ISOTOPIC RECORDS OF METEOROLOGICAL AND ATMOSPHERIC CONDITIONS FROM SUB-ANNUALLY RESOLVED TREE-RING CELLULOSE, PRECIPITATION, AND SURFACE WATERS

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In Partial Fulfillment of the Requirements for the Degree of Master of Science in the Department of Geological Sciences
University of Saskatchewan
Saskatoon

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ISOTOPIC RECORDS OF METEOROLOGICAL AND ATMOSPHERIC CONDITIONS FROM SUB-ANNUALLY RESOLVED TREE-RING CELLULOSE, PRECIPITATION, AND SURFACE WATERS

In recent decades, there has been increased global concern about observed climate change; however for future climatic impacts and anthropogenic forcings of climate change to be realistically predicted, natural climate variability in the past needs to be better understood. The aim of this research is to develop quantifiable proxy records of past climate change through the calibration of isotope values in modern surface waters and tree-ring cellulose with meteorological and atmospheric records. Terrestrial proxy records that utilize oxygen and hydrogen isotope values to reconstruct paleoclimatic and paleohydrologic conditions are limited by a paucity of data on the modification of surface water isotope values prior to sequestration into proxy material. To address this gap in our knowledge and determine the most appropriate study sites, this research focuses on...
isotopic records preserved in surface water reservoirs, precipitation, and tree-ring cellulose. In the first study, $\delta^D$, $\delta^{18}O$, and deuterium-excess values were determined for lakes and rivers from Tasmania, southeastern Australia.

The second focus of this research was to calibrate the $\delta^{18}O$, $\delta^D$, and $\delta^{13}C$ values of tree-ring cellulose from North America with instrumental records. A new high-resolution sampling procedure that uses a robotic micromilling device to very precisely map and sample along growth rings in trees is discussed. Additionally, a seasonally resolved (early/late wood) 110-year record of $\delta^{18}O$ values from tree-ring $\alpha$-cellulose from spruce species ($Picea mariana$ and $P. glauca$) from east-central Saskatchewan, Canada is compared to growing season precipitation $\delta^{18}O$ values, temperature, and relative humidity. The $\delta^{18}O$ time series from $\alpha$-cellulose display a high correlation with growing season precipitation isotope values ($r = 0.86$). $\delta^{18}O$ $\alpha$-cellulose time series from a white spruce ($Picea glauca$) also records seasonal changes in atmospheric circulation associated with the position of the circumpolar vortex and dominate modes of atmospheric variability such as the North Atlantic Oscillation and Pacific Decadal Oscillation.

Keywords: $\delta^{18}O$, $\delta^D$, $\delta^{13}C$, surface water, hydrology, paleoclimate, tree-ring cellulose, micromill, high-resolution, atmospheric circulation
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CHAPTER 1. INTRODUCTION

1.1 Climate Overview and Motivation

Increasing global concern about observed climate change in recent decades has prompted a great deal of debate as to whether these changes are due to anthropogenic or natural forcings. In order for future climatic impacts and anthropogenic forcings of climate change to be realistically predicted, there is a great need for an examination of natural climate variability in the past (Oldfield and Alverson, 2003). Instrumental records of meteorological conditions cover, at most, the last few hundred years of Earth history. Additionally, poor geographical distribution of data stations, especially in the Southern Hemisphere and the high-latitudes of the Northern Hemisphere, present a significant weakness in the present understanding of natural climate variability (Ciais et al., 1992; Gibson, 2001, Schindler and Donahue, 2006).

Stable isotope values in natural systems have been demonstrated to reliably record a variety of meteorological and atmospheric parameters. A wide range of materials contain isotope proxies, including lacustrine sediment (e.g. Kirby et al., 2001), speleothems (e.g. McDermott et al., 2001), ice cores (e.g. Alley et al., 2003), bone phosphate (e.g. Zazzo et al., 2006), biogenic carbonate (e.g. Wurster and Patterson, 2001) and tree-rings (e.g. Anderson et al., 2002, McCarroll and Loader, 2004). However, isotope values recorded in tree-rings offer a significant advantage over other terrestrial isotope proxies in that annual rings in tree stem cellulose provide unambiguous age control (Waterhouse et al., 2002, Saurer, 2003). This perfect annual resolution facilitates direct comparison and calibration of tree-ring isotope time series (such as \( \delta^{18}O \), \( \delta D \), and \( \delta^{13}C \)) with instrumental records of air temperature, relative humidity, precipitation amount, the \( \delta^{18}O/\delta D \) value of precipitation, and atmospheric circulation (Anderson et al., 2002; Saurer, 2003). Trees are abundant in many terrestrial environments and long (>5,000 years) tree-ring width chronologies have been developed in Europe (e.g. Eronen et al., 2002; Grudd et al., 2002), North America (e.g. Baillie, 1995), and Australia (Cook et al., 1992). Isotope values in tree cellulose provide additional information that is often not recorded in tree-ring width measurements, and therefore can potentially be used to
develop precise records of meteorological and environmental conditions (Saurer, 2003; McCarroll and Loader, 2004). Through development of tree-ring isotope time series, and calibration of these time series with instrumental data, it is possible to extend the (spatial and temporal) resolution of meteorological and atmospheric records.

Additionally, reconstruction of paleoclimate records contained in tree-ring cellulose hydrogen and oxygen isotope proxies is limited by a paucity of meteoric water $\delta^{18}$O/$\delta^{D}$ data and information on the modification of $\delta^{18}$O and $\delta^{D}$ values in water throughout the hydrologic cycle (Kendall and Coplen, 2001). In order to better interpret modern and paleoclimatic conditions via tree-ring cellulose H and O isotope proxies that record meteoric and surface waters it is necessary to understand the causes of geographic variability in $\delta^{D}$ and $\delta^{18}$O values of local meteoric waters. It is therefore beneficial to document the patterns of geographic variation in meteoric waters for each region of interest in order to document the concordance with and discordance from global meteorological/hydrologic models (Darling, 2004).

1.2 Methodology

Research discussed herein focuses on the use of $\delta^{18}$O, $\delta^{D}$, and $\delta^{13}$C values in tree-ring cellulose as records of environmental change. The body of the research is divided into three main chapters (2 – 4), and each of these chapters is a separate article for peer-reviewed publication. Each article consists of original work by the author with supervision by the author's co-supervisors. Chapter 2 introduces the theory behind $\delta^{18}$O and $\delta^{D}$ values in meteoric waters and the modification of these values in surface water reservoirs through case study of surface waters collected by the author from Tasmania, Australia in the summer of 2004. Chapter 3 then shifts to North America and focuses on reconstructing time series of $\delta^{18}$O, $\delta^{D}$, and $\delta^{13}$C values in tree-ring cellulose from four modern tree species (*Picea glauca*, *P. mariana*, *Larix laricina*, and *Fagus grandiflora*) from central Saskatchewan, Canada and New York, USA. Chapter 3 also describes a high-resolution sampling method for tree-ring isotope studies that has been implemented for the first time by the author. Chapter 4 brings together the concepts discussed in Chapters 2 and 3 by using the $\delta^{18}$O time series of two spruce species (*Picea glauca*, *P.
mariana) from central Saskatchewan to reconstruct the $\delta^{18}$O values of growing season precipitation. Additionally, Chapter 4 discusses the relationship between the $\delta^{18}$O time series and meteorological and atmospheric conditions for the 20th century. Although the study areas in Chapter 2 and Chapters 3-4 vary significantly in geographical location and physical characteristics, all three studies examine different aspects of isotope records as climate proxies.

1.3 References


Kirby, M.E., Mullins, H.T., Patterson, W.P., and Burnett, A.W., 2002. Lacustrine isotopic evidence for multidecadal natural climate variability related to the circumpolar vortex over northeast United States during the past millennium, Geology 29: 807-810.


CHAPTER 2. SURVEY OF OXYGEN AND HYDROGEN ISOTOPE VALUES IN TASMANIAN PRECIPITATION AND SURFACE WATERS

2.1 Abstract

Terrestrial proxy records that utilize oxygen and hydrogen isotope values to reconstruct paleoclimatic and paleohydrologic conditions are limited by a paucity of data that quantify modification of surface water isotope values prior to sequestration into proxy material. To address this gap in our knowledge and determine the most appropriate study sites and proxy materials, $\delta^D$, $\delta^{18}O$, and deuterium-excess (d-excess) values of lakes and rivers ($n=72$) from Tasmania, southeastern Australia, are presented. $\delta^D$ and $\delta^{18}O$ values of surface waters are compared to precipitation isotope values from Cape Grim, northwestern Tasmania from 1979 to 2000 (IAEA/WMO, 2001; $n=195$) and from Margate, southeastern Tasmania, from 1994 to 2000 ($n=598$; Treble et al, 2005). Local surface water lines and local meteoric water lines are defined by the relationships $\delta^D = 5.90 (\pm 0.19) * \delta^{18}O + 1.48 (\pm 1.32) (r = 0.93)$ and $\delta^D = 6.61 (\pm 0.16) * \delta^{18}O + 5.28 (\pm 0.63) (r = 0.95)$, respectively. Surface water isotope values are most significantly correlated with sample/stream head elevation and more weakly correlated with latitude/longitude. Tasmania is divided by northwest-southeast trending mountains that exert a strong orographic effect on Tasmanian precipitation amount and subsequent isotope values. Surface water isotope values record an altitude effect of 3‰/100m for $\delta^D$ and 0.4‰/100m for $\delta^{18}O$. This study provides the first regional analysis of isotope values of Tasmanian surface waters. Interpretation of proxy records of climate change in Tasmania and elsewhere will benefit from this type of surface water survey because it permits identification of the most appropriate study sites and proxy materials.

