood that single-episode lake water samples may not reflect those conditions present when the surface sediments were

deposited.

In contrast to statistically-based transfer functions, which may vary from region to region, interpretation of oxygen isotope data from cellulose in lake sediments is based on observations that the fractionation between cellulose and water is constant (Sternberg 1988; Yakir 1992); thus the $\delta^{18}O$ of the lake water can often be directly inferred from the $\delta^{18}O$ of the cellulose. This fundamental difference in the quantitative interpretation of proxy data suggested that the isotopic method provided a tool for assessing the potential hydrologic discrepancy between the time of sampling and the average conditions represented by the surface sediments.

We tested this hypothesis by comparing the oxygen isotope composition in paired lake water and surface sediment cellulose samples from 20 lakes near treeline on the western Taimyr Peninsula, Russia. Our results confirmed that the hydrologic conditions inferred from the surface sediments were, indeed, systematically different from those prevailing at the time of sampling at many lakes. The limitations of single-visit collections in characterizing seasonally averaged lake water isotope composition are clearly illustrated by this data set and reinforce the appropriateness of a mechanistic approach to the interpretation of lake sediment cellulose $\delta^{18}O$. We also stress that seasonal variability in arctic hydrology and its influence on lake water chemistry may lead to inaccurate development of microfossil-based transfer functions based on single-episode sampling, although we emphasize that integrating the mechanistic isotope approach may help to constrain transfer function interpretations.

Abstract

Systematic variability occurs between the oxygen isotope composition of lake water sampled in mid-summer 1993 and cellulose extracted from surficial sediments of a suite of lakes spanning the forest-tundra transition near Noril'sk, Russia. Some tundra and all forest-tundra lakes show greater deviation from expected cellulose-water isotopic separation than forest lakes, apparently because of greater sensitivity to ^{18}O-depleted snowmelt contributions. Cellulose derived from aquatic plants naturally integrates growing season fluctuations in lake water $\delta^{18}O$, providing a signal that is inherently more representative of average thaw season lake water $\delta^{18}O$ than the measure of instantaneous $\delta^{18}O$ obtained from an individual sample of lake water. Thus, indiscriminate use of empirical cellulose-water relations derived from "calibration" samples could lead to erroneous assessment of paleohydrology from the oxygen-isotope stratigraphy of sediment cores from arctic lakes. However, deviation from the expected cellulose-water fractionation is a source of lake-specific hydrologic information useful for qualifying paleoenvironmental interpretations and possibly constraining non-isotopic methods that rely on surface-sediment calibrations.

Introduction

Oxygen-isotope analysis of finely disseminated cellulose in lacustrine organic matter ($\delta^{18}O_{cell}$) has developed into an effective method for reconstructing past hydrologic conditions in lake watersheds (e.g. Edwards & McAndrews 1989; MacDonald *et al.* 1993; Duthie *et al.* 1996; Wolfe *et al.* 1996). In these previous investigations, interpretation has explicitly assumed that the oxygen isotope history of lake water ($\delta^{18}O_{lw}$), a function of the source composition provided by local precipitation and subsequent hydrologic processes, can be directly inferred from stratigraphic analysis of $\delta^{18}O_{cell}$. This mechanistic approach is strongly supported by independent evidence showing that the isotopic separation between cellulose and water is constant, unaffected by changes in temperature or plant species (Epstein *et al.* 1977; DeNiro & Epstein 1981; Sternberg & DeNiro 1983; Sternberg *et al.* 1984; Sternberg *et al.* 1986; Yakir & DeNiro 1990; also see reviews by Sternberg 1989 and Yakir 1992).

Microfossil-based paleolimnologic reconstructions, in contrast, commonly depend on empirical relations between taxonomic variables in surface sediment and selected parameters measured in the overlying lake water at the time of sediment sampling. Remarkably robust transfer functions can be generated from statistical analysis of microfossil species distributions from a training set of lakes that spans a broad range in the environmental parameter of interest (see recent review by Charles & Smol 1994). Examples include relations between diatoms and salinity (Fritz 1990), chironomids and water temperature (Walker *et al.* 1991), and chrysophytes and pH (Cumming & Smol 1993). Transfer functions based on single-episode sampling, however, may be subject to errors arising from the temporal inconsistency between a surface-sediment sample, which integrates conditions during an extended time interval (potentially years to decades or centuries, depending on rates of sedimentation and the sampling resolution) and a sample of overlying lake water, which provides a measure of parameters that may have taken only days or weeks to develop. This inherent uncertainty is well-recognized, though often poorly quantified, and is normally mitigated by expert judgement in the selection of calibration lakes and subsequent data analysis and interpretation.

Here we present data obtained from isotopic investigations of a small calibration set of paired surface-sediment and single-episode lake-water samples collected as part of paleoecological studies at the forest-tundra transition near Noril'sk in north-central Russia. Employment of the mechanistic isotope "transfer function" linking the $\delta^{18}O$ values of sediment cellulose and water, however, reveals systematic discrepancies between "integrated" and "instantaneous" lake water $\delta^{18}O$ in this data set. Although we focus on the hydrologic implications of these apparent isotopic differences, such data may also provide a means of independently assessing biases or uncertainties in microfossil-based transfer functions.

Study Area and Methods

Samples of surface water and short-cores of surface sediment were collected from 20 small lakes at five sites in the tundra (seven lakes), forest-tundra (eight

lakes), and forest (five lakes) near Noril'sk (Figure 2-1). Vegetation zones are defined by Davidova & Rakovskya (1990) and described by Clayden *et al.* (1996). The lakes were chosen to provide calibration sets for the establishment of transfer functions between fossil indicators (diatoms, chironomids, chrysophytes) and lake-water temperature and chemistry for application to paleoenvironmental reconstruction from several long lake-sediment cores (Duff *et al.* in prep.; Laing *et al.* in review; Velichko *et al.* in prep.). Water samples for isotopic analysis were also collected from additional lakes of various sizes (n = 12), streams (n = 6), residual snowbanks (n = 5), rain (n = 1), groundwater (n = 7), and ground-ice (n =1). All samples were collected between July 28 and August 5, 1993.

The 20 calibration lakes range in area up to about 10 ha and in maximum depth from 2.2 to 11.5 m. The lakes occupy a variety of basin types, formed as kettles in ice-contact or outwash deposits (tundra lakes TS 1-3; forest lakes TS 17 and 18), kettles and thermokarst depressions in mixed glacial drift and organic terrain (tundra lakes TS 20-23, forest-tundra lakes TS 4-11, and forest lakes TS 15 and 16), and a bedrock basin in terrain heavily mantled by organic deposits (forest lake TS 13). Water levels were high but probably declining at the time of sampling, judging by evidence of recent submersion of shoreline vegetation and active surface outflow of most lakes, and the small amount of precipitation received during the 10-day field visit. The limnological characteristics of the lakes, including aspects of the water chemistry are discussed in detail by Duff *et al.* (in prep.). Diatom assemblages from the surface-sediment samples are described by Laing *et al.* (in review); stomate and pollen distributions were reported by Clayden *et al.* (1996).

Water samples from lakes, streams, and rain were collected directly in 30-ml high-density polyethylene (HDPE) bottles. Snow and ground-ice were sealed initially in polyethylene bags, permitted to melt completely, and then transferred into HDPE bottles. Shallow groundwater was obtained by collecting water-saturated soil from near the base of the active layer. Soil samples were sealed triple-wrapped in heavy-gauge polyethylene bags to prevent vapour loss during transport to the laboratory for subsequent azeotropic distillation of porewater (Revesz & Woods 1990).

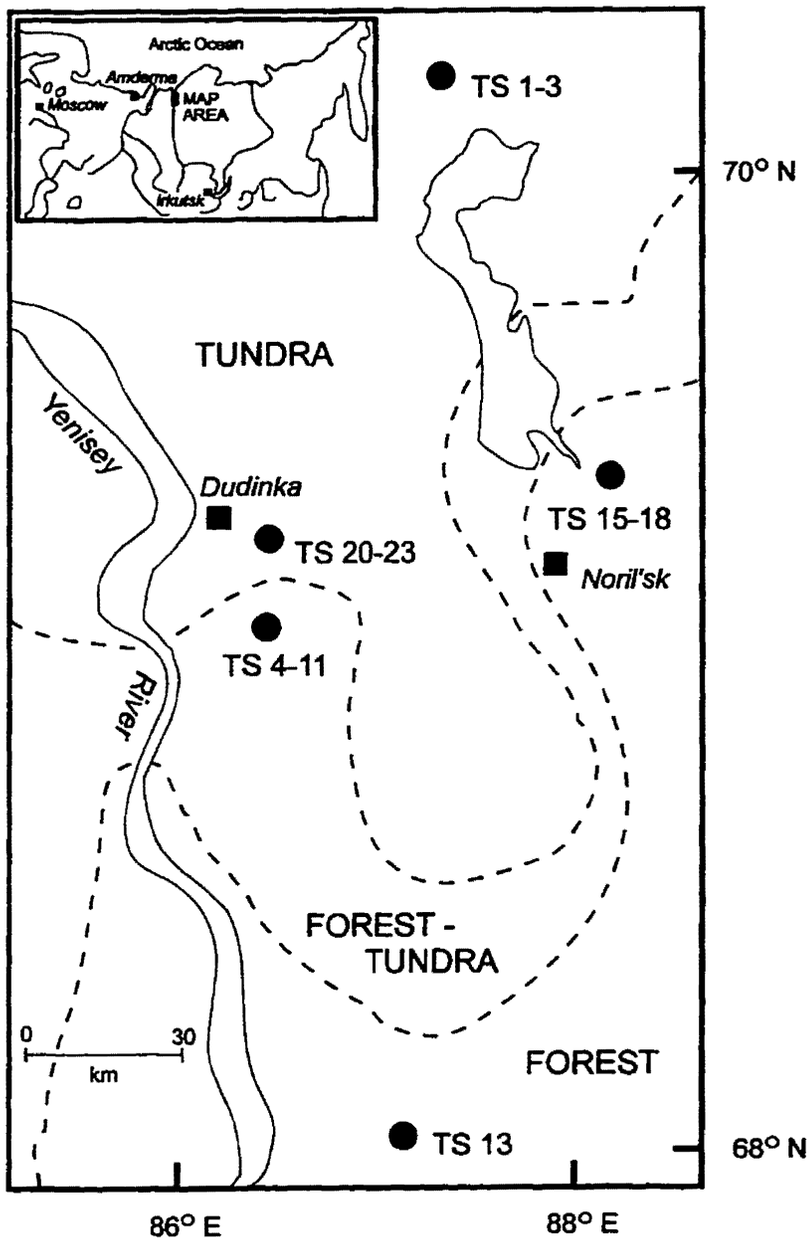


Figure 2-1. Study area including lake sites in tundra (TS 1-3, TS 20-23), forest-tundra (TS 4-11), and forest vegetation zones (TS 13, TS 15-18).

Surface sediments from the 20 calibration lakes were obtained from the uppermost portions of short cores collected using a manually operated drop-corer (Glew 1991) and sectioned in the field immediately upon retrieval. Sufficient material was obtained from the 0-1 cm interval in most of the cores, aside from TS 4, TS 13, and TS 16 (0-2 cm), and TS 17 (0-3 cm). Sediment samples were freeze-dried in the laboratory and sieved to eliminate macroscopic plant detritus (> 500 μm). Cellulose was isolated by washing at 70°C in 10% hydrochloric acid solution to remove carbonates, followed by solvent extraction, bleaching, and alkaline hydrolysis to remove non-cellulose organic components (Edwards & McAndrews 1989; Wolfe *et al.* 1996).

Isotopic analyses were carried out in the Environmental Isotope Laboratory, University of Waterloo using standard methods. Analyses of $^{18}O/^{16}O$ and $^{2}H/^{1}H$ ratios in water were undertaken on CO_2 and H_2 gases prepared by CO_2-equilibration (Epstein & Mayeda 1953) and Zn-reduction (Coleman *et al.* 1982), respectively. $^{18}O/^{16}O$ ratio in cellulose was measured on CO_2 gas produced by Ni-pyrolysis (Edwards *et al.* 1994). Results are reported as δ values, representing deviation in per mil (‰) from the international Vienna-SMOW standard such that $\delta = [(R_{sample}/R_{SMOW})-1]1000$, where R is the $^{18}O/^{16}O$ or $^{2}H/^{1}H$ ratio in the sample and standard. Analytical uncertainties are ± 0.2 ‰ and ± 2 ‰ for $\delta^{18}O$ and $\delta^{2}H$ values of water, respectively. Cellulose $\delta^{18}O$ values are considered accurate within ± 1 ‰, based on repeated analyses of natural samples.

Results and Discussion

Isotope Hydrology

Snow, rain, groundwater, and ground-ice, which should be unaffected by secondary isotopic alteration due to evaporation, define a local meteoric water line (LMWL) defined by:

$$\delta^{2}H = 8.0\delta^{18}O + 9.4 \quad (R^2 = 0.96)$$

This equation is nearly identical to the global meteoric water line of Craig (1961). Distribution of data points along the LMWL (Figure 2-2a) mainly reflects seasonal variation in temperature-dependent fractionation during condensation of atmospheric vapour, and other aspects of air mass history (Dansgaard 1964; Rozanski *et al.* 1993). As a result, our single sample of summer rain is strongly enriched in ^{18}O and ^{2}H relative to the snow samples which represent several precipitation events during the previous winter or spring. The range of snow $\delta^{18}O$ values compares well with data reported by Nikolayev & Mikhalev (1995) from the Severnaya Zemlya archipelago to the north of the Taimyr Peninsula (-24.2 to -14.4 ‰) and in the Yenisey River valley near the study area (-26.4 to -18.2 ‰). Groundwater and ground-ice data plot along the LMWL in a tight cluster intermediate between the snow and rain data, consistent with recharge by varying mixtures of snowmelt and rain.

Shallow groundwaters commonly provide a reasonable guide to the weighted mean isotopic composition of local annual precipitation (e.g., see Fritz *et al.* 1987). By this measure, recent mean annual precipitation in the study area appears to be somewhat depleted in ^{18}O and ^{2}H relative to that recorded in the early 1980s at Amderma, Russia, the nearest station in the IAEA/WMO network (Rozanski *et al.* 1993; also plotted on Figure 2-2a). More depleted values in our study area may reflect greater rain-out of contributing atmospheric vapour originating over the north Atlantic, the main source of moisture for this region (Lydolph 1977; Rogers & Mosley-Thompson 1995), compared to that reaching Amderma which lies about 1000 km to the west on the coast of the Arctic Ocean (Figure 2-1). The isotopic composition of precipitation at Amderma may also be influenced by local vapour derived from the Barents Sea.

Samples obtained from lakes and streams in the study area (Figure 2-2b) also generally lie close to, though statistically different from, the LMWL, and can be described by:

$$\delta^{2}H = 6.4\delta^{18}O - 22.0 \quad (R^2 = 0.91)$$

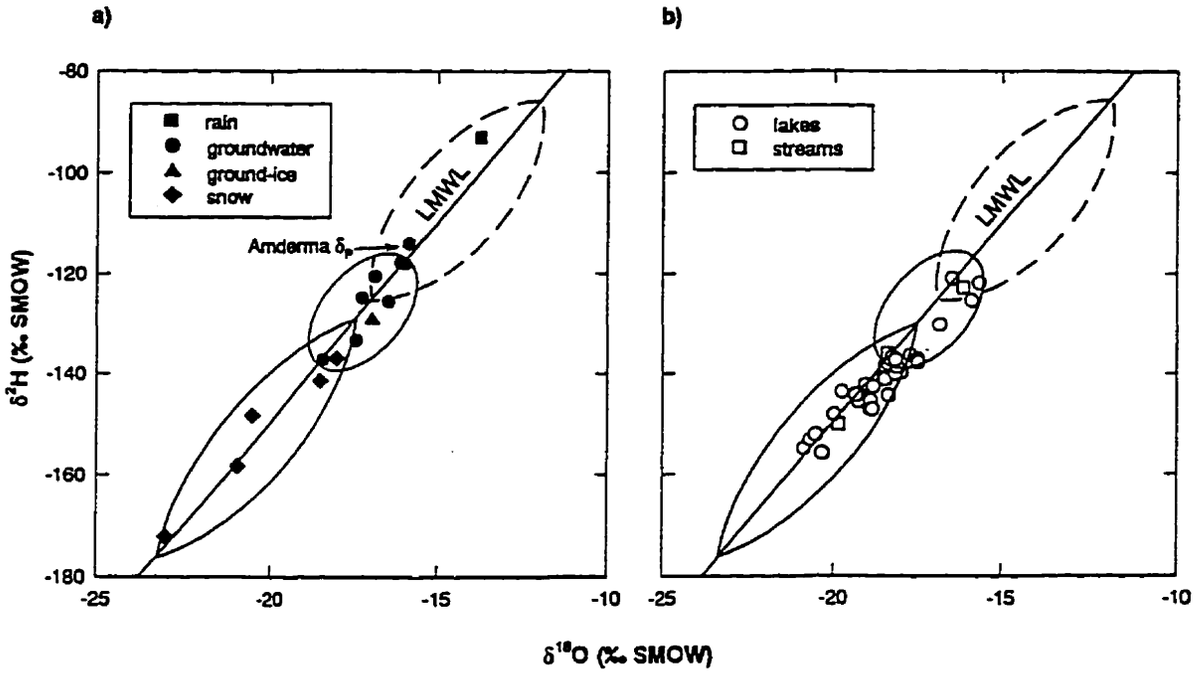


Figure 2-2. a) δ^2H versus $\delta^{18}O$ for non-evaporated waters. Local Meteoric Water Line (LMWL) is defined by $\delta^2H = 8.0\delta^{18}O+9.4$. Mean annual isotopic composition of precipitation (δ_p) for Amderma, Russia is also shown (Figure 2-1; Rozanski *et al.* 1993). Elliptical fields group isotopic compositions for snow, groundwater and ground-ice, and rain. Note that field for rain is estimated on the basis of groundwater and ground-ice isotopic compositions which likely represent mixtures of snowmelt and rain.

b) δ^2H versus $\delta^{18}O$ for surface waters. Elliptical fields as in a). Most lakes and rivers plot near the LMWL in the field for snow displaying minimal evaporative enrichment.

The systematic offset of many points to the right of the LMWL reflects kinetic isotope effects during open-water evaporation (Craig & Gordon 1965; Gonfiantini 1986); however, the scatter of the data points and high slope of this regression line suggest that it does not define a distinct local evaporation line. More likely, points are offset along a number of short, more shallowly sloping evaporation trajectories having initial compositions distributed along the LMWL, reflecting varying catchment-specific balances of seasonal precipitation and inflow. Limited evaporative enrichment is expected given the relatively early time of sampling and high thaw-season relative humidity in the area (*ca.* 70-80 % during July; Lydolph 1977). As discussed in more detail below, the marked clustering of points within the field of measured snow isotopic compositions highlights the importance of snowmelt as a component of many individual water budgets in the study area at the time of sampling, while it is also clear that snowmelt plays a much smaller role in the budgets of some lakes and streams.

$\delta^{18}O_{cell}$ - $\delta^{18}O_{lw}$ Relations

The relation between measured $\delta^{18}O_{cell}$ and $\delta^{18}O_{lw}$ for cellulose and water samples from the 20 calibration lakes is shown graphically in Figure 2-3a. $\delta^{18}O_{cell}$ values range widely, from +6.5 to +22.1 ‰, whereas $\delta^{18}O_{lw}$ values are less variable, spanning -20.8 to -15.6 ‰. The most extreme deviation from the expected separation of about 28 ‰ (Edwards & McAndrews 1989) is 12 ‰ (TS 8), while the mean deviation is about 4 ± 6 ‰, suggesting that waters from which the cellulose formed ranged from being slightly more depleted in ^{18}O compared to the water grab-sampled at the time of coring to being substantially enriched. Figure 2-3b shows the relation between $\delta^{18}O_{lw}$ inferred from cellulose $\delta^{18}O$, assuming a fixed water-cellulose fractionation of 1.028, and measured $\delta^{18}O_{lw}$, grouped according to vegetation zone.

Closer examination of our results reveals two distinct groupings on Figure 2-3a. Data points for all five forest lakes and the three most isotopically-enriched tundra lakes plot within about ± 2 ‰ of the anticipated cellulose-water isotopic separation, whereas the other four tundra lakes and all eight from the forest-tundra are offset in excess of 2 ‰. A variety of factors could account for the apparent inconsistency of

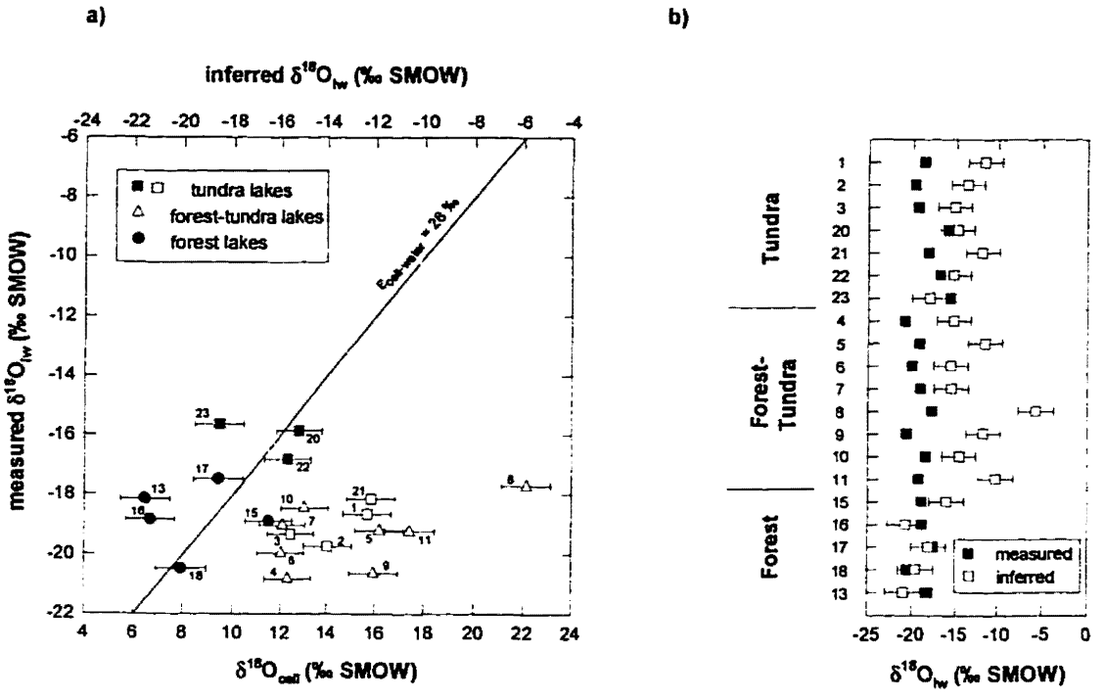


Figure 2-3. a) $\delta^{18}O_{cell}$ and inferred $\delta^{18}O_{lw}$ calculated using the expected cellulose-water isotopic separation, $\varepsilon_{cell\text{-}water}$ = 28 ‰ (from Edwards & McAndrews 1989), versus measured $\delta^{18}O_{lw}$ for tundra, forest-tundra, and forest lakes. Error bars reflect analytical uncertainty (± 1 ‰). Three tundra lakes, each identified by a solid square symbol, and all five forest lakes lie close to the line defined by $\varepsilon_{cell\text{-}water}$ indicating cellulose formed from lake water with similar oxygen isotope composition as measured lake water. The remaining tundra lakes, represented by open squares, and all forest-tundra lakes, however, plot to the right of the expected $\varepsilon_{cell\text{-}water}$ relationship suggesting higher inferred $\delta^{18}O_{lw}$.

b) Ecotone distribution of measured and cellulose-inferred $\delta^{18}O_{lw}$. Error bars for inferred $\delta^{18}O_{lw}$ incorporate uncertainties in both analysis and cellulose-water isotopic separation (± 2 ‰). Values are in reasonable agreement for forest and some tundra lakes, whereas measured $\delta^{18}O_{lw}$ is several per mil more depleted than inferred $\delta^{18}O_{lw}$ at forest-tundra and most tundra sites. See Figure 2-1 for lake locations.

$\delta^{18}O_{cell}$ and $\delta^{18}O_{lw}$ values in the latter group of lakes. Admixture of ^{18}O-enriched cellulose from terrestrial plants is an obvious candidate, yet previous studies of sediment cellulose from lakes in various settings have commonly failed to detect evidence for significant terrestrial "contamination" within the fine sediment fraction (e.g., Edwards & McAndrews 1989; MacDonald *et al.* 1993; Wolfe *et al.* 1996), even where clear evidence for increased allochthonous input of bulk organic matter existed (Duthie *et al.* 1996). Although this mechanism cannot be ruled out unequivocally, arguing against it is the fact that the five lakes in forested terrain, where there may be greater potential for delivery of terrestrial organic matter, are among those in our data set showing better agreement between $\delta^{18}O_{cell}$ and $\delta^{18}O_{lw}$ than the lakes in less densely vegetated forest-tundra or tundra.

Alternatively, and perhaps more likely, are systematic differences between measured $\delta^{18}O_{lw}$ and cellulose-inferred $\delta^{18}O_{lw}$ that arise simply because of the unavoidable mismatch in time between fossil indicators deposited gradually in sediments and parameters measured instantaneously in the overlying lake water. Strong changes in a lake's isotopic composition can occur during the thaw season, when phytoplankton that produce the cellulose are active, because of seasonal variations in the isotopic composition of inflow (runoff and precipitation) and secondary evaporative enrichment. Some lakes in northern Canada, for example, have been observed to vary seasonally by more than 5 ‰ under comparable climatic conditions (Gibson *et al.* 1993, 1996), with $\delta^{18}O_{lw}$ typically declining dramatically during ice breakup because of low-$\delta^{18}O$ snowmelt input, followed by more gradual enrichment through influx of relatively high-$\delta^{18}O$ thaw-season rain and groundwater, and evaporation. Cellulose in surface sediment naturally averages such seasonal shifts in lake-water isotopic composition. As a result, the magnitude and variability of a lake's seasonal fluctuations in relation to the timing of sampling strongly affect the likelihood of obtaining a good match between cellulose-inferred and measured $\delta^{18}O_{lw}$ (shown schematically in Figure 2-4).

Based on field observations, our visit coincided with the latter part of the "spring" freshet in most catchments. This is supported by isotopic evidence for

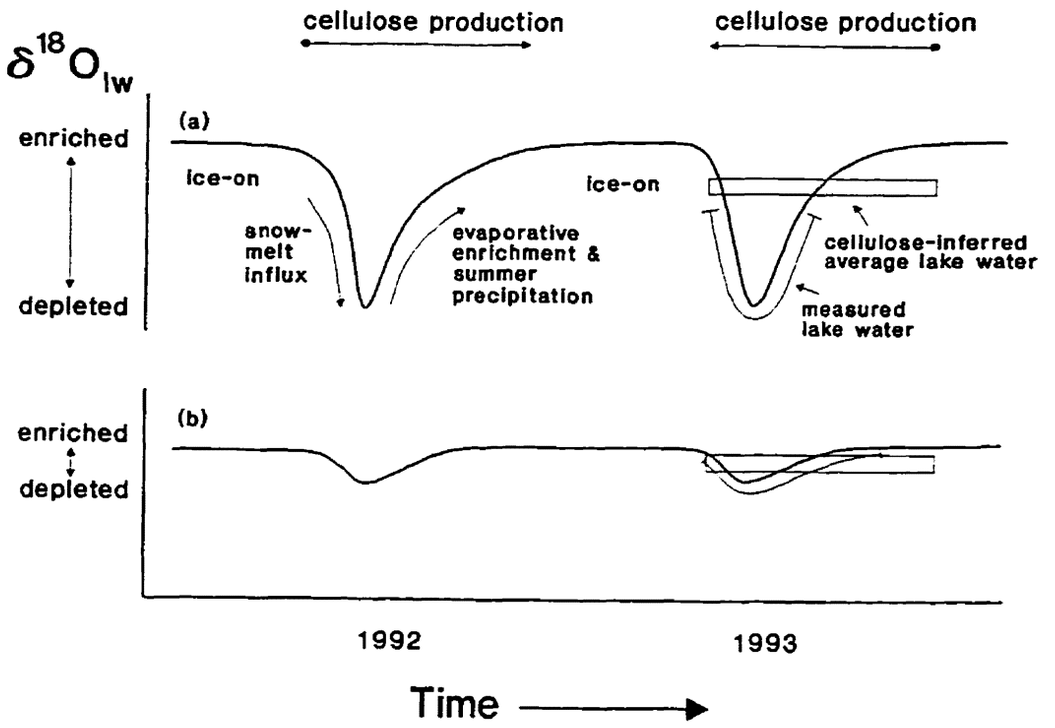


Figure 2-4. a) Average annual variation in $\delta^{18}O_{lw}$ for a typical small and well-mixed, arctic lake characterized by significant influx of ^{18}O-depleted runoff during snowmelt followed by evaporative ^{18}O-enrichment and contribution from ^{18}O-enriched summer precipitation during the thaw season. Cellulose incorporates natural fluctuations in the $\delta^{18}O_{lw}$ cycle and thus is a good proxy for average thaw season $\delta^{18}O_{lw}$. Measured $\delta^{18}O_{lw}$, however, is variably more negative than cellulose-inferred $\delta^{18}O_{lw}$ for most tundra and all forest-tundra lakes because our lake water samples were obtained during the depleted segment of the $\delta^{18}O_{lw}$ cycle at these sites. Snowmelt may also have been unusually late in 1993, given that our results are from samples collected at the end of July/beginning of August, illustrating that temporal variability in the $\delta^{18}O_{lw}$ cycle may also lead to differences between cellulose-inferred and instantaneously measured $\delta^{18}O_{lw}$.

b) Forest and some tundra lake $\delta^{18}O_{lw}$ cycles in our data set are less isotopically variable because terrain surrounding these basins appear to attenuate seasonal variations in the isotopic composition of source water. Thus, there is less potential for significant discrepancies to develop between cellulose-inferred $\delta^{18}O_{lw}$ and measured $\delta^{18}O_{lw}$ as a result of single-episode sampling.

predominant snowmelt influence, as noted above and, indeed, snowmelt was flowing directly into some lakes at tundra site TS 1-3 at the time of sampling. This also accounts for the systematic offset between inferred and measured $\delta^{18}O_{lw}$ in Figure 2-3b, reflecting the probability that we commonly captured lake water that was appreciably depleted in ^{18}O compared to the average lake water value later in the thaw season. Moreover, the varying magnitude of the discrepancy between different lakes also appears to offer meaningful lake-specific hydrologic information. For example, the extreme difference (*ca.* 12 ‰) between inferred and measured $\delta^{18}O_{lw}$ in TS 8, a shallow, headwater lake in the forest-tundra zone (Figure 2-5), can be plausibly ascribed to strong evaporative drawdown and non-steady-state isotopic enrichment equivalent to that documented by Gibson *et al.* (1993) in some similar high-boreal lakes in northern Canada. Supporting evidence for strong evaporative enrichment in this lake is provided by the displacement of TS 8 to the right of the LMWL in Figure 2-6, indicating that some evaporative enrichment had already occurred in 1993 and (or) part of the signal of evaporative enrichment from the previous year was preserved in spite of 1993 snowmelt contributions. Predictably, the much smaller difference between inferred and measured $\delta^{18}O_{lw}$ (*ca.* 3 ‰) for TS 7, a deeper, through-flow lake downstream in the same catchment (Figure 2-5), is associated with a more depleted oxygen- and hydrogen-isotope composition, lying on the LMWL (Figure 2-6).

Field observations are also consistent with the possibility that subdued seasonal isotopic variability is characteristic of the eight lakes exhibiting relatively small discrepancies between inferred and measured $\delta^{18}O_{lw}$. The terrain immediately surrounding these lakes is mantled predominantly by organic deposits (TS 13, 15, 16, 20, 22, and 23) or combinations of organic deposits and permeable coarse-grained ice-contact debris (TS 17 and 18) that limit the possibility of direct surface runoff from the surrounding catchments. Snowmelt and rain likely mix with melting ground-ice during the thaw season and flow into these lakes as shallow groundwater, naturally attenuating seasonal variations in the isotopic composition of the precipitation. Judging by the systematic offset from the LMWL, the three tundra lakes (TS 20, 22,

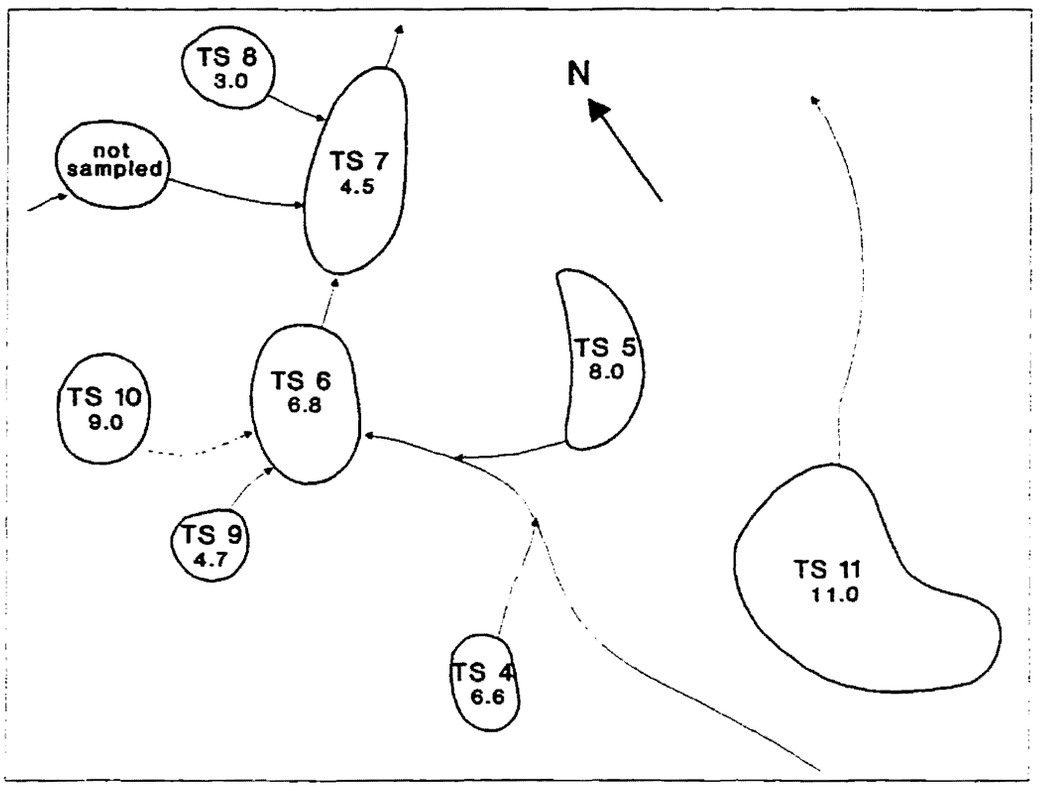


Figure 2-5. Sketch of forest-tundra lakes (TS 4-11). Solid arrows represent surface drainage; dashed arrow represents subsurface drainage. Values indicate maximum depth in metres. Not to scale.

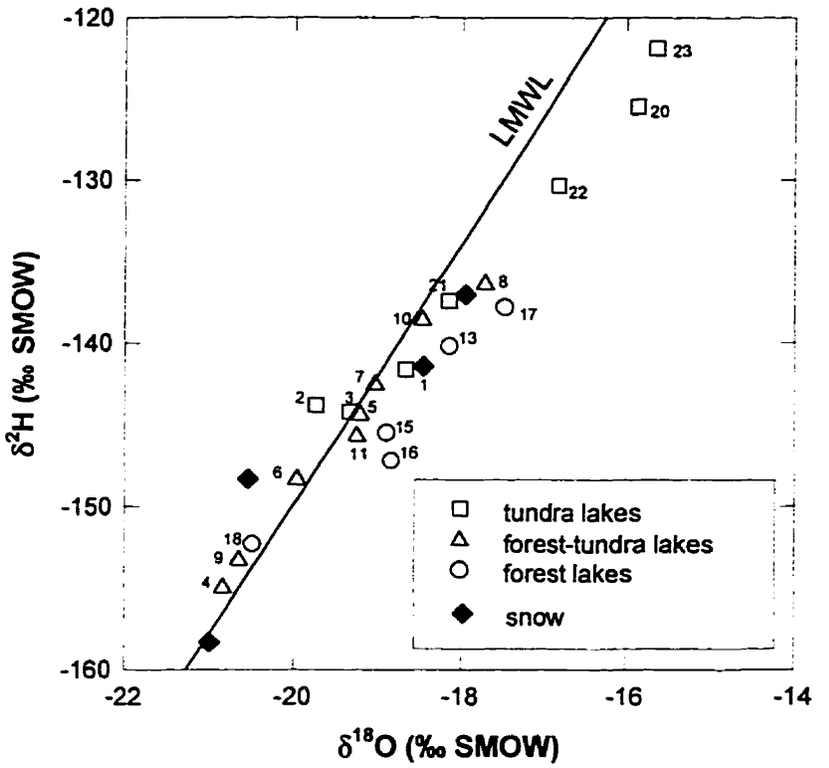


Figure 2-6. δ^2H versus $\delta^{18}O$ for lakes plotted in Figure 2-3 and selected snow samples. LMWL as in Figure 2-2.

and 23) and four of the five forest lakes (TS 13, 15, 16, and 17) do undergo detectable evaporative enrichment, although it is clear that the forest lakes generally derive a larger proportion of their water budgets from winter precipitation (Figure 2-6). Site-specific differences in the seasonal distribution of precipitation and topographically controlled differences in the ratio of contributing area to lake surface area, perhaps enhanced by greater interception losses of thaw-season rains within the forest canopy, probably account for the gross deviations in the water budgets between the forest and tundra lakes.

Interestingly, the buffering influence of shallow groundwater inflow on seasonal fluctuations in $\delta^{18}O_{lw}$ may also help to explain the relatively modest discrepancy (*ca.* 3 ‰) between inferred and measured $\delta^{18}O_{lw}$ for TS 10, one of the headwater lakes in the forest-tundra zone (Figures 2-3b, 2-5). This lake and its close neighbour TS 8 (characterized by the maximum discrepancy in our data set, as discussed above) apparently receive similar overall mixtures of seasonal precipitation, whereas TS 10 showed no signature of evaporative enrichment at the time of sampling (Figure 2-6). Outflow from TS 10 occurs via subsurface seepage through organic deposits on the downgradient shore, and the possibility exists for significant groundwater inflow through similar peat deposits located on the upgradient side of the lake, perhaps dampening seasonal fluctuations in $\delta^{18}O_{lw}$ compared to the strong variations that apparently occur in TS 8 and other headwater lakes nearby (e.g., TS 5, 9, and 11; Figures 2-3b, 2-5).

Concluding Comments

Isotopic studies at several forest-tundra and tundra lakes near Noril'sk, Russia indicate that single-episode water sampling has captured instantaneous mid-summer $\delta^{18}O_{lw}$ that is variably more negative compared to inferred $\delta^{18}O_{lw}$ from surface-sediment cellulose. Supported by field observations on local hydrologic settings, these data suggest that the isotopic mass balance in these lakes is sensitive to ^{18}O-depleted snowmelt contributions and that our grab samples of lake water had appreciable snowmelt content. At forest lakes and some tundra lakes, in contrast, good

agreement occurs between measured and inferred $\delta^{18}O_{lw}$ values. These lakes are bordered by organic substrates and/or permeable coarse-grained ice-contact debris that apparently attenuate seasonal variations in the isotopic composition of source water.

Marked seasonal variability in hydrology evident at most of the sites demonstrates that average thaw season lake water oxygen isotopic composition is difficult to obtain from a single water sample and development of an empirical cellulose - lake water $\delta^{18}O$ transfer function would be inappropriate from the available data. These results have, however, yielded a source of lake-specific hydrologic information useful in the interpretation of long-core, mechanistically-inferred $\delta^{18}O_{lw}$ from sediment cellulose. For example, frequent excursions to relatively negative values between 4000 and 2500 ^{14}C years before present at the TS 1 site may reflect short-lived, increased contribution of ^{18}O-depleted snowmelt (Velichko *et al.* in prep.). On the other hand, we speculate that the inferred $\delta^{18}O_{lw}$ record from forest site TS 13 may be relatively insensitive to abrupt fluctuations in the seasonal distribution of precipitation (Wolfe *et al.* work in progress).

Several studies from northern Canada and Alaska show that seasonal variability in arctic hydrology may also strongly influence lake water chemistry, which has important implications for microfossil-based transfer functions. For example at Colour Lake on Axel Heiberg Island, timing of snowmelt generation and lake-ice breakup strongly influence lake retention of phosphorus-rich meltwater (Adams & Allan 1987). Lakes near Saqvaqjuac, Northwest Territories, Canada are subject to widely varying amounts of soil-derived elements, including Ca and Si, depending on the seasonal pattern of runoff (Welch & Legault 1986). Two to three-fold increases in nutrient loading at Toolik Lake, Alaska, were found to be closely related to the timing of spring melt (Whalen & Cornwell 1985). On a somewhat longer timescale but perhaps also relevant seasonally, the isotopic composition of dissolved inorganic carbon and possibly dissolved CO_2 concentration in a small lake near boreal treeline in central Canada was found to be strongly tied to the hydrologic balance (Wolfe *et al.* 1996).

In remote regions such as the arctic, logistical constraints may limit the

frequency of measurements of limnological characteristics. This has been recognized as an important potential source of error in the surface-sediment calibration method (Charles *et al.* 1994). Clearly, single-episode water sampling at any of the locations mentioned above may reflect water chemistries significantly different from what prevailed during deposition of surface-sediment. In our suite of lakes in northern Russia, it is interesting to note that conductivity, Ca, Na, Sr, SO_4, and DIC show distinctly lower values in tundra and forest-tundra lakes compared to the forest sites (Duff *et al.* in prep.). Although different ion sources may account for the chemical distinction (Duff *et al.* in prep.), our isotopic studies suggest that influence of chemically dilute snowmelt in the tundra and forest-tundra lakes may also be important. If so, these measured parameters in the tundra and forest-tundra lakes may represent near-minimum values in relation to the range of chemical compositions present when the surface sediments were deposited.

CHAPTER 3: PALEOHYDROLOGY AT THE NORTHERN BOREAL TREELINE: CENTRAL CANADA

Wolfe BB, TWD Edwards, R Aravena & GM MacDonald, 1996. Rapid Holocene hydrologic change along boreal treeline revealed by $\delta^{13}C$ and $\delta^{18}O$ in organic lake sediments, Northwest Territories, Canada. *Journal of Paleolimnology* 15: 171-181.

Synopsis

Examination of multi-proxy sediment records (pollen, diatoms, elemental geochemistry, stable isotopes) from "Queen's Lake" (unofficial name) near treeline in central Canada showed that forest-tundra replaced tundra vegetation within 150 years between 5000 and 4000 ^{14}C-years BP and coincided with increased lake productivity and a positive lake water balance (MacDonald *et al.* 1993). Terrestrial vegetation changed rapidly suggesting, as had previous studies (Bryson & Wendland 1967; Nichols 1967; Ritchie & Hare 1971), that climate was the controlling factor for treeline advance in central and northwestern Canada. Changes in edaphic conditions and soil development, in contrast, would likely have led to a more gradual terrestrial vegetation response (Moser & MacDonald 1990). Pollen records from other nearby lake sites corroborated the terrestrial vegetation reconstruction from Queen's Lake and provided further supporting evidence for regional warming during the mid-Holocene (MacDonald *et al.* 1993).

In addition to contributing new insights regarding the expedient response of treeline vegetation to climate change, the Queen's Lake study also indicated that multidisciplinary analysis was an effective approach for paleoenvironmental reconstruction at the northern treeline, thus providing the framework for developing a more comprehensive research strategy (see PACT - CHAPTER 1, page 2). Our first priority within the PACT project was to analyze and interpret previously collected lake sediment cores to answer outstanding questions. For example, although regional climate warming in central Canada during the mid-Holocene appeared to be well-supported, it remained uncertain as to whether the changes in water balance at Queen's Lake reflected local hydrologic effects or were representative of a widespread increase in moisture conditions. Studies had long suggested that treeline in northern

Canada was largely controlled by summer temperature (Halliday & Brown 1943; Hopkins 1959; Bryson 1966), although more recent work showed that the northern limit of *Picea* is, in part, correlated with annual precipitation (Anderson *et al.* 1991). To better define the role of moisture in past treeline changes in central Canada, high temporal resolution stable isotope analysis was performed on sediments from "Toronto Lake" (unofficial name), one of the supplemental pollen sites published by MacDonald *et al.* (1993).

Highlighted below are important conclusions from this study:

1. *Similar to the Queen's Lake record, the cellulose oxygen isotope ($\delta^{18}O_{cell}$) results from Toronto Lake indicated that an increase in the inflow:evaporation ratio occurred during treeline advance in central Canada.* Although hydrologic effects, such as reduced wind shear and evaporation with forest cover could be responsible for the change in water balance (see Craig & Gordon 1965), consistent changes in cellulose-inferred lake water $\delta^{18}O$ at Queen's Lake and Toronto Lake as well as modern studies of Anderson *et al.* (1991) rendered support for a regional increase in moisture associated with climate warming during the mid-Holocene.

2. *Substantial oscillations in the Toronto Lake $\delta^{18}O_{cell}$ record, compared to the less variable $\delta^{18}O_{cell}$ profile at Queen's Lake, emphasized the importance of understanding the local hydrologic setting in the interpretation of lake sediment records (also see Fritz 1996).* Queen's Lake drains a small catchment and thus contains a $\delta^{18}O_{cell}$ record that is highly dependent on the hydrologic sensitivity of this single lake. In contrast, Toronto Lake is downstream of a complex drainage basin containing two subcatchments with markedly different hydrologic budgets. Abrupt changes in the size of the contributing drainage basin area, in response to changes in moisture conditions, may have led to large differences in residence time at Toronto Lake.

3. *A thorough understanding of the hydrologic history at Toronto Lake was also important in the reconstruction of the lake water carbon balance from the bulk organic*

and cellulose carbon isotope records. For example, productivity-driven ^{13}C-enrichment of dissolved inorganic carbon during periods of hydrologic closure was apparently "flushed out" by increased through-flow under more open hydrologic conditions. These data clearly illustrated that the carbon cycling was not restricted to internal lake processes, such as photosynthesis and respiration, but also intricately linked to changes in hydrology and moisture conditions.