2.2 Introduction

Oxygen and hydrogen isotope values of a wide variety of materials including speleothems, lacustrine sediment, ice cores, tree-ring cellulose and terrestrial organic material have been demonstrated to be reliable paleoclimatic proxies. Similarly, oxygen
and hydrogen isotopes are used as tracers in animal migration studies (Hobson et al., 2004), wildlife forensics (Bowen et al., 2005), and mummified human remains (Sharp et al., 2003). A common goal of these studies is to characterize the hydrogen and oxygen isotope value of the source water, and consequently the rainfall that contributed to this water body (Darling, 2004). Although isotope values of global precipitation have been characterized by the IAEA/WMO and modeled by others (e.g. Bowen and Revenaugh 2003), a complete understanding of precipitation isotope values is limited by the low density of sampling stations. Additionally, the original isotope value of precipitation can be modified in surface, soil, and groundwater reservoirs prior to preservation by proxy material (Darling, 2004). Treble et al. (2005) note that to date there have been few in-depth studies of the modification and representation of δD and δ18O values throughout the hydrologic cycle in the Australian region.

Isotope proxies used in the reconstruction of paleoclimate and as tracers of geographic origin are thus limited by a paucity of meteoric water isotope data and information on the isotopic modification of water in the hydrologic cycle (Kendall and Coplen, 2001). In order to better interpret modern and paleoclimatic conditions via proxies that record meteoric and surface waters it is necessary to understand the nature of spatial isotope variability in these waters. It is therefore beneficial to generate records for each region of interest that characterize the concordance with and discordance from global precipitation/hydrologic models.

Herein we present the spatial variability of δ18O and δD values of surface waters and precipitation in Tasmania, Australia as a means to characterize the isotope values of water incorporated into proxies such as lake sediment, trees and speleothems. Similar studies have been conducted in the UK (Darling 2004), Ireland (Diefendorf and Patterson, 2005), North America (Kendall and Coplen, 2001), and Central America (Lachniet and Patterson, 2002, 2006); however, this is the first study of surface water isotope hydrology in Tasmania. Surface water isotope values presented in this study yield information on lake water residence time, and regional hydrologic processes and serve as a useful tool in selecting appropriate locations for gathering climate change proxy materials.
2.3 Site Description

The island of Tasmania is bordered by the Tasman Sea and the Southern Pacific Ocean to the east and the Southern Ocean to the south and west. The Bass Straight to the north separates Tasmania from mainland Australia. The island is divided by northwest-southeast trending mountains (Fig. 2.1) that exert a strong orographic influence on rainfall patterns, such that the west coast receives more than 3000 mm of precipitation per year whereas the central and eastern regions of the island are limited to less than 400mm per year (Fig. 2.2, Treble et al., 2005; Commonwealth of Australia Bureau of Meteorology, 2005). Precipitation in Tasmania is derived from cyclonic systems and associated fronts embedded in the southern mid-latitude circumpolar vortex (also referred to as the westerly front), with most of the storm systems tracking from the Southern Ocean in the west (Treble et al., 2005). The high pole-to-equator temperature pressure gradients between the South Pole and tropical Indian Ocean, and the lack of land between 60°S and 40°S latitude result in exceptionally strong westerly winds in the Southern Hemisphere (Shulmeister et al., 2004). Cyclonic activity and therefore precipitation in Tasmania is greatest in the austral winter (June – August) when the mid-latitude circumpolar vortex is positioned between 60°S and 35°S (Burnett and McNicoll, 2000). During the austral winter a persistent high-pressure system is centered over the Australian continent extending from the Indian Ocean to the Western Pacific between 20°S and 40°S, whereas the Tasman Sea and Southern Ocean to the east of Tasmania are dominated by a prevalent low pressure system (Struman and Trapper, 1996).

During the austral summer (December – February) the subtropical high moves southward toward the Great Australian Bight and Tasmania, deflecting the circumpolar vortex southward thereby causing the westerlies and cyclonic activity to be concentrated south of 60°S (Burnett and McNicoll, 2000). The result is strong seasonal variation in air temperature and precipitation characterized by the meteorological station in Cape Grim, Tasmania (Figure 2.3). The relationship between Tasmanian precipitation/climate and the position of the westerly belt renders Tasmania ideal for characterizing atmospheric variability in the mid latitudes of the Southern Hemisphere. In addition, the position and strength of the westerly storm tracks are constrained by changes in sea surface temperatures related to Antarctic and low-latitude climate parameters such as El
Figure 2.1. Sample locations and sample numbers for Tasmanian surface water samples. Elevation contours illustrate the altitudinal divide through the center of the island. The IAEA/ WMO GNIP station at Cape Grim is located in the northwest corner of the island. Gray area denotes the winter rainfall zone of southeast Australia.
Figure 2.2. Precipitation patterns in Tasmania are strongly influenced by the orographic effects of the mountain ranges with more than 3000mm per year falling in the western side of the island and less than 400mm per year east of the mountains. Streamhead locations for surface water samples are also shown.
Figure 2.3. Surface temperature and precipitation amount recorded at Cape Grim are inversely related and display a strong seasonal signal. The lowest temperatures and greatest precipitation amounts are observed during austral winter (May - September).
Niño/Southern Oscillation (ENSO) and Indian Monsoon climate dynamics (Shulmeister et al., 2004).

Long-term terrestrial records of Southern Hemisphere climate are scarce. Consequently, there is a significant need to develop such records if we are to gain a better understanding of future climate change in the southern hemisphere (Villalba, 2000). Tasmania is well-positioned for the development of these kinds of records, having abundant tree-ring width chronologies covering the past few millennia (e.g. Cook et al. 1992, 2000), as well as cave and lake deposits that extend back prior to the last Ice Age (e.g. Goede et al., 1998; Calhoun, 2000).

2.4 Methods

Surface water samples were collected in July 2004 from Tasmania (Fig.2.1) as well as other areas in southeast Australia’s winter rainfall zone (New South Wales, Victoria, and South Australia). Water samples were collected in 30 ml Nalgene® bottles and sample locations determined using a Magellan® GPS and Tasmanian Government 1:250,000 topographic maps (TASMAP Tasmanian Government, 2000).

δD and δ¹⁸O analyses were conducted using a continuous flow pyrolysis technique at the Saskatchewan Isotope Laboratory. Water samples were injected in 1 µl aliquots into a Thermo Finnigan TC/EA containing a ceramic column lined with a glassy carbon tube and packed with glassy carbon fragments. Water was pyrolyzed at 1450ºC to H₂ and CO and was separated via a gas chromatograph. Gases were subsequently passed to a Conflo III for He dilution prior to analysis. Isotope ratios of D/H and ¹⁸O/¹⁶O were determined via continuous flow using a Thermo Finnigan Delta Plus XL mass spectrometer relative to H₂ and CO reference gases using the dual inlet port. Four internal standards calibrated with VSMOW, VSLAP, and GISP were used to normalize water isotope values. Sample values were corrected using a two-point calibration with two internal standards (δD/δ¹⁸O values of -171/6.1‰ and -22/11.8‰) and corrected for internal drift using a third internal standard (δD/δ¹⁸O values of -49/6.2‰). Intra-run drift was less than 2‰ for δD and 0.2‰ for δ¹⁸O. The fourth internal standard (δD/δ¹⁸O values of -81/10.8‰) was used to test inter-run reproducibility. Sample precision is ±2.0‰ for δD and ±0.2 ‰ for δ¹⁸O (1σ, n=48) with all values reported relative to
VSMOW. Conductivity of surface water samples was measured using a Radiometer Copenhagen CDM 80 Conductivity Meter calibrated at 25°C.

2.5 Isotope Values of Tasmanian Precipitation

A number of climatological and physical processes result in fractionation of hydrogen and oxygen isotope values of precipitation. These effects cause the progressive fractionation of water vapor in air masses predicted by Rayleigh distillation \((R=R_0\alpha^{-1})\); Dansgaard, 1964). Temperature is one of the primary factors that constrain the rainout process (Dansgaard, 1964); however, studies of \(\delta^{18}O\) values in Tasmanian precipitation have revealed little correlation between \(\delta^{18}O\) values of precipitation and surface temperature at the time of precipitation. Instead, \(\delta^{18}O\) values of Tasmanian precipitation appear to be best correlated with the amount of precipitation and seasonal variations in the westerly storm track (Treble et al., 2005). Studies of tropical precipitation have observed similar discrepancies between temperature and isotope values of precipitation (e.g. Fricke and O'Neil, 1999; Rozanski, 1993; Lachniet and Patterson, 2002, 2006). Although Tasmania (40 – 45ºS) is located well outside of the tropics, the large continental desert in western Australia deflects tropical air masses south resulting in a low latitudinal gradient in isotope values of precipitation over the Australian continent and Tasmania (Bowen and Revenaugh, 2003). In Tasmania, an elevation change of more than 1200 m exerts a strong orographic effect on the amount and isotope value of precipitation. Changes in topography force air upward resulting in adiabatic cooling of the air mass, driving the rainout process that produces a change in the \(\delta\)D (\(\delta^{18}O\)) in precipitation of –1 to –4‰ (–0.15 to – 0.5‰) per 100m increase in elevation (Clark and Fritz, 1997).

2.5.1 IAEA/WMO Precipitation Data

The International Atomic Energy Association and the World Meteorological Organization have operated a meteorological station in Cape Grim (40º41'S, 144º41'E; 94m elev.) in the northwestern corner of Tasmania as part of the Global Network of Isotopes in Precipitation (IAEA/WMO, 2001). The station was in operation from 1979 to 2000; however, data on precipitation amount, monthly weighted \(\delta\)D and \(\delta^{18}O\) values, and
temperature were not recorded for periods of months to years in the dataset. Weighted monthly means have been calculated for all months for which sufficient data exist and display a distinct seasonal cycle in both δD and δ¹⁸O values with highest values during austral summer and lowest values during austral winter (Fig 2.4). Weighted monthly average δD values range from −32‰ in June to −13‰ in December, whereas δ¹⁸O values range from −5.1‰ in June to −2.1‰ in December (IAEA/WMO, 2001). A linear regression of the weighted monthly values \(n = 195\) in δ¹⁸O/δD space yields a local meteoric water line (LMWL) with the following equation:

\[
\delta D = 6.61 \pm 0.16 \times \delta ^{18}O + 5.28 \pm 0.63 \quad \text{with} \quad r = 0.95.
\]

The Cape Grim LMWL has a lower slope and intercept than the Global Meteoric Water Line (GMWL), defined by \(\delta D = (8.20 \pm 0.07) \times \delta ^{18}O + (11.27 \pm 0.65)\) (Rozanski et al., 1993), indicating that δ¹⁸O and δD values are influenced by secondary evaporation during precipitation (Fig 2.5). Kinetic evaporation of precipitation falling through the air column is primarily controlled by relative humidity; high relative humidity at Cape Grim (~80% annual average) causes the Cape Grim LMWL to have a \(\delta D\) of 6.61 (Clark and Fritz, 1997).

The deuterium-excess \(d = \delta D - 8 \times \delta ^{18}O\) has been calculated for the Cape Grim data and also displays a strong seasonal signal (Fig. 2.6). The global average d-excess in precipitation is about 10‰, but varies on a regional scale with local evaporative effects on precipitation such as variations in relative humidity, air temperature, wind speed, and sea surface temperature in the vapor source region. Recycling of surface waters via evaporative contributions of moisture to precipitation increases d-excess values (Fröhlich et al., 2002). Cape Grim data exhibits the highest average monthly d-excess from April to October, peaking at 13‰ in August and decreasing to 7.1‰ in November. For Cape Grim precipitation, the seasonal variation in d-excess is primarily a result of increased westerly wind velocity over Tasmania and lower temperatures in oceanic vapor source regions during austral winter. Increased wind velocity causes greater evaporation of surface water in the Southern Ocean west of Tasmania, resulting in increased precipitation. The greater evaporation that occurs at the oceanic vapor sources during
Figure 2.4. Weighted monthly averages of $\delta^D$ and $\delta^{18}O$ values of precipitation at Cape Grim between 1979 and 2000 display a seasonal cycle with the highest isotope values occurring during austral summer (October - March) and lowest values during austral winter (April - September).
GNIP Precipitation (Cape Grim, TAS)
$\delta D = (6.61 \pm 0.16) \delta^{18}O + (5.28 \pm 0.63)$
$r = 0.95, n=195$

Tasmanian Surface Waters
$\delta D = (5.90 \pm 0.19) \delta^{18}O + (1.48 \pm 1.32)$
$r = 0.93, n=72$

*Rozanski et al. 1993

Figure 2.5. The LMWL constructed from the Cape Grim precipitation data (gray line) and SWL from Tasmanian surface water data (black) are shown with the GMWL (dashed) for comparison. The SWL displays a slightly lower slope than the LMWL indicating increased evaporation of surface water bodies as a whole.
Figure 2.6. Weighted monthly values of d-excess in Cape Grim precipitation data. Cape Grim data exhibit the highest average monthly d-excess from April to October, peaking at 13‰ in August and decreasing to 7.1‰ in November.
austral winter results in higher d-excess values in austral winter and low d-excess values during austral summer.

2.5.2 Synoptic Pattern in Precipitation

In a study of precipitation $\delta^{18}O$ values from Cape Grim and Margate (42°57'S, 147°19'E; 1176m elev.), Treble et al. (2005) demonstrate that $\delta^{18}O$ values of Tasmanian precipitation are forced by the position of mid-latitude circumpolar vortex. Daily precipitation samples were collected from Margate in southeastern Tasmania for a 5-year period (1994 to 2000) to characterize event-to-event variation in precipitation $\delta^{18}O$ values. Monthly weighted means were also compared to monthly $\delta^{18}O$ records from an IAEA/GNIP station at Cape Grim. In the precipitation data from Margate for the period between 1994 and 2000, Treble et al. (2005) observed similar average seasonal variation in $\delta^{18}O$ values of ~3‰ (-6.1‰ in June to -3.0‰ in December), with values approximately 1‰ lower at Margate than at Cape Grim due to rainout as westerly systems pass over the Tasmanian mountain range. However, daily precipitation $\delta^{18}O$ values demonstrate a greater event-to-event variability, manifested as a range in daily precipitation $\delta^{18}O$ values that range from ~0‰ to -11.5‰ between January 1994 and December 2000 (Treble et al., 2005). As is more commonly observed in tropical sites, there is little correlation between $\delta^{18}O$ values of precipitation and surface temperature. Rather, the correlation between $\delta^{18}O$ values and temperature appears to be an artifact of seasonal variability in precipitation amount forced by the position of the westerly belt. If the seasonal cycle is removed, there appears to be very little correlation between $\delta^{18}O$ values and surface temperature ($r = 0.12$ daily, $r = -0.07$ monthly). $\delta^{18}O$ values do, however, appear to demonstrate an inverse relationship with rainfall amount ($r = -0.35$ to -0.51; Treble et al., 2005).

Low $\delta^{18}O$ precipitation values at the Margate station correlate between high rainfall amounts that occur when the westerly track was shifted northward toward Tasmania. Lawrence et al. (1982) found a similar relationship between the position of cyclonic centers in the northern hemisphere circumpolar vortex and the isotope value of precipitation in New York State. When the mid-latitude vortex is positioned further south, Tasmania is located at the edge of the cyclonic activity and therefore receives
precipitation with higher $\delta^{18}O$ values. Due to the extreme convective processes and moisture recycling near the center of cyclonic low-pressure systems, precipitation that occurs near the centers of these systems will have a lower $\delta^{18}O$ value, whereas precipitation that occurs more distal to these low-pressure systems will have a higher $\delta^{18}O$ value. In addition, contribution of low latitude moisture will likely increase $\delta^{18}O$ values of precipitation.

When the mid-latitude circumpolar vortex is displaced to the south, high-pressure systems (warmer and drier air) move south along the east and west Australian coasts. In this scenario, precipitation consists of relatively more localized evaporation with higher $\delta^{18}O$ values than winter precipitation with values closer to that of seawater (~0‰; Treble et al, 2005). With the exception of the Cape Grim and Margate isotope data, however, there is little isotope data for Tasmanian precipitation and, to our knowledge these two sites provide the only isotope studies of precipitation on the island.

### 2.6 Tasmanian Surface Water: Results and Discussion

In order to gain a better understanding of hydrologic processes that influence isotope values of surface waters, we collected a suite of samples during the rainy season in July 2004 (Fig. 2.1) that provide a snapshot of isotope values of surface waters across Tasmania during the winter season (Appendix A). Rivers and other moving water bodies have comparatively short residence times and the relative effects of evaporation on these surface bodies is less than that on raindrops. Therefore riverine surface water samples are only slightly modified by evaporation and reflect, for the most part, the isotope values of precipitation averaged over short periods of time (Darling, 2004). Lakes and stagnant water bodies have a longer residence time and are therefore more significantly affected by evaporation. However, in regions with high relative humidity, evaporation has only a small effect on isotope values of lake water. In small or terminal lakes evaporation from the surface water body can greatly affect lake water isotope values, and thus significantly modify meteoric source isotope values (Gat, 1995).

$\delta D$ values range from $-56‰$ at Arthur's Lake (elev. 954m) in central Tasmania to $-3‰$ in the Forth River on the northern coast of Tasmania (elev. 6m). $\delta^{18}O$ values of surface water samples range from $-9.0‰$ in an alpine lake on Projection Bluff in central
Tasmania (elev. 1070m) to 0.4‰ in a highly evaporative pond at the headwaters of the Saltwater River in the Tasman Peninsula. Despite its name, the Saltwater River pond is at an elevation of 94m and δD/δ18O values likely reflect evaporative enrichment rather than seawater mixing.

2.6.1 Surface Water Lines and Data Correlations

Surface water lines (SWL) were calculated using a linear regression of δ18O and δD values in Tasmanian surface waters. For all surface water samples, the SWL is defined by δD = 5.90 (±0.19)*δ18O + 1.48 (±1.32) \( r = 0.93, n = 72 \) (Fig. 2.5). Surface waters are subject to a greater degree of evaporation than meteoric waters and therefore the lower slope and intercept of the Tasmanian surface waters are expected. Surface water values also fall at the lower range of Cape Grim precipitation values because surface waters were collected during austral winter when δ18O and δD values of Tasmanian precipitation are lower. Separate SWLs were calculated for lakes and rivers (Fig. 2.7), represented by the following equations:

a) Lakes and standing bodies of water

\[
\delta D = 6.25 (±0.41) \times \delta^{18}O - 0.06 (±2.09), \quad r = 0.98, \quad n = 12
\]

b) Rivers

\[
\delta D = 7.14 (±0.31) \times \delta^{18}O + 7.59 (±2.14), \quad r = 0.95, \quad n = 55
\]

Although they are not out of the range of isotope values recorded at Cape Grim, five surface samples (59, 71, 72, 75, 105) were excluded from SWL calculations and other comparisons because they appear to have abnormally high isotope values when compared to winter precipitation values. Samples 59 and 71 are stagnant bodies of water, and therefore likely reflect localized evaporative effects. Samples 72 and 75 were rivers from the extreme southeastern part of the island and likely reflect local evaporation effects as they flow through the drier region. For samples 71, 72, and 75 local evaporative effects are likely imprinted on the higher isotope value of meteoric water as air masses move across Tasmania (Treble et al., 2005). Samples 105 and 75 have been excluded because of tidal seawater (salinity ~35) mixing at the mouths of the Forth and Processor Rivers. Conductivity of these samples (59, 71, 72, 75, 105) was determined as a proxy for
Figure 2.7. δ¹⁸O and δD values of Tasmanian surface waters display a lower slope than the global and local meteoric water lines, reflecting the greater evaporation of surface water bodies. Lakes display greater evaporation than rivers, except for rivers in the extreme eastern part of the island (Prosser River and Cropping Creek). The eastern rivers as well as small-enclosed reservoirs (Saltwater River Pond and Highland Lake) plot below the meteoric water line as a result of evaporative effects on these water bodies. Saltwater mixing is likely in the Forth River.
salinity. Samples 59, 71, and 72 were significantly more saline compared to the average salinity for Tasmanian surface water samples, thereby suggesting increased evaporation of the water bodies. Samples 75 and 105 have relatively high salinity values of 22 and 31, respectively suggesting mixing with seawater (Table 2.1), therefore reaffirming the likelihood of seawater mixing in samples 75 and 105 (Linde, 2005).