Abstract

Analysis of $\delta^{18}O_{cellulose}$, $\delta^{13}C_{organic\ matter}$, and $\delta^{13}C_{cellulose}$ at about 100 year intervals from organic matter deposited in Toronto Lake, Northwest Territories, Canada, revealed an 8000-year history of rapid, post-glacial hydrologic change at the treeline zone. Several mid-Holocene phases of ^{13}C-enriched bulk organic matter and cellulose, caused by elevated lake productivity, declining $[CO_{2(aq)}]$, and closed basin conditions, were abruptly terminated by intervals of open hydrology recorded by sharply ^{18}O-depleted cellulose. Two positive excursions of $\delta^{13}C$, at 5000 and 4500 BP, are correlated with increased total organic content and *Picea mariana* pollen concentration, which indicate that high levels of productivity were also accompanied by northern treeline advances. A third treeline advance at about 2500 BP is also marked by an apparent outflow event from Toronto Lake, but this was not associated with bulk organic or cellulose ^{13}C-enrichment in the sediment record because rapid and substantial lake water renewal probably offset productivity-driven enrichment of the dissolved inorganic carbon and replenished the $CO_{2(aq)}$ supply to thriving phytoplankton. However, high sediment organic content during this period suggests increased productivity. Increases in the inflow:evaporation ratio at about 6500 and 3500 BP were also sufficient to cause Toronto Lake to overflow but the prevailing climate during these periods apparently did not favour appreciable northward treeline advance or changes in lake productivity.

Introduction

Global warming may have its greatest impact on the northern boreal forest, treeline region, and tundra (Schlesinger & Mitchell 1987). Projected 5-10°C increases in mean annual temperature (Schlesinger & Mitchell 1987; Houghton *et al.* 1990; MacCraken *et al.* 1990) and, more importantly, a rate of increase of more than 1°C/10yr by AD 2100, may have severe effects on treeline ecological communities (Svoboda & Henry 1987; Davis 1989). In addition, northward treeline migration may enhance global warming through various CO_2 generating mechanisms (BOREAS Science Steering Committee 1990; Wein 1990) and by the decrease in snow-covered

land surface albedo (Bonan *et al.* 1992; Foley *et al.* 1994). Accurate predictions of changes in global climate and management of their impact on the environment are aided by examination of past climate episodes, such as the mid-Holocene climatic optimum. To address these concerns, a joint Canadian-Russian multidisciplinary research programme (PACT - Paleoecological Analysis of Circumpolar Treeline) was initiated in 1993 and is directed at increasing our understanding of Holocene climate variation at the northern treeline and past ecological and hydrological response through the analysis of lake sediments and peat.

The sensitivity of paleoecological and paleohydrological proxy indicators in lake deposits to past climate change in the central Canadian treeline zone was examined during an exploratory study conducted at Queen's Lake (unofficial name; 64°07'N, 110°34'W; Figure 3-1), located 25 km north of the mapped extent of forest-tundra (MacDonald *et al.* 1993). Pollen data from a sediment core at this site suggested an episode of climate warming at about 5000 BP and associated conversion of the local tundra landscape to forest-tundra. There were contemporaneous changes in lake water pH represented in fossil diatom records. However, the geochemical and hydrological regime in the lake determined from major and minor element geochemistry and $\delta^{18}O_{cell}$, and total lake productivity inferred from diatom valve concentration, loss-on-ignition (LOI) and $\delta^{13}C_{cell}$, appeared to be 150-300 years slower in their response to the climate change.

Despite the apparent lag in isotopic response, the $\delta^{18}O$ record in Queen's Lake sediments suggested that strong hydrologic changes accompanied the treeline advance. Specifically, the tundra to forest-tundra transition was marked by ^{18}O-depletion in sediment cellulose, a proxy for lake water oxygen isotopic composition, and was attributed to progressively rising inflow:evaporation ratio. This interpretation was consistent with diatom and elemental geochemistry evidence for increasing water depth.

Although LOI measured from Queen's Lake sediments suggested increased productivity at the time of treeline advance, relatively low average values (≈10%) and the diatom and $\delta^{13}C$ data indicated that rather oligotrophic conditions prevailed

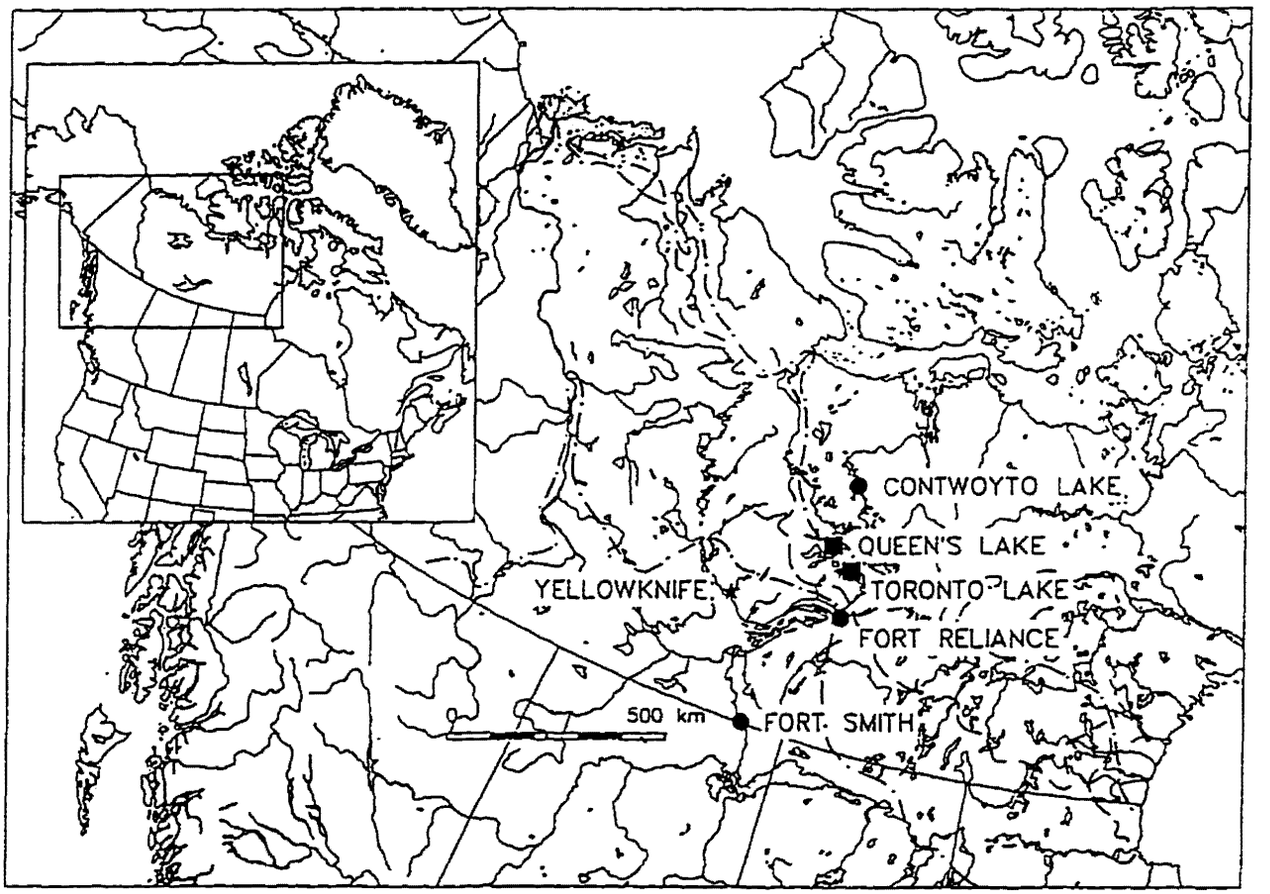


Figure 3-1. Queen's Lake (64°07'N, 110°34'W) and Toronto Lake (63°43'N, 109°21'W) located near Yellowknife north of treeline (dashed line) in central Canada. Also shown are meteorological stations at Fort Smith, Fort Reliance, and Contwoyto Lake in addition to the Arctic-Subarctic (northern dash-dotted line) and Subarctic-Boreal (southern dash-dotted line) ecoclimatic provincial boundaries (from Ecoregions Working Group 1989).

throughout the lake's history. The $\delta^{13}C$ trend displayed a general decline over the Holocene that was interpreted as the result of increased re-utilization of respired ^{13}C-depleted carbon, and only a muted and seemingly delayed response to increased productivity was visible in the isotope record during the period of treeline advance.

Pollen data for *Picea mariana*, a widely distributed and important treeline species (Black & Bliss 1980), and LOI profiles from other dated lake cores in the area, including Toronto Lake (unofficial name; 63°43'N, 109°21'W; Figure 3-1), demonstrated that the warm interval at 5000 BP intepreted from the Queen's Lake record was regional (MacDonald *et al.* 1993). However, the presence of several *Picea mariana* pollen peaks in the Toronto Lake core suggested a more complex vegetation-climate history. Here we reexamine the Toronto Lake pollen record with the isotope history investigated at a higher temporal resolution than at Queen's Lake. Buoyed by the recent development of a simplified oxygen isotope analysis technique (Edwards *et al.* 1994), $\delta^{18}O_{cell}$, $\delta^{13}C_{org}$, and $\delta^{13}C_{cell}$ were measured from Holocene sediments deposited at Toronto Lake at stratigraphic intervals corresponding to approximately every 100 years. Specific questions posed at the outset of this study included:

1. What are the isotopic signatures in the sediments of Toronto Lake, particularly at intervals associated with apparently multiple treeline advances recorded at this site, and are they similar to the Queen's Lake record?

2. Does the apparent lag in isotopic response interpreted from the Queen's Lake study represent a generalized delay in the rate of northern hydrologic change during periods of treeline advance or is the delayed response perhaps an artifact of a coarse isotopic sampling interval?

In addition, absence of detailed paleohydrologic studies in the central Canadian treeline zone warranted further investigation of isotopic responses to changing water and carbon balances.

Site Description

A 650 km south-north transect across Toronto Lake from Fort Smith to Fort Reliance to Contwoyto Lake spans three of the major ecoclimatic provinces (Boreal, Subarctic, Arctic) recognized by the Ecoregions Working Group (1989), and crosses the steep climatic gradients that characterize the treeline region (Figure 3-1). Sharp declines in mean annual precipitation (350 to 270 to 250 mm) and temperature (-3.0 to -6.8 to -11.8 °C) exhibited at these stations (Environment Canada 1993) are due to large differences in climate that prevail to the south and north of the median summer position of the Arctic Front (Bryson 1966) and changes in albedo from the forest to the tundra (Hare & Ritchie 1972).

Toronto Lake (≈414 m above sea level) is underlain by biotite granodiorite and biotite-hornblende granodiorite of the Proterozoic Great Slave Group (Department of Mines and Technical Surveys, Geological Survey of Canada 1952). The lake is small (10 ha in area) but relatively deep (6.75 m) and the high depth to area ratio is favourable for continuous and minimally disturbed sedimentation (Larsen & MacDonald 1993). Toronto Lake is hydrologically open and drains an extensive headwater catchment (*ca.* 2900 ha) that is part of the Lockhart River Basin, which is a tributary to the Mackenzie River via Great Slave Lake. Aside from direct precipitation, Toronto Lake receives essentially all of its inflow from a large, shallow lake fed by two main subcatchments (Figure 3-2). The subcatchments have markedly different hydrological budgets under present climatic conditions. The northeast subcatchment (*ca.* 2100 ha) yields continuous outflow during the thaw season, in part because of the storage capacity provided by a large lake, whereas the southwest subcatchment (*ca.* 650 ha) apparently discharges only intermittently following spring freshet. Reconnaissance water samples taken in late August 1994 after a particularly dry summer show that the isotopic signature of Toronto Lake is strongly influenced by hydrologic processes upstream (Table 3-1, Figure 3-2). Cumulative effects of evaporation are reflected in the progressive enrichment of lake water from the most upstream sample site (number 1) to Toronto Lake.

A few krummholtz *Picea mariana* currently exist near Toronto Lake, as is typical

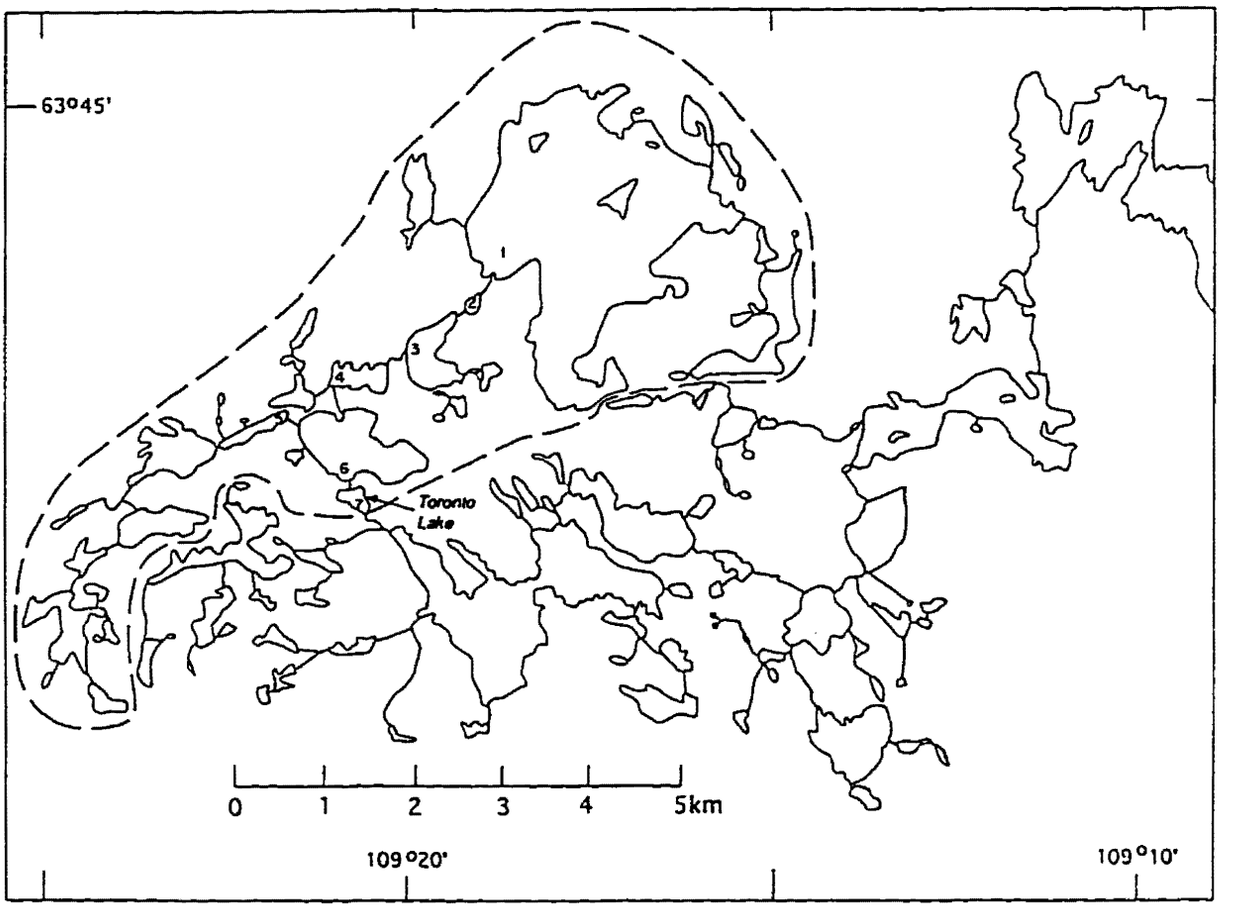


Figure 3-2. Generalized surficial drainage in the Toronto Lake area. Dashed line denotes Toronto Lake catchment. Numbered sites indicate lake water sampled for $\delta^{18}O$ and $\delta^{2}H$. See Table 3-1.

Table 3-1. Isotopic data from water samples in the Toronto Lake catchment obtained in late August 1994. See Figure 3-2 for locations. Analytical uncertainties are 0.05 ‰ for $\delta^{18}O$ and 1.0 ‰ for $\delta^{2}H$ based on sample repeats.

Site	$\delta^{18}O$ (‰ SMOW)	$\delta^{2}H$ (‰ SMOW)
1	-16.41	-138.1
2	-15.50	-135.9
3	-14.59	-130.1
4	-14.14	-128.8
5	-14.90	-132.0
6	-14.29	-132.1
7 (Toronto Lake)	-13.74	-127.1

Table 3-2. Radiocarbon dates from Toronto Lake (MacDonald *et al.* 1993).

Depth (cm)	Material	Age (yr BP ± 1σ)	Lab Number
35-40	Organic sediment	1760 ± 90	Beta-49705
80-85	Organic sediment and moss	4200 ± 80	Beta-53129
125-130	Organic sediment and moss	5460 ± 90	Beta-53130
155-160	Organic sediment	7040 ± 120	Beta-49708

of many localities beyond the mapped limits of the forest-tundra (Moser & MacDonald 1990). Some well-developed *Picea glauca* individuals are also present in a sheltered location along an esker east of the lake.

Methodology

A 170 cm-long sediment core consisting of clayey gyttja, taken from Toronto Lake in winter 1987, was sampled for carbon and oxygen isotopic analysis at mostly 2.5 cm intervals. Samples were heated in a 10% hydrochloric acid solution to remove inorganic carbon, rinsed with deionized water, and dried. Some samples required removal of coarse organic fragments, likely of terrestrial origin, by passing the sediment through a 500 μm screen. A three part extraction process that used (1) benzene, ethanol, and acetone to remove lipids, resins, and tannin, (2) acetic acid and sodium chlorite to remove lignin, and (3) sodium hydroxide to remove xylan, mannan, and other polysaccharides isolated the cellulose fraction, similar to the wood cellulose purification procedure of Green (1963).

Carbon dioxide was generated from the bulk organic material and cellulose component using a standard combustion method (Boutton *et al.* 1983), purified cryogenically, and analyzed for $^{13}C/^{12}C$. A nickel-tube pyrolysis technique (Edwards *et al.* 1994) was used to produce CO_2 from the cellulose fraction for $^{18}O/^{16}O$ assay. All isotopic ratios were determined on a VG Prism II mass spectrometer at the Environmental Isotope Laboratory, University of Waterloo, and results are expressed in δ-notation ($\delta = [(R_{sample}/R_{std}) - 1] \times 1000$, where $R = {}^{18}O/{}^{16}O$ or $^{13}C/^{12}C$) with respect to the international standards for $\delta^{13}C$ (Peedee belemnite (PDB)) and $\delta^{18}O$ (Vienna-standard mean ocean water (SMOW)). Repeated samples are normally within 0.5‰ and 1.0‰ for $\delta^{13}C$ and $\delta^{18}O$, respectively.

LOI analysis followed Dean (1974). Pollen analysis followed standard practices (Faegri & Iversen 1975). *Picea mariana* and *Picea glauca* were differentiated using the criteria proposed by Hansen & Engstrom (1985).

Radiocarbon dating provides chronological control for the core (Table 3-2). Samples of organic lake sediment were dated. The region has no calcareous or

fossiliferous rocks that would promote "old carbon" effects. Bulk organic dates from nearby lakes have corresponded well with accelerator mass spectrometry ^{14}C dates from terrestrial plant macrofossils (Moser & MacDonald 1990).

Results and Discussion

The Toronto Lake Isotopic Record

The $\delta^{18}O$ record measured from the cellulose fraction varies greatly in the bottom two-thirds of the core (Figure 3-3). Values range from +18.4‰ at the base to +4.7‰ at 50 cm depth. Near the top of the core values tend to be relatively constant around +10‰. ^{18}O-depleted spikes are present at about 145, 140, 115, 95, 70, and near 50 cm depth.

$\delta^{13}C_{org}$ varies from -30.0‰ at the base of the core to a maximum -24.4‰, which occurs at 120 cm depth (Figure 3-3). The $\delta^{13}C_{cell}$ profile is correlated with that determined from the bulk organic material ($R^2 = 0.538$), but displays more sharply ^{13}C-enriched peaks at 155, 120, 100, and 80 cm depth. $\delta^{13}C_{cell}$ is more positive than $\delta^{13}C_{org}$ by 0.5 to 5‰ with maximum separation at the ^{13}C-enriched intervals. Minimal difference in the $\delta^{13}C$ profiles occurs near 65 cm depth where the trends nearly overlap

$\delta^{18}O_{cell}$: Paleohydrology and Relationship to Past Changes in Treeline

Previous studies of several Canadian lakes have shown that the fine-grained cellulose fraction deposited offshore is dominantly aquatic in origin (Edwards & McAndrews 1989; MacDonald *et al.* 1993), perhaps due to rapid deposition and burial of phytoplankton in fecal pellets with little chance for oxidation (Edwards 1993). Other work indicates that the oxygen isotope composition of aquatic cellulose is consistently enriched by about 27 to 28‰ relative to its source water, independent of the temperature, the $\delta^{18}O$ composition of $CO_{2(aq)}$, and the plant species (Epstein *et al.* 1977; DeNiro & Epstein 1981; Sternberg & DeNiro 1983; Sternberg *et al.* 1984; Sternberg *et al.* 1986). As a result, lake water $\delta^{18}O$ histories can be directly inferred from core records of $\delta^{18}O_{cell}$. Paleohydrologic interpretation of $\delta^{18}O$ in lacustrine

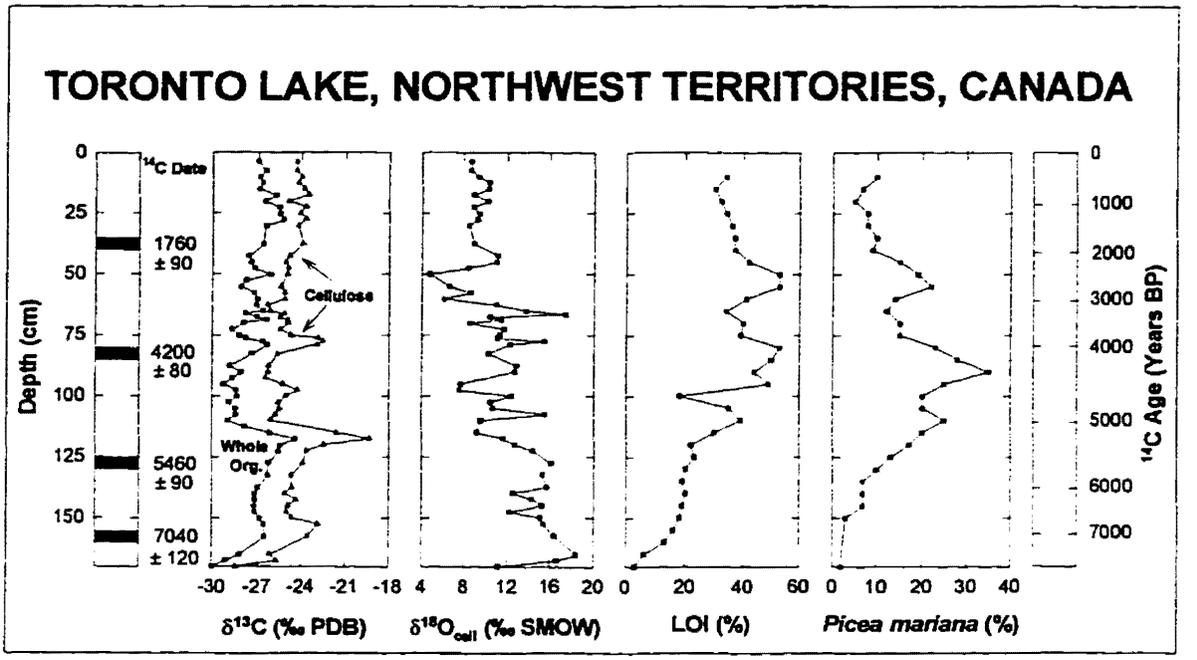


Figure 3-3. High temporal resolution isotope stratigraphy from Toronto Lake. Loss-on-ignition (LOI) and *Picea mariana* profiles reproduced from MacDonald *et al.* (1993). ^{14}C age scale determined by linear extrapolation between dated intervals.

aquatic cellulose is therefore reduced to distinguishing the degree of influence of (1) the isotopic composition of input waters determined by inflow from upstream lakes, catchment runoff, and precipitation falling directly on the lake and (2), evaporative isotopic enrichment caused by preferential evaporation of water containing the lighter isotope, ^{16}O. Hydrologic setting plays a critical role in determining the relative importance of these two factors, ultimately recorded by $\delta^{18}O_{cell}$ (Figure 3-4).

In northern regions, studies of modern hydrology indicate that changes in lake water isotope composition in basins with low inflow:evaporation ratio are mainly related to changes in water balance (Bursey *et al.* 1991; Gibson *et al.* 1993; Taal 1994). Therefore, marked fluctuations in $\delta^{18}O_{cell}$ at Toronto Lake are likely due to shifts between closed basin, strongly evaporative conditions (e.g. ^{18}O-enriched periods at 165, 77.5 and 66 cm depth - approximately 7400, 3900 and 3300 BP) and intervals of open basin hydrology when the inflow:evaporation ratio was high (e.g. ^{18}O-depleted spikes at 147.5, 110 and 95 cm depth - approximately 6500, 5000, and 4500 BP). The most recent period of apparently minimal evaporative enrichment and short residence time conditions occurred at 50 cm depth (2400 BP) and $\delta^{18}O_{cell}$ at this horizon (+4.7‰) corresponds to a lake water $\delta^{18}O$ value of -21.7 to -22.7‰, using a fractionation (α) of 1.027 to 1.028 where $\alpha_{cell\text{-}water} = (\delta_{cell} + 1000) / (\delta_{water} + 1000)$ (Sternberg 1989; Edwards & McAndrews 1989). This range is comparable to the modern mean annual precipitation value of -22‰ that persists across the continental Northwest Territories which, in part, may be due to stable Arctic Frontal air mass activity (Gibson *et al.* 1994). Close correspondence between inferred lake water isotopic composition which underwent minimal isotopic evolution and modern precipitation isotopic data provides additional support for the aquatic nature of offshore, fine-grained cellulose.

Similar to the Queen's Lake $\delta^{18}O$ record, periods of open hydrological conditions are correlated with increased productivity, suggested by high LOI, and with maxima of *Picea mariana* pollen percentage associated with treeline advances (Figure 3-3). However, trends toward ^{18}O-depleted cellulose begin synchronously to changes in the LOI and *Picea mariana* profiles suggesting that hydrologic adjustment was as

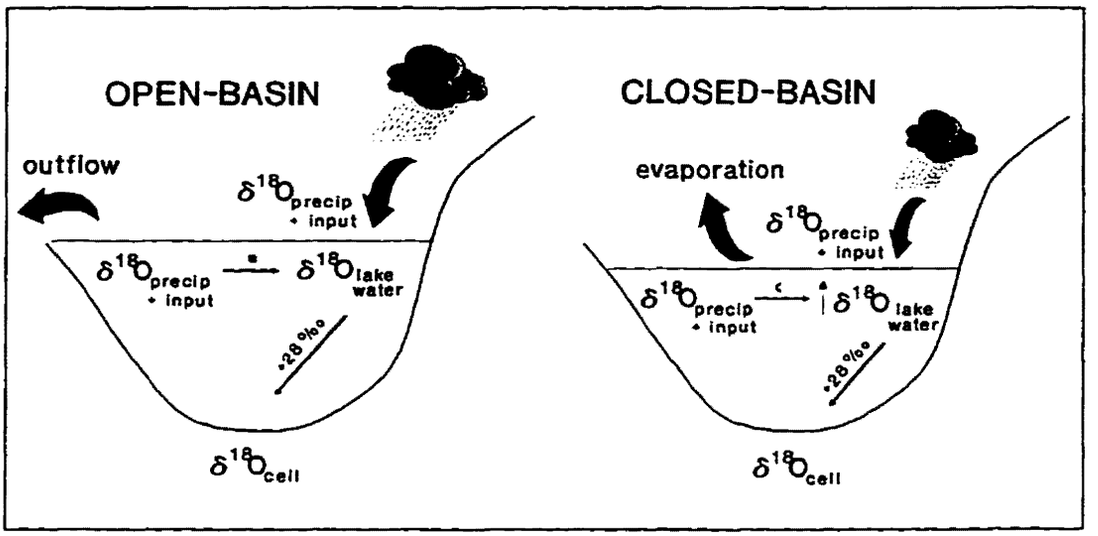


Figure 3-4. End-member hydrologic scenarios showing the effect of water balance on $\delta^{18}O$ of lake water recorded by aquatic cellulose. During intervals of open-basin conditions, lake water $\delta^{18}O$ closely resembles the isotopic composition of precipitation and input waters. Closed-basin conditions produces lake water that is enriched relative to precipitation and input $\delta^{18}O$ due to evaporation effects.

rapid as terrestrial vegetation and lake productivity in response to the climate change.

Rapid hydrologic change is in contrast to results from Queen's Lake where it appeared to lag behind the aquatic and terrestrial flora records. Although the more highly resolved sampling interval for Toronto Lake may partially account for this discrepancy, the hydrologic settings of these two lakes and their potential differences in response to climate change may also be responsible. Queen's Lake, which drains a considerably smaller catchment (*ca.* 200 ha) than Toronto Lake (*ca.* 2900 ha), contains a $\delta^{18}O$ record that is largely dependent on the hydrologic sensitivity of this one lake. As a result, it is rather subdued owing to the relatively narrow range of hydrologic conditions that occurred at this site. In contrast, modern data suggest that hydrologic factors such as residence time and evaporation upstream from Toronto Lake strongly control its isotopic composition (Table 3-1, Figure 3-2), and it is probable that these conditions were also influential in the past. Thus, the Toronto Lake oxygen isotope record is capturing hydrological changes over a large area and abrupt changes in the size of the drainage basin likely produced the rapid, several $\delta^{18}O$ per mil oscillations. These changes in watershed hydrology may have hinged on the degree of flow generated by the southwestern part of the catchment where, presently, it is limited. Specifically, the ^{18}O-depleted intervals in Figure 3-3 probably represent periods when this portion of the drainage basin became more open and substantially increased throughflow reduced the residence time of Toronto Lake. Conversely, relatively drier conditions at times in the past may have decreased flow from both the southwestern and northeastern subcatchments, thus lengthening the residence time of lakes downstream, resulting in evaporatively ^{18}O-enriched periods.

Despite the differences in response time to hydrologic change, the $\delta^{18}O_{cell}$ results from this study provide additional support for the interpretation that increased moisture, in addition to increased temperature, was also associated with treeline advance. These results are also in concert with modern studies that indicate the northern limit of *Picea* distribution correlates in part with annual precipitation (Anderson *et al.* 1991). Other outflow events distinguished by less dramatic ^{18}O-depletion at Toronto Lake, for example at 147.5 and 70 cm (6500 and 3500 BP), also

represent periods of increased inflow:evaporation but treeline position was not significantly altered perhaps due to low temperatures.

$\delta^{13}C_{org}$, $\delta^{13}C_{cell}$: Paleoproductivity and Carbon Cycling

Analysis of carbon isotopes in bulk organic lake sediments has frequently been used to acquire paleolimnologic information, despite early studies which emphasized that interpretation is complex because many different factors can invoke similar shifts in the $^{13}C/^{12}C$ ratio (Stuiver 1975; Hakansson 1985). Supply of both aquatic and terrestrial organic matter to the bulk sediment can be a major complicating variable (e.g. Aravena *et al.* 1992), although evaluation of $\delta^{13}C$ strictly from the fine-grained cellulose fraction does appear to restrict the concern for organic input from the catchment (e.g. Edwards & McAndrews 1989; MacDonald *et al.* 1993). In addition, undifferentiated organic matter may mask subtle variations in $\delta^{13}C$ compared to that measured solely from cellulose (Edwards & McAndrews 1989; Edwards 1993). Therefore, analysis of $\delta^{13}C_{cell}$ generally provides a better isotope record of the dissolved inorganic carbon (DIC), the carbon source for particulate aquatic organic carbon.

In contrast to studies by Edwards & McAndrews (1989) and Edwards (1993), the <500 μm whole organic and cellulose carbon isotope records at Toronto Lake are dominantly parallel and exhibit similarly distinct fluctuations (Figure 3-3) supporting the contention that both are largely aquatic in origin and represent carbon from the same source (viz. DIC). Variations in the offset between the two carbon isotope curves could be due to slight changes in preservation of labile components of the bulk organic matter or contribution of terrestrial material to the whole organic fraction. Although several factors can influence the $\delta^{13}C$ value of lake water DIC, which is incorporated by algae and may be reflected in the sediment record, photosynthesis and respiration are often most important (McKenzie 1985). For example, increased photosynthesis at Queen's Lake during the tundra to forest-tundra transition was reflected by ^{13}C-enrichment in cellulose due to productivity-driven enrichment in DIC (MacDonald *et al.* 1993). However, most of the carbon isotope profile at Queen's

Lake was influenced by increasing contribution of respired ^{12}C-rich CO_2, resulting in a dominantly negative-trending $\delta^{13}C_{cell}$ profile. Thus, carbon isotope records in preserved aquatic organic matter often reflect the prevailing end-member of the photosynthesis-respiration pathway.

In the more highly resolved record at Toronto Lake, many of the sharp ^{13}C-enriched peaks also suggest high levels of productivity, such as those at 117.5 and 97.5 cm depth (5200 and 4600 BP) which immediately precede increases in LOI and *Picea mariana* maxima associated with treeline advances (Figure 3-3). However, productivity-driven ^{13}C-enrichment of the DIC pool may only partially account for these excursions. Decreased fractionation between the DIC and algae, caused by low concentration of dissolved CO_2 ($[CO_{2(aq)}]$) may also be responsible (Deuser *et al.* 1968; Calder & Parker 1973; Herczeg & Fairbanks 1987; Hollander & McKenzie 1991).

Although productivity and likely $[CO_{2(aq)}]$ have largely influenced the resultant carbon isotope record preserved in the whole organic and cellulose fraction, high temporal resolution at Toronto Lake indicate that rapid changes in the hydrologic status of the catchment from relatively closed to open-basin conditions have also been critical. ^{18}O-depleted cellulose correlate with the termination of ^{13}C-enrichment trends, including at 147.5, 140, 115, 95, and 70 cm depth (6500, 6100, 5100, 4500, and 3500 BP; Figure 3-3), indicating that short residence time conditions not only restricted evaporative ^{18}O-enrichment, but also increased throughflow "flushed out" ^{13}C-enriched DIC with ^{13}C-depleted DIC and, likely, replenished the $CO_{2(aq)}$ supply to thriving phytoplankton. Regardless of the mechanism and in spite of continued high levels of productivity, as suggested by high LOI at these strata, aquatic organic matter became depleted in ^{13}C because of the hydrologic opening of the catchment and Toronto Lake and is particularly evident during the two early periods of treeline advance. This interpretation also explains the complacent $\delta^{13}C$ profile corresponding to the increase in LOI at about 55 cm depth (2700 BP; Figure 3-3), as the strong negative trend in the $\delta^{18}O_{cell}$ record at this horizon suggests rapid lake water renewal must have offset $^{13}C_{DIC}$-enrichment and $[CO_{2(aq)}]$-depletion.

This most recent interval of increased moisture may also be responsible for the

nearly overlapping carbon isotope trends at 65 cm depth (3300 BP; Figure 3-3). Elevated levels of runoff and erosion may have washed terrestrial litter into the lake, which was likely available after earlier establishment of forest-tundra vegetation in the catchment, resulting in an increase in the allochthonous component in the fine-grained bulk organic matter at this horizon.

Conclusion

Coupled $\delta^{18}O$ and $\delta^{13}C$ analyses in organic sediment demonstrate the predominant influence that catchment-lake basin hydrology has had on both water and carbon balance of Toronto Lake (Figure 3-5), and emphasizes that carbon cycling has not been restricted to internal lake processes such as photosynthesis and respiration. Toronto Lake experienced several periods of hydrological closure that resulted in evaporative ^{18}O-enrichment of lake water as recorded by $\delta^{18}O_{cell}$. $\delta^{13}C$ also became more positive in the bulk organic matter and cellulose due to photosynthetic effects on the $\delta^{13}C_{DIC}$ and, possibly, reduction in the fractionation between the DIC and organic matter/cellulose due to declining $[CO_{2(aq)}]$. At times of open hydrological conditions, the $\delta^{18}O$ of the lake water became more dependent on the ^{18}O-depleted signal provided by input waters. Interestingly, the trend of ^{18}O-depleted spikes from more enriched in the early Holocene to more depleted in the late Holocene (Figure 3-3), which is similar to the general $\delta^{18}O$ trend at Queen's Lake (MacDonald *et al.* 1993), suggests that input water $\delta^{18}O$ composition may have undergone a profound shift of as much as -6‰ over the past 8000 years. Concurrent with these intervals of short residence time, rapid lake water renewal diluted productivity-driven ^{13}C-enrichment of lake water DIC. Increased supply from the drainage basin may also have elevated the $[CO_{2(aq)}]$, contributing to the relatively ^{13}C-depleted signals in the carbon isotope composition of bulk organic matter and cellulose. These relationships, supported by the LOI record and correlated with the *Picea mariana* profile, provide strong evidence for increases in temperature and moisture that caused changes from tundra to forest-tundra at sites near the central Canadian treeline during the mid and late Holocene. Thus, $\delta^{13}C_{org}$, $\delta^{13}C_{cell}$, and $\delta^{18}O_{cell}$ were not only instrumental in reconstructing the

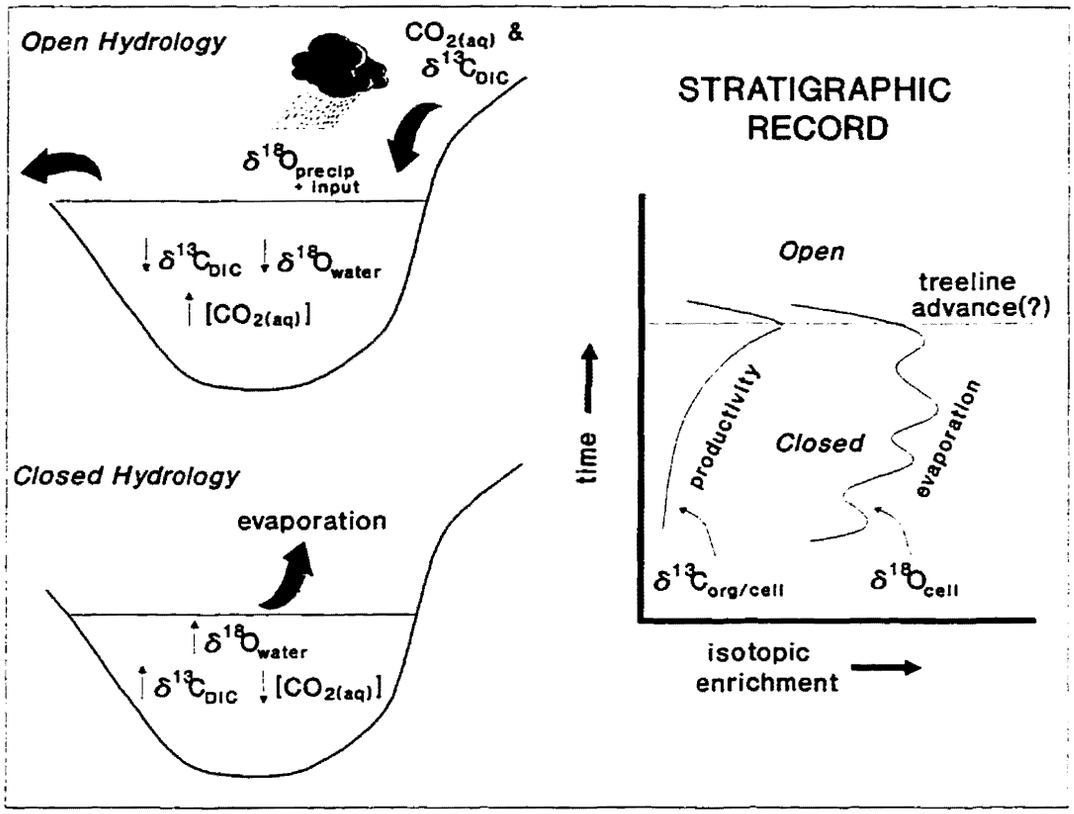


Figure 3-5. Idealized $\delta^{13}C_{org/cell}$ and $\delta^{18}O_{cell}$ variations in a typical stratigraphic segment of Toronto Lake history (right) generated by a catchment-lake basin hydrological model (left).

paleohydrology of Toronto Lake but also in monitoring the relationship between terrestrial and aquatic realms as environmental change occurred.

Multiple episodes of forest development and decline and associated changes in limnic conditions interpreted at this site portray a more complex history of Holocene climate change in this region than previously known (MacDonald *et al.* 1993). Finer temporal resolution achieved at Toronto Lake revealed three distinct episodes of a wetter and warmer climate at around 5000, 4500, and 2500 BP, compared to the evidence for a single amelioration at Queen's Lake between 5000 and 4000 BP. Analysis of Toronto Lake clearly indicates that a fine sampling approach is warranted for small Arctic lakes. In particular, future sampling sites in complex drainage networks, where catchment area modification and watershed hydrology response may be recorded in lakes downstream, could possibly provide the best sensitivity to regional hydrologic change.

CHAPTER 4: PALEOHYDROLOGY AT THE NORTHERN BOREAL TREELINE: TAIMYR PENINSULA AND LENA RIVER, RUSSIA

PART A:

Velichko AA, OK Borisova, CV Kremenetski, AA Andreev, KE Duff, TE Laing, BB Wolfe, R Aravena, LC Cwynar, TWD Edwards, JP Smol, RT Riding, GM MacDonald & D Porinchu, in prep. Holocene environmental change at treeline on the western Taimyr Peninsula of Siberia. For submission to *Quaternary Research*.

Synopsis

Lake TL1 on the western Taimyr Peninsula (informally named Middendorf Lake after an early explorer to the region) was the site for PACT's initial attempt to integrate results from multidisciplinary analyses on lake sediments from northern Russia. Based on radiocarbon dating of macrofossil wood found north of treeline, the forest (or forest-tundra) was roughly 50-100 km north of its present position between 8400 and 3100 BP. Pollen studies on the Lake Middendorf sediments were compatible with the macrofossil data, clearly displaying a decline in Larix and Picea trees at about 4000 BP. Unfortunately, the sediment record begins immediately before this event, perhaps due to thermokarst processes during the warm mid-Holocene, and does not capture the advance of treeline into the region.

Paleolimnological data were consistent in their assessment of trophic conditions in the forest and subsequent tundra periods with the former being clearly more productive. However, there were discrepancies amongst the various proxy data concerning the moisture regime. Sedimentary, isotopic and geochemical evidence indicated that a higher precipitation/evaporation ratio existed during the forest period and that drier conditions rapidly developed as treeline retreated. The abundance of benthic diatoms and chrysophytes, on the other hand, suggested that the lake may have been relatively shallow during the forest interval compared to the present. Benthic species may have responded more strongly to increased nutrients during this period, or alternatively, major changes in water level may not have been required in order to significantly alter the water balance, given that the lake is presently seasonally-closed (with seepage through a meadow) and that only a small increase

in the precipitation/evaporation ratio would be required to establish open-basin conditions during the thaw season. Following 2600 BP (and in particular between 1600 and 400 BP), both the diatom and isotopic data suggest rapidly fluctuating hydrologic conditions that, interestingly, are not associated with any known changes in terrestrial vegetation.

(Note that in this multi-authored manuscript, I am responsible for the section entitled "Oxygen Isotope Analysis" and 50 % of the "Discussion". Contributions made by other authors are duly noted in the figure captions).

Abstract

Holocene changes in treeline vegetation and lacustrine environments are reconstructed for the western Taimyr Peninsula of Siberia. Radiocarbon-dated stumps indicate Larix and Picea dominated forest or forest-tundra was located at least as far north as 70°22'N between 8400 and 3100 BP. This represents a northward extension of forested vegetation of 50-100 km from its present location. The sediments of a small lake located at 70°22'N, 87°33'E were analyzed for sedimentology, pollen, conifer stomates, diatoms, chrysophytes, loss-on-ignition, elemental geochemistry, and oxygen isotopes. Radiocarbon dates indicate that the sediment record extends back to 4400 BP. The fossil pollen and stomate records indicate that the study area supported Larix and Picea trees during the mid-Holocene. The paleolimnological record suggests that during the forest period the lake waters were warmer, less acidic and more productive. The stable isotope and sedimentological records suggest that the ratio of precipitation/evaporation was higher during the forest period and lake waters overflowed the present closed basin. As the forest vegetation declined between 4400 and 4000 BP, there is evidence of increased soil erosion into the lake. The lake became cooler, more acidic and less productive. Following 2600 BP, there were a series of marked oscillations in the diatom and isotope records that suggests rapid fluctuations in lake levels. These fluctuations are not apparent in the chrysophyte record. Neither is there any evidence from the pollen and stomate record of changes in terrestrial vegetation during these limnological events. The most recent sediments of the lake contain diatom and chrysophyte flora that have no analog in the fossil record. These unique flora likely represent the impact of atmospheric pollutants from distant sources and from the smelting center at Noril'sk, some 115 km to the SE.

Introduction

The tundra and taiga of northern Eurasia could be impacted by climatic changes due to increased levels of atmospheric greenhouse gasses (Kojima 1995; Plochl & Cramer 1995; Velichko *et al.* 1995). In the Russian Federation, the climatologically sensitive boundary between taiga and tundra occurs at roughly 68° -

70° N and it is possible that greenhouse warming will lead to northward shifts in the taiga (Plochl & Cramer 1995), although such shifts may occur gradually (Velichko *et al.* 1995). The continental tundra zone in much of Eurasia forms a relatively narrow strip along the Arctic coast. The eventual result of pronounced warming could be fragmentation or complete eradication of low elevation tundra. Even if these shifts occur slowly, managing such changes to preserve habitat, species, and genetic diversity could be difficult. The extension of forest northwards could change surface albedo, roughness and heat flux sufficiently enough to enhance the rate and magnitude of global warming (Foley *et al.* 1994; Pielke & Vidale 1995). It is thus important to know what types of change terrestrial and aquatic ecosystems might experience due to climatic warming. One line of evidence for examining potential impacts of climatic warming in Siberia is the paleoenvironmental record of past episodes of climate change (Velichko *et al.* 1993).