When compared to physical and environmental parameters (Table 2.2), $\delta D/\delta ^{18}O$ values of surface waters are most significantly correlated with stream head elevation ($r = -0.51$ and $-0.55$ for $\delta D$ and $\delta ^{18}O$, respectively). Stream head elevation was calculated for each river sampled, while the sample elevation was used for lakes and stagnant bodies (Fig. 2.2). The regression of stream head/sample elevation with $\delta D/\delta ^{18}O$ values yields an altitude effect of $3‰/0.4‰$ per 100 m rise in elevation. After sample elevation, surface water $\delta D/\delta ^{18}O$ values correlate most strongly with latitude ($r = -0.44/-0.28$) and longitude ($r = -0.37/-0.24$), reflecting fractionation associated with rainout as storms move across the island from west to east. Surface water isotope values show no significant correlation with the estimated precipitation amount at the sample site or at the stream head location (Table 2.2). Surface water bodies serve to average the large degree of variability in isotope values within and between individual storm events. In addition, surface water samples were collected during the austral winter when the evaporative modification of surface waters is less than it would be during the warmer and drier summer months.

### 2.6.2 Deuterium excess

Deuterium excess (d-excess) values of surface waters can be used as an indicator of surface water recycling through evapotranspiration, as well as precipitation source. However, variations in d-excess values of surface waters are complicated and, at present, the theoretical processes affecting d-excess values have not been fully explored. Uncertainties in the interpretation of d-excess values are in part due to uncertainties ($<2‰$) associated with $\delta D$ measurements (Fröhlich et al, 2002). Tasmanian surface waters display d-excess values that range from $-9.3‰$ to $18.5‰$ with an average value of $12.3‰$ (Appendix A). The average value of $12.3‰$ is slightly higher than the global average value of $10‰$. However, the total range in d-excess values includes abnormally
Table 2.1. Salinity of Tasmanian surface waters.

<table>
<thead>
<tr>
<th>Sample Site</th>
<th>Sample #</th>
<th>Conductivity (mS/cm)</th>
<th>Salinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Highland Lake</td>
<td>59</td>
<td>0.43</td>
<td>0.1</td>
</tr>
<tr>
<td>Saltwater River Pond</td>
<td>71</td>
<td>1.25</td>
<td>0.4</td>
</tr>
<tr>
<td>Carlton River</td>
<td>72</td>
<td>1.18</td>
<td>0.4</td>
</tr>
<tr>
<td>Prosser River</td>
<td>75</td>
<td>34.6</td>
<td>21.6</td>
</tr>
<tr>
<td>Forth River</td>
<td>105</td>
<td>47.5</td>
<td>30.8</td>
</tr>
<tr>
<td>Ave. Tasmanian surface water</td>
<td>NA</td>
<td>0.05</td>
<td>&lt;0.1</td>
</tr>
</tbody>
</table>
Table 2.2. Correlations between surface sample $\delta D$, $\delta^{18}O$, and d-excess values and sample parameters.

<table>
<thead>
<tr>
<th></th>
<th>Latitude (S) (dec. deg.)</th>
<th>Longitude (E) (dec. deg.)</th>
<th>Sample Elevation (m)</th>
<th>Elevation of streamhead (m)</th>
<th>Estimated Mean Ann. Precip. (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta D$</td>
<td>-0.44</td>
<td>-0.28</td>
<td>-0.47</td>
<td>-0.51</td>
<td>0.08</td>
</tr>
<tr>
<td>$\delta^{18}O$</td>
<td>-0.37</td>
<td>-0.24</td>
<td>-0.46</td>
<td>-0.55</td>
<td>0.00</td>
</tr>
<tr>
<td>d-excess</td>
<td>-0.09</td>
<td>-0.03</td>
<td>0.13</td>
<td>0.13</td>
<td>0.27</td>
</tr>
</tbody>
</table>
high and abnormally low values. Bowen and Revenaugh (2003) have modeled global d-excess values and noted that the area off the southwestern coast of mainland Australia has abnormally high d-excess values. They have attributed this anomaly to low relative humidity as a result of the dry continental Australia. The North and South Subtropical fronts that migrate across the Indian Ocean converge just south of western Australia before diverting southward toward Tasmania. As a result, storm systems imbedded in the subtropical front will contain a greater amount of recycled moisture and the subsequent precipitation that falls in Tasmania will therefore have d-excess values greater than the global average of 10‰.

The only correlation between the d-excess values of Tasmanian surface waters and physical/climatological parameters is that with mean annual precipitation ($r = 0.27$; Table 2.2). The same orographic effects that result in greater mean annual precipitation in western Tasmania also result in greater evaporative recycling of surface waters. Surface waters that receive more recycled precipitation are therefore located in areas that receive a greater amount of annual precipitation; however, the large error associated with $\delta$D measurements preclude more detailed comparisons of d-excess to physical/environmental parameters. In addition, increased rain, cloudiness, and orographic uplift of airmasses in the western part of the island will cause lower condensation temperatures and result in lower d-excess values (Clark and Fritz, 1997).

All of the surface water sample sites that exhibit abnormally high $\delta^D/\delta^{18}O$ values also display abnormally low d-excess values that are likely the result of evaporative increases in surface water isotope values. Two of the surface sites, the Saltwater River Pond and the Forth River (71, 105), have extremely low d-excess values of -9.3 and -2.4 respectively (Appendix A). With the exception of the Forth River, all surface samples with a d-excess less than 10‰ (50, 57, 65, 66, 67) are in central to southeastern Tasmania. In southeastern Tasmania there is less recycling of moisture since the prevailing westerly winds carry the evaporated moisture away from the island and thus cause lower d-excess values in surface waters of this region. This is in stark contrast to the western region of the island where high d-excess values and high annual precipitation is observed. The orographic barrier imposed by the Tasmanian mountains that run northwest-southwest likely captures much of the moisture evaporating from western
Tasmanian surface waters, depositing it again on the west side of the mountains and thereby increasing moisture recycling and d-excess values as well as the amount of precipitation in the western region. Additionally, precipitation that does fall on the east side of the island may come from a more southerly oceanic source. Low d-excess values have been demonstrated to correspond with high relative humidity in oceanic vapor source regions (Merlivat and Jouzel, 1979; Bowen and Revenaugh, 2003). Low d-excess values are also found in Tierra del Fuego and the Antarctic Peninsula, thus lower d-excess values in southeastern Tasmania might also be attributed to input of Southern Ocean derived precipitation.

2.6.3 Relevance to Paleoclimate and Hydrologic Studies

Tasmanian surface waters analyzed in this study characterize isotope values of precipitation over a period of weeks to months. Rainfall amount is greatest and isotope values of precipitation are lowest during austral winter. As a result, surface water values are generally weighted toward winter precipitation values. However, in drier areas such as the eastern part of the island, or in small terminal lakes (i.e. Highland Lake and Salt Water River Pond), isotope values are higher and reflective of greater evaporation of both meteoric and surface water. Consequently, paleoclimatic proxies from eastern Tasmania that utilize surface and/or ground water will reflect more evaporative conditions than those from western Tasmania. The changing position of the circumpolar vortex and imbedded westerly front is presently the dominant control on meteoric water and, in turn, surface water isotope values. Today, the circumpolar vortex and resultant westerly winds are proximal to Tasmania during winter months, resulting in more precipitation between June and August. However, changes in the seasonal position of the westerly front through time would cause dramatic changes in annual precipitation amount in Tasmania. For example, deflection of the circumpolar vortex to the south would result in drier than average conditions in Tasmania and more positive isotope values of meteoric and surface waters. Therefore, changes in precipitation isotope values, and proxies that utilize meteoric water, would likely be observed during periods such as the Little Ice Age, when the circumpolar vortex contracted toward the southern pole, or the Last Glacial Maximum when the circumpolar vortex is believed to have expanded northward.
The d-excess of surface waters in different regions can be used to ascertain the oceanic source region of Tasmanian precipitation as there is a large difference between the d-excess values of Indian Ocean derived precipitation and Southern Ocean derived precipitation (Bowen and Revenaugh, 2003). In addition, surface water d-excess indicates that moisture recycling through evapotranspiration is greater in regions where annual precipitation amount is high. In proxy materials that record both hydrogen and oxygen isotope values of source waters, such as tree-ring cellulose, changes in the relative $\delta D$ and $\delta^{18}O$ values would therefore record additional information on storm tracks and evapotranspiration.

2.7 Summary

This study is the first survey of the spatial distribution of isotope values in Tasmanian surface water. Waters analyzed range from $-56\%e$ to $-2\%e$ in $\delta D$ and from $-9.0\%e$ to $0.4\%e$ in $\delta^{18}O$ values. Isotope values of Tasmanian precipitation reflect seasonal variability in storm tracks and moisture source; however $\delta D$ and $\delta^{18}O$ values of precipitation also record physical processes, most notably rainout due to altitudinal gradients. As a result, the $\delta D$ and $\delta^{18}O$ values of Tasmanian surface waters demonstrate the highest correlation with sample/stream head elevation ($r = -0.51$ for $\delta D$ and $-0.55$ for $\delta^{18}O$). Isotope values of surface water correlate with latitude and longitude as well; however, this effect is also associated with the island's topography. As air masses travel over Tasmania from west/southwest to east/northeast precipitation isotope values decrease. This trend is produced by the island's northwest-southeast trending topographic highs that drive the rainout process. d–excess values indicate that they are most closely related to precipitation amount, and moisture recycling is likely a significant component along the west coast of Tasmania. Our data also indicate that considerable mixing of precipitation occurs in surface water bodies, although the isotope values of Tasmanian surface waters are weighted toward winter precipitation values as expected.