Climate models indicate that the Taimyr Peninsula of Siberia would have experienced marked warming during the early to mid-Holocene maximum in summer insolation (Kutzbach *et al.* 1993). Sub-fossil tree remains on the Taimyr Peninsula were first reported by A.F. Middendorf in the 1860's (Ukrainsteva 1993) and demonstrate that treeless regions once supported Larix forests. Russian scientists have obtained a number of radiocarbon dates on such stumps. These dates range from approximately 10,500 to 5000 BP (radiocarbon years before AD 1950) (e.g. Nikolskaya 1982; Khotinskiy 1984; Ukraintseva 1990, 1993) indicating that parts of the Taimyr were forested during the Holocene and good paleoenvironmental records of the response of high latitude terrestrial and aquatic environments to climatic warming should be available from the region. Examination of these records can provide insights into possible future environmental conditions on the peninsula and help to deduce how the present landscapes and environments developed during the late Holocene.

In this study we use a multidisciplinary approach to the analysis of sediments from a tundra lake on the western Taimyr Peninsula to reconstruct Holocene climate changes and the response of limnic and terrestrial ecosystems to those changes. The

analytic techniques include sedimentology, geochemistry, and analysis of pollen, stomates, diatoms, chrysophytes, and oxygen isotopes. The analysis of lake sediments is coupled with the collection and dating of sub-fossil wood from the tundra surrounding the lake. The key questions we address are: (1) Was the study area forested earlier in the Holocene and, if so, what was the nature of the terrestrial and limnic environments that existed during the forest phase, and (2) What were the patterns and rates of change that terrestrial and aquatic ecosystems experienced during the establishment of modern tundra? This is the first account from a number of key treeline sites being studied in the Russian Federation and Canada by the *Paleoecological Analysis of Circumpolar Treeline* (PACT) project. PACT is a five-year program (1993-1997) led by Andre Velichko in Russia, Les Cwynar in Canada, and Glen MacDonald in the United States.

Study Area

The study area and lake, unofficially named Middendorf Lake, is situated approximately 115 km NNW of the city of Noril'sk at 70°22'N, 87°33'E at an elevation of 200 m a.s.l. (Figure 4-1). The lake is round and about 100 m (NE-SW) by 90 m (NW-SE). The maximum depth is approximately 11.5 m. The lake is currently alkaline (pH= 9.2), oligotrophic (total phosphorus = 12 g/L, Secchi depth = 2.1 m), and freshwater (specific conductivity = 91 μS). The littoral zone is rocky with no visible macrophyte growth. The lake appears to be a hydrologically-closed basin with the only outlet being a moist meadow at the southwestern shore.

To the west of the lake lies the valley of the Yenisey River. From the river, the land rises gradually eastward over a distance of 30-50 km and gives way to the Noril'sk Plateau (650 m a.s.l.). Tectonically, the Taimyr-Yenisey region belongs to an ancient rift zone; its geological history is marked by repeated extrusions of basalts up to early Triassic time. West of the lake, the surface is subdivided into two levels: the lower level, adjacent to the Yenisey valley, mostly below 120-115 m a.s.l., and the higher one lying above 120 m a.s.l. The lower level is marked by a typical cryogenic topography, featuring numerous thermokarst lakes and polygonal microrelief. The

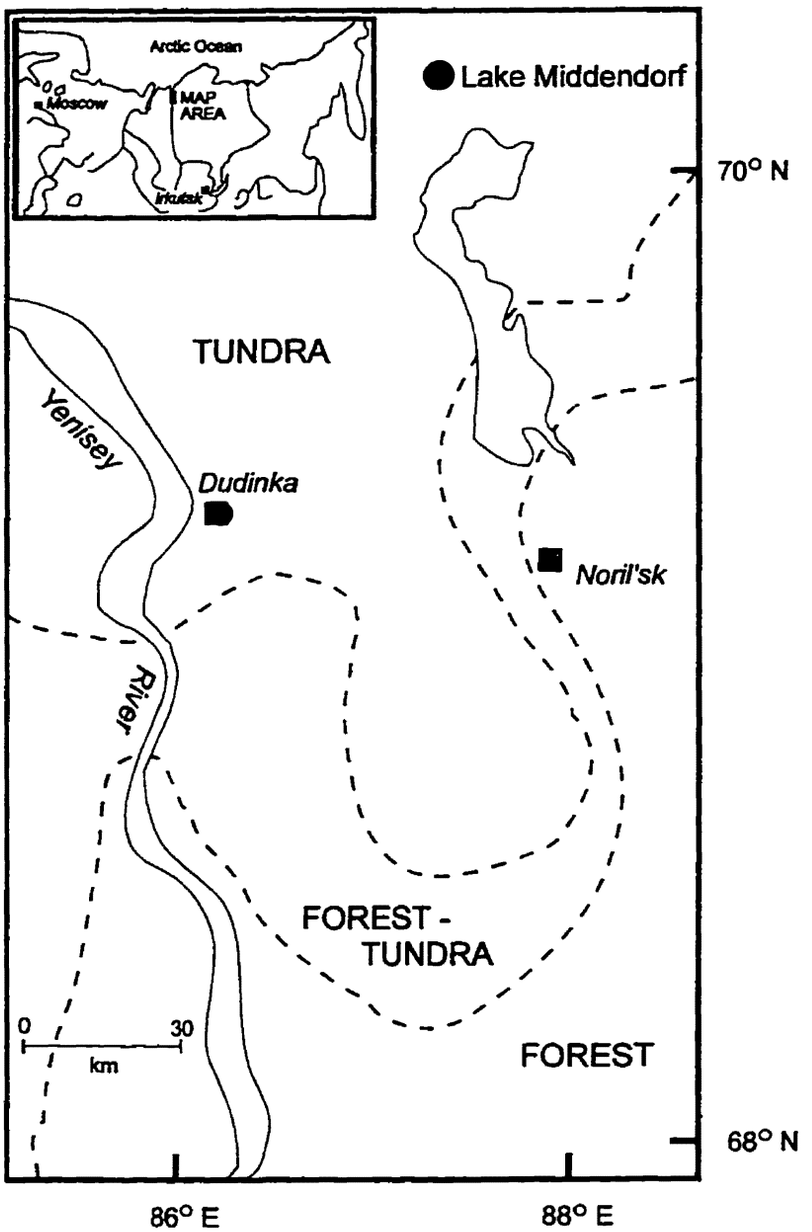


Figure 4-1. Location of Middendorf Lake and regional physiographic and vegetational setting.

higher surface is typified by hilly and irregular topography. Investigations carried out by the Noril'sk Geological Expedition (L.I.Trofimova & V.A.Fedorenko, personal communication) identified these landforms as glacial in origin, belonging to the narrow (50 to 70 km wide) marginal zone of a glacier which flowed down from the Noril'sk Plateau and Kharaelakh Plateau at the end of the Late Pleistocene (the Nyapan Stage). The glacial landforms include moraines, drumlins, and eskers. The entire area is underlain by continuous permafrost.

Middendorf Lake lies within the limits of the glacial landforms and is on the proximal side of a large arcuate morainic ridge. The lake depression is closed from the north, east, and south by the ridge, with a narrow opening westward. Local relief around the lake ranges from 10 to 30 m. The ridge slopes and crest bear large blocks of rock showing characteristic traces of glacial abrasion. The southern part of the ridge joins a small drumlin, about 8 m high and 50 to 80 m wide. Boulders and pebbles are mostly represented by fine-grained igneous rocks from the Noril'sk and Kharaelakh plateaus.

The western Taimyr region has cold winters with average January temperatures ranging from -20 to -30 °C. Summers are short and cool with average July temperatures in the region ranging from 8 to 16 °C. Annual precipitation is light, ranging from 100 to 300 mm.

The site is in the Siberian shrub tundra zone (Figure 4-1) and the vegetation around the lake is tundra dominated by Betula nana (shrub birch), with shrub Salix (willow) and Alnaster fruticosa (alder = Alnus crispa in non-Russian floras) around lakes and on favorable sites. Eriophorum wet-meadows dominate poorly drained topographic depressions. Rocky ridge tops support grasses, arctic willow, eracoids and a number of herbs. The lake lies approximately 50-75 km north and west of the mapped northern limits of Larix sibirica (western Siberian larch) forest-tundra. Extremely scattered Larix sibirica trees were observed approximately 25 km SE of the site and one krummholz individual of that species was found in the vicinity of Middendorf Lake. The nearest observed occurrences of the common northern taiga trees, Picea obovata (spruce = Picea abies in some non-Russian floras), Betula

pubescens and Betula verrucosa (tree birch) were in the vicinity of Noril'sk, approximately 100 km to the SE.

Sub-fossil Wood Collection and Analysis

Radial transects were made outward from Middendorf Lake in order to recover subfossil wood from the tundra surface. A total of 15 samples were identified to genus and radiocarbon dated (Table 4-1). Identification was based on optical analysis of hand sections, maceration and microscopic analysis. Thin-sections were also examined in the case of problematic specimens. To compare results from Russian and Canadian radiocarbon labs, samples of wood were split and dated in both countries. Wood was dated by radiocarbon at the Institute of Geography, Russian Academy of Science (IGAN) and at the University of Waterloo (WAT). The two sets of dates are closely similar (Table 4-1).

Many of the stumps were found in situ with roots still present. Most of the wood appears to have been from upright trunks and the longest trunk was almost 2 m in length. The largest trunks found were about 40 cm in diameter near their base. The nearest finds were within the drainage basin of Middendorf Lake. Stumps were found on both uplands and valley bottoms.

Stumps of both Larix and Picea were found, although the former was the most common (Table 4-1). Judging from the dates, larch grew in the region continuously from 8300 to 3100 BP, while Picea was definitely present around 6500 BP. The size of the Larix stumps and the presence of Picea suggests forested conditions, rather than sparse forest-tundra or krummholz. The occurrence of stumps both on uplands and in valleys indicates that tree cover was extensive on the landscape and not restricted to protected sites. The dates for the northward extension of Larix dominated forest correlate well with the published findings of fossil and sub-fossil wood in the southern part of the modern tundra zone on other parts of the Taimyr (e.g. Nikolskaya 1982; Khotinskiy 1984; Ukraintseva 1990, 1993). The infinite age of one sample indicates that Larix grew at the site during a previous inter-stadial or inter-glacial.

It is notable that the majority of dates from the wood fall between 8500 and

Table 4-1. Identifications and radiocarbon dates of conifer stumps found in the vicinity of Middendorf Lake. All dates are ^{13}C corrected (GM MacDonald, CV Kremenetsky & RT Riding, analysts).

Sample	Genus	^{14}C Age BP	Lab No.
M1	Larix	infinite	WAT-2715
M13	Larix	8430 ± 80	WAT-2726
M2	Larix	8260 ± 70	WAT-2716
M14	Larix	8260 ± 80	WAT-2727
		8320 ± 129	IGAN-1488
M5	Larix	8240 ± 90	WAT-2718
M10	Larix	7880 ± 80	WAT-2723
		7712 ± 62	IGAN-1484
M6	Larix	7680 ± 80	WAT-2719
M12	Larix	7050 ± 70	WAT-2725
		6923 ± 60	IGAN-1481
M15	Picea	6520 ± 70	WAT-2728
		6499 ± 47	IGAN-1479
M4	Picea	6230 ± 70	WAT-2717
M7	Larix	6100 ± 80	WAT-2720
M16	Larix	6030 ± 80	WAT-2729
M9	Larix	4610 ± 70	WAT-2722
M8	Larix	3750 ± 70	WAT-2721
		3701 ± 43	IGAN-1486
M11	Larix	3530 ± 70	WAT-2724
		3191 ± 42	IGAN-1487

6000 BP. The probability that a stump will decay or be destroyed should increase with the length of time the stump is exposed. Thus, stumps from trees that died 4000 years ago should be more likely to be present today than stumps from trees that died 8000 years ago. The large quantity of wood from the period 8500 to 6000 BP, therefore, suggests that the forest may have been denser at that time than during the period 6000 to 3500 BP.

Lake Coring and Sediment Stratigraphy

Three duplicate cores were taken during the summer of 1993 using a Livingstone piston corer from a raft. The three core holes are located about 30-40 cm apart in the central part of the lake which is 8.15 m deep. The cores penetrated the lake sediments to a depth of approximately 250 cm. The sediment stratigraphies of the three cores are practically identical (Figure 4-2). Samples collected from cores denoted TL-1-1 and TL-1-2 were analyzed in Russian and Canadian laboratories. Core TL-1-3 has been archived as a reserve. Samples from TL-1-1 were used for radiocarbon dating, pollen, stomate, diatom, chrysophyte and oxygen isotope analysis. Sediment stratigraphy and geochemical characteristics were determined using the TL-1-2 samples.

The compact gray-bluish sandy diamicton that lies below 217 cm in TL-1-1 and below 193 cm in TL-1-2 contain a considerable amount of sand, and also small gravel in abundance. Scattered terrestrial plant remains were found in the sands. Some of the gravel is well rounded. In TL-1-1, the sand content is so high that it was described as a separate layer (depth 223 to 217 cm). The sandy diamicton is overlain by organic muds with abundant plant detritus (up to 195 cm in TL-1-1, and 178 cm in TL-1-2). A Larix cone was recovered at a depth of 195.5 cm from TL-1-1. Above these organic-rich sediments, the stratigraphy is dominated by gray-bluish clays with only scattered organic macro-remains. The top 50 cm of sediment in both cores are extremely watery, uncompacted lake sediments with few plant remains.

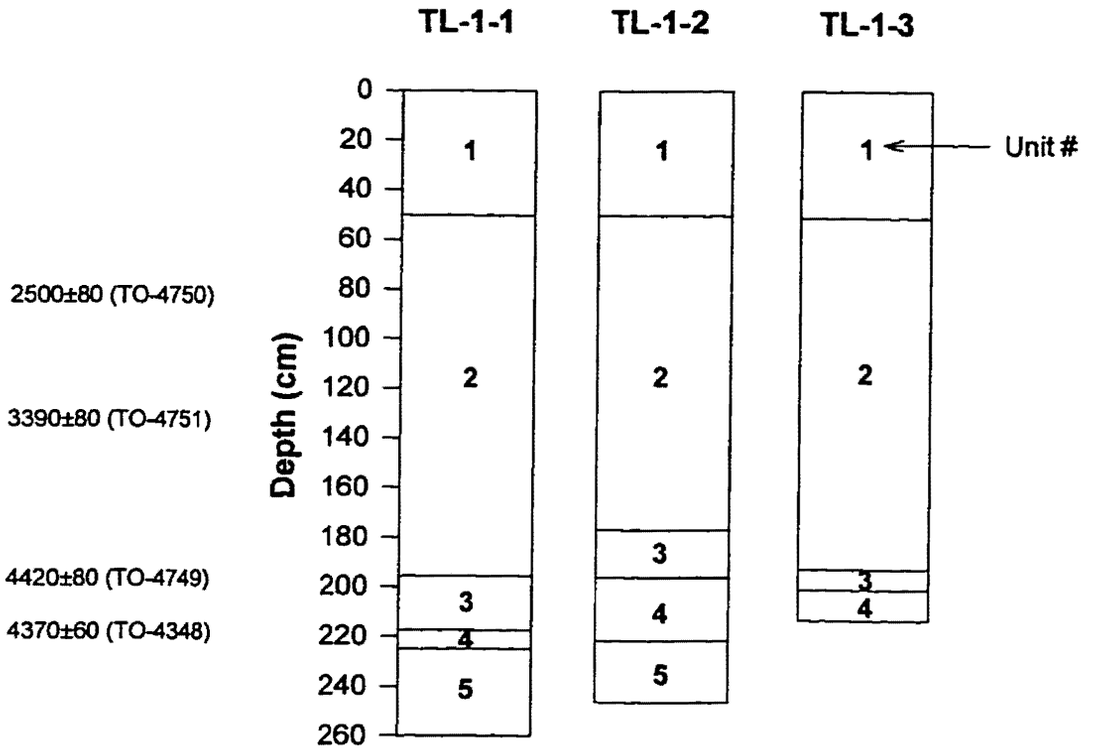


Figure 4-2. Sedimentary sequences from cores TL-1-1, TL-1-2, and TL-1-3, and radiocarbon dates from core TL-1-1 Middendorf Lake. Unit 1 is unconsolidated organic and clayey lake sediment; Unit 2 is fine dark gray-blue lake sediment with rare organic particles (1-2 mm); Unit 3 is gray-brown clay with organic inclusions (including wood) 2-4 cm in diameter; Unit 4 is bluish sandy diamicton; Unit 5 is compact gray diamicton with dark bluish spots and slightly rounded fragments of dark gray to black shale 0.8 cm in diameter (AA Velichko, analyst). All radiocarbon dates are ^{13}C corrected.

Table 4-2. Radiocarbon data obtained by accelerator mass spectrometry for Middendorf Lake sediments. All dates are ^{13}C corrected. Insufficent CO_2 was available for ^{13}C analysis for the sample at 80 cm depth.

Depth (cm)	Material	^{14}C Age BP	$\delta^{13}C$ (‰ PDB)	Lab No.
80	aquatic moss	2500 ± 80		TO-4750
135	aquatic moss	3390 ± 80	-27.35	TO-4751
196	wood fragments	4420 ± 80	-23.79	TO-4749
218	wood fragments	4370 ± 60	-29.12	TO-4348

Radiocarbon Dating of Lake Sediments

Accelerator mass-spectrometry was used to date plant macrofossils from the core (Figure 4-2; Table 4-2). The dates indicate that the organic deposits in the lake are more than 4400 years old. Sedimentation rates have been estimated from the dates without regard for sediment compaction in the lower layers. It appears that the sedimentation rate in the lower sediments amounted to 0.75 mm per year, which is almost twice the rate for the upper portion of the core. Coarser composition of the lower portion of the core and two dates which are 25 cm apart stratigraphically, but statistically indistinguishable (4420 ± 80 and 4370 ± 60) at the base of the core indicate rapid accumulation at the start of lacustrine deposition with the likelihood of some sediment reworking.

Lithochemical Characteristics

The stratigraphy established when describing the sedimentary sequence in the cores is corroborated by lithogeochemical analysis of samples from TL-1-2. Granulometric composition of Unit 2, from 50-75 cm (Figures 4-2 and 4-3) differs markedly from that of the lower ones. In the upper layer clay fractions (0.01 to 0.005, 0.005 to 0.001 and less than 0.001 mm) comprise 50 to 70 %. In contrast, Units 4 and 5 are dominated by sand, with coarse sand (1.0-0.25 mm) percentages being up to 16-18 % and fine sand up to 20-32 %.

The changes in granulometric composition reflect differences in sedimentation regime. Units 4 and 5 were likely deposited under conditions of active erosion within the catchment, possibly due to high precipitation. The sediments in the upper portion reflect a lower energy regime; predominantly fine clayey material accumulated at a slower rate. This could be attributed to a reduction of precipitation and to a lack of pronounced peak discharges or heavy rainfall in summer. Such climatic conditions corresponded in all probability to those of the relatively dry tundra around the site today, while the first stage featured quite different climates, more similar to the modern taiga.

The chemical composition of the units are very much alike (Figure 4-3), with

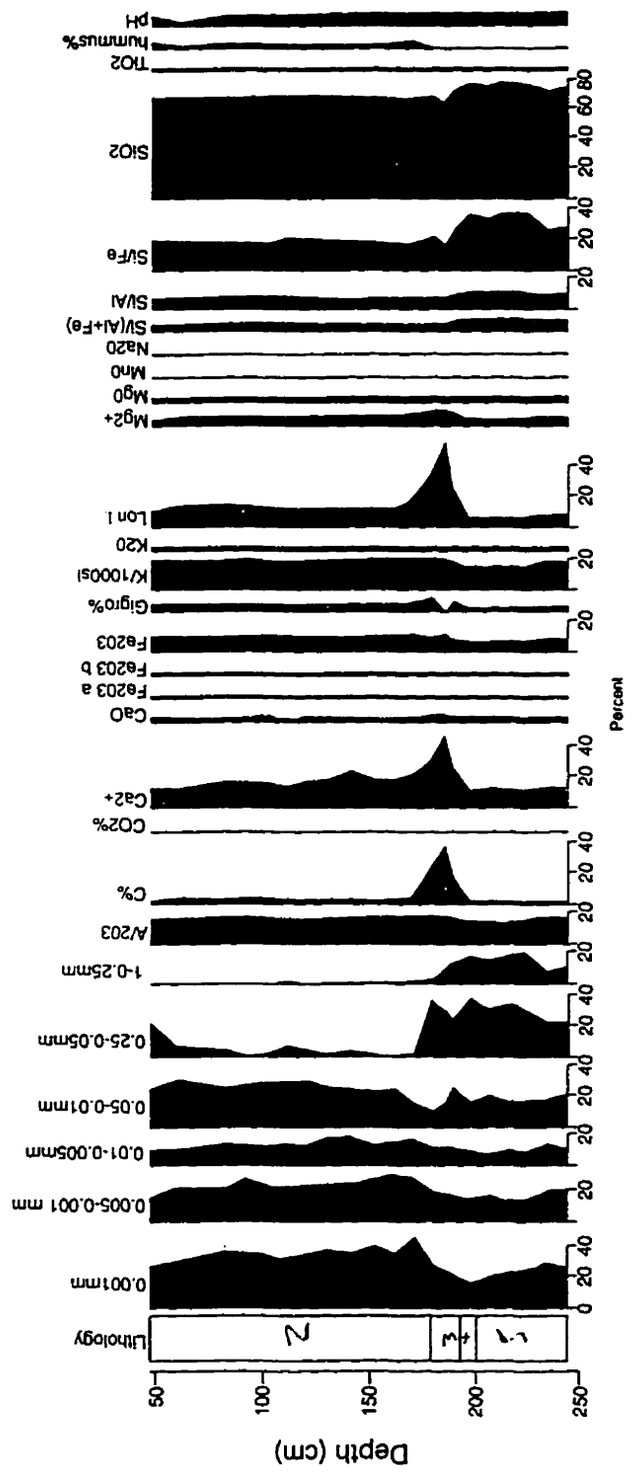


Figure 4-3. Lithochemical characteristics of lake sediments from core TL-1-2, Middendorf Lake (AA Velichko, analyst).

the exception of somewhat higher values of Si/Fe and Si/Al ratios in the lower layers. This difference may be accounted for by the presence of quartz sands. Unit 3 differs from both underlying and overlying layers in its chemical composition. It shows a peak in humus preceeded by peaks in carbon and calcium. The rise in these components may be due to calcium, organic carbon and humus that had accumulated in forest soil profiles and was subsequently redeposited in the lake by soil erosion during the period of deforestation between 4400 to 4000 BP.

Pollen Analysis

One ml sub-samples of sediment from TL-1-1 were processed for pollen and stomate analysis using standard methods (Faegri & Iversen 1975). Sub-samples were taken at 5 cm intervals along core TL-1-1. The presence or absence of stomates from conifers such as Larix and Picea are excellent indicators of the presence or absence of these trees in the immediate vicinity of lakes (Clayden *et al.* 1996; Hansen *et al.* 1996). Pre-treated tablets of Lycopodium spores were added to facilitate estimation of fossil pollen and stomate concentrations and accumulation rates. Pollen grains and stomates were identified using reference collections of the Laboratory of Evolutionary Geography in Moscow and the University of New Brunswick. A minimum of 300 pollen grains from terrestrial taxa were counted for each sample. Stomates encountered during the pollen counts were identified to genus and tabulated.

The pollen percentage diagram from Middendorf Lake (Figure 4-4) shows two distinct zones: Zone 1 (Alnaster, Betula, Larix; 218.5 to 185 cm; 4400-4000 BP) and Zone 2 (Betula, Cyperaceae; upper 185 cm; 4000 BP - Present). In Zone 1, shrub and arboreal pollen content comprises up to 90 % of the total pollen and spore amount. Alnaster and Betula pollen are dominant. Larix reaches maximum abundance (1 %). There is a maximum of Picea pollen at the base of Zone 1. Herb pollen is mostly represented by Cyperaceae and various Lycopodium species prevail among spores. Zone 2 spectra are also dominated by birch pollen (30 to 40 %), primarily of shrub varieties. Alnaster pollen declines to 10-15 %. Larix pollen is present sporadically, and only a few grains of Picea, while Pinus content is somewhat

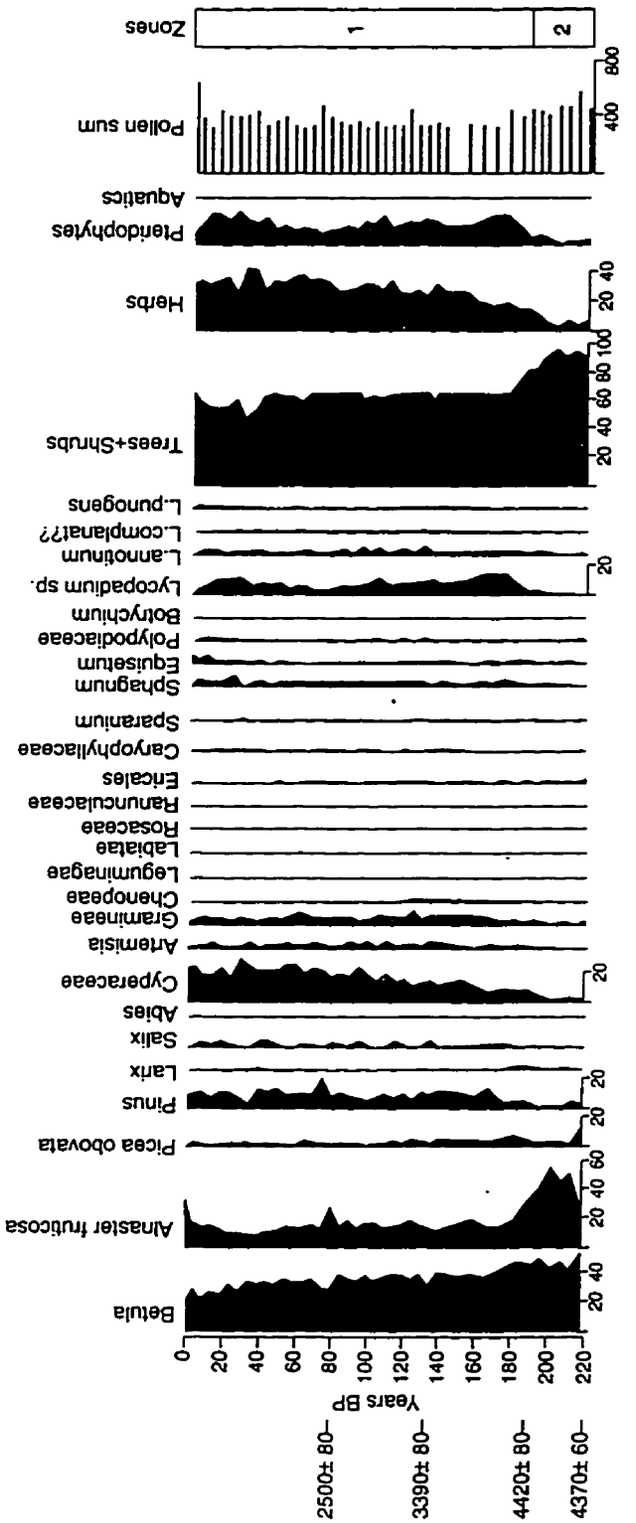


Figure 4-4. Pollen percentage diagram from core TL-1-1, Middendorf Lake (OK Borisova, analyst).

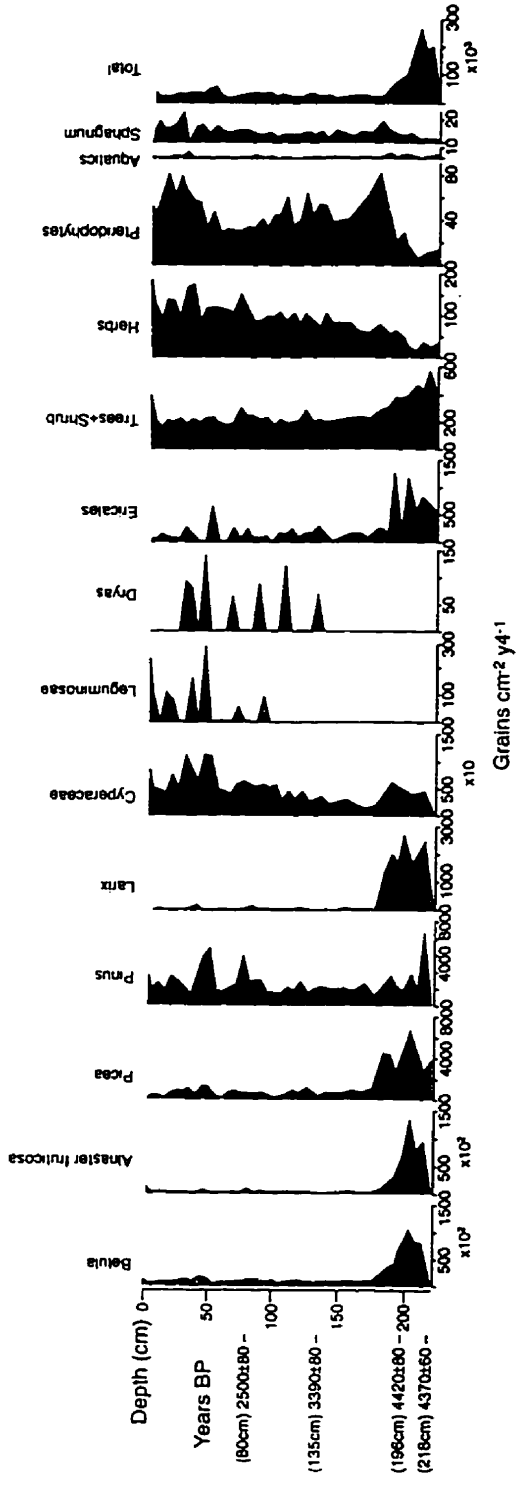


Figure 4-5. Pollen concentration diagram from core TL-1-1, Middendorf lake (OK Borisova, analyst).

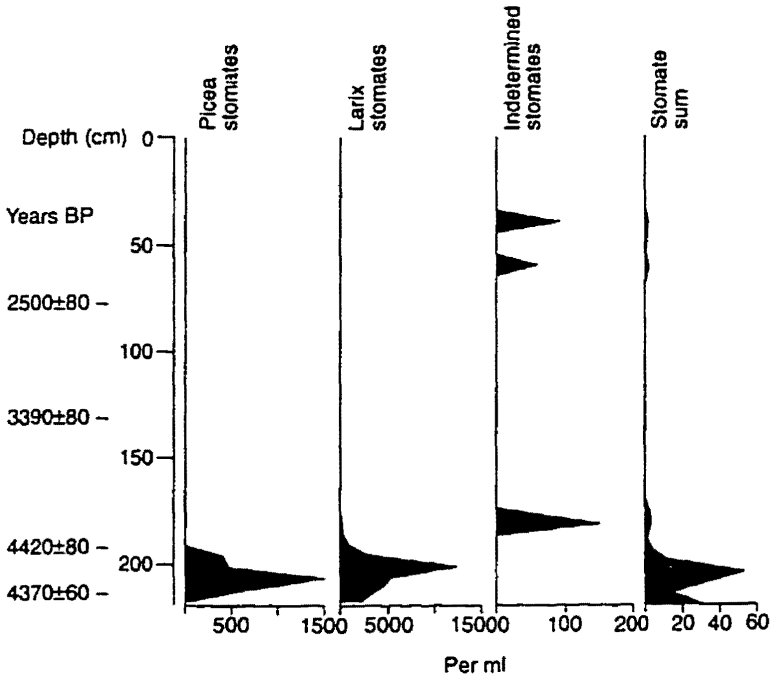


Figure 4-6. Stomata concentration diagram from core TL-1-1, Middendorf Lake (OK Borisova, analyst).

increased as compared with the lower layer. Cyperaceae pollen shows increases towards the top of the core.

Alnaster and Betula pollen concentration in Zone 1 is much higher than that in Zone 2, and Picea concentration is 6-7 times higher. Larix pollen concentration ranges up to 2500 grains per ml (Figure 4-5). Ericales dwarf shrubs also have maximum concentrations in Zone 1. In contrast, Salix, Artemisia, Gramineae, Cyperaceae and Lycopodium concentrations remain stable or increase in Zone 2.

Larix stomate abundance is up to 12,000 per ml in Zone 1 (Figure 4-6). Larch, undoubtedly existed near the lake until around 4000 BP. The date coincides closely with the time of Larix disappearance from the site deduced from the youngest radiocarbon dates from sub-fossil larch wood. Picea stomates are found in relatively small amounts (not more than 1500 per ml) in the same samples. Both the scarcity of spruce stumps and the low stomate concentrations suggest that spruce was not as common as larch in the vegetation around Middendorf Lake.

The site supported Larix and Picea from prior to 4400 BP to approximately 4000 BP. There is no evidence that Pinus was present at the site. Subsequent cooling probably resulted in the elimination of coniferous trees from the local vegetation. Around 4000 BP, the pollen and stomate record show that the forest was replaced by shrub tundra dominated by dwarf birch. However, the evidence from the radiocarbon dated stumps indicates that some trees were able to persist until 3100 BP. In the course of subsequent cooling, typical tundra communities became widespread as indicated by the presence of Dryas pollen (characteristic of dry tundra with polygonal microrelief), Leguminosae (including Hedisarum), Pedicularis, Polygonum typ viviparum, Saxifragaceae, as well as abundant sedge pollen in the upper layer of Zone 2.

Diatom and Chrysophyte Analysis

Subsamples of one ml of sediment from TL-1-1 were processed for siliceous microfossil analyses using a standard acid digestion technique (Battarbee 1986). Slides were prepared as strewn mounts, in which a small subsample of each prepared

slurry was diluted with distilled water, then transferred by pipette to glass cover slips. The cover slips were left to evaporate on a slide warmer at low heat. Once dry, the cover slips were mounted onto glass slides using Hyrax, a permanent mounting medium with a high refractive index (R.I.= 1.71). The same slides were used for both diatom and chrysophyte cyst analysis.

A minimum of 300 diatom valves (from 97 levels) and 100 chrysophyte cysts (from 40 levels) per slide were identified and enumerated using 1000X magnification with oil immersion and differential interference contrast optics. The microfossil counts are expressed as relative percentages of total diatom valves, relative percentages of total cysts, and the ratio (as a percentage) of diatom frustules to chrysophyte cysts (D:C; Smol 1985). Reference texts used for diatom taxonomy included Krammer & Lange-Bertalot (1986-1991), Lange-Bertalot (1993), Foged (1981), Camburn *et al.* (1984-1986), and Hustedt (1930-1966), as well as other sources. Cyst taxonomy followed Duff *et al.* (1995); cysts which have not yet been described using scanning electron microscopy (SEM) were given provisional letter codes (e.g. TS-AQ). Cysts that could be distinguished using SEM but not with LM were counted together (e.g. cysts 53/152/234).

The percentage diagram of the 21 most abundant diatom taxa was divided into zones using stratigraphically constrained cluster analysis (Grimm 1987), with the Edwards and Cavalli-Sforza chord distance as the dissimilarity coefficient. Similarly, the most common cyst types (with a relative percentage of ≥21% in at least one level; n=77) were divided stratigraphically using constrained cluster analysis with Euclidean distance as the dissimilarity coefficient (Grimm 1987). Only those cysts that showed distinct changes throughout the core (n=42) were plotted.

The diatom and cyst record was dominated by alkaliphilous taxa (Figures 4-7 and 4-8), indicating that the lake has remained alkaline throughout its history. Fragilaria pinnata, a cosmopolitan benthic taxon, and cyst 42, an indicator of shallow, alkaline water (Duff *et al.* in press), dominate the siliceous microfossil record for most of the core suggesting that few major limnological changes occurred overall. Nonetheless, minor changes in the aquatic environment took place, as indicated by

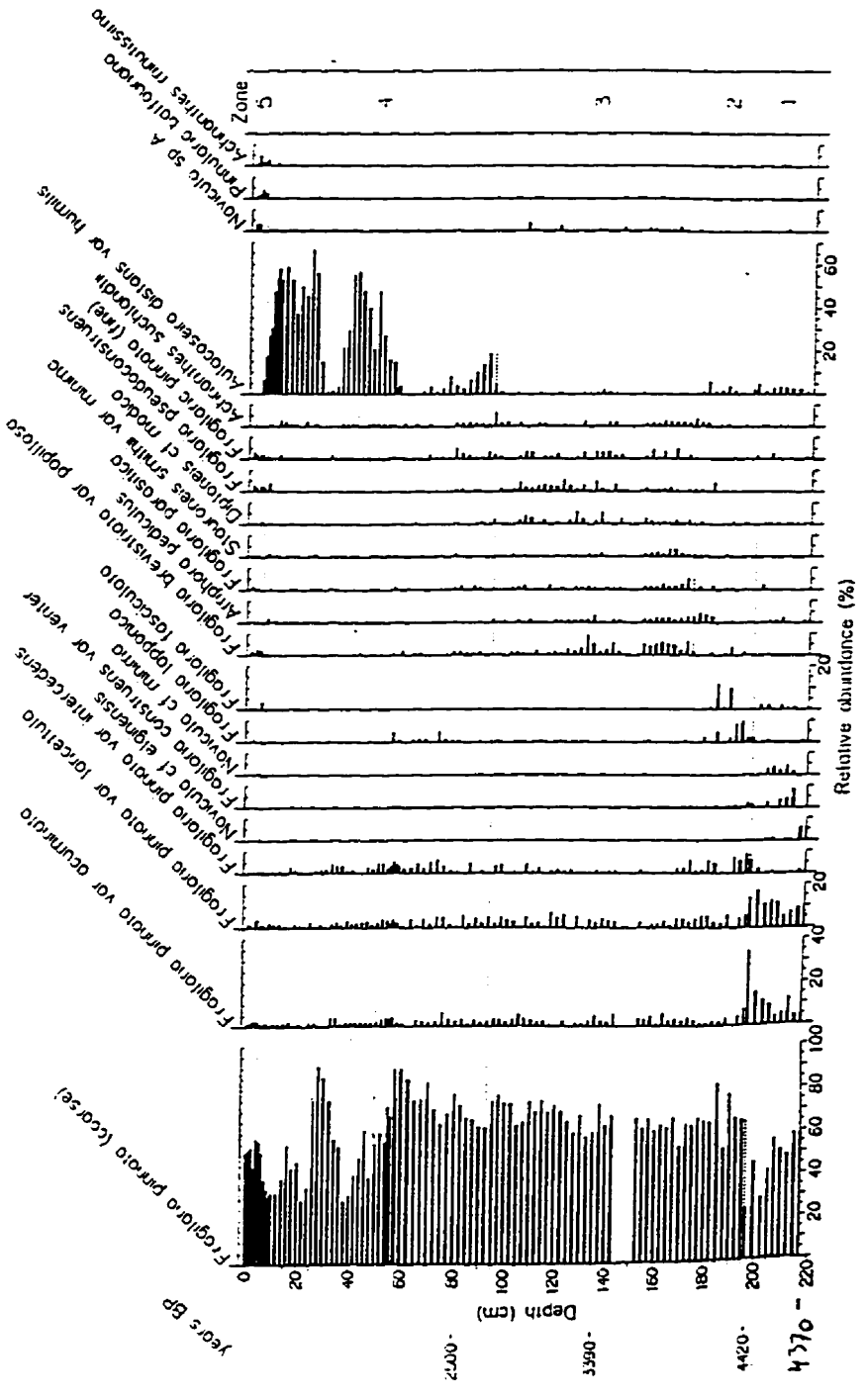


Figure 4-7. Percentage diagram of common diatom taxa from core TL-1-1, Middendorf Lake (TE Laing & JP Smol, analysts).

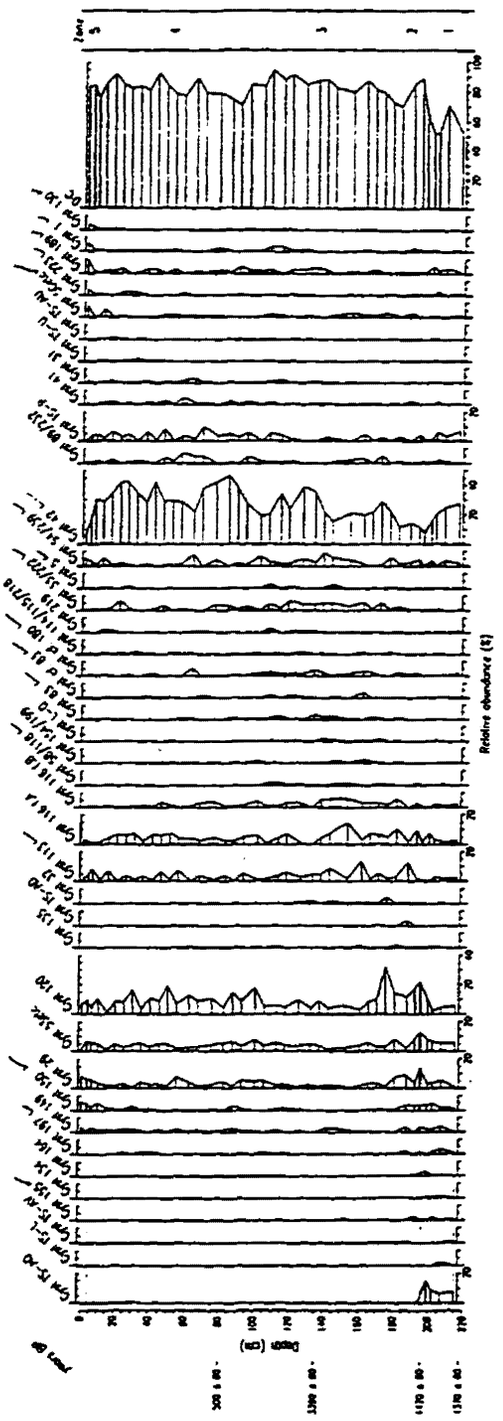


Figure 4-8. Percentage diagram of common chrysophyte cysts from core TL-1-1, Middendorf Lake. The ratio of diatom frustules to cysts (D:C) and stratigraphically constrained cluster analysis (Grimm 1987) are also shown (KE Duff, analyst).

shifts in the abundances of other taxa.

Independent cluster analyses of the diatom and cyst records identified five main zones. Interestingly, the zone boundaries occurred at nearly the same stratigraphic levels, although the degree of dissimilarity between the zones varied somewhat. Each zone is discussed in more detail below.

Zone 1 (196.5-215 cm - ≥4400 BP)

Benthic Fragilaria taxa, such as F. pinnata var. acuminata and F. construens var. venter, were abundant in this zone. Quite often these taxa dominate the initial post-glacial stage in lakes (Haworth 1975; Smol 1988), and it is possible that this assemblage may represent an early successional stage in Middendorf Lake. The cyst assemblage was composed mainly of large unornamented cysts (e.g. cysts 155, 197, 42, and 150) that are most common in shallow, meso-eutrophic lakes (Duff *et al.* 1995; Duff *et al.* in press). Although benthic diatom taxa and shallow water cysts are common, a small population of Aulacoseira distans var. humilis was present. This indicates that water depths were sufficient to support at least a small planktonic diatom community.

Zone 2 (175-195 cm - 4400-4000 BP)

This zone brackets the retreat of treeline from the region, as inferred by pollen, stomate and macrofossil evidence. The siliceous microfossils reflect climatic and limnological changes that would likely accompany a loss of trees in the catchment. For example, this zone is characterized by higher percentages of Fragilaria pinnata var intercedens and Fragilaria lapponica. In their work on treeline diatom assemblages in the Western Canadian Arctic, Pienitz *et al.* (1995) indicated that these taxa have lower temperature optima compared with the taxa in zone 1.

Fragilaria fasciculata, a taxon commonly found in waters of high conductivity (Patrick & Reimer 1966; Krammer & Lange-Bertalot 1986-1991), also increased coincidental with the boundary between pollen zones 1 and 2 at circa 185 cm. Although somewhat speculative, it is possible that weathering and catchment erosion

may have increased during this period as a result of a decline in catchment vegetation. The observed lithogeochemical changes during this period (Figures 4-2 and 4-3) provide additional evidence to support this hypothesis.

The cyst assemblages in these samples showed high levels of dissimilarity and the boundary between Zones 2 and 3 was identified as the most dramatic split in the cyst cluster analysis. The cyst flora is characteristic of alkaline, shallow, fairly productive water (Duff *et al.* 1995; Duff *et al.* in press) but was characterized by a decline in larger cysts and an increase in smaller cysts, likely reflecting a shift in the chrysophycean flora from netplankton to nannoplankton. At this point, the reasons for such a shift are unclear. However, the continued presence of a small population of Aulacoseira distans var. humilis indicates that at least some planktonic diatoms persisted during this period.

Zone 3 (92.5-172.5 cm - 4000-2600 BP)

Zone 3 is marked by increases in diatom species typically found in tundra lakes, such as Fragilaria brevistriata var. papillosa (Pienitz 1993). Taxa characterized by lower temperature optima, for example Stauroneis smithii var. minima and Fragilaria pseudoconstruens (Pienitz *et al.* 1995), also became more prominent. Cysts that are produced by cold-water taxa (e.g. cyst cf. 180, probably Spiniferomonas bourrellyi, and cyst 58/118, probably Mallomonas akrokomos) increased in abundance, as did cysts that are common in alpine and arctic lake sediments (cysts 113, 83, cf. 83, 33/222, 5 and 94/239; Duff *et al.* 1995; Duff *et al.* in press). These data indicate that temperatures were cooler during this zone.

Other stratigraphic changes that characterize zone 3 are the consistently high (>80%) D:C values and the near disappearance of the planktonic Aulacoseira distans var. humilis. With colder conditions, it is possible that lake ice cover was more persistent, and this may have hindered the development of planktonic diatom taxa (Smol 1988).