Isotope values of Tasmanian surface waters provide useful information about modern meteorological and physical parameters that influence Tasmanian precipitation. Additionally, this study provides critical information about the modification of precipitation isotope values by surficial processes such as evaporation, hydrologic
residence time, and the time averaging of seasonal variability. Perhaps most importantly, development and interpretation of multi-proxy records of climate change in Tasmania and elsewhere will benefit significantly by surface water surveys such as this, in that they permit selection of the most appropriate study sites and proxy materials.

2.8 Acknowledgements

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2.9 References


2.10 Manuscript's Relationship to Thesis

Chapter 2 discusses modification δ18O and δD values in precipitation by surface water processes. Although Tasmania is vastly different, geographically and physically, than the other areas discussed Ch 2 and 3, modification of precipitation δ18O and δD values through the hydrologic cycle is a critical component of other isotope proxies, such as those preserved in tree-ring cellulose.
CHAPTER 3. A NEW TOOL FOR OBTAINING SUB-SEASONAL SAMPLES OF TREE-RING CELLULOSE FOR ISOTOPE STUDIES: ADVANTAGES OF ROBOTIC MICROMILLING

3.1 Abstract
High-resolution, intra-ring analysis of $\delta^{18}$O, $\delta^D$, and $\delta^{13}$C values of modern tree species (Picea glauca, P. mariana, Larix laricina, and Fagus grandiflora) were sampled using a robotic micromill. The micromilling apparatus allows growth bands to be accurately mapped and sampled at a resolution of few $\mu$m. Milling produces a fine, homogenous powder that facilitates the chemical processing and analyses of very small samples (~100$\mu$g). Considerable intra-ring isotope variability observed in all tree samples correlates with temperature, relative humidity, and precipitation data indicating that intra-ring variability in $\delta^{18}$O, $\delta^D$, and $\delta^{13}$C has great potential for reconstructing high-resolution variations in meteorological conditions throughout the growing season.

3.2 Introduction
Isotope studies of tree-ring cellulose (e.g. $\delta^D$, $\delta^{18}$O, and $\delta^{13}$C analyses) are increasingly used as proxies for terrestrial climate variability (Epstien et al., 1977; Wilson and Grinsted, 1977; Saurer et al., 1997; Switsur and Waterhouse, 1998; McCarroll and Loader, 2004). Isotope time series developed from tree-ring cellulose have advantages over other proxies such as speleothems and lake sediments in that they provide annual and even sub-seasonal samples that can be precisely dated. Developments in online, continuous flow gas isotope ratio mass spectrometry technology permit analysis of increasingly smaller samples (~100$\mu$g). Intra-ring sampling of cellulose for H, O and C isotope analyses provides records of meteorological and atmospheric conditions at monthly or even weekly resolution (Leavitt and Long, 1991; Loader et al., 1995, Evans and Schrag, 2004). High-resolution studies are particularly useful for reconstructing seasonal variability in precipitation source (i.e. monsoonal rain and tropical storm activity), temperature and relative humidity (Loader et al., 1995; Evans and Schrag, 2004,
Poussart et al., 2004, Miller et al., *in press*. Additionally, researchers have used high-resolution isotopic time-series to elucidate seasonality in tropical trees where growth banding does not necessarily record annual cycles (Evans and Schrag, 2004, Poussart et al., 2004).

Traditionally, high-resolution sampling has been conducted with a fixed blade and rotary microtome (Loader et al., 1995; Evans and Schrag, 2004; Poussart et al., 2004). Microtomes are capable of extracting small wood slivers (~20-30µm thick), although there are drawbacks to this method. First, because microtomes utilize a rotary blade, samples must be removed as linear segments parallel to each other. As a result, only rings or ring segments that are linear or nearly linear can be sampled. Rings that are very narrow or rings that have tight curvatures cannot be reliably sampled without crosscutting growth rings, thereby mixing material from adjacent time periods and reducing the temporal resolution of sampling. Secondly, microtomes compress tree-ring cellulose and distort the true sample thickness. Robotic micromills are increasingly used for high-resolution sampling of gastropod and mollusk shells (e.g. Wurster and Patterson, 2001), fish otoliths (e.g. Patterson et al. 1993), animal teeth (e.g. Zazzo et al., 2005), and speleothems (e.g. Lachniet et al., 2004); however, to our knowledge, this is the first time it has been applied to tree ring cellulose. Herein, we describe the use of a robotic micromilling device that recovers high-resolution time-specific subseasonal samples of cellulose concordant with growth rings. An additional advantage of micromilling is that it generates a fine, homogenous powder that facilitates the processing and analyses of small samples.

### 3.3. Experimental Section

#### 3.3.1 Sample Preparation

In order to compare methods for recovery of high-resolution cellulose samples, trees were sampled using a 1.2cm Haglof™ increment bore tree corer and by cutting disks from felled trees. Samples discussed herein include spruce (*Picea glauca* and *P. mariana*), and tamarack (*Larix laricina*) from central Saskatchewan, Canada as well as beech (*Fagus grandiflora*) from the Green Lake region of upstate New York, USA. Increment core samples were trimmed into 10 to 15cm lengths by slicing along ring
boundaries with a scalpel while disks where cut with a band saw into blocks approximately 15 x 5 x 2cm (length x width x height). Samples were sanded with 100- to 500-grit sand paper to facilitate identification of rings and prevent sampled powder from becoming caught in pores and cracks. Subsequently, specimens were affixed to glass dissection slides and attached to a moveable stage for micromilling.

3.3.2 Micromilling Apparatus

Wood specimens were milled using a computer-controlled micromilling apparatus that facilitates micron-scale sampling of tree-rings (Wurster et al., 1999). Increment cores and sections were attached to a movable stage beneath a fixed micro drill. Stage motion is controlled by three linear actuators with a step resolution of 0.05 µm on the x- and y-axis, and 1µm on the z-axis. The apparatus is manipulated by a computer via a motion controller with a range of x, y, and z-axis motion of 17.78 x 7.62 x 4.54 cm, respectively.

Tree-rings, though generally sequentially concordant, often display complex patterns or curves that are difficult if not impossible to sample at high-resolution using standard techniques. Tree-rings are thus mapped using a real-time digital color camera mounted on a fourth linear actuator. Digital characterization of tree-rings entails touching the tip of the drill to the surface of the sample at several points along the growth ring and recording these points in x-y-z space. We then employ a cubic spline interpolation between the digitized points that mimics the characteristics of growth rings. By characterizing two successive growth rings multiple intermediate paths can be interpolated (Fig. 3.1). Spacing of intermediate paths can be regulated to insure that adequate material is recovered to generate sufficient gas for analyses. Due to the removal of up to 70% of wood material (lignin, resins, and other non-cellulose compounds) during α-cellulose processing, we found that approximately 600µg of raw wood is necessary for each isotope analysis. For the increment core samples this generally requires a minimum thickness of 400µm; however for the slabs where longer sample paths could be milled, individual path widths of 100µm were possible.

Samples were milled using coarse cut carbide burs from Advanced Carbide Tool Company™. The total bur diameter (2.4mm) is significantly greater than sample path
Figure 3.1. Screen capture during the milling of a white spruce 12mm core sample from central Saskatchewan. The growth ring boundaries (marked by white asterisks) are easily distinguished as well as previous sample paths (dashed lines). By discretely sampling with only the edge of the drill, samples that are much smaller than the diameter of the drill are collected. In this image, sample paths are 400µm in width and the drill is moving left to right parallel to the ring boundaries.
widths. However, recovery of much smaller increments is made possible by milling (rather than drilling) concordant with ring boundaries such that only the edge of the bit comes in contact with the sample (Fig. 3.2). Milling depth is dependent upon the three-dimensional characteristics/orientation of growth rings and the amount of powder that must be obtained for analyses. For example, longer paths allow for minimal milling depths (less than 200µm). Alternatively, when path length is limited, as in tree core samples, greater depths are required to obtain sufficient powder for isotope analyses. The resulting wood powder is collected into 1.5ml polypropylene microcentrifuge tubes. Wood powder particles generated by the micromill are approximately 150 to 500 µm (100- to 35-mesh sieve).

3.3.3 Alpha-cellulose processing

Tree rings are principally composed of cellulose and several other compounds such as lignin, waxes, lipids, oils, and resins. Non-cellulose compounds can vary significantly in relative abundance and isotope values throughout a given tree ring (Wilson and Grinsted, 1977; Brendel et al., 2000). Most studies that make use of isotope records of tree rings isolate purified cellulose (commonly referred to as α-cellulose) to derive paleoclimatic signals (Gaudinski et al., 2005). α-cellulose is ideally suited for paleoclimatic studies because once formed, carbon and oxygen atoms in the cellulose molecule do not exchange with other environmental compounds and therefore preserve the isotope values at the time of cellulose formation (Sternberg et al., 1986).