Other limnological changes also occurred during this time. For example, the diatom taxa were mostly oligohalobous species (Patrick & Reimer 1966; Foged 1981),

indicating that lake conductivity may have decreased slightly. Similarly, there was an increase in cyst morphotypes that are typical of oligotrophic, circumneutral and less alkaline lakes (e.g. cysts 5 and 94/239; Duff *et al.* in press), suggesting slight declines in lake pH and productivity.

Zone 4 (4-90 cm - 2600-100 BP)

Zone 4 was possibly a period of slight climatic warming and possibly reduced ice cover, as indicated by declines in the abundances of cold-water diatoms and cysts and a modest decline in the D:C ratio. The presence of Aulacoseira populations in zone 4, as in zones 1 and 2, may reflect a decrease in the extent of ice cover compared with zone 3. The high abundances of Aulacoseira in zone 4 compared with zones 1 and 2 suggests that lake turbulence was greater during this period. Most Aulacoseira species form heavy resting cells during their life cycle that require resuspension from the sediments into the water column to establish planktonic populations (Round *et al.* 1990). In addition, the vegetative cells themselves often require strong turbulence to maintain their position in the photic zone. As trees were no longer in the drainage basin during zone 4, more wind mixing would be likely, possibly explaining the high abundances of Aulacoseira in the lake during this time.

Zone 4 was also characterized by the most striking successional changes recorded in the diatom record. These changes are marked by a series of oscillations between the two dominant diatom taxa: Fragilaria pinnata, a small benthic diatom, and Aulacoseira distans var. humilis, a heavily silicified tychoplanktonic species. At least two possible hypotheses may explain this phenomenon. First, F. pinnata is generally most abundant in shallow lakes (Rawlence & Senior 1988), while Aulacoseira species, being planktonic, tend to be more representative of deep water lakes (Pienitz 1993). One possibility is that the oscillations may represent fluctuations in lake water levels. Alternatively, the cycles of Aulacoseira relative abundances may indicate changes in the mixing regime within the lake as a result of altered wind patterns and lake stratification (Smol *et al.* 1984; Smol 1988). The D:C ratio, while fluctuating, showed no clear correspondence with the Fragilaria/Aulacoseira oscillations.

The diatom record clearly indicates that limnological conditions were relatively unstable throughout Zone 4. Interestingly, though, the limnological changes apparently affected the chrysophytes to a much lesser degree. Chrysophytes, however, are flagellated, and are not as dependent on wind-induced turbulence. Thus, the aquatic algal populations differed in their responses to environmental shifts during this period. Moreover, the pollen record does not display coincident changes, suggesting that the diatoms were responding to external factors not apparent as changes in the terrestrial ecosystem during this time.

Zone 5 (0-3 cm - Recent)

Recent diatom assemblages in the lake are characterized by a shift to species previously rare in the diatom record, for example Pinnularia balfouriana and Achnanthes minutissima. Similar changes have been observed in other arctic regions, such as eastern Ellesmere Island (Douglas *et al.* 1994). Similarly, the chrysophyte assemblage in the most surficial sample was unique, with the lowest recorded abundances of cyst 42, and increases in previously rare cysts such as cysts 50/52/110/small 51, 223, 189, 1 and 130. These changes are probably the result of post-industrial anthropogenic disturbances altering the lake from its natural state. The nearby city of Noril'sk is a major center for nickel smelting and appreciable damage to forest vegetation is clearly observable near the city. In addition, the Taimyr Peninsula is located along a major route for the transport of atmospheric pollutants into the Arctic, and consequently receives significant amounts of pollutants through atmospheric deposition (Barrie *et al.* 1992; Krasovskaya 1987).

In summary, the diatom and chrysophyte record for Middendorf Lake indicate the following limnological changes. First, a pioneering benthic diatom assemblage dominated during the period in which the catchment of the lake was forested. The cyst data suggest a relatively warm, productive and possibly shallow lake at this time. Between 4400 and 4000 BP, a slight decline in lake temperatures and a modest increase in lake conductivity coincided with a decline in catchment forest vegetation. Following the departure of forest from the area (4000 BP), temperatures became

cooler, persistent ice cover may have increased and lake conductivity, pH and productivity decreased slightly. A period of limnological instability occurred between circa 2600 to <100 BP, characterized by enhanced mixing or fluctuating lake levels. Finally, anthropogenic factors appear to have influenced the composition of recent aquatic communities.

Oxygen Isotope Analysis

Samples taken at mostly 5 cm intervals from core TL-1-1 were pre-treated in a 10% hydrochloric acid solution at 70 °C for two hours to dissolve any trace amounts of shell or mineral carbonate. Additional sample preparation on the <500 μm acid-washed residue involving solvent extraction, bleaching, and alkaline hydrolysis removed non-cellulose organic components (Edwards & McAndrews 1989). The cellulose fraction was subject to oxygen isotope ($^{18}O/^{16}O$) determinations using nickel-tube pyrolysis (Edwards *et al.* 1994). Cellulose $^{18}O/^{16}O$ was also measured on surface sediment from an additional short core. Bulk organic and cellulose stable carbon isotope ratios, bulk organic nitrogen isotope ratios, bulk organic carbon content, and bulk organic nitrogen content are reported elsewhere (Wolfe *et al.* in prep.).

Oxygen isotope ratios were measured on a VG Prism II mass spectrometer at the Environmental Isotope Laboratory, University of Waterloo, and results are reported in δ-notation ($\delta = [(R_{sample}/R_{std}) - 1] \times 1000$, where $R = {}^{18}O/{}^{16}O$) with respect to Vienna-standard mean ocean water (SMOW). Repeated samples are normally within 1.0 ‰ reflecting both method uncertainty and the natural heterogeneity of the samples.

Results from the cellulose $\delta^{18}O$ ($\delta^{18}O_{cell}$) analysis vary significantly, spanning over 10 ‰ from +7.7 to +18.9 ‰ (Figure 4-9). In the bottom 15 cm of the core, $\delta^{18}O_{cell}$ values are low, ranging from +8 to +11 ‰. From 196.5 to 190 cm, the $\delta^{18}O_{cell}$ profile rapidly becomes several per mil more positive to about +18 ‰. The $\delta^{18}O_{cell}$ record is relatively invariant to 48.5 cm oscillating between +16 and +19 ‰ except for brief negative excursions to less positive values between +12 and +15 ‰ at 187.5, 172.5, 157.5, 107.5, 92.5, and 82.5 cm. At 48.5 cm $\delta^{18}O_{cell}$ values rapidly return to a level similar to the bottom of the core, roughly +10 ‰, until 14.5 cm except for two

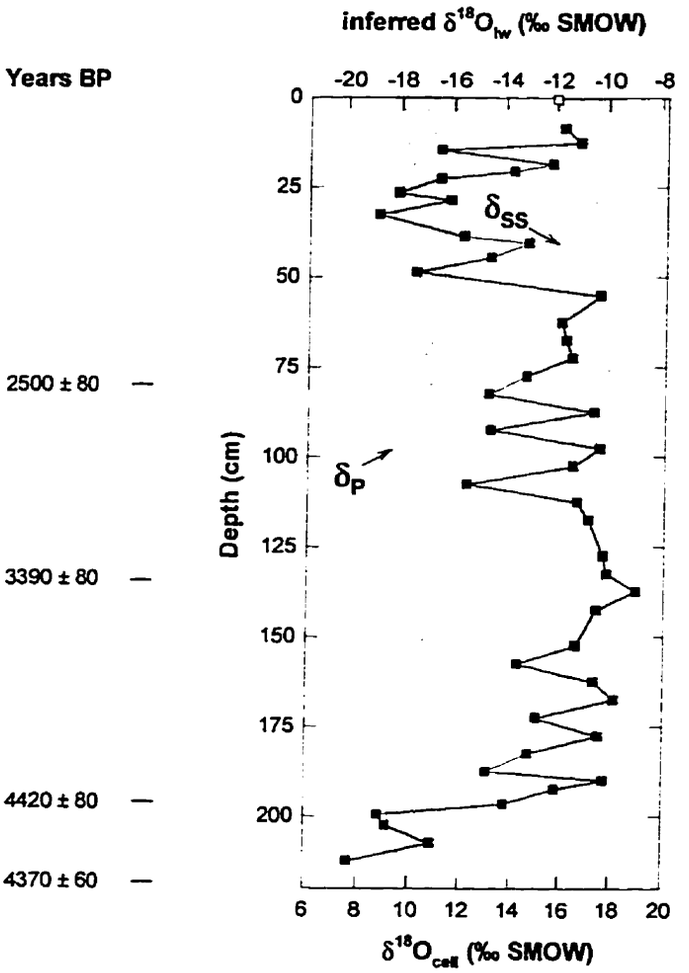


Figure 4-9. Oxygen isotope stratigraphy for core TL-1-1, Middendorf Lake (BB Wolfe, TWD Edwards & R Aravena, analysts). $\delta^{18}O_{cell}$ from a short core is plotted separately. Inferred $\delta^{18}O_{lw}$ calculated assuming cellulose is dominantly aquatic in origin (Wolfe *et al.* in prep.) and using a $\alpha_{cell\text{-}lw}$ of 1.028 (Edwards & McAndrews 1989). Mean annual isotopic composition of precipitation (δ_P) is estimated from a range of shallow groundwater and ground-ice samples collected in the region (Wolfe & Edwards in press). Steady state isotopic composition (δ_{ss}) is based on theoretical relationships for a closed basin and modern climate/isotope data (see text).

positive peaks centred at 40.5 and 18.5 cm. At 12.5 cm $\delta^{18}O_{cell}$ values rapidly increase and stabilize at about +16 ‰, similar to the interval between 190 and 48.5 cm. $\delta^{18}O_{cell}$ data obtained from surface sediment of the short core compares well with the uppermost sample from the long core.

Interpretation of inferred lake water $\delta^{18}O$ ($\delta^{18}O_{lw}$) histories derived from $\delta^{18}O_{cell}$ requires differentiation of source signals, reflecting the integrated isotopic composition of surface and subsurface inflow and precipitation, from hydrologic factors that may modify the isotopic content of the lake water (e.g. Edwards & McAndrews 1989; Edwards 1993; MacDonald *et al.* 1993; Duthie *et al.* 1996; Edwards *et al.* 1996; Wolfe *et al.* 1996). Middendorf Lake receives most of its water via precipitation falling directly on the lake, supplemented by limited runoff from its small catchment and perhaps minor flow from active layer groundwater. For headwater lakes the oxygen isotope composition of input waters can be approximated by the mean annual oxygen isotope composition of precipitation ($\delta^{18}O_P$), with the long-term average often reflected in shallow groundwaters (Gat 1981). Based on a small number of shallow groundwater and ground-ice samples collected in the region, which show no isotopic evidence of selective recharge or evaporative enrichment, $\delta^{18}O_P$ is estimated to be roughly -17 ‰ (Wolfe & Edwards in press).

In seasonally closed basins such as Middendorf Lake, however, evaporation should also play a role in the isotopic composition of the lake water. This process results in ^{18}O-enrichment of lake water due to preferential removal of water containing ^{16}O. Under stable hydrologic and climatic conditions, $\delta^{18}O_{lw}$ becomes increasingly positive until isotopic steady state is reached (i.e. $\delta^{18}O_{evap} = \delta^{18}O_{input}$; Craig *et al.* 1963; Gat & Levy 1978) with the rate dependent on the residence time of the basin (Lister *et al.* 1991). The theoretical, closed basin steady state isotopic composition for Middendorf Lake can be estimated using climatic data from Dudinka, Russia (Lydolph 1977) and the following expression (Craig & Gordon 1965; Lister *et al.* 1991):

$$\delta^{18}O_{ss} = \varepsilon + h(\delta^{18}O_A - \delta^{18}O_{input}) + \delta^{18}O_{input}.$$

ε incorporates both the equilibrium fractionation factor, ε^*, and the kinetic fractionation factor, ε_K, h = relative humidity, $\delta^{18}O_A$ = isotopic composition of atmospheric vapour, and $\delta^{18}O_{input}$ = average isotopic composition of input waters. Assuming isotopic equilibrium between $\delta^{18}O_A$ and $\delta^{18}O_P$ (i.e. $\delta^{18}O_A = \delta^{18}O_P - \varepsilon^*$), $\delta^{18}O_{input} \approx \delta^{18}O_P \approx -17$ ‰, $\varepsilon^* = +10.7$ ‰ (using equation (1) in Table 3-1 of Gonfiantini (1986) and an average ice-free air temperature of 7 °C), and $\varepsilon_K = 14.2(1-h)$ (Gonfiantini 1986), yields $\delta^{18}O_{ss}$ = -12 to -9.5 ‰ for h = 0.7 to 0.8. This is in good agreement with modern average $\delta^{18}O_{lw}$ for Middendorf Lake, estimated at about -12 ‰ (Figure 4-9) on the basis of the surface sediment sample $\delta^{18}O_{cell}$ (+15.7 ‰) and a fractionation (α) of 1.028, where $\alpha_{cell\text{-}lw} = (\delta^{18}O_{cell} + 1000) / (\delta^{18}O_{lw} + 1000)$ (Edwards & McAndrews 1989). These calculations suggest that Middendorf Lake is currently at isotopic steady state and that the $\approx$ 5 ‰ difference between $\delta^{18}O_P$ and $\delta^{18}O_{lw}$ is attributable to lake water evaporative isotopic enrichment (Figure 4-9).

If $\delta^{18}O_P$ can be assumed to have varied little over the past 4400 years, then in contrast to the modern relationship, $\delta^{18}O_{lw}$, inferred from $\delta^{18}O_{cell}$, and $\delta^{18}O_P$ merge at two stratigraphic intervals (4400 to 4100 BP, 215 to 199.5 cm and 1500 to 400 BP, 48.5 to 14.5 cm; Figure 4-9). An increase in the inflow/evaporation (I/E) ratio during these periods, including when forest dominated the terrestrial vegetation, likely accounts for the negative shifts in $\delta^{18}O_{lw}$ and implies that Middendorf Lake has previously been hydrologically open with rapid flushing rates. Wetter conditions were also interpreted from $\delta^{18}O_{cell}$ records during mid-Holocene intervals of forest development near treeline in central Canada (MacDonald *et al.* 1993; Wolfe *et al.* 1996).

A $\approx$ 9 ‰ increase in $\delta^{18}O_{lw}$ from 4100 to 4000 BP (196.5 to 190 cm) is interpreted to reflect conditions which rapidly became drier during the transition from forest to tundra, resulting in lake water evaporative isotopic enrichment. The $\delta^{18}O_{lw}$ record abruptly stabilizes in the range estimated for isotopic steady state based on modern data (Figure 4-9), suggesting that the lake became hydrologically closed and moisture levels similar to modern conditions may have prevailed by 4000 BP. Occasional, but brief excursions to more negative $\delta^{18}O_{lw}$ at 4000, 3800, 3700, 2900,

2700, and 2500 BP (187.5, 172.5, 157.5, 107.5, 92.5, and 82.5 cm depth) may reflect increased contribution of ^{18}O-depleted snowmelt (Wolfe & Edwards in press) or flood events in which the lake overflowed, flushing out evaporatively ^{18}O-enriched lake water with the more negative signature of $\delta^{18}O_p$.

The hydrologic regime rapidly changed again at 1500 BP (48.5 cm). High I/E ratios minimized the difference between $\delta^{18}O_p$ and $\delta^{18}O_{lw}$ as moisture conditions may have become similar to the forest period. This more recent increase in moisture, however, is apparently not accompanied by any change in the terrestrial vegetation. At least two brief intervals in which moisture conditions were more favourable for evaporation are suggested by the positive $\delta^{18}O_{lw}$ trends at 1300 and 600 BP (40.5 and 18.5 cm), probably caused by temporary drawdown of lake level. Modern, closed basin hydrologic conditions were established at 400 BP (12.5 cm depth) with a rapid increase to more positive $\delta^{18}O_{lw}$ values.

Discussion

The radiocarbon dated stumps, fossil Larix cone, and the fossil pollen and stomate records all confirm the presence of trees in this portion of the western Taimyr Peninsula during the early and mid Holocene. The stumps indicate that Larix was present shortly after 9000 BP and persisted until 3100 BP. The stumps, pollen and stomate records all indicate that Picea was also present, but at far lower densities than Larix. The presence of stumps on both uplands and valleys indicates widespread occurence of trees. The likely modern equivalent to the paleoforest occurs at the northern edges of continuous forest and southern edges of forest-tundra some 100 to 50 km south and east of the site.

Although Picea obovata was sparse at the study site, the range limits of the species was undoubtedly to the north of Middendorf Lake. Judging by pollen evidence from other sites (Nikolskaya 1982), spruce in Central Siberia reached as far as 72° N during the mid-Holocene. Spruce needles have been found in a Holocene peat deposits north of Khatanga (È-10 section, 72°12'N, 102°32'E, Nikolskaya 1982); unfortunately, no radiocarbon dates of the peat are available. Additional evidence is

available which shows that forest shrub species such as raspberry (Rubus idaeus *L.*) and cranberry (Oxycoccus palustris *Pers*) also had ranges north of their present limits in the Yenisey-Taimyr region during the early to mid-Holocene (Firsov *et al.* 1974; Badinova *et al.* 1976).

The tundra vegetation of the study site is a late Holocene phenomenon. Progress towards the development of tundra likely had already begun by the time the Middendorf Lake record commenced. By 4500 BP, the summer insolation maximum and associated summer warming had already decreased markedly from the early to mid-Holocene maximum (Kutzbach *et al.* 1993). The lower number of stumps recovered for the period 5000 to 3000 BP in comparison with the number recovered for 9000 to 6000 BP suggests that forest cover had begun to thin by 4400 BP. All lines of evidence show that between 4400 and 3000 BP trees disappeared almost completely and the present tundra was established. The decline in Larix and Picea pollen and stomates is sharp between 4400 and 4000 BP. During this phase of deforestation there was significant erosion of forest soils. However, the radiocarbon dated stumps show that scattered trees persisted until 3100 BP. Indeed, the single krummholz Larix sibirica found near the site may be a last relict of the early to mid-Holocene forest phase.

The evidence presented here clearly indicates that forest was able to persist on the Taimyr during the Holocene and the region supported Larix during at least one previous inter-stadial or inter-glacial. The extension of forest in the past indicates that the tundra zone in this region has likely experienced geographic compression along the arctic coast and fragmentation in mountainous areas earlier in the Holocene. Under conditions of climatic warming, forest could eventually return to the study site. Scattered krummholz, such as the one found near Middendorf Lake, may serve as invasion foci, helping to promote reforestation during climatic warming (MacDonald *et al.* 1993).

Changes in the limnic environment during the transition from forest to tundra are striking. Conclusive evidence from diatom, chrysophyte, sedimentary, and geochemical profiles indicates that the lake was clearly more productive during the

forest interval than during the later tundra period. Furthermore, the decline in trophic conditions appears to have occurred rapidly over a few centuries.

Interpretation of hydrologic changes is less straightforward amongst the various records during the forest to tundra transition. Oxygen isotope data suggest the area became drier as the forest retreated, although a flush of clastics, organics, and nutrients into the lake implies that relatively moist conditions conducive to intense erosion persisted at least until final deforestation. Chrysophyte cyst data, however, indicate that Middendorf Lake was shallow during the forest period and no significant change in water depth occurred as the landscape became dominated by tundra vegetation. The rapid decrease in grain size apparent from the sedimentological analysis may be consistent with the $\delta^{18}O$ interpretation, reflecting reduced precipitation and influx of coarse detrital sediment, or may alternatively indicate an increase in water depth and lower energy conditions at the coring site.

A key assumption in the oxygen isotope interpretation is that $\delta^{18}O_P$ has remained relatively constant over the past 4400 years. Support for the hydrologic end-member interpretation comes from several lines of evidence. Of primary note are the large (6 - 9 ‰) and rapid $\delta^{18}O_{lw}$ shifts at 4100, 1500, and 400 BP which cannot easily be explained by factors that commonly influence $\delta^{18}O_P$. At 4100 BP, the trend in $\delta^{18}O_{lw}$ towards more positive values is opposite in direction to that expected if principally due to mean annual temperature (MAT) effects on $\delta^{18}O_P$, assuming modern $\delta^{18}O_P$-MAT relations (Dansgaard 1964; Rozanski *et al.* 1993) and that MAT decreased with treeline retreat. Changes in the seasonal distribution of precipitation are also probably not responsible for ^{18}O-enrichment at this horizon based on modern data in which ^{18}O-depleted winter precipitation represents a greater proportion of annual precipitation in the tundra compared to the boreal forest (Lydolph 1977). Lack of modern $\delta^{18}O_P$ data east of the Urals (Rozanski *et al.* 1993) precludes speculation on the possible role of a shift in moisture sources or air mass dynamics, although the rate and magnitude of the $\delta^{18}O_{lw}$ shift makes these explanations seem unlikely. A rapid change to drier conditions, however, is consistent with changes in the carbon and nitrogen cycling regimes (Wolfe *et al.* in prep.), modern meteorological records in the

forest and tundra regions (Lydolph 1977), and large-scale paleobotanical reconstructions of Eurasian climate during the mid-Holocene (Velichko *et al.* 1995). At 1500 and 400 BP, there are no major changes in the pollen or stomate records that might signal large shifts in MAT, but hydrologic change at these strata is in strong agreement with the diatom record. Finally, basal porewater from a peat section obtained near treeline in the study area show similar $\delta^{18}O$ values as modern estimated $\delta^{18}O_P$, suggesting the isotopic composition of source water to Middendorf Lake during the mid-Holocene may have been similar to present (Wolfe *et al.* 1997).

Observations at Middendorf Lake suggest that major changes in *water level* may not be required to significantly alter the *water balance*. Seepage occurs through a meadow along the southwestern edge of the lake and we speculate that a small rise in lake level could lead to a substantial increase in the rate of outflow. Thus, a moderate increase in the precipitation/evaporation ratio could potentially decrease the residence time of the basin significantly (leading to more negative $\delta^{18}O_{lw}$), while the water depth may only change marginally. An increase in the proportion of the lake area defined by the littoral zone during the forest interval may account for the presence of shallow water chrysophyte cysts (and benthic diatoms) preserved in the sediment record. Alternatively, these taxa may have responded more strongly to increased nutrients during this time.

Increased moisture at the close of the early to mid Holocene forest period may also be responsible for the establishment of the lake and explain why lacustrine deposition did not commence until 4400 BP. Although the lake basin lies in an area of glacial deposits and continuous permafrost, the lake cannot be purely the result of water filling a glacial depression as sedimentation should have began with deglaciation. Alternatively, the basin may have originated through thermokarst processes and the timing of its inception does not strongly reflect climate variation. Thermokarst subsidence would explain why the basal organic sediments are relatively young and why the lake may have been initially shallow despite high precipitation.

The transition in the terrestrial and limnic environments following 4400 BP certainly reflects climatic cooling at the close of the early to mid Holocene insolation

and thermal maximum. Evidence for treeline retreat during the late Holocene is widespread from pollen records from Fennoscandia and the Russian Federation (e.g. Hyvarinen 1976; Khotinskiy 1984; Seppa 1996). During the period of roughly 8000 to 4000 BP, the vegetation around Middendorf Lake was likely similar to that found in the region south of Dudinka in the Yenisey valley. Using the modern summer climate of Dudinka as a conservative analog, this would imply a mean July temperature of around 12 to 14 °C at Middendorf Lake during the early and mid-Holocene. This is consistent with the conclusion of Velichko *et al.* (1995) that July temperatures in this region were 3 to 4 °C warmer than present during the mid-Holocene.

The late Holocene record from Middendorf Lake contains two important additional pieces of information pertaining to late Holocene tundra ecosystems on the Taimyr. First, there is evidence from the diatom and isotope records that the lake has witnessed a series of rapid changes in hydrologic conditions in the late Holocene, particularly after 1600 BP. The causes of these changes, and what, if any coincidental changes occurred in the terrestrial environment remains unknown. Second, in the very recent past the lake has undergone a shift in its diatom and chrysophyte flora to assemblages that have not previously been evident at the site. The impact of airbone pollutants is a possible explanation for this latest change.

PART B:

Wolfe BB, TWD Edwards & R Aravena, in prep. Changes in carbon and nitrogen cycling during treeline retreat recorded in the isotopic content of lacustrine organic matter, western Taimyr Peninsula, Russia. For submission to *The Holocene*.

Synopsis

Multidisciplinary investigations of Velichko *et al.* (in prep.) indicated that marked changes in the limnic environment of Lake Middendorf, western Taimyr Peninsula, Russia, occurred during the transition from forest to tundra *ca.* 4000 ^{14}C years BP. Evidence from diatom, chrysophyte cyst, sedimentary, and geochemical profiles suggested that the lake was clearly more productive during the forest interval than during the following tundra period. Oxygen isotope data from fine-grained cellulose indicated that relatively moist conditions prevailed during the forest period and that a drier climate ensued as the boreal forest retreated. The decline in trophic conditions and shift in hydrologic regime occurred rapidly, perhaps over a few centuries.

Our understanding of the terrestrial vegetation, lake trophic, and hydrologic history at Lake Middendorf made this an ideal site to explore the utility of nitrogen isotopes in lacustrine organic matter ($\delta^{15}N_{org}$). $\delta^{15}N_{org}$ has rarely been used in paleolimnology studies perhaps because of the lack of nitrogen isotope data in modern lake settings and also the formerly-less-than routine method of analyzing the $^{15}N/^{14}N$ ratio in organic material. However, recent development of continuous-flow isotope ratio mass spectrometry with coupled elemental analyzers has made analysis of $\delta^{15}N_{org}$, along with C (%), N (%), and $\delta^{13}C_{org}$, readily attainable on the same milligram-sized sample.

Results from this pilot study of Lake Middendorf sediments show that a shift in $\delta^{15}N_{org}$ (as well as C (%), N (%), $\delta^{13}C_{org}$, and $\delta^{13}C_{cell}$) occurs during the transition from forest to tundra suggesting that this proxy may be a sensitive recorder of nitrogen cycle response to climate change. Interpretation of these data are necessarily speculative given our lack of modern nitrogen isotope information (e.g. $\delta^{15}N$ in forest and tundra soil nitrate, $\delta^{15}N$ in atmospheric-derived nitrate, $\delta^{15}N$ in forest and tundra soil organic matter, etc.). However, multidisciplinary analysis has enabled the

proposal of a tentative unified model that strongly links the elemental and isotopic trends to changes in soil development processes and the hydrologic regime, and is consistent with previous isotopic studies near treeline in central Canada (Wolfe *et al.* 1996; see CHAPTER 3). These promising results suggest that further study of nitrogen isotope systematics in both the modern and paleolimnological context near treeline sites is warranted.

Abstract

Bulk organic and cellulose stable carbon isotope and bulk organic nitrogen isotope profiles from a small tundra lake on the western Taimyr Peninsula, Russia, show changes that are correlated with climate cooling and treeline retreat during the mid to late Holocene. Increased soil organic matter decomposition, combined with a moist climate, likely provided a ^{13}C-depleted source of $CO_{2(aq)}$ to lake phytoplankton thriving under favourable conditions during the forest period. Bulk organic and cellulose carbon are more enriched in ^{13}C after the boreal forest retreated probably because CO_2 from the atmosphere became the dominant source of carbon to the lake as soil organic decomposition rates declined and the climate became drier. Interpretation of the $\delta^{15}N_{org}$ record is considerably more speculative but similar factors that appear to have controlled the carbon cycling in the lake, including soil development and the hydrologic regime, may also have strongly influenced the lake water nitrogen balance. These results suggest that lake sediment organic matter $\delta^{13}C$, $\delta^{15}N$, and cellulose $\delta^{13}C$ may be useful indicators of past nutrient dynamics in boreal treeline watersheds.

Introduction

The response of arctic treeline nutrient cycles to elevated atmospheric CO_2 and temperature has the potential to significantly influence climatic and ecologic change. For example, enhanced greenhouse gas release due to rapid decomposition of soil organic matter and peatlands (BOREAS Science Steering Committee 1990) and CO_2 loading of the atmosphere as a result of increased forest fires (Wein 1990) may provide important positive climate feedbacks. In northern Alaska, there already appears to be evidence for tundra soils becoming a source of CO_2 to the atmosphere during the warming of the past century (Oechel *et al.* 1993). Over longer time scales (centuries to millennia) however, northern ecosystems may act as a small carbon sink in a warmer climate (Marion & Oechel 1993) as a result of elevated rates of productivity, development of new plant communities, and increased carbon storage in plant biomass (Oechel & Billings 1992). The capacity for both positive and negative

responses highlights the importance of understanding interactions amongst the northern treeline region, carbon balance, and climate change.

A key factor that will contribute to determining the importance of many of these feedback scenarios is the fate of mineralized nitrogen, often the limiting nutrient in arctic ecosystems (Chapin & Bledsoe 1992) and which is expected to increase with soil organic matter decomposition under a warmer climate (Nadelhoffer *et al.* 1992; Hobbie & Chapin 1996). If retained within the terrestrial environment, greater nutrient availability could provide the stimulus for increased productivity and withdrawal of additional CO_2 from the atmosphere. However, recent studies in Alaskan tussock tundra suggest that nitrogen is primarily released during spring thaw when it is predominantly unavailable to plants or soil microbes due to low soil temperatures and may instead be transported to aquatic ecosystems via snowmelt (Hobbie & Chapin 1996). Increased nitrogen mineralization, in concert with higher soil temperatures and oxygen levels, may also lead to greater production of nitrate which is more readily leached downslope than ammonium. If re-utilized, however, plant community structure may alter because of species-dependent nitrate-uptake potential and assimilation efficiencies (Nadelhoffer *et al.* 1992). Greater understanding of factors controlling the seasonal timing of nitrogen release, and the response of soil microclimate, microbial activity, and hydrology under a warmer climate are required for accurate predictions of nitrogen cycling and availability.

Dynamics of arctic watershed carbon and nitrogen cycling in the context of climate change have previously been assessed primarily through the use of carefully orchestrated field programs (e.g. Hobbie & Chapin 1996), via laboratory experiments (Marion & Black 1986; Nadelhoffer *et al.* 1991), and by process-based model simulations (McKane *et al.* 1997). Although these research strategies can often determine the likely *direction* of change in the event of climate warming, evaluation of the *rate* of change on relevant timescales is more uncertain. A paleoclimate approach using records preserved in soils (e.g. Marion & Oechel 1993) or lake sediments (e.g. Wolfe *et al.* 1996) on the other hand, can provide an indication of rate of nutrient cycle change and also insight to long-term variability. Here we examine

the response of carbon and nitrogen nutrient dynamics, inferred from elemental and stable isotope records in lacustrine organic matter, during a period of climate cooling at the end of the mid-Holocene Climatic Optimum in north-central Russia *ca.* 4000 ^{14}C years before present (4000 BP).

Paleoecologic and Paleoclimatic Setting

The western Taimyr Peninsula, Russia represents one of several northern sectors that has been targeted by the *Paleoecological Analysis of Circumpolar Treeline* research project to examine the relationship between treeline ecosystems and climate change during the Holocene. In this region, Larix and Picea stumps radiocarbon-dated between 8400 and 3100 BP have been found as far north as 70° 22' N representing northward extension of taiga of at least 100 km (Velichko *et al.* in prep.). Sediments from a small tundra lake 70 km northwest of treeline (Middendorf Lake, unofficial name; 70° 22' N, 87° 33' E; Figure 4-10) contain a 4400-year fossil pollen and stomate record that captures the end of the forest period, treeline retreat, and establishment of tundra vegetation consistent with the macrofossil radiocarbon data (Velichko *et al.* in prep.). The forest to tundra transition recorded at this site is rapid, perhaps taking place over a few centuries *ca.* 4000 BP.

In addition to terrestrial ecosystem-focused studies, Velichko *et al.* (in prep.) also examined the paleolimnology of Middendorf Lake using a multidisciplinary stratigraphic approach. Analyses using physical (grain size), chemical (element geochemistry, oxygen isotopes in cellulose) and biological (diatoms, chrysophyte cysts) techniques revealed significant changes in the trophic and hydrologic regimes, particularly during the forest to tundra transition. Lake water was more productive and warmer, while the precipitation/evaporation ratio (Figure 4-11) was higher during the forest period. Drier and less productive conditions developed rapidly and contemporaneous with changes in landscape vegetation as the climate deteriorated *ca.* 4000 BP. Between 1600 and 400 BP, oxygen isotope (Figure 4-11) and diatom data suggest that short-lived fluctuations in lake level may have occurred although these hydrologic changes are not associated with any known alterations in terrestrial

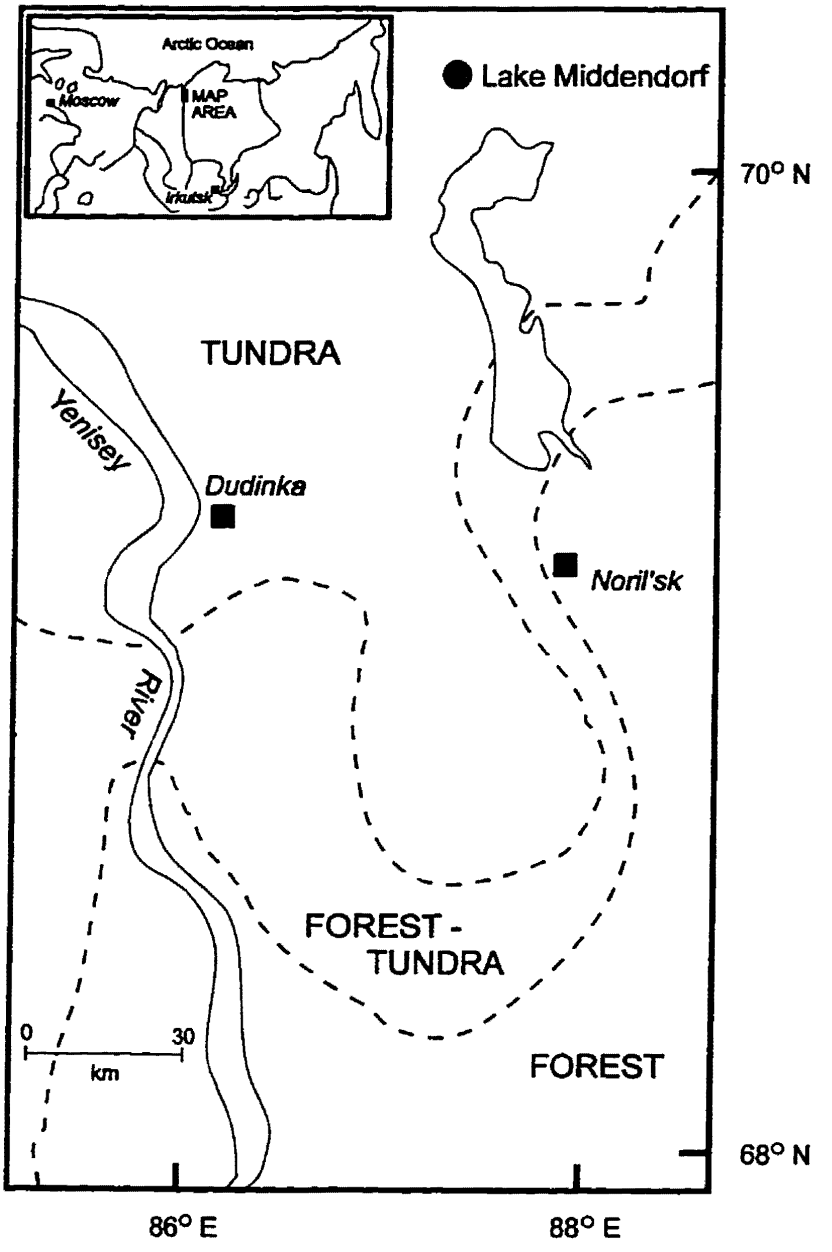


Figure 4-10. Lake Middendorf is located about 115 km NNW of Noril'sk on the tundra, approximately 50-75 km north and west of the mapped northern limits of Larix sibirica (western Siberian larch) forest-tundra. The lake is a seasonally-closed headwater basin, circular (roughly 100 x 90 m), and oligotrophic. Maximum depth is about 11.5 m. Coring depth was 8.15 m. Detailed local geomorphic and vegetation descriptions can be found in Velichko *et al.* (in prep.).

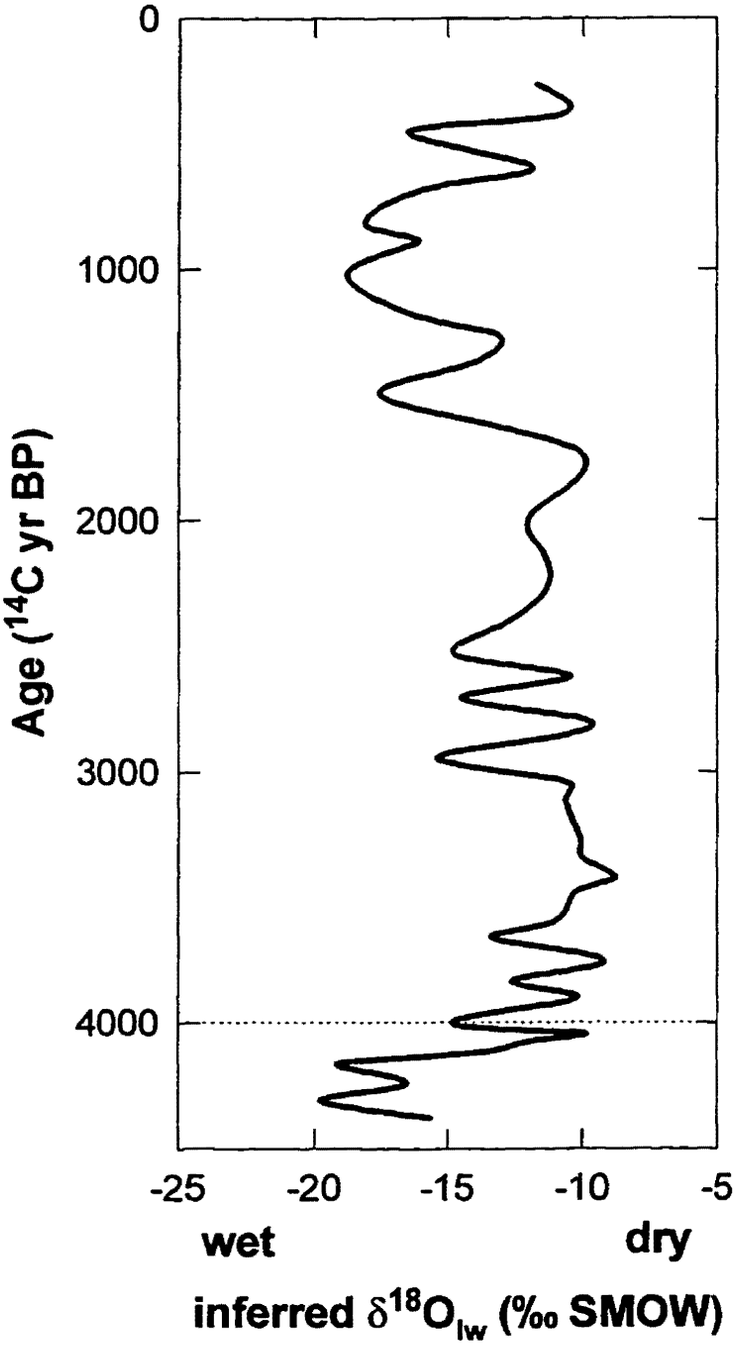


Figure 4-11. Inferred lake water $\delta^{18}O$ from oxygen isotope analysis of sediment cellulose. Data is considered to largely reflect changes in water balance arising from changes in moisture conditions (see Velichko *et al.* in prep.). Dotted line defines approximate transition between forest (lower) and tundra (upper) vegetation.

vegetation.

Methods

Sediment samples from Middendorf Lake were pre-treated in a 10% hydrochloric acid solution at 70 °C for two hours to dissolve trace amounts of shell and mineral carbonate. Stable carbon and nitrogen isotope ratios ($^{13}C/^{12}C$, $^{15}N/^{14}N$), carbon content (C %), and nitrogen content (N %) were measured on the <500 μm acid-washed residue. Additional sample preparation involving solvent extraction, bleaching, and alkaline hydrolysis removed non-cellulose organic components (Edwards & McAndrews 1989). The cellulose fraction was subject to $^{13}C/^{12}C$ analysis. All analyses were conducted at 2.0 to 2.5 cm depth intervals except $^{15}N/^{14}N$ which were analyzed at 4.0 to 5.0 cm depth intervals.

Carbon isotope analysis was performed using a standard combustion method (Boutton *et al.* 1983) and isolated CO_2 was analyzed on a VG Prism II mass spectrometer. Samples for nitrogen isotope determination were loaded in tin cups and measured on a continuous flow Isochrom mass spectrometer. All isotopic ratios were measured at the Environmental Isotope Laboratory, University of Waterloo, and results are reported in δ-notation ($\delta = [(R_{sample}/R_{std}) - 1] \times 1000$, where R = $^{13}C/^{12}C$ or $^{15}N/^{14}N$) with respect to the international standards for $\delta^{13}C$ (PDB) and $\delta^{15}N$ (AIR). Repeated samples are normally within 0.5 ‰ for $\delta^{13}C$ and $\delta^{15}N$, respectively, reflecting both method uncertainty and the natural heterogeneity of the samples.

Carbon and nitrogen content were measured on a Carlo Erba EA1108 elemental analyzer. Repeated samples are normally within 0.4 % for C and 0.04 % for N. The carbon/nitrogen ratio (C/N) is expressed as a weight ratio.

Results

The most striking stratigraphic change in the C and N elemental and stable isotope data is during the transition from forest to tundra *ca.* 4000 BP, although the rates of change differ amongst the profiles (Figure 4-12). Carbon and N are markedly high during the forest zone (≈ 25 % and 1.5 %, respectively) and then rapidly decline

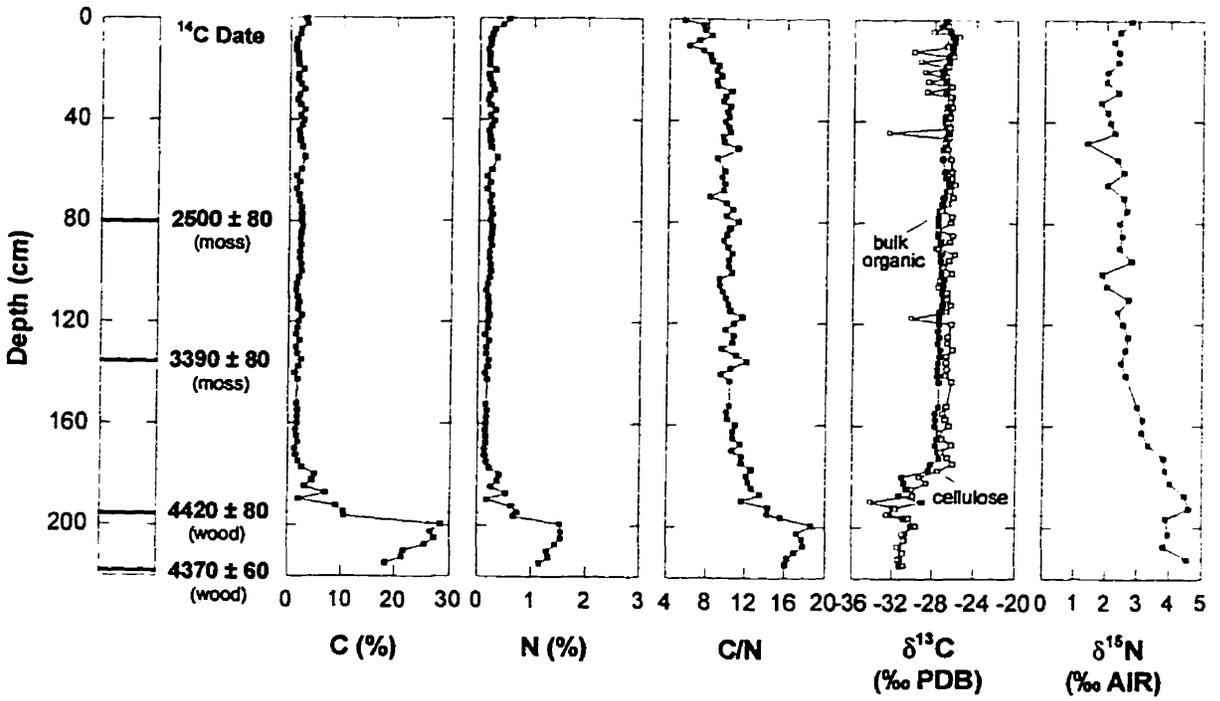


Figure 4-12. Carbon and nitrogen elemental and isotope stratigraphy for Lake Middendorf. See Table 4-3 for radiocarbon data. Dotted line defines approximate transition between forest (lower) and tundra (upper) vegetation.

Table 4-3. Radiocarbon data obtained by accelerator mass spectrometry for Middendorf Lake sediments (Velichko *et al.* in prep.). All dates are ^{13}C corrected. Insufficent CO_2 was available for ^{13}C analysis for the sample at 80 cm depth.

Depth (cm)	Material	^{14}C Age BP	$\delta^{13}C$ (‰ PDB)	Lab No.
80	aquatic moss	2500 ± 80		TO-4750
135	aquatic moss	3390 ± 80	-27.35	TO-4751
196	wood fragments	4420 ± 80	-23.79	TO-4749
218	wood fragments	4370 ± 60	-29.12	TO-4348

with treeline retreat (≈ 2 % and 0.2 %). C/N displays a similar pattern (≈ 18 in the forest interval; ≈ 10 in the tundra). $\delta^{13}C_{cell}$ and $\delta^{13}C_{org}$ both increase by about 4 ‰ (-31 to -27 ‰), although not until slightly after the main period of transition. $\delta^{13}C_{cell}$ displays a more gradual trend than $\delta^{13}C_{org}$. Finally, $\delta^{15}N_{org}$ shows the most gentle change decreasing for several hundred ^{14}C years from ≈ +4 ‰ during the forest interval to ≈ +2.5 ‰ in the tundra zone. Data are relatively complacent within both the forest and tundra intervals except for oscillations in $\delta^{13}C_{cell}$ in the upper part of the profile and small increases in C and N % (with corresponding decline in C/N) at the top of the core.

Discussion

Origin of Organic Matter

Fundamental to the interpretation of $\delta^{13}C$ and $\delta^{15}N$ in the organic fraction of lake sediments is knowledge of the origin of the organic matter. In the forest interval, relatively high C/N ratios measured on the <500 μm bulk organic fraction are consistent with abundant macrofossils of terrestrial origin found in these strata (Velichko *et al.* in prep.), although high levels of aquatic productivity suggest that both allochthonous and autochthonous sources are responsible for the rich organic content (Figure 4-12). The carbon isotope data, however, indicates that the <500 μm organic fraction may be dominantly aquatic in origin. $\delta^{13}C$ values obtained from bulk organic matter, which range between -32 and -30 ‰, are several per mil more negative than the $\delta^{13}C$ average of two wood samples from these sediments analyzed for ^{14}C-dating (-26.5 ‰; see Table 4-3). The $\delta^{13}C_{org}$ and $\delta^{13}C_{cell}$ values are also more negative than generally found in soil organic matter (Deines 1980; Boutton 1991) and high-latitude forest soils (-27.3 ± 0.7 ‰; Bird *et al.* 1996). Based on these $\delta^{13}C$ values for wood and soil, it appears that terrestrial organic matter input to Lake Middendorf during the forest period has, at most, reduced the magnitude of the ^{13}C-enrichment trend across the forest to tundra transition.

C/N ratios gradually decrease in the tundra zone to values more typical for aquatic organic matter (Figure 4-12; Meyers & Ishiwatari 1993a; Meyers 1994).

Similar $\delta^{13}C$ values for bulk organic matter, cellulose, and ^{14}C-dated aquatic moss (see Table 4-3) provides additional support for an autochthonous origin for the organic fraction of these sediments.

Carbon Cycling Regime

The carbon-isotope composition of fine-grained cellulose ($\delta^{13}C_{cell}$) contained within the organic fraction of lake sediments has proven to be an effective tracer of biogeochemical processes in freshwater lakes (e.g. MacDonald *et al.* 1993; Duthie *et al.* 1996; Wolfe *et al.* 1996; Wolfe *et al.* in review). Although $\delta^{13}C$ in bulk organic matter has also been used for paleolimnologic investigations (e.g. Oana & Deevey 1960; Schelske & Hodell 1991, 1995; Meyers & Horie 1993), mixing of terrestrial and aquatic source material and changes in the relative proportion of organic constituents having differing isotopic compositions can complicate interpretation (e.g. Aravena *et al.* 1992; Spiker & Hatcher 1984). In contrast, cellulose deposited in offshore lake sediments is frequently aquatic in origin and is well-preserved, perhaps due to rapid deposition and burial of phytoplankton in fecal pellets with little chance for oxidation (Edwards 1993).

The carbon isotope composition of aquatic cellulose is primarily determined by the $\delta^{13}C$ of lake water dissolved inorganic carbon (DIC), which is controlled by a dynamic balance of processes including isotopic exchange with atmospheric CO_2, input of DIC from the catchment, ^{13}C-enrichment deriving from preferential uptake of ^{12}C by phytoplankton during photosynthesis, and recycling of ^{13}C-depleted carbon from the decay of organic matter in the water column and bottom sediments. The balance between photosynthesis and respiration commonly provides the dominant signal preserved in the $\delta^{13}C$ of organic matter in sediment cores with positive excursions frequently interpreted as increased lake productivity (McKenzie 1985; Schelske & Hodell 1991, 1995; Meyers *et al.* 1993; Dean & Stuiver 1993; Duthie *et al.* 1996).

In the forest interval of the Lake Middendorf sediment record, however, $\delta^{13}C_{org}$ and $\delta^{13}C_{cell}$ are relatively negative compared to the less organic-rich tundra sediments suggesting that processes other than lake productivity have played a significant role

in controlling the carbon balance of the lake (Figure 4-12). Based on our understanding of the hydrologic and ecologic conditions (see Figure 4-11), the most likely explanation for the relatively negative $\delta^{13}C$ values is influx of ^{13}C-depleted dissolved CO_2 ($CO_{2(aq)}$) generated by soil development processes when forest vegetation occupied the catchment. Rapid hydrologic flushing of the lake (with ^{13}C-depleted $CO_{2(aq)}$) may have counteracted the carbon isotope effects of lake productivity on the DIC. Similar hydrologic scenarios have been presented by Aravena *et al.* (1992) and Wolfe *et al.* (1996) to explain negative $\delta^{13}C$ trends in organic lake sediments associated with past periods of increased lake productivity and forest cover in western and central Canada. In lacustrine sediments of southern Sweden, increased soil $CO_{2(aq)}$ production at the Pleistocene-Holocene transition may also have been responsible for widespread bulk organic ^{13}C-depletion in spite of increased organic matter deposition (Hammarlund 1993).

The forest to tundra transition is marked by significant shifts in the carbon isotope and elemental records. Changes in the carbon balance of the lake are clearly indicated by the trend to more ^{13}C-enriched values observed in the carbon isotope profiles. Drier conditions and increased lake water residence time may have led to an increase in the role of lake water DIC exchange with atmospheric CO_2, a ^{13}C-enriched source of carbon to the lake (cf. Turner *et al.* 1983), as influx of ^{13}C-depleted $CO_{2(aq)}$ from the catchment was reduced. The gradual change in the carbon isotope profiles at the forest to tundra transition may be related to the lake water residence time of $CO_{2(aq)}$ or declining rates of soil organic matter decomposition and $CO_{2(aq)}$ production. The carbon isotope composition of the DIC stabilized by about 3900 BP (180 cm). Rapid decline in organic matter content is probably due to decreased lake productivity.

The carbon isotope trends are generally complacent for the remainder of the record suggesting relatively stable levels of lake water DIC - atmospheric CO_2 exchange, lake productivity, and $CO_{2(aq)}$ supply from the catchment. Exceptions include negative oscillations in the $\delta^{13}C_{cell}$ profile at 3100 and 1400 BP (117.5 and 44.5 cm) and between 1000 and 400 BP (30 and 12.5 cm). Most of these occur during a

recent wet phase (Figure 4-11) and may be attributed to subtle changes in the $\delta^{13}C$ of the DIC caused by variable influx of soil generated, ^{13}C-depleted $CO_{2(aq)}$.

Roughly two-fold increases in C (%) and N (%) and corresponding decline in C/N ratios in the near surface sediment occur probably because recently deposited organic matter has had less exposure to oxidation. The $\delta^{13}C$ profiles, in contrast, show no diagenetic effects at the top of the core. Lakes with low organic carbon concentrations frequently exhibit no diagenetic carbon isotope effect (Meyers & Ishiwatari 1993b).

Nitrogen Cycling Regime

In contrast to $\delta^{13}C$, analysis and interpretation of $\delta^{15}N$ in organic lake sediments has received limited attention. This is perhaps due to the complexity of the nitrogen cycle and lack of modern process studies that have traced nitrogen isotope transformations in the catchment and water column to organic matter deposition in lacustrine environments. Few lake sediment data sets exist, yet it appears that $\delta^{15}N_{org}$ can exhibit a wide range of values depending on the nitrogen sources, nitrogen cycling, and nitrogen metabolism of the dominant taxa (see Table 4-4).

Table 4-4. $\delta^{15}N$ in organic lake sediments.

Location	$\delta^{15}N_{org}$ (‰ AIR) Range	Reference
Lake Superior	+5	Pang & Nriagu 1977
Green River Formation	+10.8 to +20.7	Collister & Hayes 1991
Lake Bosumtwi	+1.2 to +18.0	Talbot & Johannessen 1992
Lake 18, NWT	+2.3 to +4.7	Ramlaal *et al.* 1994
Devil's Lake	+8.5 to +28.0	Lent *et al.* 1995
Florida lakes	-2 to +8	Gu *et al.* 1996

Dissolved inorganic nitrogen (DIN - principally nitrate and ammonium) and atmospheric nitrogen are the primary reservoirs utilized by phytoplankton (Talbot &

Johannessen 1992). Nitrate and ammonium mainly originate in aerobic and anaerobic environments, respectively, through the recycling of organically-fixed N. Strong kinetic isotope effects can occur during nitrate and ammonium assimilation although where combined nitrogen is limiting, isotopic fractionation may not be significant (Fogel & Cifuentes 1993). $\delta^{15}N_{org}$ values produced by nitrate assimilation can be variable while large equilibrium fractionation effects can occur as a result of ammonia volatization, leaving a DIN pool enriched in ^{15}N; assimilation of this N results in high $\delta^{15}N_{org}$ values (Collister & Hayes 1991). In contrast, negligible fractionation occurs during fixation of atmospheric N (Heaton 1986). $\delta^{15}N_{org}$ values generated in this manner (e.g. by cyanobacteria in N-limited eutrophic lakes) are typically near 0 ‰.

Although our understanding of modern nitrogen isotope systematics may be limited, studies do suggest that paleo-nutrient cycling information may be stored in this archive. For example, Talbot & Johannessen (1992) found that high $\delta^{15}N_{org}$ values (≈ +15 to +20 ‰) in Lake Bosumtwi sediments were likely related to enhanced ammonia loss by volatization whereas low $\delta^{15}N_{org}$ values (≈ 0 to +5 ‰) reflected a major change from a DIN-utilizing algal community to a system dominated by nitrogen-fixers. Interpretation of past nitrogen cycling within the water column were directly related to changes in lake water circulation and prevailing climatic conditions. Very high $\delta^{15}N_{org}$ values in sediments (≈ +8 to +28 ‰) from Devil's Lake, North Dakota were considered to be a result of sufficiently available and non-limiting quantities of DIN (Lent *et al.* 1995). Low lake level and decreased primary productivity appeared to be associated with the more extreme positive values within this range. In their study of the Tertiary Green River Formation in the western United States, Collister & Hayes (1991) proposed complex nitrogen cycle models to explain high $\delta^{15}N_{org}$ values. Stratigraphic intervals with values of ≈ +10 ‰ were attributed to a mixture of assimilated isotopically-heavy ammonium and fixated light atmospheric N_2. These occurred during dry periods which led to decreased nutrient supply from the catchment. Conversely, zones with higher $\delta^{15}N_{org}$ values (≈ +20 ‰) were thought to reflect uptake of ^{15}N-enriched ammonium and nitrate. DIN was readily available during these wet periods and thus N_2-fixation was not an important process.

At Lake Middendorf, the $\delta^{15}N_{org}$ profile appears to record a change in the nitrogen cycling regime gradually occurring over several hundred ^{14}C years during the transition from forest to tundra vegetation (Figure 4-12). Several possible factors and processes may be responsible for this trend towards more ^{15}N-depleted values. On the basis of the studies mentioned above that have outlined major controls on the $\delta^{15}N$ in bulk organic matter, we suggest that the most likely candidates include 1) a decrease in allochthonous organic matter influx, 2) a decline in lake productivity, 3) a change in algal community structure resulting in an increase in N_2-fixation relative to nitrate assimilation, and 4) a decrease in the $\delta^{15}N$ of the nitrogen source.

As discussed above, the C/N ratio data suggest that some of the <500 μm organic matter fraction in the forest sediments may be terrestrial in origin. $\delta^{15}N$ values in peat from the northern boreal forest of the Lena River to the east vary between +1 and +6 ‰ (Aravena unpublished data), similar to the narrow span of $\delta^{15}N$ values measured in this part of the Lake Middendorf sediment core. We note, however, that the trend to lower C/N values occurs more rapidly than the decline in $\delta^{15}N$ values suggesting that an additional explanation is also likely.

In a survey of surface-sediment from several Florida lakes, Gu *et al.* (1996) found that the $\delta^{15}N$ of phytoplankton increased from oligotrophic to eutrophic lakes, (although complications did arise in hypereutrophic lakes because of increasing importance of N_2-fixers). This relationship is consistent with the $\delta^{15}N$ trend at our study site, although the gradual trend to more ^{15}N-depleted values contrasts with the rapid change to oligotrophic conditions suggested by the carbon and nitrogen elemental data (Figure 4-12) and fossil diatom and chrysophyte evidence (Velichko *et al.* in prep.) as the landscape altered to tundra conditions.

Although a change in algal community structure resulting in an increase in N_2-fixation relative to nitrate assimilation could theoretically account for the $\delta^{15}N_{org}$ trend, this explanation is perhaps least likely, given that this would demand sufficient supply of other nutrients, particularly phosphorus, yet diatom and chrysophyte evidence indicates that the lake was oligotrophic during the tundra period (Velichko *et al.* in prep.).

Finally, a decrease in the $\delta^{15}N$ of the nitrogen source may provide the most favourable explanation. In soils, bulk organic matter $\delta^{15}N$ values generally increase with organic matter age, depth, and extent of decomposition (Nadelhoffer & Fry 1988). Nitrate leached from soil generally has a $\delta^{15}N$ value reflecting these factors so with increased decomposition, nitrate also becomes increasingly enriched in ^{15}N (Nadelhoffer & Fry 1994). We propose that high rates of soil organic matter decomposition during the forest period generated ^{15}N-enriched nitrate that was leached and utilized by phytoplankton in Lake Middendorf. This hypothesis is directly compatible with the interpretation of ^{13}C-depleted values observed in the bulk organic and cellulose records (Figure 4-12) as well as moist conditions inferred from the oxygen isotope data (Figure 4-11). The decline in $\delta^{15}N_{org}$ may then reflect decreased soil organic matter decomposition (and leaching of nitrate) and a relative increase in the importance of atmospheric-derived nitrate as a source of nitrogen, which generally has a more ^{15}N-depleted composition compared to soil-derived nitrate (Létolle 1980; Nadelhoffer & Fry 1994). If this hypothesis is correct, then the gradual decline in $\delta^{15}N_{org}$ values suggests that rates of soil organic matter decomposition may be relatively slow to respond to climate cooling compared to changes in lake productivity, water balance, and terrestrial vegetation.

Summary and Concluding Comments

Knowledge of trophic state and water balance changes associated with treeline retreat and climate cooling at Lake Middendorf (Velichko *et al.* in prep.) provided a strong foundation to examine the response of nutrient cycling dynamics using carbon and nitrogen isotopes in lacustrine organic matter. Similar to our previous investigations near treeline in northern Canada (MacDonald *et al.* 1993; Wolfe *et al.* 1996), we found that the lake water carbon balance was strongly regulated by catchment hydrology in addition to terrestrial soil and vegetation development (Figure 4-13). In this study, similar factors also appear to have played a significant role in determining the lake water nitrogen balance history (Figure 4-13).

During the forest interval (>4400 - 4000 BP), elevated carbon and nitrogen

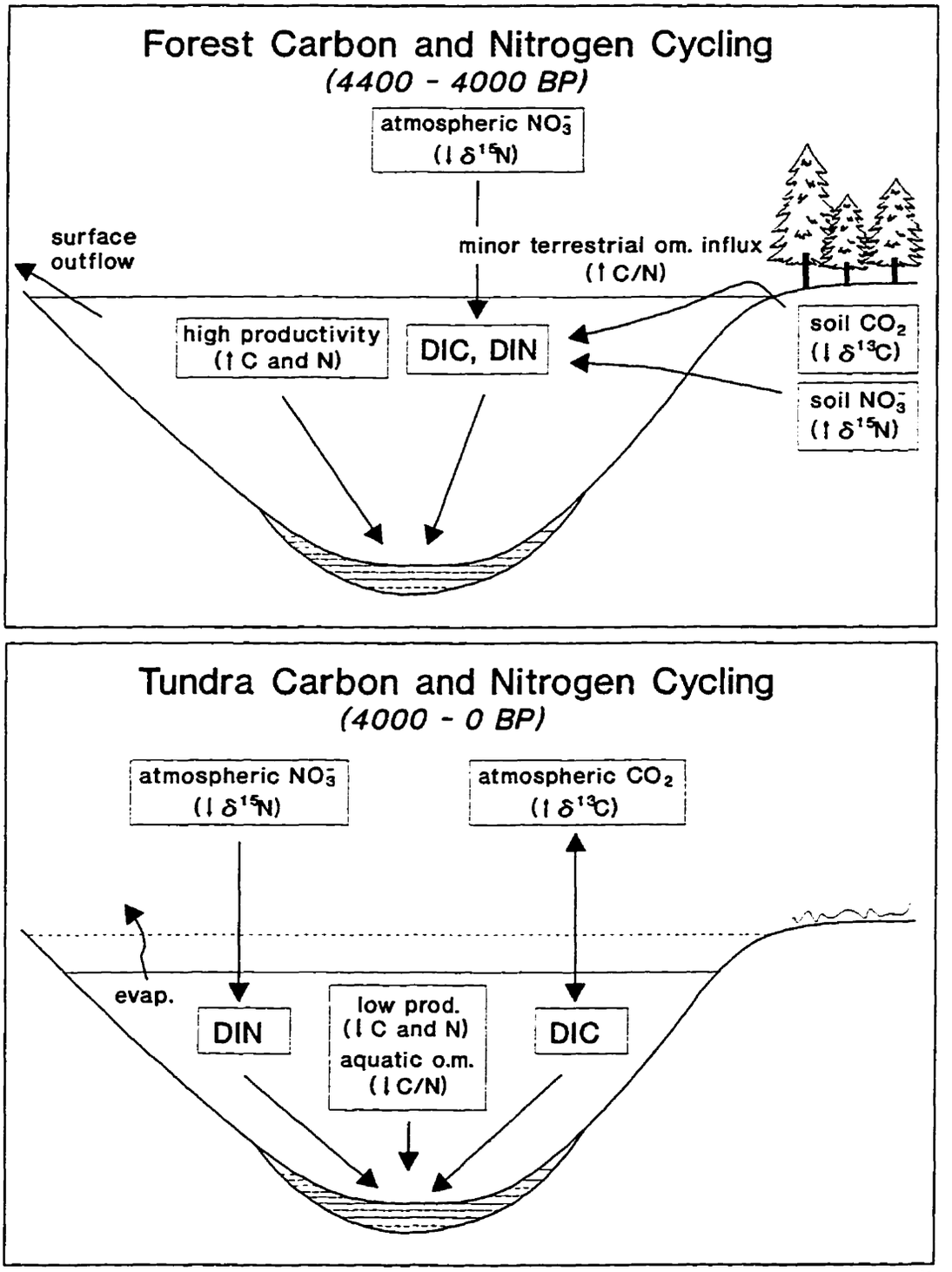


Figure 4-13. Summary cartoons of forest and tundra carbon and nitrogen cycling and probable sources of elemental and isotope trends observed in the lake sediment profiles. Note that between 1600 and 400 BP, wetter conditions resulted in lake outflow and possibly minor influx of soil-derived ^{13}C-depleted $CO_{2(aq)}$.

concentrations corroborate fossil diatom and chrysophyte evidence and are indicative of a relatively productive lake. The bulk organic and cellulose profiles do not display strong enrichment in ^{13}C, typical of so many other studies however, probably because influx of ^{13}C-depleted soil $CO_{2(aq)}$ and rapid hydrologic flushing of the lake counteracted the carbon isotope effects of primary productivity on lake water DIC. ^{13}C-enrichment in the bulk organic matter and cellulose profiles during the transition from forest to tundra is likely a reflection of atmospheric CO_2 becoming the primary source of carbon to the lake as lake water residence time increased and soil organic matter decomposition rates declined. Influx of ^{13}C-depleted soil $CO_{2(aq)}$ likely played a minor role in modifying the $\delta^{13}C$ of the DIC during the more recent wet interval (1600 - 400 BP).

Relatively ^{15}N-enriched values during the forest interval may also be related to soil development processes and prevailing hydrologic conditions. Enhanced soil organic matter decomposition rates and production and leaching of ^{15}N-enriched nitrate may have provided an important source of nitrogen to phytoplankton in Lake Middendorf. Other contributing factors may include allochthonous input of terrestrial organic matter and high rates of aquatic productivity. However, the gradual decline in $\delta^{15}N$ values across the forest-tundra transition, which is in contrast to more rapid changes in the C/N ratio and proxy data (diatom, chrysophyte cysts) for lake productivity seems to suggest that these latter two mechanisms may be less important. Lower $\delta^{15}N_{org}$ values in the tundra zone may primarily reflect decreased soil organic matter decomposition as conditions became colder and a corresponding, relative increase in the importance of ^{15}N-depleted atmospheric nitrate as a source of nitrogen to the lake.

These results suggest that the dynamics of treeline carbon and nitrogen cycles have been quite sensitive to climate change and that the fate of these nutrients appear to have been intricately linked to changes in the hydrologic regime. Quantitative assessment of the fate of nitrogen during past periods of climate change is currently beyond our capabilities due to the lack of modern process-oriented studies. Nevertheless, exploratory investigations using $\delta^{15}N$ in bulk organic matter

indicate that this may be a useful proxy for identifying past changes in nitrogen cycling in this ecotone, particularly when coupled with other isotopic and biological proxy data. We further suggest that incorporation of fossil pigment analysis, to assess past algal community structure and nitrogen-source uptake preferences (e.g. Leavitt & Findlay 1994), may be an especially valuable additional technique to consider in future studies.

PART C:

Contribution to MacDonald GM, AA Velichko, LC Cwynar, M Pisaric, D Porinchu, TE Laing, BB Wolfe, AA Andreev, OK Borisova, TWD Edwards & JP Smol, in prep. A continuous record of Late Quaternary climatic and environmental change from Arctic Siberia. For submission to *Science*.

Synopsis

Radiocarbon dating of terrestrial macrofossils found on the Lena River delta indicated that treeline extended north of its present limits between 8000 and 4000 BP, temporally consistent with results from the Taimyr Peninsula to the west. Successful recovery of a 386 cm core from lake LS9 on the Lena River delta, a hydrologically-open lake ^{14}C-dated at 12,310 years BP at 300 cm core depth, provided the opportunity to investigate environmental changes associated with Holocene treeline fluctuations as well as the Younger Dryas in this region.

Palynological studies on the lake sediment core also revealed significant changes in terrestrial vegetation (Pisaric 1996; Pisaric *et al.* 1997). The early part of the record indicates that the region supported a shrub birch, herb, grass and sedge tundra that became increasingly productive and dominated by birch to roughly 11,500 BP. A sharp reversion to sparser vegetation cover dominated by herbs, grasses and sedges at this time provides the first clear evidence of the classical Younger Dryas in eastern Siberia. Between 8500 and 3500 BP, the sediments record increases in Picea and Larix pollen, similar to the macrofossil radiocarbon data. After 3500 BP, the modern vegetation consisting of herb and shrub tundra became established.

The most significant result from oxygen isotope analysis of cellulose in the LS9 lake sediment core is substantial increase (≈ 7 ‰) during the early phase of northward treeline migration (9000 to 6500 BP). These data are considered to reflect dry conditions (and subsequent evaporative isotopic enrichment of lake water) that accompanied warming in this region, in contrast to earlier studies on the western Taimyr Peninsula and in central Canada. This preliminary interpretation is supported by radiocarbon dating of bottom sediments from a nearby small, hydrologically-closed lake which indicate that lacustrine deposition did not begin until ≈ 6800 BP (Aravena

unpublished data), perhaps because the climate was too dry.

Carbon isotope analysis revealed considerably less striking changes although a rapid 4 ‰ decrease at 10,600 BP may be associated with cooler conditions during the Younder Dryas and modest ^{13}C-enrichment in the bulk organic matter during the warm, early Holocene may reflect an increase in lake productivity.

We are currently in the process of compiling and interpreting data from multidisciplinary analyses at this site. A manuscript is in preparation describing these findings; below is an excerpt that describes the isotopic and elemental results.

Methods

Sediment samples for elemental and stable isotope analysis were taken at mostly 5-7 cm intervals from core LS9-3. Samples were pre-treated in a 10 % hydrochloric acid solution at 70 °C for two hours to dissolve trace amounts of shell or mineral carbonate. Bulk carbon/nitrogen weight ratios and bulk organic $^{13}C/^{12}C$ ratios on the <500 μm acid-washed residue were determined on a Carlo Erba elemental analyzer interfaced with a continuous flow Isochrom mass spectrometer at the Environmental Isotope Laboratory (EIL), University of Waterloo. Additional sample preparation on the fine-grained acid-washed residue involving solvent extraction, bleaching, and alkaline hydrolysis removed non-cellulose organic components (Edwards & McAndrews 1989). Breakseal combustion (Boutton 1991) and nickel-tube pyrolysis (Edwards *et al.* 1994) were used to produce CO_2 from the cellulose fraction for $^{13}C/^{12}C$ and $^{18}O/^{16}O$ determination, respectively, on a Prism mass spectrometer at the EIL. Stable isotope results are reported as δ values, representing deviation in per mil (‰) from the international Vienna-SMOW and Vienna-PDB standards such that $\delta = [(R_{sample}/R_{std})-1]*1000$, where R is the $^{13}C/^{12}C$ or $^{18}O/^{16}O$ ratio in sample and standard. Analytical uncertainties are ± 0.5 ‰ for $\delta^{13}C$ and ± 1.0 ‰ for $\delta^{18}O$ reflecting both method uncertainty and the natural heterogeneity of the samples.

Interpretation

Wide variation in carbon/nitrogen (C/N) weight ratios (10-20) and correlation with bulk organic $\delta^{13}C$ ($\delta^{13}C_{org}$), cellulose $\delta^{13}C$ ($\delta^{13}C_{cell}$), and cellulose $\delta^{18}O$ ($\delta^{18}O_{cell}$) prior to 12,000 ^{14}C years BP (below 300 cm depth; Figure 4-14) suggests fluctuating deposition of terrestrial and aquatic organic matter. Between 12,000 and 1500 BP (300 to 50 cm depth), low C/N ratios (10-15) indicate that the lacustrine organic matter is primarily of autochthonous origin.

After 12,000 BP, $\delta^{18}O_{cell}$ appears to provide a good proxy for lake water $\delta^{18}O$ (Figure 4-14; see Edwards & McAndrews 1989; Edwards 1993; Wolfe *et al.* 1996). Fluctuations in $\delta^{18}O_{cell}$ during this part of the record are most likely a reflection of changes in lake water balance, based on preliminary evidence from peat porewaters

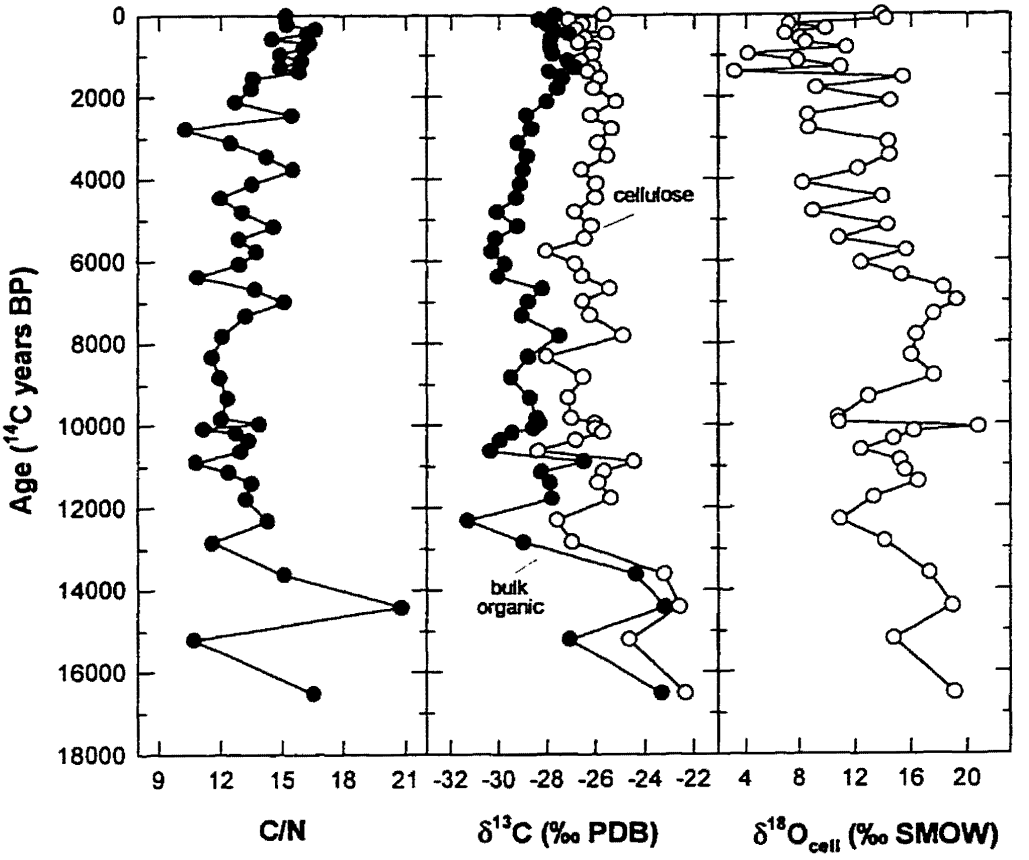


Figure 4-14. C/N and isotope stratigraphy for LS9.

and modern meteoric waters that suggest no significant variation in $\delta^{18}O$ of mean annual precipitation has occurred since, perhaps, the early Holocene (Wolfe *et al.* 1997). ^{18}O-enriched values between 9000 and 6500 BP (also immediately prior to and briefly at the end of the Younger Dryas) are therefore likely due to drier conditions and evaporative isotopic enrichment that accompanied climate warming. Oscillating decline in $\delta^{18}O_{cell}$ between 7000 and 4000 BP may be due to an overall increase in inflow relative to evaporation caused by a wetter and cooler climate. High-frequency and large fluctuations in $\delta^{18}O_{cell}$ during the past 1500 ^{14}C years are strikingly similar to $\delta^{18}O_{cell}$ records near treeline on the western Taimyr Peninsula, northern Russia (Wolfe *et al.* 1997), suggesting that highly variable hydrologic conditions have recently characterized a broad region of the Siberian tundra.

The most significant change in the $\delta^{13}C_{org}$ and $\delta^{13}C_{cell}$ records following 12,000 BP is an abrupt 4 ‰ negative shift at about 10,600 BP (Figure 4-14), perhaps reflecting a decline in productivity-driven ^{13}C enrichment of dissolved inorganic carbon (DIC), less demand on dissolved CO_2 leading to increased fractionation between DIC and phytoplankton, or a change in plant community in response to cooler conditions. Slight ^{13}C-enrichment in bulk organic matter (about 2 ‰) during the early Holocene warm interval (10,000 to 7000 BP) relative to the mid-Holocene (7000 to 4000 BP) may conversely be caused by increased lake productivity or carbon cycle isotope effects related to hydrologic closure (inferred from the $\delta^{18}O_{cell}$ data) such as increased residence time of DIC or increased atmospheric CO_2 exchange. The small difference in $\delta^{13}C_{org}$ values recorded during the early and mid-Holocene, however, is not observed in the $\delta^{13}C_{cell}$ profile. Since 1500 BP, positive shifts in C/N and $\delta^{13}C_{org}$ values likely represent increased flux of terrestrial bulk organic matter input to the lake arising from fluctuations in hydrologic conditions and erosion of organic deposits along the shore of the lake.

CHAPTER 5: REGIONAL SYNTHESES

PART A:

Edwards TWD, BB Wolfe & GM MacDonald, 1996. Influence of changing atmospheric circulation on precipitation $\delta^{18}O$-temperature relations in Canada during the Holocene. *Quaternary Research* 46: 211-218.

Synopsis

Oxygen isotope analysis of sediment cellulose ($\delta^{18}O_{cell}$) from Queen's Lake and Toronto Lake indicated that rapid shifts to increasingly negative values were associated with intervals of northward treeline advance in central Canada during the mid-Holocene (MacDonald *et al.* 1993; Wolfe *et al.* 1996; see CHAPTER 3). These isotopic trends were interpreted to reflect increases in the inflow:evaporation ratio due to more humid conditions that accompanied climate warming. Comparison of the Queen's Lake and Toronto Lake oxygen isotope records, however, also revealed another similarity: a smoothed curve fitted to both profiles displayed a common millennial-scale negative shift of several per mil over the past 8000 ^{14}C-years. Was this trend representative of the more long-term water balance, as originally proposed by MacDonald *et al.* (1993), or was it a proxy for the regional isotopic composition of precipitation which may also contain useful paleotemperature or paleohydrologic information (see CHAPTER 1)?

To distinguish between these two possible interpretations, we analyzed the $\delta^{18}O_{cell}$ in archived sediment from a third site, "Whatever Lake" (unofficial name; see Figure 1-1), located 125 km north of treeline and 200 km south of Baker Lake, Northwest Territories. Whatever Lake was ideally suited to assist deconvolution of water balance and source water isotopic signals in the previously studied lakes for several reasons. Most importantly, isotope analysis of modern meteoric and lake water from the catchment suggested that Whatever Lake is isotopically insensitive to changes in hydrology, in contrast to Queen's Lake and Toronto Lake, because of the large volume-to-surface area ratio (Bursey *et al.* 1991; Figure 5-1). Since no major environmental or hydrological changes had occurred following the termination of

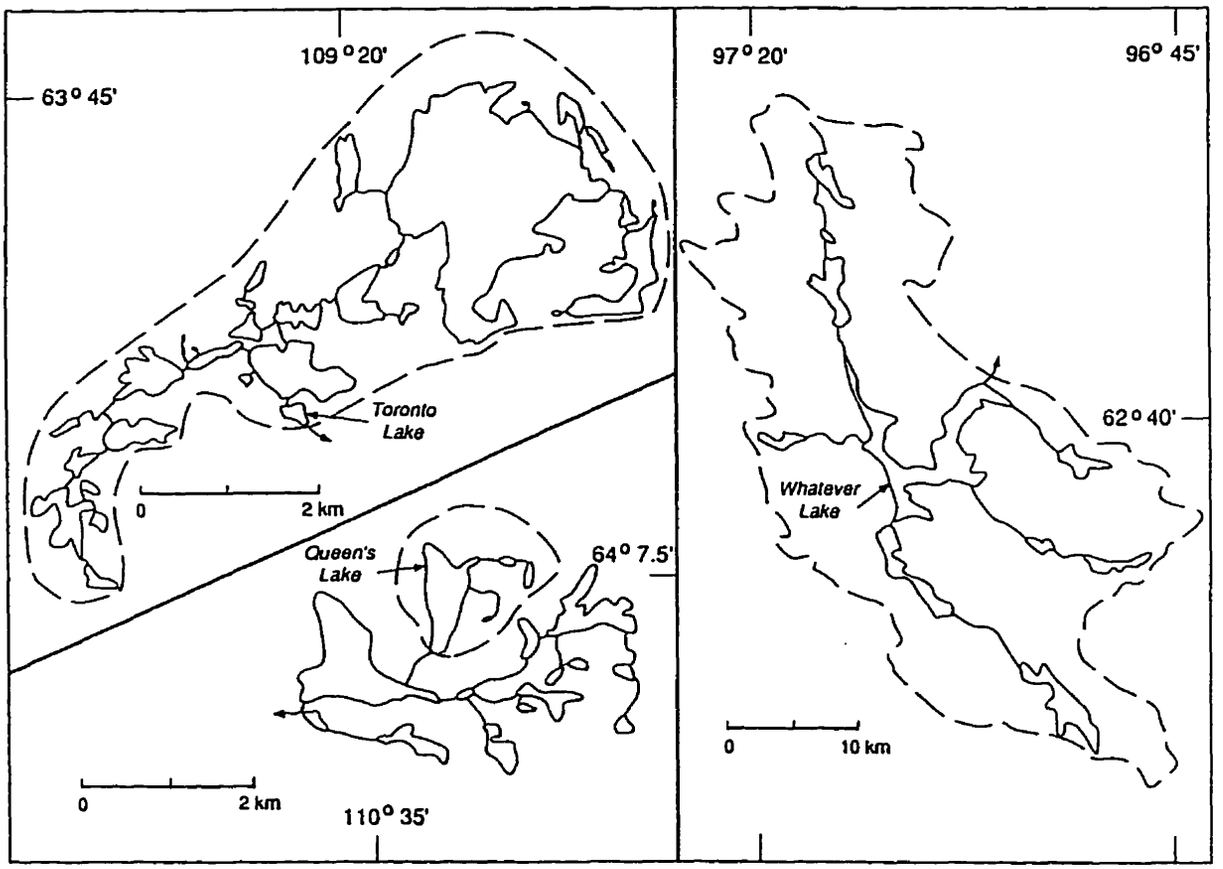


Figure 5-1. Drainage basin maps for Queen's Lake, Toronto Lake and Whatever Lake. Maximum depth (3.5, 6.8 and 32 m, respectively), size (50, 10, 3400 ha), and catchment area (200, 2900, 85000 ha) vary considerably as does the position of the lakes within their respective drainage basins. Note different scale for Whatever Lake map.

marine influence at about 6500 BP (see $\delta^{13}C$ data in APPENDIX 2; also Edwards 1980), we anticipated that the $\delta^{18}O_{cell}$ in Whatever Lake sediments should contain a long-term record that largely reflects the oxygen isotope composition of precipitation ($\delta^{18}O_P$). In addition, combining stable isotope data from Whatever Lake with the records from Queen's Lake and Toronto Lake, which are located several hundred kilometres to the west, created the opportunity to generate a truly regional perspective on isotope paleohydrology at the central Canadian treeline.

Results from the $\delta^{18}O_{cell}$ analysis of Whatever Lake sediments did, in fact, show a similar long-term trend as Queen's Lake and Toronto Lake which provided support for a regionally consistent but changing record of $\delta^{18}O_P$. Reconstruction of $\delta^{18}O_P$ is utilized to estimate changes in summer relative humidity by using an isotope-mass balance approach. The model, where

$$I/E = h/(1-h) \times (\delta^{*}-\delta_{lw})/(\delta_{lw}-\delta_P) \qquad \text{(Gat \& Levy 1978)}$$

and I = inflow,

E = vapour outflow,

h = relative humidity,

δ^{*} = limiting isotopic enrichment,

δ_{lw} = lake water isotopic composition,

δ_P = precipitation isotopic composition,

assumes long-term hydrologic steady state (i.e. $I/E = 1$; for theoretical development, see Gibson *et al.* 1993). Residual changes in the Queen's Lake $\delta^{18}O_{lw}$ record, independent of changes in $\delta^{18}O_P$, is primarily used for model δ_{lw} input because Queen's Lake is considered to have behaved essentially as a closed basin and its record is not complicated by changes in the contributing drainage basin area (i.e. Toronto Lake, see CHAPTER 3). These calculations suggest that the central Canadian treeline may have experienced a 10-15 % rise in summer relative humidity during the warm mid-Holocene.

Perhaps the most significant outcome of the $\delta^{18}O_P$ reconstruction, however, is that the early part of the record (8000 to 5500 BP) departs from the expected relationship with mean annual temperature, the climatic parameter traditionally cited as controlling temporal records of $\delta^{18}O_P$ (e.g. ice cores). In this manuscript, we propose that ^{18}O-enriched precipitation in central Canada during the early Holocene may have primarily resulted from a small increase in long-distance moisture transport efficiency (leading to a decrease in rain-out effects), which is consistent with the high zonal index that is thought to have existed at this time. A higher summer:winter precipitation ratio could also have been a factor as low snow accumulation may have, in part, delayed northward treeline advance.

Note that we have also presented data from southern Ontario in this manuscript in an effort to compile our current state of knowledge of Late Glacial/Holocene $\delta^{18}O_P$ history for mainland Canada. This represents the first, preliminary step towards the long-term goal of preparing paleo-$\delta^{18}O_P$ maps for North America. These maps will help to gain a greater understanding of past climate dynamics and provide quantitative data for testing general circulation models that incorporate isotopic tracers.

(Note that in this multi-authored manuscript, I collaborated in equal partnership with Edwards on the scientific development and literary presentation).

Abstract

Postglacial precipitation $\delta^{18}O$ history has been reconstructed for two regions of Canada. Long-term shifts in the oxygen-isotope composition of annual precipitation ($\delta^{18}O_P$) in southern Ontario appear to have occurred with a consistent isotope-temperature relation throughout the past 11,500 ^{14}C years. The modern isotope-temperature relation in central Canada near present boreal treeline evidently became established between 5000 and 4000 years ago, although the relation during the last glacial maximum and deglaciation may also have been similar to present. In the early Holocene, however, unusually high $\delta^{18}O_P$ apparently persisted, in spite of low temperatures locally, probably associated with high zonal index. A rudimentary sensitivity analysis suggests that a small reduction in distillation of moisture in Pacific air masses traversing the western Cordillera, perhaps accompanied by higher summer:winter precipitation ratio, could have been responsible for the observed effect. Equivalent isotope-temperature "anomalies" apparently occurred elsewhere in western North America in response to changing early-Holocene atmospheric circulation patterns, suggesting that a time-slice map of $\delta^{18}O_P$ for North America during this period might provide a useful target for testing and validation of atmospheric general circulation model simulations using isotopic water tracers.

Introduction

The isotopic composition of past precipitation is commonly considered a proxy for paleotemperature at mid- to high latitudes, because of systematic linear relations observed between mean annual air temperature (MAT) and weighted mean oxygen- or hydrogen-isotope composition of annual precipitation ($\delta^{18}O_P$ or $\delta^{2}H_P$)[1] (Dansgaard 1964; Rozanski *et al.* 1992, 1993). Applicability of $\delta^{18}O_P$ or $\delta^{2}H_P$ as a paleotemperature proxy is well-supported by various evidence, including direct archives of past precipitation such as ice cores (e.g. Jouzel *et al.* 1993; Grootes *et al.*

[1] $\delta^{18}O$ and $\delta^{2}H$ values represent deviations in per mil (‰) from the V-SMOW standard, such that $\delta = ((R_{sample}/R_{VSMOW})-1)1000$, where R is the $^{18}O/^{16}O$ or $^{2}H/^{1}H$ ratio.

1993) and old groundwaters (e.g. Rozanski 1985), simulations based on atmospheric general circulation model (AGCM) experiments (e.g. Jouzel *et al.* 1994), and data from various indirect archives such as lake sediments, cave deposits, and tree rings. On the other hand, changing moisture sources and recycling, conditions at the site of evaporation, air mass history, seasonality and amount of precipitation, and other factors can also influence the isotopic composition of local precipitation (e.g. Dansgaard 1964; Lawrence & White 1991; Plummer 1993; Charles *et al.* 1994). These factors can perhaps confound attempts to reconstruct paleotemperature, but can potentially yield other climatically relevant information.

Reconstructions of weighted mean $\delta^{18}O$ of annual precipitation ($\delta^{18}O_P$) for two regions in Canada spanning the postglacial provide contrasting views of the isotopic signals of changing climate. As we discuss below, the $\delta^{18}O_P$ record for southern Ontario seems to be a good indicator of MAT throughout the past 11,500 ^{14}C yr, suggesting a consistent linear isotope-temperature relation. In contrast, a shorter $\delta^{18}O_P$ chronology (*ca.* 8000 yr) from central Canada offers evidence that a single isotope-temperature relation did not persist, apparently as a consequence of changing atmospheric circulation. Although these results emphasize the uncertainties involved in teasing paleoclimate information out of isotopic archives, they also highlight the value of primary isotopic signals independent of their usefulness as proxies for parameters such as paleotemperature.

Modern Climate of Southern Ontario and Central Canada

The modern climatic settings of the study areas can be readily characterized in terms of seasonally shifting air mass influence (Bryson 1966; Bryson & Hare 1974). The cool temperate climate of southern Ontario reflects the varying seasonal influence of three distinct air masses: (1) cold, very dry Arctic air arising in northern Canada, (2) warm, moist Maritime-Tropical air from the south, which originates in the sub-tropic North Atlantic and Gulf of Mexico and traverses northward up the Mississippi and Missouri valleys before being deflected eastward across the Great Lakes basin, and (3) seasonally warm, relatively dry air from the west, which originates over the North

Pacific, but subsequently loses much of its moisture during passage across the western Cordillera. Summers in southern Ontario are typically warm and humid, reflecting the dominance of Maritime-Tropical air, punctuated by short incursions of dry Pacific air. Southward shifting of frontal zones in winter leads to cold and relatively dry conditions due to strong Arctic air influence. Precipitation, which is mainly derived from Maritime-Tropical air masses, is well-distributed throughout the year.

The arid subarctic to low-arctic climate of central Canada is strongly influenced by Arctic air masses in all seasons. Summer conditions are moderated by Pacific air that also brings most of the limited moisture to the region, but winters are long and severe owing to persistent Arctic air dominance.

Precipitation $\delta^{18}O$ History

Southern Ontario

Precipitation $\delta^{18}O$ history in southern Ontario is based on isotopic studies of terrestrial plant matter, and organic and inorganic lake sediments. The initial $\delta^{18}O_P$ chronology was developed from oxygen and hydrogen isotopes in fossil wood cellulose, using a semi-empirical model to separate humidity-dependent isotopic enrichment of leaf water during evapotranspiration from the primary isotopic signature of water taken up by the trees (Edwards & Fritz 1986). Calibration of the model using modern trees permitted quantitative reconstruction of both the isotopic composition of local precipitation ($\delta^{18}O_P$) and growth season relative humidity (RH). These preliminary paleo-isotope and paleo-humidity records were supported and supplemented by independent evidence from the oxygen isotope stratigraphy of aquatic cellulose and carbonate in sediment cores from several lakes in the region, using analogous reasoning to separate lake-specific isotopic responses to changing RH from the common signal imposed by the changing isotopic composition of catchment source waters, controlled by $\delta^{18}O_P$ (Edwards 1987; Edwards & Fritz 1988; Edwards & McAndrews 1989). The basis for this approach was addressed in detail by Edwards & McAndrews (1989) and revisited by Edwards (1993). New oxygen

isotope data from aquatic cellulose in sediments underlying Hamilton Harbour, a bay at the western end of Lake Ontario, have recently verified and further supplemented the later part of the $\delta^{18}O_P$ record, from about 8000 yr B.P. to present (Duthie *et al.* 1996). The resulting composite $\delta^{18}O_P$ and RH records derived from these studies are shown in Figure 5-2.

The $\delta^{18}O_P$ history of southern Ontario is characterized by low values during late-glacial and early-Holocene times, rising to a maximum by about 5000 yr B.P., before declining to values approaching those of the past few decades sometime after 4000 yr B.P. Summer RH was evidently closely coupled to changing $\delta^{18}O_P$, also rising from a late-glacial minimum to a maximum in the mid-Holocene, though with a lag centred on about 7000 yr B.P. as $\delta^{18}O_P$ converged on and subsequently exceeded the modern value.