Waxes, resins and lipids were removed from milled whole wood powder by solvent extraction using 2:1 toluene and methanol and rinsed with ethanol and deionized water (Leavitt and Danzer, 1993). α-cellulose was subsequently isolated following a modified Brendel et al. (2000) procedure reported by Evans and Schrag (2004) for small samples. One hundred and twenty µl of 80% acetic acid and 12µL of 69% nitric acid were added to batches of 48 powdered wood samples that ranged between 600µg and 1000µg in 1.5ml polypropylene microcentrifuge tubes. Samples were then capped and heated to 120ºC in convection oven for 30 minutes and allowed to cool. Samples were subsequently rinsed in four successive steps using 400µl of 100% ethanol, 300µl of deionized water, and 150 µl of 100% ethanol, followed by a final rinse with acetone. Between each rinse samples
Figure 3.2. Tree-rings (a) can be mapped and sampled using a computer-controlled robotic micromilling apparatus (b). A section of a tree slab or core sample is fixed to a glass slide and attached to a movable stage. The stage then moves past the drill along a digitized sample path so that only the edge of the drill scraps the sample. Full range of motion in x-y-z space allows rings to be followed with resolution of 0.05μm.
were centrifuged at 15,000rpm for 10min. Samples were then dried at 70ºC for 1 hr and overnight in a vacuum desiccator. The resulting α-cellulose was a pure white cotton-like, fibrous material with a processing yield of 35 (±3)% the original volume, that is in agreement with other studies (Brendel et al., 2000; Evans and Schrag, 2004).

Gaudinski et al. (2005) have suggested that the modified Brendel method does not sufficiently remove lipids and waxes in comparison to other methods. They noted that samples processed with the Brendel method had higher δ⁸¹⁸O values than the samples processed with the Jayme-Wise method as reported by Green (1963), but could not explain the difference. Lignin, lipids, and other non-cellulose compounds generally have lower δ¹⁸O and δ¹³C values and therefore incomplete removal should result in lower, rather than higher values (Leavitt and Danzer 1993; Schmidt et al., 2001; Loader et al., 2003). Leavitt and Danzer obtained similar unexpected results when samples were exposed to sodium chlorite for extended periods of time and suggested that extreme chlorite delignification processes might be too harsh for fine samples and result in cellulose degradation (Leavitt and Danzer, 1993). Additionally, Gaudinski et al. (2005) did not use the toluene/alcohol solvent extraction prior to α-cellulose conversion, perhaps explaining the presence of resins and waxes in their samples. We believe the method described by Evans and Schrag (2004) is suitable for α-cellulose conversion in our study because the same process was applied to δ¹⁸O time series in spruce species from central Saskatchewan (not shown) which appear to be well correlated with growing season source water values.

Hydrogen atoms in α-cellulose are not as strongly bound as carbon and oxygen in that 30% of the hydrogen atoms can exchange with xylem and other waters subsequent to cellulose production (Epstein et al., 1976; Grinsted and Wilson, 1977). α-cellulose in samples analyzed for δD, were converted to cellulose nitrate using the acetic anhydride method to remove exchangeable hydrogen atoms (Sternberg, 1989). One ml of 40% fuming nitric acid and 60% reagent grade acidic anhydrite was added to samples that were capped and placed on ice for 4 hours, after which the reaction was terminated by adding deionized ice water. Samples were subsequently rinsed with deionized water and methanol and centrifuged between each rinse. Because nitrated cellulose has a rather low
combustion temperature (65°C), samples were freeze-dried under vacuum at –50°C over night (12 to 20 hours).

3.3.4 Isotope analyses

Isotope analyses were conducted at Saskatchewan Isotope Laboratory on 150 to 200 µg of α-cellulose, or cellulose nitrate. Oxygen and hydrogen analyses were preformed by online pyrolysis using a Thermo Finnigan Thermal Conversion Elemental Analyzer (TC/EA) at 1450°C. Isotope ratios of $^{18}$O/$^{16}$O and D/H of the resulting CO and H$_2$ gases were determined via continuous flow using a Thermo Finnigan Delta Plus XL mass spectrometer relative to CO and H$_2$ reference. Sample reproducibility is constrained by international benzoic standards (IAEA-601 and IAEA-602) for δ$^{18}$O analyses (±0.1‰, 1σ) and IAEA-CH-7 and NBS-22 for δD analyses (±2‰, 1σ). Carbon isotope values were determined using a continuous flow online combustion technique on a Thermo Finnigan Elemental Analyzer (EA) coupled to a Thermo Finnigan Delta Plus XL mass spectrometer. Sample reproducibility for δ$^{13}$C is ±0.2‰ 1σ) and constrained by international cellulose and sucrose standards (IAEA-CH-3 and IAEA-CH-6). All isotope values are reported relative to VSMOW (δ$^{18}$O and δD) and VPDB (δ$^{13}$C) in delta notation ($\delta_{\text{sample}} = \{R_{\text{sample}}/R_{\text{standard}} - 1\} \times 1000$).

3.4 Results

Considerable intra-ring variability is observed in δ$^{18}$O values of all trees analyzed in this study (Fig. 3.3-5). White spruce and tamarack from central Saskatchewan, Canada, were collected with a 1.2cm increment borer and milled at a resolution of 2 to 12 samples per ring (average of 4). Ring widths in the white spruce range from <0.5mm to 4mm and from 1 to 3mm in the tamarack. Each core contained only enough material for δ$^{18}$O analyses at this resolution. By collecting multiple cores the milling process could be repeated to generate δ$^{13}$C and δD values at the same resolution as the δ$^{18}$O time series. Both white spruce and tamarack δ$^{18}$O values display a seasonal cycle with highest values generally early in the growing season and lower values in the late growing season (Fig. 3.4). In years when average growing season δ$^{18}$O values do not change from year to year (for example 1993 to 1997 in Fig. 3.4), intra-ring variability is often quite high, thus
Figure 3.3. High-resolution sampling of white spruce from Prince Albert, Saskatchewan, Canada (53°13’ N, 105° 40’W). Individual samples represent 400µm thickness and between 2 and 12 samples were collected per ring between 1985 and 2004. The average δ¹⁸O value for each growing season as well as the time span represented by those average values are depicted as gray boxes (early wood) and black boxes (late wood). In most cases the late wood portion is much only one or two samples (< 800µm) and therefore boxes are much larger than the actual time represented. δ¹⁸O values are generally highest early in the growing season and lowest late in the growing season. Analytical error is smaller than the dots that represent each sample.
Figure 3.4. High-resolution $\delta^{18}$O time series of tamarack from east central Saskatchewan, Canada (54° 40' 37" N, 103° 11'11"W) from 1990 to 2004. Similar to the white spruce in figure 3.3, the tamarack $\delta^{18}$O time series display a general seasonal pattern; however there is more seasonal variation than observed in the white source. Again the average $\delta^{18}$O value for each growing season as well as the time span represented by those average values are depicted as gray boxes (early wood) and black boxes (late wood). Note that between 1993 and 1997 average $\delta^{18}$O values change very little, yet intra-annual variation remains quite high (e.g.,~4‰ in 1993).
Figure 3.5. Unlike the white spruce and tamarack presented in figures 3.3 and 3.4, the beech tree used in this study was from a complete disk rather than a tree core from the Green Lakes region of central New York, USA. The disk allowed for recovery of more material and therefore analyses of $\delta^{18}O$ (a) as well as $\delta^{13}C$ (b) and $\delta^D$ (c) for the same sample. Between 1944 and 1998, 388 samples were collected with an average of 6 samples per ring. Shown here are a portion of those data from 1946 to 1956. The average isotope value for each growing season as well as the time span represented by those average values are depicted as gray boxes.
years that have extreme, but oppositely trending $\delta^{18}$O values in the early and late wood would appear to be "normal" or "average" in $\delta^{18}$O values if cellulose comprising the entire width of the annual rings were sampled.

For the beech tree from upstate New York, a complete slab (or cookie) was available, allowing for recovery of more material and therefore $\delta^{18}$O, $\delta$D, and $\delta^{13}$C analyses were conducted on cellulose from each sample path (Fig 3.5). The micromill proved particularly useful for sampling slabs as it allowed for the curvature of growth bands to be mapped across several centimeters of the disk (see Fig. 3.2). A total of 383 samples were collected between 1944 and 1998 in the beech tree. Average sample width for the beech tree was 200 µm, and up to 12 samples were collected per growth ring. The range of $\delta$D, $\delta^{18}$O, and $\delta^{13}$C values in the beech is 36‰, 4.5 and 2.3‰, respectively. The intra-ring $\delta^{18}$O, $\delta$D, and $\delta^{13}$C time series in the beech tree therefore also display considerable variability that is not recorded by annual or even late wood/early wood portions of the ring. Additionally, all the intra-ring variability in $\delta^{18}$O, $\delta$D, and $\delta^{13}$C in the beech specimen display a strong seasonal cycle. $\delta^{18}$O and $\delta^{13}$C values in the beech are generally low in the earliest and latest parts of the season with the highest values occurring in the midsummer, when temperature is highest and relative humidity is the lowest; however $\delta$D values for the beech tree display a less coherent seasonal pattern.