Edwards & Fritz (1986) noted that the systematic shifts in past $\delta^{18}O_P$ (if interpreted as annual temperature) and summer RH are strongly consistent with changing air mass influence in eastern North America inferred from other evidence (e.g. Bryson & Wendland 1967; Bartlein *et al.* 1984; Dean *et al.* 1996). Thus the long-term coupling between temperature and humidity is in good agreement with progressive postglacial warming and moistening to a mid-Holocene "climatic optimum", as the influence of Arctic air diminished and Atlantic air increased, followed by slight climatic deterioration as the modern intermediate balance became established. Superimposed on this meridional fluctuation in atmospheric circulation is a shorter-term episode of enhanced zonal index in the early Holocene, that accounts for a lag between rising temperature and humidity between about 7500 and 6000 yr B.P., caused by increased incursion of warm, dry Pacific air into the region during the summer months. This general sequence of events is readily visualized through the division of the postglacial climate history of southern Ontario into four climatic intervals, based on qualitative differences between past and present annual temperature and summer humidity (Edwards & Fritz 1986): (1) a postglacial period of colder and drier conditions culminating around 7400 yr B.P., (2) a warmer and drier "early hypsithermal", ending about 6000 yr B.P., (3) a warmer and moister "main

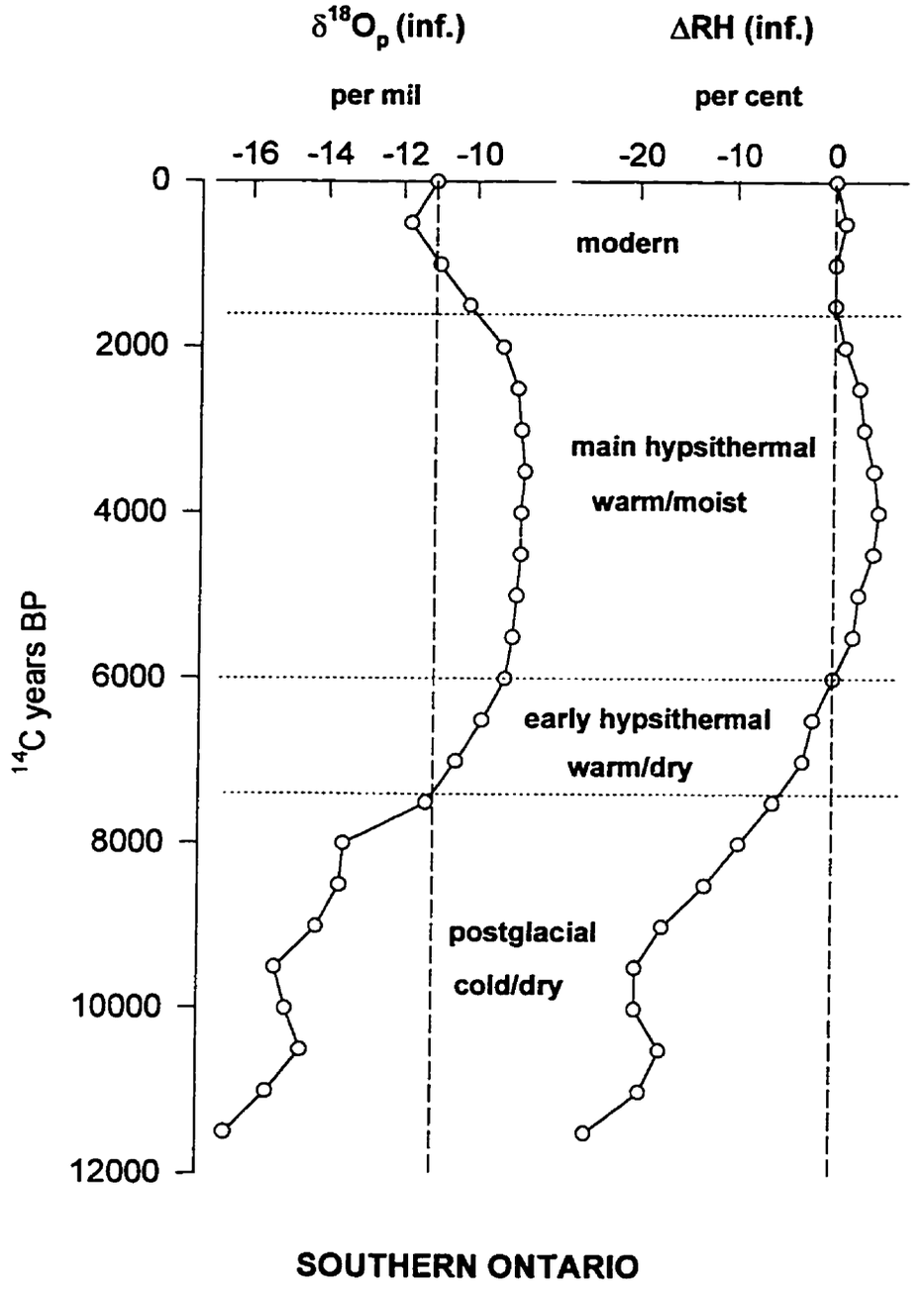


Figure 5-2. Reconstructed $\delta^{18}O_P$ and ΔRH for southern Ontario, expressed as 500-year averages, based on oxygen and hydrogen isotopes in cellulose and inorganic carbonate from lake sediments and fossil wood cellulose (see Edwards 1987; Edwards & Fritz 1986, 1988; Edwards & McAndrews 1989; Duthie *et al.* 1996). ΔRH is scaled to represent difference from present average summer relative humidity. Estimated uncertainties in the reconstructed values are on the order of ± 1 ‰ and ± 5 %.

hypsithermal", leading to (4) the cool, temperate climate of today sometime within the last two millennia.

As observed by Edwards & Fritz (1986), the $\delta^{18}O_P$ history can be translated quantitatively into a plausible MAT record by assuming a constant linear $\delta^{18}O_P$-MAT relation having a slope of about 0.65‰/°C, approximating the modern spatial isotope-temperature relation in the Great Lakes region. This yields a paleotemperature curve that is remarkably consistent with the regional time-series reconstruction for southeastern Canada reported by Kutzbach (1987, Figure 13), based on atmospheric general circulation model simulations. Notably, strong qualitative agreement is also evident between inferred RH and modelled precipitation from the same simulations, providing support for both the successful deconvolution of the raw isotopic records and the general validity of the $\delta^{18}O_P$ record as a proxy for paleotemperature. The $\delta^{18}O_P$ curve is also broadly comparable to previous quantitative reconstructions based on pollen data (McAndrews 1981; Bartlein *et al.* 1984) and the limited information available from fossil insects and relict permafrost for the earlier part of the record (Edwards *et al.* 1985). General agreement is evident with mapped representations of inferred changes in temperature and precipitation from the COHMAP project, based on pollen response surfaces (Webb *et al.* 1993), although direct comparison is hampered by the coarse COHMAP spatial resolution. Lake-level information for southern Ontario in the COHMAP data base is too limited to support an adequate comparison with inferred effective moisture.

Central Canada

Postglacial $\delta^{18}O_P$ and summer RH chronologies for an area in central Canada have been developed from the oxygen-isotope stratigraphies of cellulose in lake sediments (Figure 5-3), as part of multiple-proxy investigations of circumpolar treeline fluctuations (MacDonald *et al.* 1993; Wolfe *et al.* 1996). Environmental change in this region following local deglaciation around 9000 yr B.P. (Dyke & Prest 1987) was characterized by the advance and subsequent retreat of boreal treeline, accompanied by profound limnologic and hydrologic changes, in response to shifts in the mean

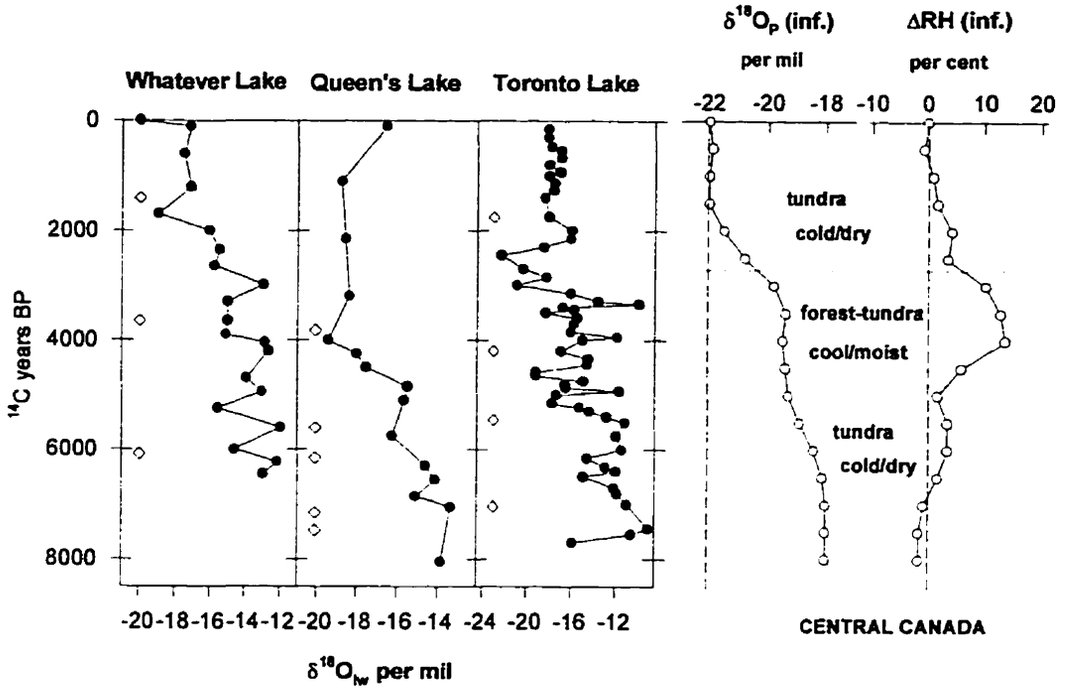


Figure 5-3. Reconstruction of $\delta^{18}O_P$ and ΔRH for central Canada, expressed as 500-year averages, based on oxygen isotopes in lacustrine cellulose from three lakes. Chronologic control for each lake record is provided by ^{14}C-dated samples represented by diamonds (see Table 5-1). $\delta^{18}O_P$ and RH were derived by deconvolution of the inferred lake water $\delta^{18}O$ histories ($\delta^{18}O_{lw}$) for informally-named Queen's Lake (64°07'N; 110°34'W), Toronto Lake (63°43'N; 109°21'W), and Whatever Lake (64°41'N; 97°03'W) reported previously by MacDonald *et al.* (1993) and Wolfe *et al.* (1995, 1996). The $\delta^{18}O_P$ history is strongly constrained by the low-frequency $\delta^{18}O_{lw}$ trend from Whatever Lake, which is hydrologically insensitive (see Bursey *et al.* 1991) and thus expected to shift in parallel to long-term changes in $\delta^{18}O_P$, while the ΔRH history is mainly constrained by the residual changes in $\delta^{18}O_{lw}$ independent of changes in $\delta^{18}O_P$ in Queen's Lake, which is believed to have behaved essentially as a closed basin. The long-term evaporative-enrichment response of Toronto Lake is consistent with that of Queen's Lake, but is overprinted by "noise" inherited from its hydrologically complex catchment (see Wolfe *et al.* 1996). The tundra and forest-tundra zonation is based on pollen and loss-on-ignition data from Queen's Lake, which lies about 25 km north of the mapped limit of forest-tundra (MacDonald *et al.* 1993). In order to permit comparison with the southern Ontario reconstruction (Figure 5-2), ΔRH has been scaled to approximate deviation from present average summer relative humidity, assuming evaporative enrichment under conditions of long-term hydrologic steady state. Uncertainties in the reconstructed values are somewhat higher than for southern Ontario, on the order of ± 1.2 ‰ and ± 6 %.

Table 5-1. Radiocarbon dates from lake sediment cores.

Depth (cm)	Material	Age (^{14}C yr B.P.)	Laboratory #
Whatever Lake			
20-22	Organic sediment	1410 ± 110	TO-4526
89.0-91.5	Organic sediment	3650 ± 130	TO-4527
172.5-175	Organic sediment	6080 ± 80	TO-4528
Queen's Lake			
15-20	Organic sediment	3820 ± 60	WAT-1770
45-50	Organic sediment	5600 ± 60	WAT-1771
60-65	Organic sediment	6150 ± 60	WAT-1772
100-105	Organic sediment	7150 ± 70	WAT-1773
105	Twig	7470 ± 80	TO-827
Toronto Lake			
35-40	Organic sediment	1760 ± 90	Beta-49705
80-85	Organic sed. & moss	4200 ± 80	Beta-53129
125-130	Organic sed. & moss	5460 ± 90	Beta-53130
155-160	Organic sediment	7040 ± 120	Beta-49708

summer position of the Arctic frontal zone. Terrestrial vegetation abruptly shifted from dwarf shrub tundra to *Picea mariana* forest-tundra around 5000 yr B.P., as the frontal zone moved northward. Minor local fluctuations in treeline position or forest density occurred during the subsequent 2000 years, followed by return to the modern dwarf shrub tundra vegetation after 3000 yr B.P.

$\delta^{18}O_p$ was apparently higher than present when organic lake-sediment accumulation began shortly before 8000 yr B.P., and decreased progressively to about 4500 yr B.P. Values subsequently increased slightly to a localized maximum around 4000 yr B.P. before declining to near modern values by about 1500 yr B.P., followed by a small rise to the modern level, which has persisted for the past 1000 years. Summer RH during this 8000-year period shows a simpler pattern of change, oscillating between low values prior to and following a pronounced maximum during the forest-tundra event. Correspondence between RH and forest expansion even occurred on the scale of centuries, as shown by high-resolution sampling of one core (see Wolfe *et al.* 1996).

The post-5000 yr B.P. part of the $\delta^{18}O_p$ record reveals evidence of a straightforward isotope-climate linkage, with higher values than present corresponding to maximum forest-tundra development between 5000 and 3000 yr B.P., followed by a decline as treeline receded. This is consistent with the expected temperature shift as the strong Pacific air mass influence in summer that triggered the treeline advance was reduced by southward movement of the Arctic frontal zone. However, reconstructed $\delta^{18}O_p$ values of about 4 ‰ higher than present during the earlier tundra period, when temperatures must have been at least as cold as present, are clearly not in harmony with the isotope-temperature relation that became established after 5000 yr B.P.

Discussion

Isotope-Temperature Relations in Precipitation

Calibration of isotope-temperature relations using modern data is inherently limited by the short temporal range of observational records at individual sites. As a

result, calibrations of paleotemperature are commonly based on empirical $\delta^{18}O_P$-MAT or $\delta^{2}H_P$-MAT relations derived using data from several scattered sites within a region. This approach has been applied extensively to interpret isotopic records from various archives.

The $\delta^{18}O_P$-MAT relation used by Edwards & Fritz (1986), based on a survey of limited modern data available from sites in the Great Lakes region, is described by:

$$\delta^{18}O_P = 0.65MAT - 15.5 \quad (1)$$

which has essentially the same slope, but more negative intercept than the "global" empirical $\delta^{18}O_P$-MAT relation for sites having MAT less than 15°C (Jouzel *et al.* 1994) given by:

$$\delta^{18}O_P = 0.64MAT - 12.8 \quad (2)$$

Although the modern spatial and temporal $\delta^{18}O_P$-MAT relations in the study area in central Canada are less well-defined than in eastern Ontario, local $\delta^{18}O_P$ and MAT (*ca.* -22‰ and -10°C) are also in good agreement with (1). The occurrence of more depleted modern $\delta^{18}O_P$ values for a given temperature in both areas compared to the "global" relation probably reflects continental effects due to rain-out from long-distance transport of moisture, perhaps reinforced in the Great Lakes region by recycling of isotopically depleted vapour from the lakes (Gat *et al.* 1994).

As expected, (1) yields highly reasonable MAT values for the past 5000 years from the central Canada $\delta^{18}O_P$ history, suggesting cooling of about 3 °C since the time of maximum treeline advance. However, isotope-inferred MAT values of 6 °C or more above present for the older part of the record are clearly incompatible with pollen and diatom evidence that MAT was no higher than present during this time (Moser & MacDonald 1990; MacDonald *et al.* 1993; MacDonald 1995; Pienitz R & JP Smol, personal communication 1995). This discrepancy is shown schematically on a plot of MAT versus $\delta^{18}O_P$ (Figure 5-4). The entire southern Ontario record and the later part

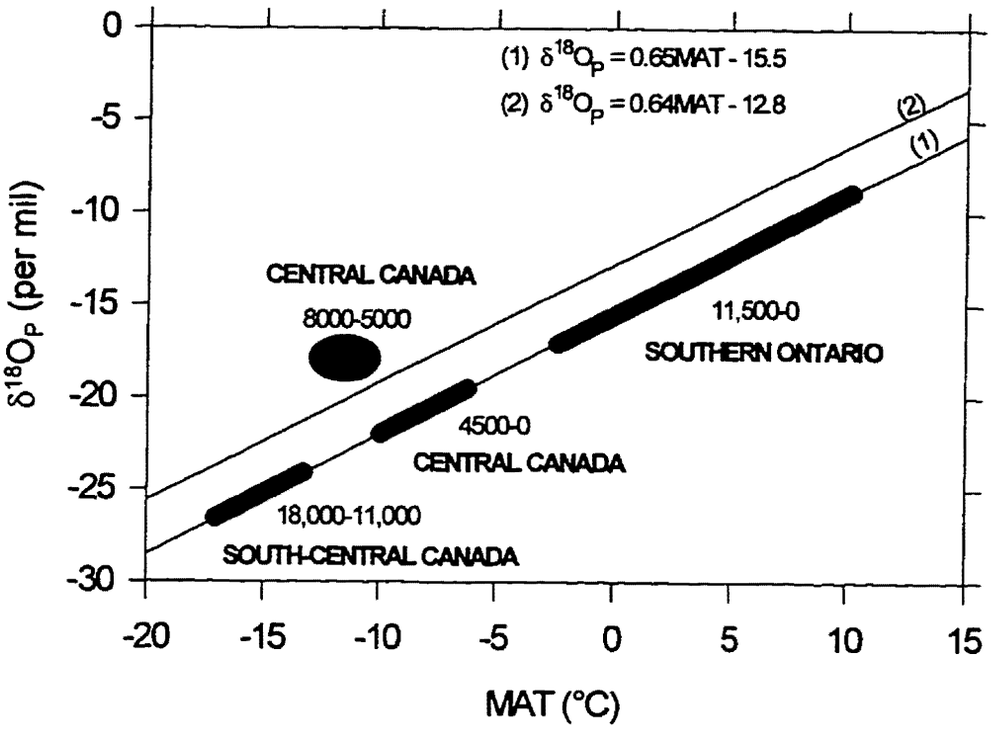


Figure 5-4. Schematic diagram showing apparent $\delta^{18}O_P$-MAT relations for central Canada and southern Ontario. Isotope-temperature relations in both areas seem to lie close to the "continental" line defined by (1), except for the earlier part of the central Canada record, which plots above the "global" line defined by (2) (Jouzel *et al.* 1994). $\delta^{18}O_P$-MAT in the area of the Laurentide Ice Sheet during deglaciation of southwestern and central Canada probably also lay near the continental line.

of the central Canada record apparently lie near the continental line defined by (1), whereas the earlier part of the central Canada record is distinctly offset, plotting above the global line defined by (2). AGCM simulations (Jouzel *et al.* 1994) and the isotopic composition of late-glacial groundwater (Remenda *et al.* 1994) suggest that (1) also approximates isotope-temperature relations in central and south-central Canada during the last glacial maximum and the early stages of deglaciation. Thus the "anomalous" isotope-temperature relation in central Canada appears to have been limited to a discrete time interval during the early Holocene, beginning sometime after 11,000 yr B.P. and culminating shortly after 5000 yr B.P.

Possible Origin of "Anomalous" $\delta^{18}O_P$-MAT Relation in Central Canada

Two likely mechanisms can be invoked to explain elevated $\delta^{18}O_P$ in central Canada during the early Holocene, both linked to the high zonal index that is believed to have persisted at this time (Bryson & Wendland 1967; Bryson *et al.* 1970; Bartlein *et al.* 1984; Vance *et al.* 1995; Dean *et al.* 1996). Abundant evidence supports the existence of elevated alpine treeline in the western Cordillera from prior to 9000 until at least 6000 yr B.P., accompanied by pronounced dryness at lower altitudes (see Clague *et al.* 1992 and references cited therein) and drought in western Canada (e.g. MacDonald 1989; Schweger & Hickman 1989; Vance *et al.* 1995). As noted by Clague *et al.* (1992), higher cloud base enhanced the efficiency of moisture transport through the mountains. This should have led to decreased rain-out effects on the isotopic composition of residual vapour (and ultimately precipitation derived from it), which can be simulated assuming a simple Rayleigh distillation process, described by the equation

$$R_{Vr}/R_{Vo} = f^{(\alpha-1)} \qquad (3)$$

where R is the $^{18}O/^{16}O$ ratio in residual (Vr) and initial (Vo) vapour, f is the fraction of residual vapour remaining at any time, and α is the liquid-vapour equilibrium isotopic fractionation occurring during condensation ($= R_L/R_V$). Manipulation of (3) using a

plausible value of -15 ‰ for the $\delta^{18}O$ of original vapour and α of 1.010 suggests that the present $\delta^{18}O_P$ of -22 ‰ represents an f of about 0.18. Assuming all else remained constant, a relatively moderate increase in moisture transport efficiency (from an f of 0.18 to 0.28) would be sufficient to generate the observed 4 ‰ increase in $\delta^{18}O_P$.

Moreover, any isotopic enrichment generated in this way is likely to have been reinforced by an increase in the summer:winter precipitation ratio, because the effect of higher cloud base would be more pronounced in summer. Sensitivity to this effect can also be readily simulated. Based on isotope hydrology studies in the region (Gibson *et al.* 1993, 1994) and meteorological records (Environment Canada 1982), the modern $\delta^{18}O_P$ value of -22 ‰ represents roughly a 55:45 mixture of summer rain and winter snow (water equivalent) having average $\delta^{18}O$ values of about -17 and -28 ‰, respectively. Mass balance considerations show that a modest shift to a 65:35 mixture in the annual budget would cause an increase in $\delta^{18}O_P$ of over 1 ‰, in the absence of changes in other factors.

These simple calculations demonstrate that the magnitude of the early-Holocene $\delta^{18}O_P$ "anomaly" in central Canada can be reasonably explained by small changes in rain-out effects and seasonality of precipitation, independent of change in MAT. Although there are certainly other factors that might influence spatial and temporal isotope-temperature relations, such as changing sea-surface conditions where vapour originates or changing moisture sources, we speculate that the above mechanisms may be the major ones operating at the coarse resolution of our existing $\delta^{18}O_P$ time-series. Most importantly, this provides the basis for a unified model that reconciles inferred climate and isotope-climate histories readily within the established framework of shifting postglacial atmospheric circulation (shown schematically in Figure 5-5).

"Anomalous" $\delta^{18}O_P$-MAT Relations Elsewhere in North America

Several examples of unusually high $\delta^{18}O_P$ (or $\delta^{2}H_P$) in relation to MAT have been identified previously in North America. These include pre-Holocene episodes

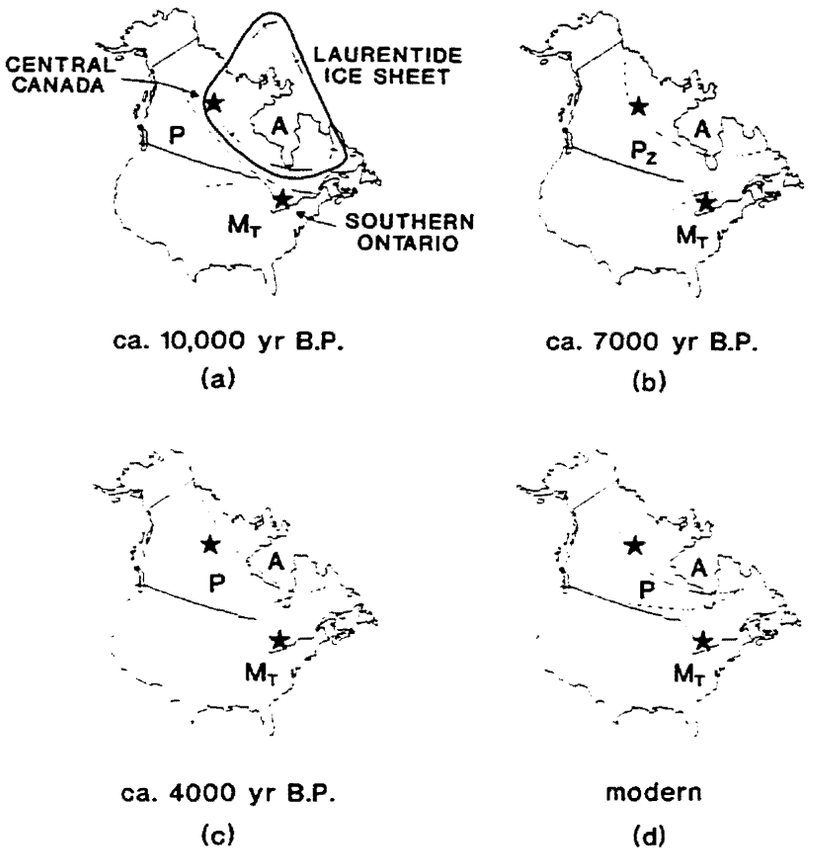


Figure 5-5. Schematic representation of mean summer frontal zone positions at selected times during the Holocene in relation to southern Ontario and central Canada (*cf.* Bryson & Wendland 1967). (A = Arctic; M_T = Maritime-Tropical; P = Pacific; P_Z = high-zonal Pacific).

a) Earliest Holocene (*ca.* 10,000 yr B.P.): central Canada ice-covered; southern Ontario strongly influenced by Arctic air interacting with Maritime-Tropical air.
b) High Zonal Index (*ca.* 7000 yr B.P.): central Canada strongly influenced by Arctic air interacting with high-zonal Pacific air; southern Ontario strongly influenced by Maritime-Tropical air with subsidiary high-zonal Pacific air influence.
c) "Climatic Optimum" (*ca.* 4000 yr B.P.): central Canada strongly influenced by Pacific air; southern Ontario strongly influenced by Maritime-Tropical air.
d) Modern: central Canada strongly influenced by Arctic air with subsidiary Pacific air influence; southern Ontario strongly influenced by Maritime-Tropical air.

revealed by isotope study of fossil wood cellulose at several U.S. sites (Yapp & Epstein 1977), groundwater along the southeast Atlantic coastal plain (Plummer 1993), and soil carbonate in Wyoming (Amundson *et al.* 1996). Possible early-Holocene examples that may correspond in time with high $\delta^{18}O_P$ in central Canada have been inferred from isotopes in tree-ring cellulose from the White Mountains of California (Feng & Epstein 1994) and the San Juan Mountains of Colorado (Friedman *et al.* 1988), lake sediment kerogen from western Michigan (Krishnamurthy *et al.* 1995), and fossil hackberry endocarp carbonate in the midwest U.S. (Jahren *et al.* 1995). Although detailed analysis would be required to verify teleconnection to events in central Canada, it is likely that these episodes are also a manifestation of the same atmospheric circulation changes outlined in Figure 5-5 and that "anomalous" $\delta^{18}O_P$-MAT relations along the Arctic frontal zone in the north may have been mirrored by analogous effects along the Pacific frontal zone in the south.

Concluding Comments

Our results are strongly consistent with the notion that "the $\delta^{18}O$ values of precipitation in North America are controlled by a complex array of processes that occasionally shows a strong dependence on MAT" (Amundson *et al.* 1996: 26). Further investigation and analysis of isotopic data from precipitation, both past and present, are clearly needed to better document isotope-climate relations. We view our compilation and interpretation of $\delta^{18}O_P$ histories for two areas in Canada as a preliminary step towards preparation of continental-scale paleo-isotope maps that can be used to gain deeper understanding of climate dynamics through synoptic-climatological analysis. As well, such time-slice maps will have obvious value for validation of AGCM simulations incorporating isotopic tracers and may indeed provide isotopic boundary conditions necessary for future-generation AGCMs to explore other aspects of global paleoclimate. Growing evidence for "anomalous" isotopic distribution in parts of North America during the early Holocene, in concert with differing circulation than present, suggests that a mapped time-slice within this interval might be a particularly fruitful target for a climate modelling experiment.

PART B:

Wolfe BB, TWD Edwards & R Aravena, 1997. Paleohydrology at treeline, northern Russia: A multi-faceted isotope approach. *Proceedings, International Symposium on Isotope Techniques in the Study of Past and Current Environmental Changes in the Hydrosphere and the Atmosphere.* International Atomic Energy Agency, Vienna, IAEA-SM-349/9.

Synopsis

In central Canada, multiple records of cellulose-inferred $\delta^{18}O_{lw}$, combined with several years of field investigations (Bursey *et al.* 1991; Gibson *et al.* 1993, 1994), were used to disentangle hydrologic effects (primarily evaporative enrichment) from the changing oxygen isotope composition of precipitation (MacDonald *et al.* 1993; Wolfe *et al.* 1996; Edwards *et al.* 1996). Successful deconvolution of the $\delta^{18}O_{lw}$ records was facilitated largely due to the varying hydrologic sensitivity of the study lakes owing to their strongly contrasting settings.

In northern Russia, however, we have used a slightly different research approach beacuse we do not have the benefit of extensive field-based studies of modern isotope hydrology nor, at present, the fortunate occurrence of a regional suite of sediment cores from lakes in very different hydrologic environments. Based on the the recent work by Vardy *et al.* (1997), which showed that peat porewater $\delta^{18}O$ can be a useful tracer of past hydrologic change, we re-examined the $\delta^{18}O_{lw}$ profiles from TL1 (Lake Middendorf: Velichko *et al.* in prep., see CHAPTER 4) and LS9 (MacDonald *et al.* in prep., see CHAPTER 4) as well as an additional site on the western Taimyr Peninsula (TL5) in light of new data provided by isotopic analysis of peat porewater. Integration of these data allows us to tentatively separate evaporative enrichment effects from the isotopic composition of precipitation in the $\delta^{18}O_{lw}$ records. Results from the two main study areas, the western Taimyr Peninsula and lower Lena River delta, are compared and speculative regional interpretations of Holocene moisture conditions are made.

Our studies suggest that a strong moisture gradient may have developed between these two regions during the early Holocene when the boreal forest expanded to the Arctic coast. The initial advance of the forest closely corresponds

to deglaciation of Scandinavia, enhanced thermohaline circulation and northward movement of the north Atlantic polar front (Koc *et al.* 1993; Bjorck *et al.* 1996; Jones 1994; Macdonald *et al.* in review). These factors likely led to increased flow of warm Atlantic water into the Arctic Ocean, expansion of the Icelandic Low, and enhanced transport of warm and moist air into arctic Siberia (Khotinskiy 1984; Koc *et al.* 1993; Rogers & Moseley-Thompson 1995; Macdonald *et al.* in review). At the Lena River delta, however, more continental conditions were promoted because the arctic coastline may have been located as much as 150 km north of its modern location between 9000 and 6000 BP (Macdonald *et al.* in review). Since 3500 ^{14}C-years BP, both the Taimyr Peninsula and Lena River delta appear to have experienced highly variable but comparable moisture conditions.

We view these preliminary interpretations as a working model that can be used to develop more comprehensive paleohydrologic reconstruction in northern Russia following several planned additional studies. These include a more thorough isotopic investigation of the peat records (completion of porewater δ^2H analysis, porewater tritium analysis and peat cellulose δ^{18}O analysis) to better evaluate the significance of evaporation, porewater mixing, and modern water infiltration. Additional lake sediment cores in the Lena River, Pechora, and Kola Peninsula regions are in various stages of sample preparation and analysis. Results from these sites will increase spatial coverage and help to constrain our paleohydrologic reconstructions. As well, paleoceanographic work in the Barents Sea and Arctic Ocean currently being conducted by Steve Forman (University of Illinois) will contribute greater understanding of important climate forcing mechanisms in northern Russia during the Holocene.

Abstract

Reconstruction of lake-water oxygen isotope histories, based on stratigraphic analysis of finely disseminated sediment cellulose, provide insight to Holocene paleohydrologic changes on the remote and largely unstudied tundra landscape of northern Russia. Oxygen and hydrogen isotope evaluation of local meteoric water and frozen porewater from nearby peatlands has enabled speculative deconvolution of the isotopic composition of precipitation from evaporative isotopic enrichment in the lake-water records. These collective data suggest that the western Taimyr Peninsula may have been relatively humid compared to more arid conditions on the Lena River delta during the early to mid-Holocene when the boreal forest expanded to the Arctic coast. Enhanced transport of moisture to the western Taimyr Peninsula from warm North Atlantic water penetrating the Barents Sea and increased continentality at the Lena River delta due to large tracts of exposed shelf may provide the forcing mechanisms for these different moisture records. Since the establishment of modern tundra vegetation at *ca.* 3500 BP, these two regions have apparently experienced highly variable yet regionally similar changes in moisture conditions.

Introduction

The *Paleoecological Analysis of Circumpolar Treeline* (PACT) project is an international research effort designed to increase our knowledge of treeline ecosystem response to climate change. Our primary method of investigation is to examine paleoenvironmental records contained in lake sediments and peat deposits using a multi-proxy approach (e.g. MacDonald *et al.* 1993; Vardy *et al.* 1997). Paleohydrologic reconstruction, based on inferred lake-water oxygen isotope profiles from analysis of lacustrine cellulose, is an important component of these studies.

Interpretation of lake-water oxygen isotope records requires separating isotopic effects caused by hydrological processes, which can provide information regarding past moisture conditions, from shifts in the isotopic composition of source water supplied to the lake, which in turn may reflect changes in temperature, vapour sources, seasonal distribution of precipitation, or other aspects of air mass circulation.

Near the boreal treeline in northern Canada, we have previously utilized records of inferred lake-water oxygen isotope composition from a series of lakes in different hydrologic settings, combined with several years of field investigations (Gibson *et al.* 1993, 1994), to disentangle evaporative enrichment effects from the changing isotopic composition of precipitation (MacDonald *et al.* 1993; Wolfe *et al.* 1996; Edwards *et al.* 1996).

Here we use a different approach to interpret cellulose-inferred lake-water oxygen isotope records from near treeline on the western Taimyr Peninsula (TL1, TL5) and the Lena River delta (LS9) in northern Russia (Figure 5-6). Single-season samples of modern meteoric water, including precipitation, groundwater, and ground-ice provide a temporally limited, yet important modern database in the absence of IAEA/WMO network stations and years of field studies. We also investigate the archival potential of peat porewater, extracted from sites in permafrost terrain near the study lakes (Figure 5-6), to provide an independent record of the mean annual oxygen isotope composition of precipitation.

Field and Laboratory Methods

Samples of rain were collected in 30-ml high-density polyethylene (HDPE) bottles. Snow and ground-ice were sealed initially in polyethylene bags, permitted to melt completely, and then transferred into HDPE bottles. Shallow groundwater was obtained from springs at the site of discharge or by collecting water-saturated soil from near the base of the active layer. Soil samples were sealed triple-wrapped in heavy-gauge polyethylene bags to prevent vapour loss during transport to the laboratory for subsequent azeotropic distillation of porewater (Revesz & Woods 1990). Samples from the western Taimyr Peninsula were collected between 28/07/93 and 05/08/93 and from the lower Lena River basin between 23/07/94 and 07/08/94.

A 3.5 m thick section of peat (68°10'N, 87°09'E), located on the western Taimyr Peninsula, was sampled from 2.15 m below the surface to the bottom of the section in 5 cm-thick slices at 10 cm intervals for porewater isotope analysis. Insufficient water was present in the upper part of the exposure. In the Lena River study region,

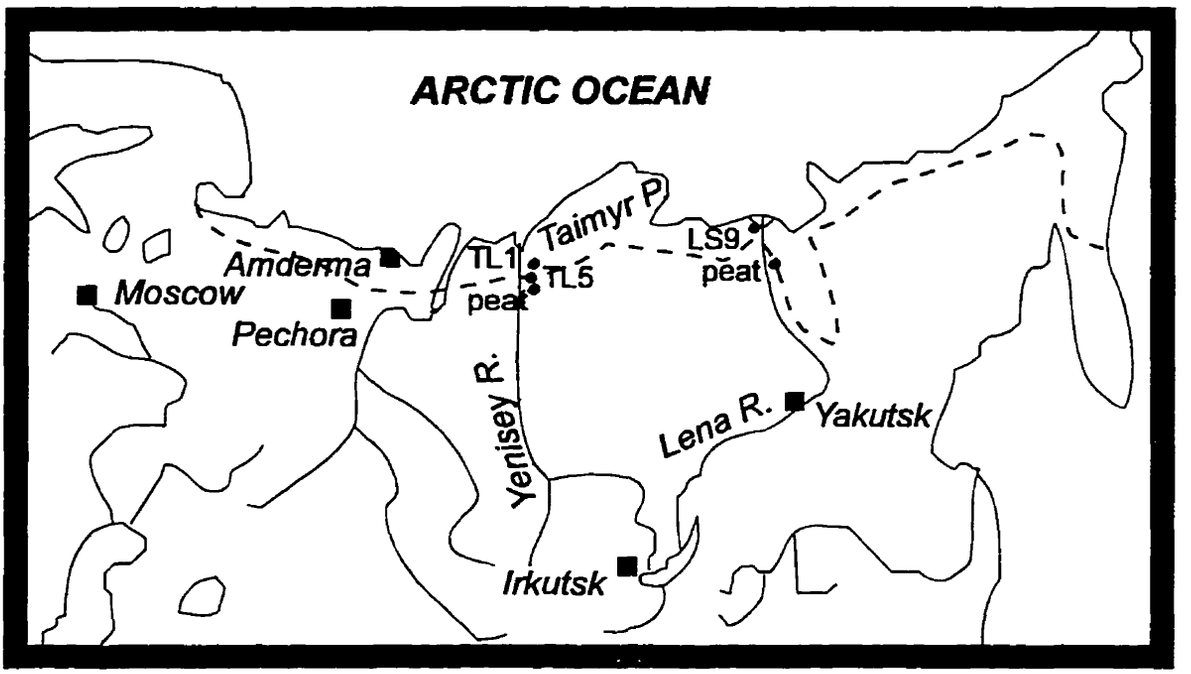


Figure 5-6. Locations of lakes TL1, TL5, LS9 and peat sites. Approximate position of treeline is represented by the dashed line. Lakes TL1 and LS9 are both headwater basins in small permafrost catchments. Lake TL5 is fed by several lakes and streams. Coring depth for lake TL1 was 8.15 m. Lake TL1 is a seasonally-closed basin. Coring depth for lake TL5 was 4.50 m. Lake TL5 is a through-flow lake. Coring depth for lake LS9 was 4.50 m. At the time of sampling, outflow was observed from lake LS9.

a 3.9 m peat core (69°23'N, 125°08'E) was obtained. Below 50 cm depth, 2-3 cm sections at 10-20 cm intervals were obtained for porewater isotope analysis. Water thawed from frozen peat samples was extracted using a centrifuge and transferred to HDPE bottles. Peat characteristics (bulk density, organic and inorganic content), pollen, and plant macrofossil stratigraphy are reported elsewhere (Andreev *et al.* in prep.; Jasinski *et al.* 1997).

Sediment cores from lakes TL1 (70°22'N, 87°33'E), TL5 (69°14'N, 86°34'E), and LS9 (71°52'N, 127°04'E) spanning 2.7 m, 4.2 m, and 3.5 m, respectively, were obtained using a Livingstone piston corer for multidisciplinary analysis (i.e. grain size, elemental geochemistry, loss-on-ignition, pollen, stomates, diatoms, chrysophyte cysts, chironomids, stable isotopes). Sediment samples for oxygen isotope analysis were taken at mostly 5 cm intervals from core TL1, 10 cm from core TL5, and 7 cm from core LS9. Samples were pre-treated in a 10 % hydrochloric acid solution at 70 °C for two hours to dissolve trace amounts of shell or mineral carbonate. Additional sample preparation on the <500 μm acid-washed residue involving solvent extraction, bleaching, and alkaline hydrolysis removed non-cellulose organic components (Edwards & McAndrews 1989). Nickel-tube pyrolysis (Edwards *et al.* 1994) was used to produce CO_2 from the cellulose fraction for $^{18}O/^{16}O$ determination.

Analyses of $^{18}O/^{16}O$ and $^{2}H/^{1}H$ ratios in water samples were performed at the Environmental Isotope Laboratory (EIL), University of Waterloo using CO_2-equilibration (Epstein & Mayeda 1953) and Zn-reduction (Coleman *et al.* 1982), respectively. Results are reported as δ values, representing deviation in per mil (‰) from the international Vienna-SMOW standard such that $\delta = [(R_{sample}/R_{SMOW})-1]*1000$, where R is the $^{18}O/^{16}O$ or $^{2}H/^{1}H$ ratio in sample and standard. Analytical uncertainties are ± 0.2 ‰ for $\delta^{18}O$ and ± 2 ‰ $\delta^{2}H$. Oxygen isotope ratios from cellulose-derived CO_2 are also reported in δ-notation with respect to Vienna-SMOW. Repeated cellulose analyses are normally within 1.0 ‰, reflecting both method uncertainty and the natural heterogeneity of the samples.

Results and Discussion

Meteoric Water

Non-evaporated water sampled on the western Taimyr Peninsula and lower Lena River basin define local meteoric water lines (Figure 5-7). Summer rain is predictably enriched in ^{18}O and ^{2}H relative to snow, whereas groundwater and ground-ice data are intermediate due to recharge by varying mixtures of snowmelt and rain. Estimated oxygen isotope composition of mean annual precipitation ($\delta^{18}O_P$) from groundwater and ground-ice data is more negative in our study regions, compared to IAEA/WMO network stations at Moscow (-10.8 ‰), Pechora (-14.7 ‰), and Amderma (-15.8 ‰), consistent with greater rain-out of atmospheric vapour largely originating over the North Atlantic as well as the southwest (i.e. Mediterranean Sea, Black Sea, Caspian Sea).

Peat Porewater

Peat porewater $\delta^{18}O$ profiles from the Taimyr Peninsula and Lena River sites are largely complacent (Figure 5-8a). Analyses of $\delta^{2}H$ are currently in progress but preliminary results suggest that porewater at the Lena River site have not been subjected to evaporative isotopic enrichment (Figure 5-8b), including samples displaying the 1-2 ‰ increase at the top of the core. Overall, these peat porewater profiles appear to integrate seasonal variations in the isotopic composition of precipitation and close correspondence to the modern inferred $\delta^{18}O_P$ values suggests little variation has occurred in this parameter since perhaps the mid-Holocene.

Lake Sediment Cellulose

Reconstruction of lake-water $\delta^{18}O$ ($\delta^{18}O_{lw}$), based on analysis of cellulose extracted from sediment cores at lakes TL1, TL5, and LS9, show similar variations during the modern tundra interval but contrasting behaviour during the early to mid-Holocene when the boreal forest advanced to the present-day coastline (Figure 5-9). The source water for these lakes is primarily derived from local precipitation (potentially modified by upstream evaporation in the case of lake TL5), whose average

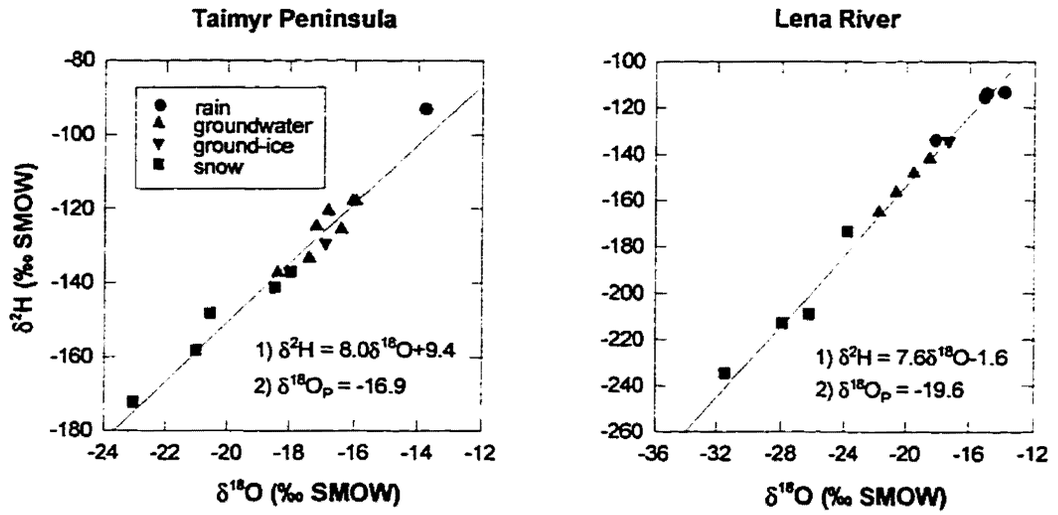


Figure 5-7. Non-evaporated meteoric water samples from the western Taimyr Peninsula and the lower Lena River basin, northern Russia. Equation 1) defines local meteoric water lines in respective regions by linear regression. Equation 2) defines estimated mean annual oxygen isotope composition of precipitation ($\delta^{18}O_P$) from average of groundwater and ground-ice data.

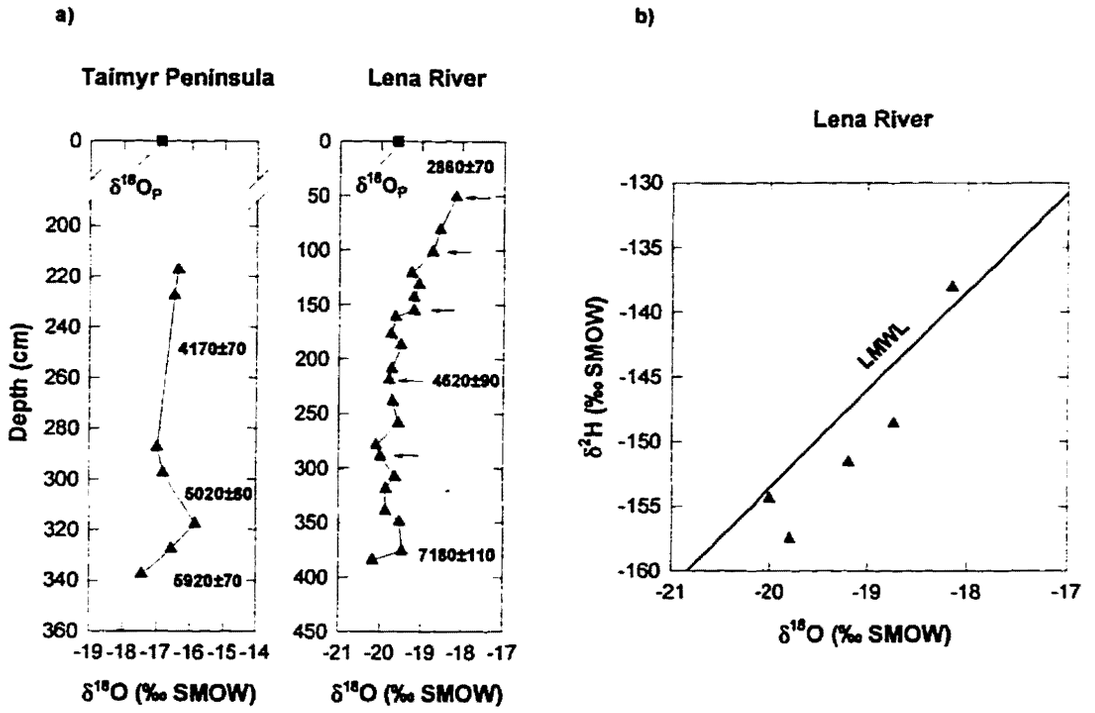


Figure 5-8a). Peat porewater $\delta^{18}O$ profiles and estimated mean annual oxygen isotope composition of precipitation ($\delta^{18}O_p$) from average of groundwater and ground-ice data (see Figure 5-7). Arrows identify samples for which $\delta^{2}H$ values are available (see **Figure 5-8b**). The ^{14}C-dates were obtained on peat.

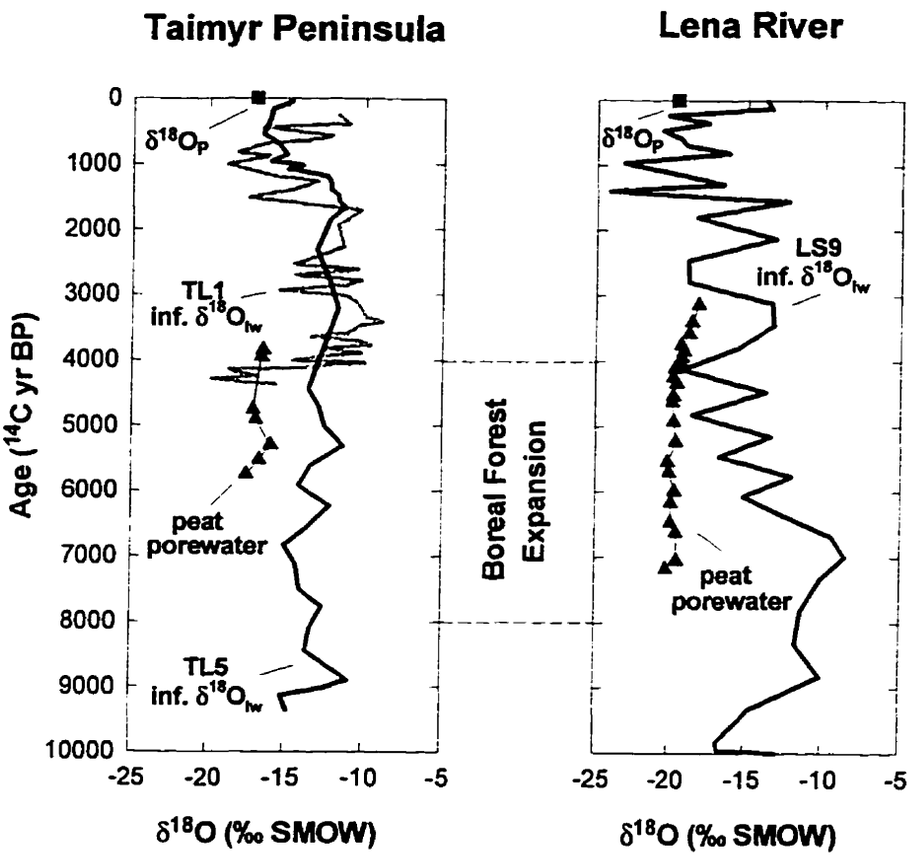


Figure 5-9. Cellulose-inferred lake-water $\delta^{18}O$ ($\delta^{18}O_{lw}$; $\alpha_{cell\text{-}water}$ = 1.028, Edwards & McAndrews 1989) and peat porewater $\delta^{18}O$ stratigraphy. Modern mean annual oxygen isotope composition of precipitation ($\delta^{18}O_p$) is from data in Figure 5-7. The interval of boreal forest expansion (8000-4000 ^{14}C-years BP) is inferred from palynology of lake sediment cores and ^{14}C-dated macrofossil Betula, Larix, and Picea found on the present-day tundra landscape. Peat porewater chronology is based on ^{14}C-dating of peat and therefore represents maximum ages. Lake-water $\delta^{18}O$ chronologies are based on accelerator mass spectrometry of terrestrial and aquatic macrofossils sampled from the sediment cores.

oxygen isotope value appears to have remained relatively constant (Figure 5-8). This suggests that $\delta^{18}O_{lw}$ at these sites has responded predominantly to changes in humidity and subsequent hydrologic effects on lake-water balance.

During the forest interval at *ca.* 7000 BP, high $\delta^{18}O_{lw}$ values at lake LS9 relative to $\delta^{18}O_{P}$ (inferred from the Lena River peat porewater $\delta^{18}O$) are suggestive of dry conditions and considerable evaporative enrichment. Preliminary calculations based on a steady state model suggest that mean summer relative humidity at lake LS9 may have been about 10 % lower at *ca.* 7000 BP compared to the present. In contrast, inferred $\delta^{18}O_{lw}$ values at lake TL5 at this time may only be marginally enriched relative to the local $\delta^{18}O_{P}$, reflecting moist conditions and rapid lake-water through-flow. During the past 3500 ^{14}C-years, all three lakes have responded similarly to humidity and water balance changes.

These inferred $\delta^{18}O_{lw}$ records may be responding to large-scale changes in North Atlantic circulation and Arctic coastline configuration (Forman, personal communication 1997). During the early to mid-Holocene, greater penetration of North Atlantic water into the Barents Sea, due to rising sea level and isostatically-depressed oceanic crust, may have provided increased warmth and moisture to the western Taimyr Peninsula. Further to the east at the Lena River delta, however, subsequent rain-out of air masses derived from the North Atlantic combined with a still emergent coastline may have resulted in a more continental climate compared to the present-day, relatively maritime conditions. Reduced atmospheric influence of North Atlantic water and establishment of the modern coastline position has perhaps led to similar, yet highly variable hydrologic conditions in both regions during the late Holocene.

Concluding Comments

The combination of results from isotope analysis of modern meteoric water, peat porewater, and lake sediment cellulose has yielded a provisional working model for Holocene paleohydrologic reconstruction in northern Russia. Preliminary data from peat porewater analyses are especially promising in providing an independent record of the mean annual oxygen isotope composition of precipitation. Completion of

porewater δ^2H analysis and $\delta^{18}O$ evaluation of the cellulose fraction of the peat will supply additional information concerning the possible role of evaporation and porewater mixing in these profiles.

Interpretation of peat porewater $\delta^{18}O$ results suggests that cellulose-inferred $\delta^{18}O_{lw}$ variations at lakes TL1, TL5, and LS9 primarily reflect changes in water balance in response to altering moisture conditions. During the early and mid-Holocene, development of a strong moisture gradient between the western Taimyr Peninsula and the Lena River delta may have resulted from changes in North Atlantic circulation and global sea level. These forcing mechanisms may have also contributed to the northward migration of the boreal forest. During the last 3500 ^{14}C-years, similar $\delta^{18}O_{lw}$ records at all three sites suggest a weakened moisture gradient and a common, regional hydrologic history.

CHAPTER 6: SUMMARY AND RECOMMENDATIONS

Summary of Significant Results

This dissertation is a series of independent manuscripts that focus on investigations of Holocene paleohydrology near treeline in central Canada and central and eastern Russia based on stable isotope analysis of lake sediment cores. Results and interpretations are a contribution to the multidisciplinary *Paleoecological Analysis of Circumpolar Treeline* (PACT) project led by Canadian and Russian researchers. Oxygen isotope analysis of lake sediment cellulose has been used to reconstruct lake water $\delta^{18}O$ records for several lakes from which interpretations regarding water balance and source water isotopic composition history have been made. Carbon isotope analysis of bulk organic and cellulose fractions have provided a record of watershed carbon balance as well as supplementary information on paleohydrologic conditions.

Results indicate that (often rapid) changes in moisture conditions have occurred during mid-Holocene intervals of northern boreal treeline advance (Figure 6-1). These warmer intervals appear to have been associated with higher summer relative humidity in central Canada and Russia, and a drier climate in eastern Russia. Although the latitudinal position of the forest-tundra ecotone has been traditionally viewed as being largely controlled by thermal factors, these data suggest that northern forest development may also be strongly linked to the moisture regime.

The carbon isotope records indicate that past changes in carbon balance in small boreal treeline lakes have been strongly influenced by prevailing hydrologic conditions. Increased lake productivity (inferred primarily from diatom records) is associated with warmer conditions and treeline advance at all of our study sites. However, the carbon isotope records frequently show excursions to ^{13}C-depleted values (or only muted enrichment) during these intervals in contrast to the strong relationship between increased lake productivity and ^{13}C-enrichment in bulk organic and cellulose fractions reported in many other locations (e.g. Schelske & Hodell 1991, 1995; Meyers *et al.* 1993; Dean & Stuiver 1993; Duthie *et al.* 1996). Increased

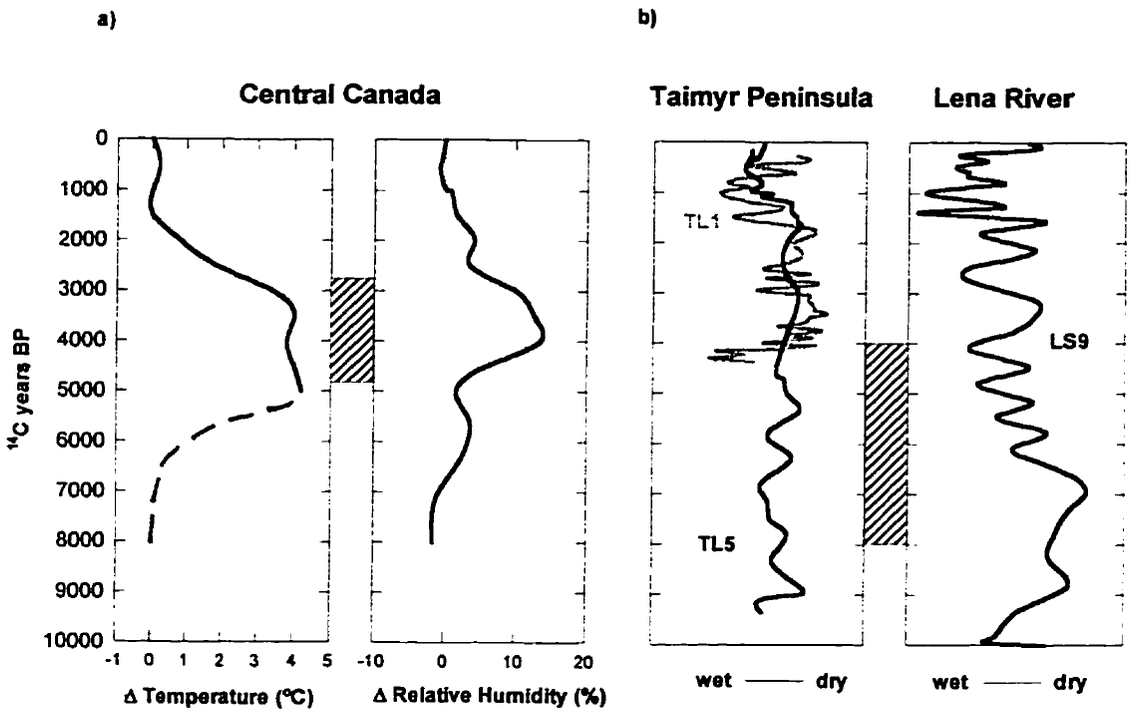


Figure 6-1. a) Holocene record of mean annual paleotemperature and summer paleohumidity change for central Canada based on lake sediment cellulose $\delta^{18}O$ from three lakes. Paleotemperature is derived from reconstructed $\delta^{18}O_P$ values and the relation, $\delta^{18}O_P = 0.65$ MAT - 15.5. Note that the older part of the record is constrained by pollen and diatom data. Uncertainties in reconstructed values are on the order of ± 2 °C and ± 6 % (see Edwards *et al.* 1996, also CHAPTER 5). b) Qualitative paleomoisture trends for the western Taimyr Peninsula and Lena River, northern Russia based on lake sediment cellulose $\delta^{18}O$ from three lakes (see Wolfe *et al.* 1997, also CHAPTER 5). Uncertainty in $\delta^{18}O_P$ record hinders quantitative reconstruction of paleohumidity in these regions. Note that hatched zones represent intervals of forest expansion.

production of ^{13}C-depleted soil $CO_{2(aq)}$ by root respiration and oxidation of organic matter combined with elevated surface runoff and rapid hydrologic flushing of lake water (particularly at the central Canadian and Russian sites) may be responsible for these isotopic signatures.

The Holocene record of northern treeline expansion, summer relative humidity and the oxygen isotope composition of precipitation ($\delta^{18}O_p$) in central Canada can uniformly be ascribed to shifting patterns of atmospheric circulation (Figure 6-2). Enhanced zonal circulation of dry Pacific air during the early Holocene led to arid conditions and likely contributed to ^{18}O-enriched precipitation ($\approx$ -18 ‰). By 5500 BP, zonal circulation weakened and treeline repeatedly advanced and retreated in association with latitudinal shifts of the Arctic Front. Forest development was, in part, aided by wetter conditions probably due to increased snow cover. Enhanced rain-out effects with the deceleration of Pacific vapour transport and decrease in the summer:winter precipitation ratio were likely important factors leading to a decline in $\delta^{18}O_p$. An estimated value of -20 ‰ for $\delta^{18}O_p$ at *ca.* 4000 BP corresponds to the period of maximum treeline advance and may reflect a $\approx$ 3 °C increase in mean annual temperature with respect to the present (see Figure 6-1). The modern tundra vegetation and regional $\delta^{18}O_p$ of -22 ‰ were established by 2000 BP as the Arctic Front migrated to a more southerly position and the region became dominated by dry, Arctic air.

Treeline in northern Russia is much closer to the coast than in central Canada and therefore advance and retreat are likely more directly linked with changes in oceanic circulation and subsequent effects on thermal and moisture regimes. Interpretation of Holocene paleohydrology in northern Russia associated with changes in treeline is, however, somewhat more speculative than in central Canada due to greater uncertainties in our reconstruction of regional $\delta^{18}O_p$ and also the lack of modern isotope hydrology studies. Nevertheless, our records appear to show that a strong moisture gradient may have developed between the western Taimyr Peninsula and the Lena River delta during the early to mid-Holocene when the boreal forest expanded to the Arctic coastline. Enhanced transport of moisture to the western

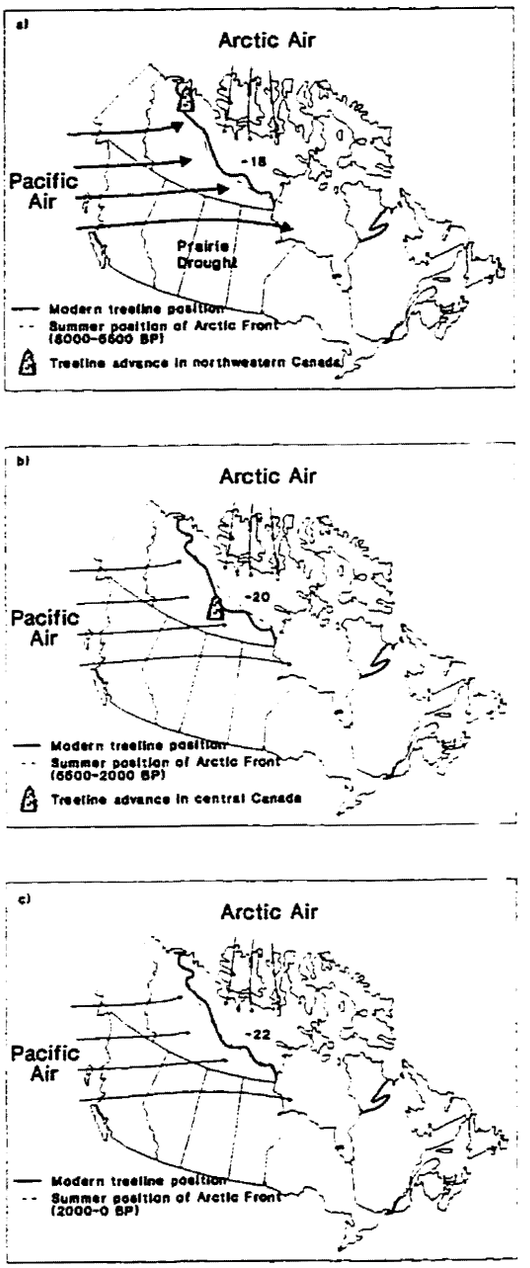


Figure 6-2. Reconstruction of summer position of Arctic Front and related treeline fluctuations in northern Canada during the a) early (8000-5500 BP); note treeline advance in northwestern Canada (Ritchie *et al.* 1983), b) mid- (5500-2000), and c) late (2000-0 BP) Holocene. Values in central Canada refer to estimated $\delta^{18}O_p$ (see Edwards *et al.* 1996, also CHAPTER 5).

Taimyr Peninsula from warm North Atlantic water penetrating the Barents Sea (as a result of isostatically-depressed ocean floor) and increased continentality at the Lena River delta due to large tracts of exposed shelf (because of low global sea level) may have been important climate forcing mechanisms during this time (Figure 6-3). Since the establishment of modern tundra vegetation at *ca.* 3500 BP, these two regions have apparently experienced highly variable yet regionally similar changes in moisture conditions.

Recommendations for Future Research

Circumpolar Treeline Paleohydrology

Reconstruction of Holocene paleohydrology in northern Russia is largely dependent on the first-order approximation of the isotopic composition of precipitation record, which is based on a small number of peat porewater $\delta^{18}O$ results. The first priority for further research should clearly be to complete porewater $\delta^{2}H$ determinations and to initiate porewater tritium and peat cellulose $\delta^{18}O$ analyses to evaluate the role of evaporation, porewater mixing and modern water infiltration in these profiles. Stable isotope analysis of other lake sediment cores collected in 1994 from the Lena River region will help to place constraints on preliminary interpretations based on the LS9 lake sediment record (Figure 6-4). Lake sediment cores collected in the Pechora region during the 1995 PACT field season and on the Kola Peninsula, as part of a new project led by Glen MacDonald (UCLA), will increase spatial coverage in northern Russia (Figure 6-4) and help to establish linkage with similar investigations in Scandinavia (e.g. Hammarlund & Edwards 1997). Preliminary analyses by Forman (1997) suggests that increased study of paleoceanographic conditions in the North Atlantic and Arctic Oceans will also be critical for reconciling the Russian terrestrial paleohydrologic records.

Holocene reconstruction of arctic treeline hydrology is in its infancy and clearly much work remains. Although vegetation histories have been studied in many other circumpolar regions (e.g. Ritchie *et al.* 1983; Payette *et al.* 1989; Peterson 1993; Anderson & Brubaker 1993; Cwynar & Spear 1995), these reconstructions have

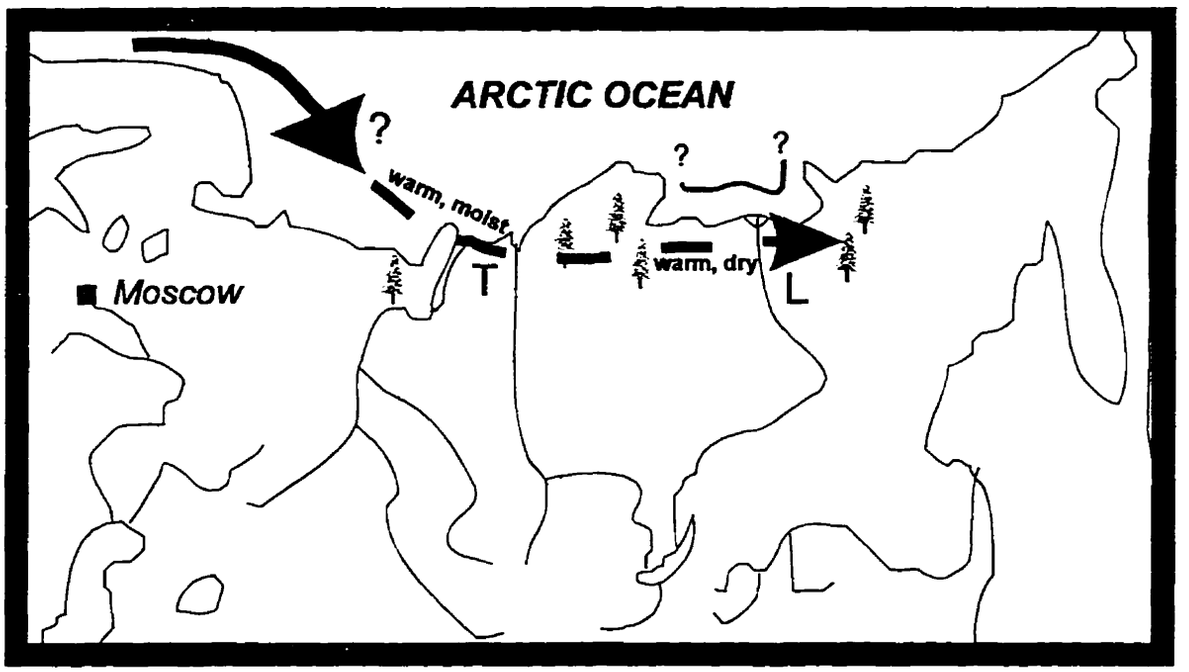


Figure 6-3. Possible climate forcing mechanisms in northern Russia during the early to mid-Holocene (see text; Forman 1997).

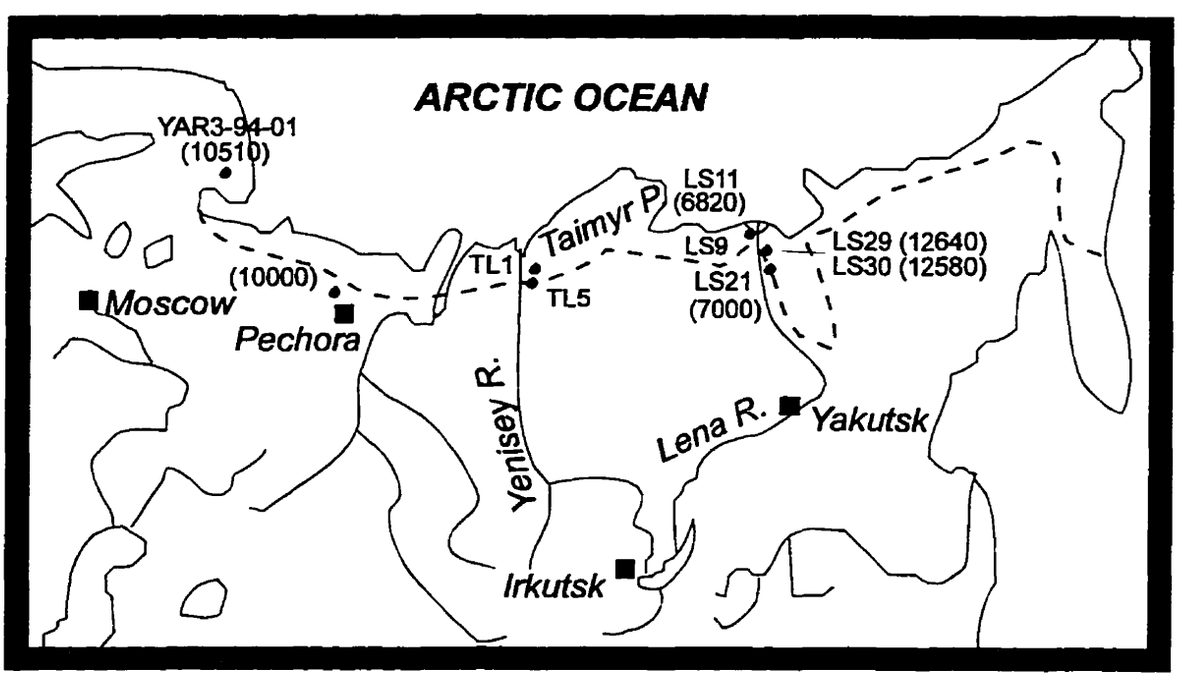


Figure 6-4. Available lake sediment cores in northern Russia for isotope analysis with basal estimated (Pechora site, LS21) or radiocarbon (all other sites) dates in brackets.

generally been related to changes in summer temperature. Associated hydrologic change is considerably less well known and frequently restricted to qualitative interpretations (i.e. moister, drier). These regions require intensive study in order to develop a unified quantitative Holocene record of *circumpolar* paleohydrology that, together with the thermal record, can be confidently linked with changes in atmospheric and oceanic circulation. Our studies in central Canada and central and eastern Russia indicate that oxygen and carbon isotope analysis of organic lake sediments (in association with peat isotopic records) combine to form a powerful approach to paleohydrologic reconstruction and may be a useful tool in these poorly studied regions as well. Even at this early stage, however, there appears to be evidence for similar large-scale processes influencing past hydrologic change in different regions and that hemispheric teleconnection may indeed exist. For instance, Hammarlund & Edwards (1997) suggested that ^{18}O-enriched fine-grained calcite in a small treeline lake in the Scandes Mountains of northern Sweden may be related to a high zonal index and reduced rain-out effects during the early Holocene, similar to the explanation for ^{18}O-enriched precipitation in central Canada at this time.

Research Design

Interpretation of reconstructed lake water $\delta^{18}O$ records would certainly benefit from coupled estimation of lake water $\delta^{2}H$ (see Figure 1-2). Unsuccessful attempts to relate $\delta^{2}H$ in cellulose to water in which it formed arising from species-dependent $^{2}H/^{1}H$ fractionation (see references in Edwards 1993) has recently spurred efforts to examine the $\delta^{2}H$ composition in other organic substrates as a possible tracer of lake water $\delta^{2}H$. Studies on the hydrogen isotope composition of kerogen (Krishnamurthy *et al.* 1995) and lipids (Buhay 1997), in particular, are especially promising new research directions. Perhaps one of the remaining surface sediment transects obtained during PACT field seasons 1995-97 (Lena, Pechora, Northwest Territories) could provide an appropriate testing ground for these potential $\delta^{2}H$ archives where results could readily be combined with lake water $\delta^{2}H$ and $\delta^{18}O$ and cellulose $\delta^{18}O$ data. Alternatively, a series of lakes near Lupin, Northwest Territories where several

years of lake water δ^2H and $\delta^{18}O$ data have been collected (Gibson 1996), may also prove to be a useful site for sediment organic - lake water δ^2H "calibration" studies.

Development of the continuous-flow isotope ratio mass spectrometer with option to couple with an elemental analyzer has made $\delta^{15}N$ data readily attainable on the organic component of lake sediments. The usefulness of this proxy for recording past nutrient balance was explored on a well-studied site in which there was a good understanding of past hydrology, carbon balance and ecology. Although promising results were obtained, our ability to interpret these data are limited by the lack of detailed process studies that trace ^{15}N sources through the complex lacustrine nitrogen cycle to final organic matter deposition, as well as the paltry number of published lake sediment $\delta^{15}N$ profiles. Because ^{15}N fractionation is species-specific, future paleo-$\delta^{15}N$ studies may be most useful if combined with pigment analysis (e.g. Leavitt & Findlay 1994), in addition to elemental and carbon and oxygen isotope assessment, to evaluate algal community structure history.

APPENDIX 1: TECHNICAL PROCEDURES

Edwards TWD, RJ Elgood & BB Wolfe, 1997. Cellulose extraction from lake sediments for $^{18}O/^{16}O$ and $^{13}C/^{12}C$ analysis. Technical Procedure 28.0, Environmental Isotope Laboratory, Department of Earth Sciences, University of Waterloo, Waterloo.

Elgood RJ, BB Wolfe, WM Buhay & TWD Edwards, 1997. $\delta^{18}O$ in organic matter and water by nickel-tube pyrolysis. Technical Procedure 29.0, Environmental Isotope Laboratory, Department of Earth Sciences, University of Waterloo, Waterloo.

ENVIRONMENTAL ISOTOPE LABORATORY
DEPARTMENT OF EARTH SCIENCES
UNIVERSITY OF WATERLOO
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Technical Procedure 28.0

CELLULOSE EXTRACTION FROM LAKE SEDIMENTS FOR $^{18}O/^{16}O$ AND $^{13}C/^{12}C$ ANALYSIS

AUTHORS:

T.W.D. Edwards R.J. Elgood B.B. Wolfe

APPROVAL:

R.J. Drimmie, LABORATORY MANAGER DATE

1.0 INTRODUCTION

Cellulose was first extracted from lake sediments for isotopic analysis by Edwards (1987) in the course of paleohydrologic studies in southern Ontario. The technique was used to reconstruct postglacial lake water $\delta^{18}O$ history of a lake from cores containing gyttja and organic silt. These studies also demonstrated the sensitivity of sediment cellulose $\delta^{13}C$ as an alternative to bulk organic $\delta^{13}C$ as a tool for paleolimnologic investigations (Edwards & McAndrews 1989).

1.1 Precautions

The precautions listed below are guidelines only. Refer to the relevant Material Safety Data Sheets (MSDS) which are kept in the EIL office and in an MSDS binder in each lab. Retain waste for processing in the Hazardous Waste Handling Facility in ECS 150.

1. Carbon Dioxide (CO_2) is a clear, colourless, odourless gas at room temperature. In solid form (i.e. "dry ice"; sublimation temperature -78 °C), it can cause severe frostbite and continuously releases gas which displaces air and can result in asphyxiation. Use in a well ventilated area wearing thermal gloves and safety glasses.

2. Methanol (CH_3OH) is a clear, colourless, flammable and poisonous liquid. Acute effects of exposure by ingestion, inhalation or percutaneous absorption include headache, fatigue, nausea, visual impairment or complete blindness (may be permanent), acidosis, convulsions, mydriasis, circulatory collapse, respiratory failure or death.

3. Nitrogen (N_2) is a colourless, odourless gas at room temperature. In liquid form (condensation temperature -196 °C), it can produce severe frostbite. Wear safety glasses and thermal, impervious gloves to prevent frostbite. It is a simple asphyxiant; use under well ventilated conditions.

4. Acetic acid (CH_3COOH) is a colourless liquid and has a vinegary odour. Inhalation of the corrosive gas or fumes may be immediately dangerous to life or health. It may cause severe burns on contact. It reacts exothermically with water to produce toxic and corrosive fumes. Wear gloves and dust mask and handle with care in the fumehood.

5. Sodium chlorite ($NaClO_2$) is an off-white crystal, odourless, oxidizable material. It irritates skin, eyes, and in contact with wet skin can cause burns. Wear gloves, dust mask and safety glasses in the fumehood.

6. Benzene (C_6H_6) is a clear and colourless liquid with an aromatic odour. It is volatile, flammable and toxic. Acute effects of exposure by ingestion and inhalation absorption are flushing, headaches, shortness of breath, respiratory collapse, coma and death. It irritates skin and eyes. Wear gloves, dust mask and safety glasses in the fumehood.

7. Acetone ($CH3COCH_3$) is a colourless, volatile, flammable, poisonous and mobile liquid. Boiling point is 56 °C. Avoid all sources of ignition. Use gloves and safety glasses in the fumehood.

8. Ethanol (C_2H_5OH) is a clear, colourless, flammable, volatile liquid. Boiling point is 79°C. Use gloves and safety glasses in the fumehood.

2.0 PREPARATION PROCEDURE

Preparation of sediment cellulose from organic lake sediments follows the technique of Green (1963) and Sternberg (1989) for extracting cellulose from wood powder (see T.P. 10.0), with modifications to accomodate the much finer grain size typical of sediments. Following removal of carbonate (see T.P. 22.0) and freeze-drying, lake sediment samples are sieved to < 500 μm (if necessary) to eliminate macrofossil plant debris (which is commonly of terrestrial origin). Scattered fragments may be removed with tweezers.

Cellulose preparation is a three-part process involving sequential extraction of non-cellulose organic components. All extractions are performed in the fumehood. Batches of 10 or more may be run simultaneously, depending on the size of the bottles and space restrictions in the fumehood and water bath.

Part 1. Solvent Extraction (removes lipids, resins, tannin)

1. Extract 2-5 g of freeze-dried sediment in a covered 125 ml glass wide-mouth, screw-top bottle with about 100 ml of 2:1 benzene:ethanol, swirling the solution occasionally. Decant/aspirate the solution after 48 hours. If the liquid is deeply coloured (i.e. darker than weak tea), repeat the extraction with fresh solvent for an additional 24 to 48 hours.

2. Add about 100 ml of acetone and replace cover. After 24 hours, decant/aspirate and allow samples to air-dry in the fumehood.

Part 2. Bleaching (removes lignin)

1. Add about 75 ml of deionized water to the air-dried sample and place in a water bath at 70 °C. Add 0.5 ml of glacial acetic acid, followed by 0.5 g of sodium chlorite, stir, and cover.

2. After one hour, add fresh aliquots of acetic acid and sodium chlorite (always adding the acetic acid first), and stir. Repeat 5 times or until sediment residue is a pale grey to yellowish-grey colour.

3. Allow sediment residue to settle, decant/aspirate supernatant liquid, and re-fill with deionized water. Repeat 5-10 times, or until odour of the bleach solution fades, to completely displace bleach solution. **Do not test the odour until the solution is thoroughly diluted.**

4. After the final dilution, decant/aspirate to within about 1 cm of the residue.

Part 3. Alkaline hydrolysis (removes xylan, mannan, other polysaccharides)

1. Add about 100 ml of 17 % sodium hydroxide solution to the wet sample. Let stand for 45 minutes, decant/aspirate, and fill with deionized water. Rinse with deionized water 3-4 times or until solution is near neutral.

2. Dilute once with 10 % acetic acid and allow to stand for 15 minutes. Thoroughly wash the residue by repeated rinsing with deionized water until the odour of acetic acid fades. (Test the pH with indicator paper to confirm that it matches that of the deionized water).

3. After the final dilution, decant the water to within about 1 cm of the grey cellulose residue (see Note (3) below if the residue is reddish or orange-brown, indicating oxyhydroxide contamination). Cover the bottle with aluminum foil and freeze the remaining water and cellulose residue. Puncture foil with several pinholes and place bottles in freeze-drier.

4. After the sample is thoroughly dry, transfer to clean, dry, labelled vial for subsequent isotopic analysis by pyrolysis for $^{18}O/^{16}O$ (see T.P. 29.0) or combustion for $^{13}C/^{12}C$ (see T.P. 22.0).

3.0 NOTES

1. Label bottles carefully, keeping in mind that solvents used in the initial steps will dissolve almost any ink.

2. Carbon dioxide yields during pyrolysis and combustion suggest that refractory (non-cellulose) material (mostly fine-grained mineral matter) may be present in some samples, although this has no apparent effect on the isotopic results.

3. Oxygen isotope results may be severely affected (and the pyrolysis chamber contaminated) if iron or manganese oxyhydroxides are present (indicated by distinctive reddish or orange-brown colour of the final cellulose concentrate). If present, oxyhydroxides must be removed using the following leach solution:

Dissolve in 1 L of water:
- 35.16 g sodium dithionite
- 52.14 g ammonium citrate
- 14.33 g hydroxylamine hydrochloride

Extract oxyhydroxide-contaminated cellulose concentrate with about 75 ml of leach solution at room temperature for 24 hours. If oxide colour remains, repeat with fresh dose of leach solution. Wash by repeated dilution and decanting/aspirating with deionized water, and freeze-dry.

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EIL Technical Procedures:

Technical Procedure 10.0. ^{18}O Analysis in Cellulose by Pyrolysis.

Technical Procedure 22.0. Breakseal Combustion Method.

Technical Procedure 29.0. $\delta^{18}O$ in Organic Matter and Water by Nickel-Tube Pyrolysis.

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Technical Procedure 29.0

$\delta^{18}O$ IN ORGANIC MATTER AND WATER BY NICKEL-TUBE PYROLYSIS

AUTHORS:

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APPROVAL:

R.J. Drimmie, LABORATORY MANAGER DATE

1.0 INTRODUCTION

Prior to 1992, the Environmental Isotope Laboratory (EIL) at the University of Waterloo used the Thompson & Gray (1977) method for the determination of $\delta^{18}O$ in organic material. In this technique (T.P. 10.0), the sample is pyrolysed in an evacuated nickel vessel. Hydrogen released during pyrolysis diffuses through the walls of the nickel chamber, while carbon and oxygen combine to form carbon dioxide, on which $^{18}O/^{16}O$ ratio measurements are made by mass spectrometry.

The nickel-tube pyrolysis method of Brenninkmeijer & Mook (1981) permits more rapid analysis of oxygen isotope ratios in organic matter or water than the original nickel-pyrolysis technique; however it is complicated by the need to cut and weld the tubes prior to each sample analysis. Furthermore, the technique requires the use of a nickel powder catalyst and a spark chamber to ensure quantitative recovery of oxygen.

The Brenninkmeijer technique has been further modified at the EIL where resealable nickel vessels have replaced the need to cut and weld tubes. This technique permits greatly increased service life of individual tubes and has led to considerable simplification of the procedure.

1.1 Precautions

The precautions listed below are guidelines only. Refer to the relevant Material Safety Data Sheets (MSDS) which are kept in the EIL office and in an MSDS binder in each lab.

1. Carbon Dioxide (CO_2) is a clear, colourless, odourless gas at room temperature. In solid form (i.e. "dry ice"; sublimation temperature -78 °C), it can cause severe frostbite and continuously releases gas which displaces air and can result in asphyxiation. Use in a well ventilated area wearing thermal gloves and safety glasses.

2. Ethanol (C_2H_5OH) is a clear, colourless, flammable, volatile liquid. Boiling point is 79°C. Use gloves and goggles in the fumehood.

3. Nitrogen (N_2) is a colourless, odourless gas at room temperature. In liquid form (condensation temperature -196 °C), it can produce severe frostbite. Wear safety glasses and thermal, impervious gloves to prevent frostbite. It is a simple asphyxiant; use under well ventilated conditions.

4. Argon (Ar) is a colourless gas at room temperature. It can cause rapid suffocation and exposure can cause nausea, headache, and vomiting. At high concentrations argon functions as a simple asphyxiant by displacing air.

2.0 MATERIALS

Pyrolysis vessels are machined from nickel rod, which is left sealed at one end, welded to stainless steel VCR metal gasket face seal fitting with raised circular seats. A resealable fitting consists of a stainless steel nut and modified VCR plug used to compress a nickel gasket between raised circular seats. The puncturing device consists of two components machined from brass (see Edwards *et al.* 1994). Vertical movement of the needle is achieved by a threaded handle on the puncturing hilt. Three o-rings provide a vacuum-tight seal within the unit, and a machined stainless steel Rotulex-type fitting allows connection to a vacuum extraction line.

3.0 PROCEDURE

The following is a detailed description of the procedure used by the EIL to prepare CO_2 for ^{18}O analysis. Following sample pretreatment (T.P. 10.0 for wood cellulose; T.P 28.0 for sediment cellulose), the sample is pyrolysed in a nickel vessel at 1050 °C. Diffusion of H_2 through the nickel tubing at high temperature drives the reaction to completion, producing CO_2, CO, and C plus minor traces of non-condensible gases arising from trace contaminants. Tests indicate that capture of CO (and conversion to CO_2) is unnecessary (Aravena 1982; Edwards *et al.* 1994). The CO_2 is purified cryogenically and collected for oxygen isotope analysis by mass spectrometry (see T.P. 15.0/24.0).

3.1 Preparation of Sample Vessels Prior to Combustion

3.1.1 Bomb Conditioning

New pyrolysis vessels require conditioning before analysis. Standards should be loaded, pyrolysed and the resulting gas released for at least two runs before CO_2 is collected. Repeated runs with a water standard should then be undertaken until consistent reproducibility is obtained. After extended periods of non-use, standards should be run in each vessel to re-establish the catalytic activity of the nickel.

3.1.2 Bomb Cleaning

Prior to use, pyrolysis vessels must be carefully cleaned to remove all debris remaining from the previous sample.

1. Clean the interior of vessel using a stainless steel brush (1/4" diameter). Gently tap out debris.
Note: Care must be taken not to score the raised circular seats at the opening of the vessel as this will result in a poor seal and loss of gas during pyrolysis.

2. Flush interior of vessel with acetone and allow to air-dry.

3. Place clean vessels in oven at 60 °C or keep in a desiccator under vacuum.
Note: During periods of prolonged non-use, the pyrolysis vessels should be kept in a desiccator to minimize oxidation of nickel surfaces.

4. Vessels should frequently be cleaned by immersing in Extran solution in an ultrasonic bath for several hours followed by thorough rinsing with deionized water and acetone.

3.1.3 Loading Sample Vessels and Pyrolysis

3.1.3.1 Water Samples

1. Clean and dry vessels as described in section 3.1.2.

2. Load prebaked carbon (T.P. 31.0) (1 mg / 1 μl H_2O) into vessels and place in desiccator. 5 μl of H_2O typically produces ≈ 1.5 cc of CO_2.
Note: Gloves should be worn to prevent contamination of sealing surfaces.

3. Attach desiccator to freeze dryer or extraction line and evacuate. Leave vessels under vacuum for a period of at least 12 hours.

4. Close desiccator and remove from freeze dryer/extraction line. Place desiccator in glovebox.

5. Flood glovebox with argon. Check that glovebox has been fully flushed by determining the flow from the upper vent.
Note: Argon should be passed through a moisture trap to ensure that no moisture is passed into the chamber during loading.

6. Attach desiccator to argon tank and flood with argon.

7. Place nut in holder and transfer vessel from desiccator to holding rack in glovebox.
Note: Gloves should be worn to prevent contamination of sealing surfaces.

8. Draw sample into syringe.

9. Flush vessel with thin stream of argon to further ensure that all atmosphere is displaced.

10. Lower needle as far as possible into the vessel and inject sample.

11. Quickly place nickel gasket and plug on vessel and tighten.

12. Rinse sealed vessel in acetone and allow to air-dry.

13. Insert sealed vessel into quartz envelope and evacuate on vacuum extraction line (Figure 3).

14. Bake sealed vessel in evacuated quartz envelope at 1050 °C for 50 minutes and then 500 °C for 30 minutes. After baking, allow quartz envelope and vessel to cool to room temperature (30 minutes).
Note: Reaction oven requires approximately 2 hours to stabilize at 1050 °C (variac setting of about 91 %, 120 v).

3.1.3.2 Organic Matter

Although samples are vacuum dried during the process of cellulose extraction (T.P. 10.0/28.0), it has been demonstrated that moisture is readily absorbed from the air (Edwards *et al.* 1994). Furthermore, due to the small sample size any moisture will have a significant effect on the final analysis. It is therefore extremely important to adhere to the following procedure.

1. Place samples in desiccator and attach to freeze dryer or extraction line. Desiccate samples for 12-24 hours.

2. Load samples (see Table 1) into the pyrolysis vessels, place in desiccator chamber and attach to freeze dryer/extraction line. Keep under vacuum for a period of at least twelve hours. Note: Gloves should be worn to prevent contamination of sealing surfaces.

Table 1. Suggested sample sizes.

Material	Organic content	Sample size	CO_2 Yield
lake sediment	5 %	60 mg	≈ 0.5 cc
lake sediment	10 %	40 mg	≈ 0.5 cc
lake sediment	30 %	20 mg	≈ 0.5 cc
cellulose	100 %	5 mg	≈ 1.5 cc

Notes:
1) Suggested lake sediment sample sizes are based on organic content prior to cellulose extraction.
2) For lake sediment samples with very low organic content, it is important not to overload vessels as the pyrolysis reaction will not go to completion.

3. Close desiccator and remove from freeze dryer/extraction line. Place desiccator in glovebox.

4. Flood glovebox with argon.

5. Attach desiccator to argon tank and flood with argon.

6. Place nut in holder and transfer vessel from desiccator to holding rack in glovebox.
Note: Gloves should be worn to prevent contamination of sealing surfaces.

7. Flush vessel with thin stream of argon to further ensure that all atmosphere is displaced.
Note: Pure cellulose is easily blown out of vessel!

8. Quickly place nickel gasket and plug on vessel and tighten.

9. Rinse sealed vessel in acetone and allow to air-dry.

10. Insert sealed vessel into quartz envelope and evacuate on vacuum extraction line.

11. Bake sealed vessel in evacuated quartz envelope at 1050 °C for 50 minutes and then 500

°C for 30 minutes. After baking, allow quartz envelope and vessel to cool to room temperature (30 minutes).
Note: Reaction oven requires approximately 2 hours to stabilize at 1050 °C (variac setting of about 91 %, 120 v).

3.2 Collection of CO_2

1. Preheat extraction line oven to 350 °C at least one hour in advance to permit thermal stabilization (Figure 1).

2. Establish a vacuum downstream of valve #1 (i.e. open valves #2, #3, #4, and #5).

3. Remove the head unit from the puncturing device and place a cooled pyrolysis vessel inside the sample shaft. Check that the puncturing needle is withdrawn to the correct height and that o-rings are clean. Replace headunit and screw head tightly to the sample shaft.

4. Attach the puncturing device to the vacuum line; open valve #1 to evacuate the puncturing device. Pump on the entire line for several minutes until vacuum is obtained. Zero the pressure gauge.

5. Place liquid nitrogen dewar on bottom of trap A. Close valve #1. Carefully screw down the puncturing hilt (resistance will indicate that cap has been pierced). Slowly raise the hilt to remove the needle from the cap and allow the contained gases into the heated portion of the line.