A major issue associated with isotopic analyses of very small (<200 µm) samples of α-cellulose or cellulose nitrate is sample heterogeneity (Rinne et al., 2005). Much of this heterogeneity is the result of the high intra-ring variability that is observed in $\delta^{18}$O, $\delta$D, and $\delta^{13}$C values. High-resolution, intra-ring sampling generates very small amounts of material and therefore often prevents multiple analyses of single samples. In order to assess the homogeneity of the micromilled samples at the 100 µg scale, multiple $\delta^{18}$O analyses were conducted on 25 samples of early and late wood from a black spruce from central Saskatchewan (Table 3.1). Micromilled samples have also been compared to the same 25 samples collected with the traditional scalpel method (Fig. 3.6; Table 3.1). Samples collected using the traditional scalpel method were homogenized using an agate mortar and pestle, while powder from the micromilled samples required no further grinding. Samples collected with the micromill display considerably less variability (average $s.d. = 0.1‰, 1\sigma$) than those collected by scalpel (average $s.d. = 0.5‰, 1\sigma$).
Table 3.1. Homogeneity: Scalpel vs. Micromill Sampling of cellulose

<table>
<thead>
<tr>
<th>Year</th>
<th>Season</th>
<th>Sampled with Micromill</th>
<th>Sampled with Scalpel</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>δ¹⁸O (‰)</td>
<td>s.d. (1σ)</td>
</tr>
<tr>
<td>1951</td>
<td>Early</td>
<td>22.2</td>
<td>0.3</td>
</tr>
<tr>
<td>1951</td>
<td>Late</td>
<td>21.6</td>
<td>0.1</td>
</tr>
<tr>
<td>1952</td>
<td>Early</td>
<td>21.9</td>
<td>NA</td>
</tr>
<tr>
<td>1952</td>
<td>Late</td>
<td>22.1</td>
<td>0.1</td>
</tr>
<tr>
<td>1953</td>
<td>Early</td>
<td>22.8</td>
<td>0.2</td>
</tr>
<tr>
<td>1953</td>
<td>Late</td>
<td>22.7</td>
<td>NA</td>
</tr>
<tr>
<td>1954</td>
<td>Early</td>
<td>24.5</td>
<td>0.1</td>
</tr>
<tr>
<td>1954</td>
<td>Late</td>
<td>23.4</td>
<td>0.1</td>
</tr>
<tr>
<td>1955</td>
<td>Early</td>
<td>22.0</td>
<td>0.1</td>
</tr>
<tr>
<td>1955</td>
<td>Late</td>
<td>23.9</td>
<td>0.1</td>
</tr>
<tr>
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<td>22.9</td>
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</tr>
<tr>
<td>1956</td>
<td>Late</td>
<td>24.1</td>
<td>0.1</td>
</tr>
<tr>
<td>1957</td>
<td>Early</td>
<td>24.8</td>
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<tr>
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<td>Late</td>
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</tr>
<tr>
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<td>Early</td>
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</tr>
<tr>
<td>1958</td>
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<td>0.3</td>
</tr>
<tr>
<td>1959</td>
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</tr>
<tr>
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<tr>
<td>1961</td>
<td>Early</td>
<td>23.3</td>
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<td>23.9</td>
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<tr>
<td>1962</td>
<td>Early</td>
<td>25.7</td>
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<tr>
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<td>Late</td>
<td>24.0</td>
<td>NA</td>
</tr>
<tr>
<td>1963</td>
<td>Early</td>
<td>26.7</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Average: 0.1  0.5

* Note most sample reruns were analyzed in the same run and standard deviations reflect sample heterogeneity not analytical reproducibility.
Figure 3.6. In order to assess the homogeneity of $\delta^{18}O$ values in the micromilled samples we analyzed early wood and late wood portions from a black spruce from east central Saskatchewan, Canada ($54^\circ 40' 37''$ N, $103^\circ 11' 11''$ W) that had been collected using both micromill and scalpel techniques. The micromilled samples (black line) were considerably more homogeneous than those collected with a scalpel (gray line). The average standard deviation (depicted by vertical bars on each sample point) of the micromilled samples was 0.1‰, while samples collected with a scalpel had an average standard deviation of 0.5‰ (1σ; Table 1). Analytical error for $\delta^{18}O$ analyses is 0.2‰ and therefore the error associated with the heterogeneity of the scalpel sampled cellulose is significantly higher. Note sample reruns were often analyzed in the same run and therefore do not reflect true analytical reproducibility.
Micromilled samples are therefore very homogenous and appear to represent the average value of the given sample interval within the range of analytical error.

3.5 Discussion and Conclusions

Seasonal cyclicity observed in the intra-ring variations in $\delta^{18}$O, $\delta^D$, and $\delta^{13}$C values indicate that high-resolution sampling of tree-ring cellulose offers the potential to reconstruct variation in meteorological conditions throughout the growing season. The climate of a region is characterized not only by the average growing season conditions but also the seasonal extremes; high-resolution reconstructions of intra-ring isotope variability can therefore provide critical information about the timing and magnitude of changes in past meteorological conditions such as temperature, relative humidity, precipitation amount, and precipitation $\delta^{18}$O/$\delta^D$ values. Additionally, many major climate events such as monsoonal rain and tropical storm activity occur during small portions of the growing season and would therefore not be apparent in samples averaged over the entire growing season (Poussart et al., 2004, Miller et al., in press). Although some seasonal information can be ascertained from studies that divide wood into early wood and late wood portions, the division along the late wood boundaries is sometimes problematic. In white spruce and tamarack from central Saskatchewan, the late wood growth period is very short and results in late wood widths that are often less than 400µm in thickness. It is therefore difficult to discretely sample the late wood in these, and other boreal trees, even by micromilling. However, by sampling at a very high-resolution across the growth ring it is possible to reconstruct isotope time series of the entire season regardless of the early wood late wood boundary.

Intra-ring $\delta^{18}$O time series from Saskatchewan trees are well correlated with relative humidity and temperature. The early growing season conditions are typically characterized by low relative humidity and high temperatures, whereas the late growing season is higher in relative humidity and lower in temperature. This causes tree-ring $\delta^{18}$O values to be high in the early part of the growing season and lower near the end. A similar seasonal cycle is observed in $\delta^{18}$O values of precipitation in central Saskatchewan with the highest $\delta^{18}$O values in the early growing season (May – July) and lowest $\delta^{18}$O values in the late growing season (Sep. – Oct.; Fritz et al., 1987). Intra-ring $\delta^{18}$O, $\delta^D$, and
Figure 3.7. Although intra-ring samples of equal width may not represent equal periods of time, it does appear that they are very close to equal. Intra-ring $\delta^{18}$O values from the beech tree have a strong relationship with the average monthly temperature recorded during the growing season (April to October). Both temperature and $\delta^{18}$O values display a similar seasonal cycle with highest values occurring in the early part of the growing season and lowest values late in the growing season.
\( \delta^{13}C \) values in the beech from central New York are well correlated with relative humidity, temperature, precipitation \( \delta^{18}O/\delta D \) values, and precipitation amount. For example, there is a strong relationship between the seasonal variations in intra-ring \( \delta^{18}O \) values of the beech tree and average monthly temperatures (Fig. 3.7).

A robotic micromilling device has many advantages over other methods of high-resolution sampling such as a microtome. The micromilling approach allows for growth bands to be accurately mapped and sampled, preventing crosscutting of growth bands as would often be the case if a scalpel or microtome were used. Micromilling of tree-ring wood also produces a very fine, isotopically homogeneous powder, which would benefit sampling of wood at any spatial resolution. Continuing work is focused on relating the seasonal changes in the \( \delta^{18}O, \delta D, \) and \( \delta^{13}C \) time series to meteorological and atmospheric data. Once calibrated, high-resolution isotope time series can provide valuable information about seasonal and sub-seasonal changes in relative humidity, temperature, and precipitation.

3.6 Acknowledgments

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3.8 Manuscript's Relationship to Thesis
Chapter 3 provides a detailed examination of the methods used in sampling and processing tree-ring cellulose for δ18O, δD, and δ13C analysis. Chapter 3 also explains the justification for using a robotic micromilling apparatus to sample tree rings and demonstrates the applicability of intra-ring variations in δ18O, δD, and δ13C to studies of sub-seasonal meteorological and atmospheric variability.
CHAPTER 4. A 110YR SEASONAL PRECIPITATION AND ATMOSPHERIC CIRCULATION RECORD: EVIDENCE FROM $\delta^{18}$O VALUES OF TREE-RING $\alpha$–CELLULOSE IN MODERN SPRUCE

4.1 Abstract
A seasonally resolved (early/late wood) 110-year time series of $\delta^{18}$O values from tree-ring $\alpha$-cellulose from modern spruce species ($Picea mariana$ and $P. glauca$) from east-central Saskatchewan, Canada is presented as a record of growing season precipitation and atmospheric circulation. Isotope values of source-water utilized by the trees are reconstructed using a modified leaf-water equation (Anderson et al., 2002) that incorporates relative humidity and temperature measurements to account for leaf water modification through stomatal evaporation. The reconstructed $\delta^{18}$O source water values display a high correlation with growing season precipitation isotope values ($r = 0.86$) recorded at The Pas, Manitoba approximately 150 km to the southeast. $\delta^{18}$O $\alpha$-cellulose time series also record seasonal changes in atmospheric circulation associated with the position of the circumpolar vortex and dominate modes of atmospheric variability such as the North Atlantic Oscillation and Pacific Decadal Oscillation.

4.2 Introduction
Oxygen isotope records preserved in tree ring $\alpha$-cellulose are valuable proxies of environmental change that are particularly useful for reconstructing secular records of oxygen isotope values in precipitation (Epstein et al., 1977, DeNiro and Epstein, 1979, Roden et al., 2000, Anderson et al., 2002, Waterhouse et al., 2002, Saurer, 2003, McCarroll and Loader, 2004, Weigou et al. 2004, Miller et al., in press). Although the IAEA/WMO have constructed an extensive database of precipitation isotope values and others have modeled the spatial distribution of isotopes in global precipitation (Bowen and Revenaugh 2003), precipitation isotope records are only available for the later part of the 20th century, at best, and for only a few years at many stations. Tree-ring isotope studies have the potential to extend the record of precipitation isotope variability well
beyond the range of IAEA/WMO data and thus provide indispensable records of past variation in the hydrologic cycle (Darling, 2004). Unlike other terrestrial climate proxies such as lacustrine sediment, speleothems, and ice cores, tree-rings isotope studies provide unambiguous age control in the form of annual rings (Waterhouse et al., 2002, Saurer, 2003). The perfect annual resolution in tree-rings facilitates direct comparison with instrumental records of air temperature, relative humidity, precipitation amount, and the $\delta^{18}O$ value of precipitation. In addition, the abundance of trees in many terrestrial environments provides an opportunity to characterize the spatial distribution of precipitation isotope values over much of the Earth for the past several thousand years (Saurer, 2003).