6. Allow the gases to remain in the heated portion of the line for 2 minutes. Close valve #2. Slowly open valve #1 and allow the CO_2 gas to condense in trap A.

7. Record change in pressure from the presence of non-condensible gases (mainly argon and CO).

8. Raise liquid nitrogen dewar halfway up trap A, wait several minutes and then raise to about 3 cm from top of trap.

9. Bleed off non-condensible gas by opening valve #2 slowly. Pump on the trapped CO_2 to remove non-condensible gases and to ensure complete transfer from punctured sample vessel. When the initial (full vacuum) reading on the pressure gauge is restored, close valves #1 and #2.

10. Replace liquid nitrogen dewar with ethanol/dry ice dewar on trap A to vaporize the CO_2. Record the new reading on the pressure gauge.

11. Place a liquid nitrogen dewar on the bottom of sample breakseal and close valve #4 to isolate the line from the vacuum pump. Slowly open valve #2 and allow the CO_2 to condense in the sample breakseal. Raise liquid nitrogen dewar over condensed CO_2.

12. After a few minutes, during which the pressure gauge should have returned to near its full-vacuum reading, raise liquid nitrogen dewar. Open valve #4 to pump off any residual CO that might have remained in the solid CO_2.

13. Flame off sample breakseal. Ensure that the sample vessel is correctly labelled and remove it for analysis by mass spectrometry (T.P. 15.0/24.0).

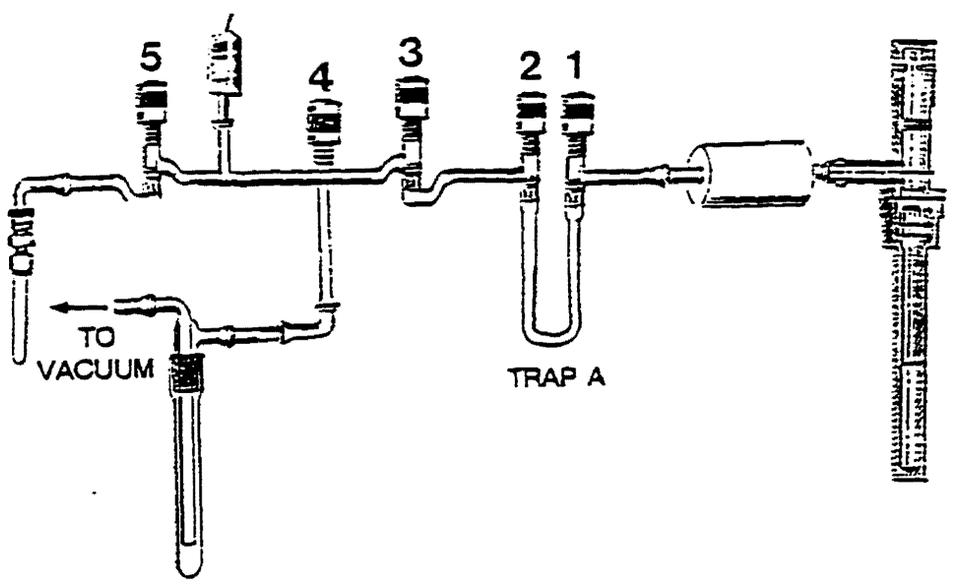


Figure 1. Vacuum extraction line.

14. Close valves #1 and #2. Heat for 2-3 minutes and check for an increase in pressure. A change may indicate the presence of water vapour suggesting that the pyrolysis reaction was incomplete. Open valve #2 to check vacuum recovery. A substantial fall in the vacuum also suggests residual water. Replace sample breakseal, pyrolysis vessel in puncturing device, and evacuate line.

4.0 VALUE REPORTING AND ERROR IDENTIFICATION

A water or cellulose standard should be routinely run with each sample batch, rotating the vessel in which the standard is loaded to monitor vessel performance. Repeats on water, lake sediment and pure cellulose are typically within 1.0 ‰.

Note that PDB values from the PRISM mass spectrometer are converted to SMOW by an empirical calibration (SMOW = 1.264 x PDB + 50.277) developed through analysis of known water and cellulose standards, ranging from -15 ‰ to +30 ‰ (SMOW). Good results have been obtained, however, for water samples as negative as -25 ‰ (SMOW) (Buhay & Wolfe unpublished data).

4.1 Trouble-Shooting Guide

<u>If water standards are too enriched:</u>

1. incomplete pyrolysis reaction?
   - check for water in trap following transfer
   - ensure pyrolysis oven temperature
   - ensure pyrolysis time

2. atmospheric CO_2, O_2 contamination?
   - ensure vessels are completely flushed with argon prior to sealing (1 minute of steady flow is normally sufficient)
   - run cellulose standards; if contamination is approximately equal in volume, less enrichment should be seen with a more enriched standard

<u>If water standards are too depleted:</u>

1. residual debris in vessels?
   - clean vessels in ultrasonic bath with Extran solution for several hours; rinse thoroughly with deionized water and acetone

2. leakage during pyrolysis?
   - check initial evacuation in quartz envelope; slow recovery may indicate poor seal or a leak has developed at weld between nickel rod and stainless steel
   - pyrolyse standard for different lengths of time to ensure smooth evolution to stable value

3. incomplete line transfer?
   - following check for water, open valve #1; if vacuum collapses, enriched CO_2 may still be in line; ensuring complete vacuum recovery when removing non-condensible gases prior to closing valves #1 and #2 and maintaining a clean nickel trap should alleviate this problem

4. atmospheric vapour contamination?
   - rebake carbon
   - check argon moisture trap
   - ensure vessels are dry prior to carbon loading
   - run cellulose standards; if contamination is approximately equal in volume, more depletion should be seen with a more enriched standard

5.0 REFERENCES

Aravena RO, 1982. ^{18}O, ^{2}H and ^{13}C in tree rings and their relation to the environment. M.Sc. Thesis, University of Waterloo, Waterloo. 142 pp.

Brenninkmeijer CAM & WG Mook, 1981. A batch process for direct conversion of organic oxygen and water to CO_2 for $^{18}O/^{16}O$ analysis. *International Journal of Applied Radiation and Isotopes* 32: 137-141.

Brenninkmeijer CAM, 1983. Deuterium, Oxygen-18 And Carbon-13 In Tree Rings And Peat Deposits In Relation To Climate. Ph.D. Thesis. 146 pp.

Edwards TWD, WM Buhay, RJ Elgood & HB Jiang, 1994. An improved nickel-tube pyrolysis method for oxygen isotope analysis of organic matter and water. *Isotope Geoscience* 114: 179-183.

Thompson P & J Gray, 1977. Determination of $^{18}O/^{16}O$ ratios in compounds containing C, H and O. *International Journal of Applied Radiation and Isotopes* 18: 411-415.

EIL Technical Procedures:

Technical Procedure 10.0. ^{18}O Analysis in Cellulose by Pyrolysis.

Technical Procedure 15.0. CO_2 Mass Spectrometer (903).

Technical Procedure 24.0. Prism.

Technical Procedure 28.0. Cellulose Extraction from Lake Sediments for $^{18}O/^{16}O$ and $^{13}C/^{12}C$ Analysis.

Technical Procedure 31.0. Sulphate ^{18}O By Combustion in Metallic Foil.

APPENDIX 2: ISOTOPE/GEOCHEMISTRY DATA

Toronto Lake Watershed Water Data (sampled August 22, 1994)

Sample	Lake*	$\delta^{18}O$		$\delta^{2}H$	
BW-TLC-1	1	-16.41		-138.3	-137.9
BW-TLC-2	2 - inflow	-16.28		-134.1	-136.5
BW-TLC-3	2	-15.52	-15.48	-135.9	
BW-TLC-4	3	-14.59		-130.1	
BW-TLC-5	4	-14.14		-128.8	
BW-TLC-6	5	-14.90		-132.6	-131.3
BW-TLC-7	6	-14.34	-14.23	-132.1	
BW-TLC-8	7- Toronto Lake	-13.74		-127.1	

* See Figure 2 of Wolfe BB, TWD Edwards, R Aravena & GM MacDonald, 1996. Rapid Holocene hydrologic change along boreal treeline revealed by $\delta^{13}C$ and $\delta^{18}O$ in organic lake sediments, Northwest Territories, Canada. *Journal of Paleolimnology* 15: 171-181. Also Chapter 3, Figure 3-2 in this document.

Taimyr Peninsula Water Data (sampled July 28 - August 5, 1993)

	Sample	Lake*	$\delta^{18}O$		$\delta^{2}H$	
Rain:						
	TE-93032		-13.63	-13.88	-93.05	-93.05
Groundwater:						
	TE-93003		-16.81		-120.6	
	TE-93008		-15.98	-15.90	-118.1	
	TE-93020		-17.38		-133.4	
	TE-93029		-18.37		-139.1	-135.5
	TE-93037		-16.41		-125.7	
	TE-93008		-17.18		-124.9	
	TE-93045		-16.05		-117.9	
Ground-Ice:						
	TE-93039		-16.81	-16.98	-129.3	
Snow:						
	TE-93005		-17.96		-137.0	
	TE-93009		-18.46		-141.4	
	TE-93011		-21.00		-158.3	
	TE-93030		-23.04	-23.06	-174.5	-169.9
	TE-93031		-20.55		-148.3	
Tundra Lakes:						
	TE-93001	TS-1	-18.67		-141.1	-142.1
	TE-93002		-16.47		-121.0	
	TE-93004	TS-2	-19.81	-19.67	-143.8	
	TE-93006	TS-3	-19.34		-144.2	
	TE-93012		-18.25		-136.8	
	TE-93051	TS-20	-15.87		-125.5	
	TE-93052	TS-21	-18.15		-137.4	
	TE-93053	TS-22	-16.83		-129.8	-130.9
	TE-93054	TS-23	-15.64		-121.9	
	TE-93007	(stream)	-19.08		-142.5	
	TE-93010	(stream)	-16.12	-16.13	-122.9	
Forest-Tundra Lakes:						
	TE-93015	TS-6	-19.97		-147.5	-149.2
	TE-93016	TS-7	-19.04		-142.5	
	TE-93017	TS-8	-17.72		-136.4	
	TE-93021	TS-4	-20.84		-155.0	
	TE-93022	TS-5	-19.21		-144.4	
	TE-93024	TS-9	-20.65		-153.3	
	TE-93025		-18.47		-141.3	
	TE-93026	TS-10	-18.47		-138.6	

TE-93027		-18.82	-18.84	-142.7	
TE-93028	TS-11	-19.25		-145.7	
TE-93014	(stream)	-18.41		-136.1	
TE-93018	(stream)	-18.38		-138.3	
TE-93019	(stream)	-18.39	-18.56	-141.0	
Forest Lakes:					
TE-93034		-17.51		-137.2	
TE-93035	TS-13	-18.00		-139.9	
TE-93036	TS-13	-18.15		-140.2	
TE-93040		-18.38		-138.2	
TE-93041	TS-12	-18.92		-147.2	
TE-93042	TS-14	-18.40	-18.34	-144.0	-144.9
TE-93043	TS-15	-18.90		-145.5	
TE-93044	TS-16	-18.84		-147.2	
TE-93046		-18.11		-138.7	
TE-93047	TS-17	-17.53	-17.45	-137.8	
TE-93048		-19.31		-144.4	
TE-93049	TS-18	-20.49		-152.3	
TE-93050		-20.30		-156.0	
TE-93033	(stream)	-19.85		-150.2	

• See Figure 1 in Wolfe BB & TWD Edwards, 1997. Hydrologic control on the oxygen isotope relation between sediment cellulose and lake water, western Taimyr Peninsula, Russia: Implications for the use of surface-sediment calibrations in paleolimnology. *Journal of Paleolimnology* (in press). Also Chapter 2, Figure 2-1 in this document. Note that Lakes TS-12 and TS-14 are located near TS-13.

Lena River Water Data (sampled July 23 - August 7, 1994)

	Sample		$\delta^{18}O$		$\delta^{2}H$	
Rain:						
	BW-1-18		-15.08		-115.4	
	BW-2-10		-18.15		-133.9	
	BW-5-2		-14.95		-113.8	
	BW-5-8		-13.86		-113.3	
Groundwater:						
	BW-1-12		-18.54		-141.8	
	BW-3-9		-19.56		-148.2	
	BW-5-6		-20.67		-156.3	-156.6
	BW-5-7		-21.91	-21.56	-165.1	
Ground-Ice:						
	BW-1-23		-17.32		-134.0	
Snow:						
	BW-1-13		-28.07	-27.86	-213.1	
	BW-1-14		-26.31		-209.2	
	BW-2-18		-23.79		-173.5	
	BW-2-19		-31.48	-31.48	-234.6	
		Lake*				
Tundra Lakes:						
	BW-1-1	LS-2	-16.42		-134.0	
	BW-1-2	LS-4	-17.41		-136.4	-137.2
	BW-1-3		-18.95		-143.6	
	BW-1-4		-17.48		-140.6	
	BW-1-6		-17.04		-137.9	
	BW-1-7		-15.16		-120.6	
	BW-1-8		-17.42	-17.48	-137.3	
	BW-1-9	LS-1	-18.35		-138.5	
	BW-1-10	LS-3	-16.85		-133.5	
	BW-1-11		-19.77		-152.7	
	BW-1-16		-19.74	-19.78	-153.0	
	BW-1-17		-17.22		-140.8	
	BW-1-19	LS-5	-18.20	-18.17	-139.9	
	BW-1-20	LS-6	-18.31		-142.1	
	BW-1-21	LS-7	-17.98		-139.6	
	BW-1-22	LS-8	-18.63		-146.2	
	BW-2-1	LS-9	-20.18		-154.2	-155.4
	BW-2-2	LS-10	-17.57		-138.8	
	BW-2-3	LS-11	-18.07	-18.07	-141.3	
	BW-2-4	LS-12	-17.50		-141.3	-139.8
	BW-2-5	LS-13	-18.40		-141.8	
	BW-2-6	LS-14	-20.06		-152.0	

BW-2-8	LS-15	-18.40	-18.28	-141.4	
BW-2-11	LS-16	-17.91		-138.6	
BW-2-12	LS-17	-14.43		-118.4	
BW-2-13	LS-18	-17.44		-135.6	-137.0
BW-2-14	LS-19	-16.29		-130.4	
BW-2-15	LS-20	-20.04	-19.87	-156.8	
BW-2-16	LS-9	-20.15		-157.1	
BW-1-24	(stream)	-20.68		-151.6	
BW-2-17	(stream)	-23.45		-175.5	
Forest-Tundra Lakes:					
BW-5-3	LS-29	-19.64		-159.3	
BW-5-4	LS-30	-18.74		-152.3	
BW-5-5	LS-31	-19.02	-19.04	-152.5	
Forest Lakes:					
BW-3-1	LS-21	-18.55		-154.9	
BW-3-2	LS-22	-19.63		-162.1	-160.9
BW-3-3	LS-23	-19.43		-160.5	
BW-3-4	LS-24	-16.61		-143.3	
BW-3-5	LS-25	-19.17		-157.2	
BW-3-6	LS-26	-16.19		-142.7	
BW-3-8		-17.09	-17.06	-143.1	
BW-4-1	LS-27	-17.95		-146.2	
BW-4-2	LS-28	-18.87		-151.5	-149.7
BW-3-7	(stream)	-18.01		-141.8	

* See Figure 1 in Duff KE, TE Laing, JP Smol & DRS Lean, in prep. Limnological characteristics of Siberian lakes spanning the northern treeline. For submission to *Hydrobiologia*.

Taimyr Surface Sediment Data

	Lake*	Depth (cm)	cell-$\delta^{18}O$ (SMOW)	
Tundra:				
	TS-1	0-1	15.7	
	TS-2	0-1	14.1	
	TS-3	0-1	12.5	
	TS-20	0-1	12.8	
	TS-21	0-1	15.8	
	TS-22	0-1	12.2	12.4
	TS-23	0-1	9.5	
Forest-Tundra:				
	TS-4	0-2	12.3	
	TS-5	0-1	16.2	
	TS-6	0-1	12.0	
	TS-7	0-1	12.1	
	TS-8	0-1	21.2	23.1
	TS-9	0-1	15.9	
	TS-10	0-1	13.0	
	TS-11	0-1	17.4	
Forest:				
	TS-13	0-2	6.5	
	TS-15	0-1	11.5	
	TS-16	0-2	6.7	
	TS-17	0-3	8.7	10.1
	TS-18	0-1	7.9	

*See Figure 1 in Wolfe BB & TWD Edwards, 1997. Hydrologic control on the oxygen isotope relation between sediment cellulose and lake water, western Taimyr Peninsula, Russia: Implications for the use of surface-sediment calibrations in paleolimnology. Journal of *Paleolimnology* (in press). Also Chapter 2, Figure 2-1 in this document.

Toronto Lake Sediment Core Data

Sample	Depth (cm)	bulk-$\delta^{13}C$ (PDB)		cell-$\delta^{13}C$ (PDB)		cell-$\delta^{18}O$ (SMOW)	
BW-S31-1	3.75	-27.0		-24.3		8.5	9.0
BW-S31-2	7.50	-26.5		-24.4		8.7	
BW-S31-3	10.00	-26.9		-24.0		9.3	
BW-S31-4	12.50	-26.7		-24.2		9.7	10.9
BW-S31-5	15.00	-26.9		-23.9	-23.8	9.7	10.8
BW-S31-6	17.50	-25.8		-23.5		8.9	
BW-S31-7	20.00	-26.5		-24.9		10.2	
BW-S31-8	22.50	-25.5		-23.7		8.6	9.2
BW-S31-9	25.00	-25.5		-24.1		9.4	
BW-S31-10	27.50	-25.3	-25.2	-23.7		9.0	9.6
BW-S31-11	30.00	-26.4		-24.1		8.5	
BW-S31-12	37.50	-26.6		-23.9		9.4	8.6
BW-S31-13	42.50	-27.6		-24.8		11.1	
BW-S31-14	45.00	-27.5		-25.1		11.0	
BW-S31-15	47.50	-27.2		-25.1	-24.8	8.5	8.3
BW-S31-16	50.00	-26.1		-25.0		4.7	
BW-S31-17	52.50	-27.8					
BW-S31-18	55.00	-28.2		-25.4		6.6	
BW-S31-19	57.50	-27.3		-25.1		8.7	
BW-S31-20	60.00	-27.2	-26.8	-25.1		6.1	
BW-S31-21	62.50	-27.1		-26.3		11.0	
BW-S31-22	65.00	-26.6		-26.1		13.7	
BW-S31-23	66.25	-27.8		-25.2		16.6	18.2
BW-S31-24	67.50	-27.1		-25.5		10.4	
BW-S31-25	68.75	-26.4		-25.0	-24.9	11.7	11.2
BW-S31-26	70.00	-28.0		-24.9		8.6	
BW-S31-27	72.50	-28.7		-25.5		11.7	
BW-S31-28	75.00	-28.2		-24.7		11.4	
BW-S31-29	76.25	-27.8		-22.8		11.1	
BW-S31-30	77.50	-26.9	-26.4	-22.5		15.3	15.6
BW-S31-31	78.75	-26.3		-22.9		12.3	
BW-S31-32	82.50	-27.4		-25.6		10.3	
BW-S31-33	87.50	-28.9		-26.2		12.9	
BW-S31-34	90.00	-28.1		-26.3		12.7	
BW-S31-35	92.50	-28.7		-26.6	-26.3		
BW-S31-36	95.00	-29.3		-25.3		7.7	
BW-S31-37	97.50	-28.4		-24.3		7.6	
BW-S31-38	100.00	-28.3		-25.1		12.4	
BW-S31-39	102.50	-28.9		-25.6		10.5	
BW-S31-40	105.00	-28.7	-28.2	-25.5		10.3	11.1
BW-S31-41	107.50	-28.4		-25.8		14.9	16.2
BW-S31-42	110.00	-29.0		-26.1		9.6	
BW-S31-43	112.50	-27.9					
BW-S31-44	115.00	-26.1		-21.5		9.2	

BW-S31-45	117.50	-24.4		-19.3	-19.3	11.4	11.8
BW-S31-46	120.00	-25.4		-22.4		12.7	
BW-S31-47	122.50	-25.5		-23.6		14.4	
BW-S31-48	127.50	-26.2		-23.9		16.1	
BW-S31-49	132.50	-26.3		-24.7		15.3	
BW-S31-50	137.50	-27.0	-27.0	-24.6		15.7	
BW-S31-51	140.00	-27.2		-25.1		12.5	
BW-S31-52	142.50	-27.2		-24.4		14.3	
BW-S31-53	145.00	-27.2		-24.9		15.3	
BW-S31-54	147.50	-27.2		-25.0		12.2	
BW-S31-55	150.00	-26.8		-24.6		14.8	15.5
BW-S31-56	152.50	-26.6		-22.8		15.4	
BW-S31-57	157.50	-26.5		-23.6		16.4	
BW-S31-58	165.00	-28.2		-26.1		18.4	
BW-S31-59	167.50	-29.1		-25.7		16.6	
BW-S31-60	170.00	-30.0	-30.0	-28.4		11.2	

Whatever Lake Sediment Core Data

Sample	Depth (cm)	C (%)		N (%)		C:N	bulk-$\delta^{13}C$ (PDB)	cell-$\delta^{13}C$ (PDB)		cell-$\delta^{18}O$ (SMOW)	
TE-1863	0-1.0						-28.9	-28.7		9.8	
TE-1868	9.0-11.5						-27.4	-28.5		9.5	
TE-1872	17.0-19.5	3.65		1.01		3.60	-28.1	-28.5	-27.9	9.9	
TE-1877	28.0-30.5						-27.7	-28.7		7.3	8.8
TE-1882	38.5-41.0	3.21		0.45		7.08	-27.5	-28.6		11.0	
TE-1887	48.0-50.5	1.30		1.43		0.91	-28.2	-28.5		11.0	12.2
TE-1891	59.0-61.5	3.16		0.43		7.41	-27.4	-27.9	-28.1	12.0	
TE-1895	68.0-70.5	3.27		0.57		5.78	-28.0	-28.7		9.8	10.2
TE-1899	78.0-80.5	3.01		0.34		8.74	-27.9	-28.2		12.2	
TE-1903	89.0-91.5	2.34		0.34		6.86	-28.2	-28.2		9.7	9.1
TE-1906	97.5-100.0	2.10		0.42		5.02	-27.5	-28.4	-28.2	12.0	
TE-1908	103.0-105.5	2.63		0.32		8.35	-27.6	-27.9		14.4	
TE-1912	112.0-114.5	2.67		0.32		8.46	-27.0	-28.2		14.5	14.6
TE-1917	124.0-126.5	2.79		0.35		8.08	-26.2	-27.6		13.3	
TE-1921	134.0-136.5	2.23		0.28		7.94	-26.2	-27.0		14.4	14.1
TE-1925	144.0-146.5	2.01		0.25		8.10	-25.9	-27.6		11.0	12.0
TE-1930	155.0-157.5	2.29		0.32		7.05	-26.6	-27.8		15.0	15.7
TE-1934	167.0-169.5	1.57		0.23		6.81	-27.3	-27.4		11.9	9.3
TE-1938	177.0-179.5						-27.1	-27.8		15.2	
TE-1942	186.5-189.0	0.16	0.14	0.03	0.03	4.78	-24.5	-26.7		14.3	
TE-1944	193.0-195.5	0.11		0.02		4.74	-25.2				
TE-1948	204.0-206.5	0.06		0.02		3.79	-24.8				
TE-1952	214.0-216.5	0.04		0.02		1.87	-26.2				
TE-1956	224.0-226.5	0.06		0.02		3.39	-22.9				

TL-1-1 Sediment Core Data

Sample	Depth (cm)	C (%)		N (%)		C:N	bulk-δ^{13}C (PDB)		cell-δ^{13}C (PDB)		cell-δ^{18}O (SMOW)		bulk-δ^{15}N (AIR)	
TL-1-1-0-1	0-1	3.01		0.54		5.6	-26.9						2.8	
TL-1-1-2-3	2-3	3.30		0.44		7.6	-27.3		-26.8					
TL-1-1-4-5	4-5	2.09		0.27		7.7	-26.5		-28.2				2.2	2.7
TL-1-1-6-7	6-7	2.00		0.24		8.4	-26.3		-25.7					
TL-1-1-8-9	8-9	1.47	1.31	0.21	0.18	7.1	-26.2		-26.6		16.0		2.2	
TL-1-1-10-11	10-11	1.17		0.20		6.0	-26.3		-26.9					
TL-1-1-12-13	12-13	1.16		0.15		7.5	-26.3		-29.6	-30.5	16.6		2.4	
TL-1-1-14-15	14-15	1.50		0.18		8.2	-26.6		-26.2		11.1			
TL-1-1-16-17	16-17	1.48		0.18		8.4	-26.7		-29.1	-29.8			2.4	
TL-1-1-18-19	18-19	1.66	1.63	0.18	0.18	9.1	-26.8		-26.7		15.5			
TL-1-1-20-21	20-21	2.60		0.29		8.9	-27.2		-28.7	-29.4	13.9		2.0	
TL-1-1-22-23	22-23	1.62		0.17		9.4	-27.1	-27.2	-26.9		11.0			
TL-1-1-24-25	24-25	1.65		0.19		8.9	-26.9		-28.7				2.0	
TL-1-1-26-27	26-27	2.09		0.23		9.0	-26.5		-26.4		9.4			
TL-1-1-28-29	28-29	3.35	2.11	0.30	0.22	10.4	-26.9		-28.8	-28.8	11.2	11.7	2.4	
TL-1-1-30-31	30-31	1.87		0.19		9.8	-26.4		-26.5					
TL-1-1-32-33	32-33	1.53		0.16		9.6	-26.5		-26.6		9.5	7.8	2.0	1.7
TL-1-1-34-35	34-35	2.04		0.20		10.3	-26.8		-26.3					
TL-1-1-36-37	36-37	2.83		0.28		10.0	-26.6		-26.9				2.0	
TL-1-1-38-39	38-39	2.00	2.18	0.19	0.22	10.2	-27.0		-26.5		12.0			
TL-1-1-40-41	40-41	2.69		0.27		9.8	-27.0		-26.8		14.6		2.1	
TL-1-1-42-43	42-43	2.32		0.23		10.2	-26.8		-26.5					
TL-1-1-44-45	44-45	1.84		0.18		10.4	-26.6		-32.4	-32.7	13.0		2.3	
TL-1-1-46-47	46-47	1.96		0.20		9.6	-26.8		-26.6					
TL-1-1-48-49	48-49	1.93	2.14	0.19	0.23	9.8	-26.9		-27.0		10.1	10.1	1.4	1.3
TL-1-1-50-52	50-52	2.46		0.22		11.2	-27.1		-26.8					
TL-1-1-55	55.0	2.99		0.33		9.0	-27.2		-26.4		17.5		2.4	
TL-1-1-57.5	57.5													
TL-1-1-60	60.0	2.22		0.23		9.8	-27.0		-26.3				2.5	
TL-1-1-62.5	62.5	1.40		0.15		9.5	-26.9		-26.3		16.0			

TL-1-1-65	65.0	2.19	1.80	0.21	0.19	9.8	-26.6		-26.0			2.0	2.1
TL-1-1-67.5	67.5	1.67	1.20	0.18	0.12	9.7	-26.8		-26.5		16.1		
TL-1-1-70	70.0	1.81		0.22		8.2	-27.1		-26.2			2.7	2.4
TL-1-1-72.5	72.5	1.97		0.20		9.9	-27.2		-26.7		16.4		
TL-1-1-75	75.0	2.38		0.22		10.6	-27.5		-27.2			2.6	
TL-1-1-77.5	77.5	2.04	2.82	0.20	0.29	9.9	-27.6		-26.3		14.5		
TL-1-1-80	80.0	2.29	2.54	0.21	0.22	11.2	-27.6		-26.4			2.4	
TL-1-1-82.5	82.5	2.59		0.25		10.4	-27.6		-27.6		13.0		
TL-1-1-85	85.0	2.41		0.24		10.1	-27.6		-26.2			2.5	
TL-1-1-87.5	87.5	2.17	2.28	0.23	0.23	9.8	-27.3		-26.5		17.3		
TL-1-1-90	90.0	2.41		0.24		10.2	-27.8		-27.6			2.4	
TL-1-1-92.5	92.5	2.17		0.21		10.6	-27.3		-26.0		13.6	12.6	
TL-1-1-95	95.0	2.07		0.20		10.3	-27.3		-26.5			2.8	
TL-1-1-97.5	97.5	2.37		0.23		10.3	-27.2		-27.1		17.5		
TL-1-1-100	100.0	2.32	2.59	0.22	0.24	10.6	-27.3		-26.3			1.8	1.9
TL-1-1-102.5	102.5	1.96		0.21		9.3	-27.0		-27.4		16.4		
TL-1-1-105	105.0	1.65		0.18		9.4	-27.0	-27.1	-27.5			2.1	2.0
TL-1-1-107.5	107.5	1.50		0.16		9.6	-27.2		-26.8	-26.6	12.0	12.4	
TL-1-1-110	110.0	1.76		0.18		10.0	-27.0		-26.7			2.7	
TL-1-1-112.5	112.5	1.95	1.97	0.19	0.19	10.2	-27.1		-26.3		16.6		
TL-1-1-115	115.0	1.83		0.18		10.4	-27.4		-26.8			2.6	2.2
TL-1-1-117.5	117.5	2.45		0.21		11.7	-27.4		-30.2	-30.3	17.1		
TL-1-1-120	120.0	1.97		0.18		10.8	-27.5		-26.3			2.6	
TL-1-1-122.5	122.5	1.77		0.18		10.0	-27.5						
TL-1-1-125	125.0	1.47	1.46	0.13	0.14	10.8	-27.4		-26.6			2.7	
TL-1-1-127.5	127.5	2.16		0.20		10.7	-27.5		-26.6		17.7		
TL-1-1-130	130.0	1.51		0.16		9.5	-27.3		-26.1			2.6	
TL-1-1-132.5	132.5	1.72		0.16		11.0	-27.4		-26.8		17.8		
TL-1-1-135	135.0	2.46		0.20		12.1	-27.5		-26.7			2.5	
TL-1-1-137.5	137.5	1.94	1.94	0.18	0.19	10.5	-27.6		-26.7		18.9		
TL-1-1-140	140.0	1.33		0.14		9.5	-27.5		-26.8			2.6	
TL-1-1-142.5	142.5	1.86		0.18		10.4	-27.4		-26.2		17.4		
TL-1-1-152.5	152.5	1.65		0.16		10.4	-27.4		-26.6		16.6	3.0	
TL-1-1-155	155.0	1.82		0.18		10.2	-27.7		-27.0				
TL-1-1-157.5	157.5	1.72	1.69	0.16	0.18	10.2	-27.8		-26.8		14.2	3.2	
TL-1-1-160	160.0	1.70		0.16		11.0	-27.8		-26.5				

TL-1-1-162.5	162.5	1.53		0.14		10.7	-27.4		-27.4		17.3		3.1	
TL-1-1-165	165.0	1.64		0.15		10.7	-27.7		-27.1					
TL-1-1-167.5	167.5	1.83		0.16		11.5	-27.8		-26.2		18.1		3.2	3.4
TL-1-1-170	170.0	1.33	1.41	0.13	0.13	10.7	-27.5		-27.2					
TL-1-1-172.5	172.5	1.57		0.13		11.6	-27.4		-26.6		15.0		3.8	
TL-1-1-175	175.0	1.97		0.17		11.6	-28.2		-26.1					
TL-1-1-177.5	177.5	2.72		0.22		12.6	-28.4		-27.5		17.5		3.9	
TL-1-1-180	180.0	5.00		0.41		12.1	-31.0		-29.3					
TL-1-1-182.5	182.5	4.68	4.50	0.37	0.37	12.3	-30.9		-28.6		14.7		4.0	
TL-1-1-185	185.0	3.25		0.26		12.6	-30.6		-30.1					
TL-1-1-187.5	187.5	7.09		0.53		13.5	-31.4		-29.9	-30.0	13.0		4.5	
TL-1-1-190	190.0	2.12		0.18		11.7	-29.0		-34.4	-34.0	17.3	18.2		
TL-1-1-192.5	192.5	9.06		0.63		14.4	-31.9		-31.6		15.8		4.6	
TL-1-1-195	195.0	10.48		0.74		14.3	-32.1	-32.4	-32.5					
TL-1-1-196.5	196.5	10.53		0.67		15.6	-30.9		-30.3		13.8		3.9	
TL-1-1-199.5	199.5	28.50		1.53		18.6	-30.2		-29.7		8.8			
TL-1-1-202.5	202.5	26.67		1.54		17.3	-30.8		-31.1		9.1		4.0	
TL-1-1-205	205.0	26.25	28.37	1.47	1.60	17.8	-30.8		-30.9					
TL-1-1-207.5	207.5	25.59		1.43		17.9	-31.3		-31.5		10.9		3.8	
TL-1-1-210	210.0	21.85		1.29		16.9	-31.0		-30.9					
TL-1-1-212.5	212.5	21.50		1.32		16.3	-31.3		-31.4		7.7		4.3	4.8
TL-1-1-215	215.0	18.40		1.15		16.0	-31.2		-30.8					
TL-1-1-218.5	218.5	0.58	0.58	0.05	0.06	10.0	-25.7		-27.3		11.9			

TL-5-1 Sediment Core Data

Sample	Depth (cm)	C (%)			N (%)			C:N	bulk-$\delta^{13}C$ (PDB)	cell-$\delta^{13}C$ (PDB)		cell-$\delta^{18}O$ (SMOW)	
TL-5-1-0.5	0.5	2.12			0.28			7.6	-28.2	-24.1			
TL-5-1-4.5	4.5	3.21			0.30			10.7	-28.7	-27.1		12.9	
TL-5-1-9.5	9.5	2.56			0.18			14.3	-28.1	-25.3			
TL-5-1-14.5	14.5	3.44			0.25			13.8	-27.8	-25.5		11.6	
TL-5-1-19.5	19.5	1.21	1.83		0.08	0.12		14.7	-27.4	-24.0	-25.0		
TL-5-1-25	25	2.56	2.23	1.87	0.10	0.14	0.11	19.1	-27.4	-25.9		12.1	11.0
TL-5-1-35	35	0.80			0.06			12.5	-27.1	-24.2			
TL-5-1-40	40	0.80			0.06			12.5	-27.7	-26.8	-26.0	11.1	
TL-5-1-45	45	1.54			0.11			14.1	-27.3	-24.5			
TL-5-1-50	50	3.01	2.35		0.21	0.16		14.6	-27.6	-27.5		12.1	
TL-5-1-55	55	4.02	3.88	2.38	0.20	0.25	0.16	16.9	-27.7	-26.3			
TL-5-1-60	60	2.29			0.17			13.5	-27.6	-27.4		12.5	
TL-5-1-65	65	3.22			0.23			14.0	-26.8	-26.0			
TL-5-1-70	70	2.31			0.14			16.5	-27.4	-26.6		11.6	
TL-5-1-75	75	2.38	1.98		0.18	0.16		13.0	-27.7	-26.1			
TL-5-1-80	80	3.28	2.32		0.26	0.23		11.4	-27.7	-26.9		13.6	
TL-5-1-85	85	3.29			0.21			15.5	-27.6	-25.8			
TL-5-1-90	90	2.22			0.16			13.8	-27.7	-27.1		12.8	12.4
TL-5-1-95	95	2.02			0.16			12.9	-27.6	-25.8			
TL-5-1-100	100	2.01	2.52		0.15	0.18		13.5	-27.9	-27.4		14.0	
TL-5-1-105	105	2.29			0.18			13.0	-27.9	-26.3			
TL-5-1-110	110	2.36			0.18			13.5	-27.9	-27.6		15.3	
TL-5-1-115	115	3.13			0.23			13.5	-28.2	-26.5			
TL-5-1-120	120	3.50			0.31			11.4	-28.4	-27.8		15.5	
TL-5-1-132.	132.5	2.71	2.68		0.23	0.22		12.0	-28.8	-26.1			
TL-5-1-135	135	4.13			0.37			11.3	-28.7	-27.7		15.5	
TL-5-1-140	140	1.75			0.13			13.0	-27.6	-25.7			
TL-5-1-145	145	5.00			0.42			11.9	-27.6	-28.6		16.5	15.5
TL-5-1-150	150	3.48			0.29			11.9	-29.0	-26.9			
TL-5-1-155	155	4.83			0.41			11.9	-29.4	-28.7		16.0	

TL-5-1-160	160	3.53	3.42	0.30	0.29	11.7	-28.9		-27.0			
TL-5-1-165	165	5.92		0.55		10.7	-29.9		-29.1		16.4	
TL-5-1-170	170	6.73		0.62		10.8	-30.1		-27.3			
TL-5-1-175	175	5.95		0.52		11.5	-30.1		-28.7		15.4	
TL-5-1-180	180	3.83		0.34		11.4	-29.4		-28.0			
TL-5-1-185	185	4.42	4.48	0.39	0.38	11.6	-29.6		-29.1		14.6	
TL-5-1-190	190	6.42		0.55		11.6	-30.4		-29.9			
TL-5-1-190	195	3.88		0.30		12.9	-29.2		-27.9	-27.4	15.4	
TL-5-1-200	200	5.59		0.42		13.2	-30.3		-29.6			
TL-5-1-205	205	9.72		0.75		13.0	-30.7		-31.6		16.0	
TL-5-1-208.	208.5	5.60	5.67	0.41	0.42	13.6	-29.6		-29.0			
TL-5-1-232	232	4.29		0.33		13.1	-29.8		-28.4		14.0	14.3
TL-5-1-235	235	4.12		0.30		13.8	-29.4		-28.0			
TL-5-1-240	240	4.69		0.36		13.0	-31.0		-28.7		14.8	
TL-5-1-245	245	7.12		0.60		11.9	-30.9		-32.1			
TL-5-1-250	250	6.32	6.19	0.54	0.53	11.6	-31.3		-32.6	-32.0	15.2	
TL-5-1-255	255	9.47		0.81		11.7	-31.3		-32.1			
TL-5-1-260	260	4.40		0.37		11.9	-30.3		-30.0		16.4	15.7
TL-5-1-265	265	5.13		0.44		11.5	-31.4		-30.9			
TL-5-1-270	270	3.07		0.26		11.6	-30.5		-29.2		14.2	
TL-5-1-275	275	5.32	5.31	0.46	0.46	11.5	-31.5		-30.4			
TL-5-1-280	280	2.92		0.24		12.1	-30.1		-30.0		13.5	
TL-5-1-285	285	4.44		0.38		11.6	-31.1		-29.7			
TL-5-1-290	290	3.99		0.35		11.3	-30.7		-32.0		15.6	16.9
TL-5-1-295	295	1.30		0.10		12.5	-26.6	-26.6	-25.2	-26.0		
TL-5-1-300	300	3.58		0.32		11.3	-30.2		-29.1		14.2	
TL-5-1-305	305	1.29		0.14		9.0	-27.6		-25.8			
TL-5-1-310	310	0.94		0.10		9.3	-26.9		-25.9		12.6	
TL-5-1-315	315	1.32		0.11		11.8	-27.0		-25.0			
TL-5-1-320	320	2.00		0.19		10.5	-29.1	-29.1	-28.1		13.3	
TL-5-1-325	325	1.49	1.45	0.14	0.14	10.5	-27.2		-25.4			
TL-5-1-332	332	2.06		0.18		11.2	-28.9		-28.0		13.6	
TL-5-1-335	335	2.16		0.18		12.2	-28.8		-26.8			
TL-5-1-340	340	1.09		0.11		10.0	-26.4	-26.2	-25.2		15.1	15.9
TL-5-1-345	345	3.87		0.37		10.5	-31.0	-31.3	-31.4	-30.1		
TL-5-1-350	350	1.50	1.47	0.14	0.14	10.8	-27.8		-26.4		14.3	

TL-5-1-355	355	1.04		0.11		9.8	-26.4	-26.5	-25.1		
TL-5-1-360	360	1.39		0.13		10.7	-28.2		-25.9	14.0	13.7
TL-5-1-370	370	4.35		0.35		12.6	-30.8	-29.5	-27.4		
TL-5-1-375	375	1.31		0.13		9.9	-26.1		-25.0	16.9	
TL-5-1-380	380	1.11	1.12	0.10	0.10	11.4	-26.5		-25.0		
TL-5-1-385	385	1.99		0.17		11.9	-27.7		-25.8	15.3	
TL-5-1-390	390	11.19		0.73		15.4	-26.6		-26.2		
TL-5-1-395	395	10.60		0.69		15.3	-26.4		-25.2	12.5	
TL-5-1-400	400	8.50		0.49		17.5	-26.6		-26.3		
TL-5-1-415	415	6.58		0.43		15.3	-26.6		-25.2	12.9	
TL-5-1-419	419	2.50	1.61	0.16	0.11	15.3	-25.7		-25.6		

LS-9-3 Sediment Core Data

Sample	Depth (cm)	C (%)		N (%)		C:N	bulk-$\delta^{13}C$ (PDB)		cell-$\delta^{13}C$ (PDB)		cell-$\delta^{18}O$ (SMOW)	
LS-9-3-0.5	0.5	11.36	11.01	0.74	0.73	15.2	-27.5	-27.9	-25.7		13.9	
LS-9-3-5.5	5.5	10.56		0.70		15.2	-28.3		-27.1		14.2	
LS-9-3-10.5	10.5	8.94		0.59		15.2	-28.0		-26.6		7.2	
LS-9-3-15.5	15.5	9.56		0.57		16.6	-27.7		-26.8		9.9	
LS-9-3-20.5	20.5	8.18		0.50		16.2	-27.1		-25.7	-25.4	6.9	
LS-9-3-25.5	25.5	7.35		0.51		14.5	-27.8		-26.5		8.1	
LS-9-3-30.5	30.5	9.32		0.57		16.4	-27.9		-26.7		8.5	
LS-9-3-35.5	35.5	7.88	9.79	0.51	0.59	16.1	-27.7	-28.0	-26.1		11.4	
LS-9-3-42.5	42.5	7.93		0.53		14.9	-27.8		-26.2		4.2	
LS-9-3-49.5	49.5	7.52		0.47		16.0	-27.1		-26.6		7.9	
LS-9-3-56.5	56.5	6.04		0.41		14.9	-26.8		-26.1		11.0	
LS-9-3-61	61	11.65		0.74		15.8	-27.9		-26.3		3.2	
LS-9-3-68	68	7.00		0.52		13.6	-27.4		-25.9		15.4	
LS-9-3-75	75	7.90		0.59		13.5	-27.6		-26.1		9.2	
LS-9-3-82	82	6.63	7.21	0.54	0.56	12.7	-28.2	-27.8	-25.2		14.5	
LS-9-3-89	89	8.32		0.54		15.5	-28.8		-26.2		8.6	
LS-9-3-96	96	7.26		0.71		10.3	-28.6		-25.4		8.7	
LS-9-3-103	103	7.56		0.61		12.5	-29.2		-26.0		16.2	12.5
LS-9-3-110	110	8.39		0.59		14.2	-28.8		-25.6		14.5	
LS-9-3-117	117	10.35		0.67		15.5	-29.0		-26.6	-26.6	12.2	
LS-9-3-124	124	7.95		0.59		13.5	-29.1		-26.0		8.3	
LS-9-3-131	131	8.53	8.49	0.71	0.71	12.0	-29.3	-29.2	-26.0		14.0	
LS-9-3-138	138	9.31		0.72		13.0	-30.1		-26.9		9.0	
LS-9-3-145	145	9.76		0.67		14.6	-29.2		-26.2		16.0	12.7
LS-9-3-152	152	11.67		0.91		12.9	-30.1		-26.5		10.8	
LS-9-3-159	159	12.40		0.90		13.7	-30.3		-28.0	-28.0	15.1	16.3
LS-9-3-166	166	9.22		0.72		12.9	-29.7		-26.8		12.4	
LS-9-3-173	173	7.10		0.66		10.8	-30.0		-26.6		15.3	
LS-9-3-180	180	6.77	6.96	0.49	0.52	13.6	-28.1	-28.3	-25.5		18.3	
LS-9-3-187	187	10.24		0.68		15.1	-28.8		-26.5		20.2	18.4

LS-9-3-194	194	11.38		0.86		13.2	-29.0		-26.3		17.6	
LS-9-3-201	201	8.47	11.51	0.69	0.96	12.1	-27.4	-27.6	-24.9		16.4	
LS-9-3-208	208	10.68		0.93		11.5	-28.8		-28.2	-27.9	16.0	
LS-9-3-215	215	8.91		0.75		11.9	-29.5		-26.5		17.6	
LS-9-3-222	222	9.59		0.78		12.3	-28.7		-27.1		12.9	
LS-9-3-229	229	16.11		1.34		12.0	-28.4		-27.0		10.8	
LS-9-3-236	236	12.32		0.89		13.9	-28.3		-26.0		10.9	
LS-9-3-243	243	12.05		1.08		11.2	-28.6		-26.0		20.8	20.7
LS-9-3-249	249	9.60	9.68	0.75	0.76	12.7	-29.4	-29.5	-26.1	-25.4	16.2	
LS-9-3-256	256	11.20		0.84		13.3	-29.9		-26.8		14.8	
LS-9-3-263	263	14.24		1.10		13.0	-30.4		-28.4		12.4	
LS-9-3-270	270	8.48		0.79		10.8	-26.5		-24.5		15.2	
LS-9-3-277	277	8.80		0.71		12.3	-28.2		-25.7		15.5	
LS-9-3-284	284	12.60		0.94		13.5	-27.9		-25.9		16.9	
LS-9-3-291	291	11.49		0.87		13.2	-27.8		-25.4		13.3	
LS-9-3-298	298	11.57	13.16	0.83	0.90	14.3	-31.2	-31.4	-27.6		10.9	
LS-9-3-305	305	6.12		0.53		11.6	-29.0		-27.0		14.1	
LS-9-3-315.5	315.5	1.45		0.10		15.1	-24.4		-23.0	-23.4	17.1	17.6
LS-9-3-326	326	3.26		0.16		20.8	-23.2		-22.6		18.9	
LS-9-3-336.5	336.5	7.94		0.74		10.7	-27.0		-24.6		14.8	
LS-9-3-354	354	2.50		0.15		16.5	-23.3		-22.3		19.1	

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