Recent studies have demonstrated that high latitude environments may be particularly sensitive to global climate change, yet our understanding of natural climate variability in these regions is hindered by the poor temporal and spatial resolution of paleoclimate records (Gibson, 2001; Schindler and Donahue, 2006). Instrumental records of temperature and precipitation amount for western Canada are only available for the most recent 100 to 150 years; weather patterns that were experienced during the 20th century are generally considered as "normal" climate conditions. However, other proxies such as drought sensitive tree-ring chronologies indicate that western Canada was considerably drier prior to the 20th century (Sauchyn and Skinner, 2001; Schindler and Donahue, 2006).

Presented herein is a detailed (early/late wood) 110-year record of seasonal $\delta^{18}O$ values in tree-ring $\alpha$-cellulose of boreal forest white and black spruce (Picea mariana and P. glauca) from east-central Saskatchewan, Canada. The $\delta^{18}O$ cellulose record is compared to meteorological data measured at The Pas, Manitoba and Prince Albert, Saskatchewan (Environment Canada, 2005) and $\delta^{18}O$ values in precipitation recorded by the International Atomic Energy and the World Meteorological Organization (IAEA/WMO) at The Pas, Manitoba (IAEA/WMO, 2001). The $\delta^{18}O$ records are compared to secular changes in the position of the circumpolar vortex (NCEP/NCAR Reanalysis Project, 2000) and other records of atmospheric circulation such as the Pacific Decadal Oscillation (PDO) and the North Atlantic Oscillation (NAO) indices (Hurrell, 1995, 1996; Mantua et al, 1997; Zhang et al., 1997)
Using a modified leaf-water equation (after Anderson et al., 2002) $\delta^{18}O$ values of water utilized by the trees during the growing season have also been reconstructed and are well correlated with $\delta^{18}O$ values of growing season (April – October) precipitation at the Pas, Manitoba. The modified leaf-water equation (Anderson et al., 2002) used in the $\delta^{18}O$ source water reconstruction is empirically calibrated with daily relative humidity and temperature measurements, and therefore accounts for isotopic modification of source water $\delta^{18}O$ values in a manner that is broadly applicable for reconstruction of the $\delta^{18}O$ values of growing season precipitation from tree-ring $\alpha$-cellulose.

### 4.2.1 Oxygen isotope values of tree-rings

The woody tissue of tree rings consists of multiple compounds such as lignin, lipids, resins, and other non-cellulose compounds that generally have lower $\delta^{18}O$ values relative to cellulose (Wilson and Grinsted, 1977; Brendel et al., 2000). Most studies that make use of isotope studies of tree rings have focused on purified cellulose (commonly referred to as $\alpha$-cellulose) to derive paleoclimatic and paleoenvironmental signals (Gaudinski et al., 2005). $\alpha$-cellulose is ideally suited for paleoclimatic studies because once formed, carbon and oxygen atoms in the cellulose molecule do not exchange with other environmental compounds and therefore preserve the $\delta^{13}C$ and $\delta^{18}O$ values at the time of cellulose formation (Sternberg et al., 1986).

The oxygen atoms in tree-ring $\alpha$-cellulose are primarily derived from water taken into the tree by the roots, which in the case of shallow rooted trees is predominantly derived from soil moisture. The $\delta^{18}O$ value of soil moisture reflects local precipitation, averaged over some period of time prior to utilization by the tree. Evaporation of water from the soil, long soil moisture residence times, and mixing of groundwater can distort the precipitation $\delta^{18}O$ signal; therefore in studies that attempt to reconstruct past $\delta^{18}O$ values of precipitation, it is desirable to study trees growing in shallow, well-drained soil with limited evaporation (Tang and Feng, 2001, Buhay and Edwards, 1995). The $\delta^{18}O$ value of water in the tree is subsequently modified by: (1) evaporation of water in the leaf through the stomata during transpiration (Dogmann et al. 1974), (2) biologic fractionation between water and cellulose (DeNiro and Epstein, 1979, Sternberg et al. 1986), (3) and exchange of oxygen atoms between sucrose produced during photosynthesis and water in
the leaf and stem-wood cellulose (Sternberg et al., 1986). For an in-depth discussion of fractionation processes see Yakir and DeNiro (1990), Roden et al. (2000), Waterhouse et al. (2002), and McCarroll and Loader (2004).

Anderson et al. (2002) reconstructed $\delta^{18}$O values of the source water ($\delta^{18}$O$_{sw}$) utilized by the tree using a modified-leaf water equation (Eq. 1) developed from equations by Dogmann et al. (1974) and Aucour et al. (1996) that accounts for evaporative modification of $\delta^{18}$O values during transpiration constrained by temperature ($t$), relative humidity ($h$), and tree growth rate (represented by measured tree-ring index values, $r_x$) to calculate a variable damping factor $f$ (Eq. 2).

$$\delta^{18}O_{sw} \approx \delta^{18}O_{cellulose} - (1 - f)(1-h)(\epsilon_e + \epsilon_k) - \epsilon_{biochem}$$  \hspace{1cm} (1)

$$f = -1.47(h) + 0.03(t) + 0.11(r_x) + 0.62$$  \hspace{1cm} (2)

As used in this equation, the water liquid-vapor kinetic fractionation across the leaf boundary ($\epsilon_k$) and the biologic fractionation factor ($\epsilon_{biochem}$) are 28‰ and 27‰, respectively. A value of 28‰ for $\epsilon_k$ reflects the nearly stagnant boundary layer conditions observed in fine spruce needles (Anderson et al., 2002; Allison et al., 1985, Buhay et al., 1996). The biologic fractionation factor accounts for the fractionation of oxygen isotopes in leaf water during photosynthesis and a value of 27‰ is most common in the literature (DeNiro and Epstein, 1979; Roden et al., 2000, Yakir and DeNiro, 1990). $\epsilon_e$ is the liquid-vapor equilibrium fractionation factor for water from Manjoube (1971) and can be calculated using the average growing season temperature at the sample site. The damping factor $f$ provides an estimate of the modification of the precipitation $\delta^{18}$O value of water utilized by the tree through soil and leaf evaporation, groundwater mixing, and exchange of oxygen atoms between xylem water and photosynthate. Relative humidity and temperature are dynamic environmental parameters and by calculating a variable $f$ factor that incorporates these processes, the equation developed by Anderson et al. (2002) is able to more accurately predict the $\delta^{18}$O value of water utilized by the tree than equations that assume fixed value for $f$.

### 4.3 Site Description

Modern tree samples were collected near the north end of Limestone Lake in east-central Saskatchewan, Canada (54° 40' 37 N, 103° 11' 11 W; Fig. 4.1) at about 350m
Figure 4.1. The position of the Limestone Lake sample site (54° 40' 37 N, 103° 11' 11W) as well as meteorological stations at Prince Albert, Saskatchewan (53° 13' N, 105° 40' W, ~300km southwest of Limestone Lake) and The Pas, Manitoba (53° 58' N, 101° 6' W ~150km to the southeast). These sites are positioned between the Northern and Central contours of the circumpolar vortex. Both vortex contours seasonally contract to the north during the summer and expand to the south during the winter. Summer conditions are therefore dominated by the position of the central vortex contour.
above sea level. The sample area is part of the southern boreal forest/aspen plains transition zone with mixed wood boreal forests containing softwood (spruce, pine, fir, and tamarack) and hardwood (birch, aspen, and balsam poplar) growing in muskeg bog and shallow acidic soil underlain by metavolcanic and metasedimentary bedrock at the southern edge of the Canadian Shield.

Instrumental records from Prince Albert, Saskatchewan are available since 1889 for precipitation and temperature and since the early 1950s for relative humidity, sky conditions, and wind speed. Meteorological data for The Pas are less complete with reliable records from 1943 to present (Environment Canada, 2005). Monthly $\delta^{18}O$ values of precipitation are available from the IAEA/WMO at The Pas somewhat sporadically from 1975 to 1982 (IAEA/WMO, 2001; Fritz et al, 1987). Over the period of instrumental data (1889 – 2005), the study area received an average of 327mm of precipitation a year, with most (175mm on average) falling during the summer months (June - August). Sub-freezing temperatures are generally observed from late October through early April, and therefore April – October represents the maximum possible growing season for trees in the area.

The central Canadian boreal forest is dominated by three climate regimes influenced by Pacific, Arctic and Tropical/Atlantic air masses (Fritz et al, 1987). The relationship of these air masses to the study site is largely influenced by the position and strength of westerlies associated with the jet stream (Burnett, 1993; Frauenfeld and Davis, 2003; Fig. 4.1). The main band of westerly winds generally encircles the polar region and is therefore also referred to as the circumpolar vortex (Burnett, 1993). The center of the circumpolar vortex is defined as the region with the strongest meridional gradient within the main belt of westerly flow (Frauenfeld and Davis, 2003). To better characterize the geometry and circulation on the circumpolar vortex at higher and lower latitudes, the main westerly belt is divided into three contours, the central, northern and southern. The central contour of the circumpolar vortex best describes the core of the westerly flow while the northern and southern contours generally describe the northern and southern limits of the main westerly belt. Continental scale variations in the circumpolar vortex have strong geographic preferences and have a dominant influence on mid-latitude climates. In North America, the position of the circumpolar vortex is
confined by Canadian Rockies in the west and thermal contrast between the Atlantic Ocean and continental North America in the east. The geographic boundary conditions result in a relatively stable ridge, or northward deflection of the vortex, over the mountains and a trough over northeastern North America. The average position of the vortex varies seasonally, with a general expansion to the south during the winter months and a contraction to the north in the summer (Burnett, 1993). When the circumpolar vortex moves southwards during the winter months, the study area is dominated by cold, dry Arctic and Pacific air masses. Warmer and wet conditions persist as the circumpolar vortex migrates northwards in the spring (Burnett, 1993; Frauenfeld and Davis, 2003). Seasonal changes in the position of the circumpolar vortex cause seasonal changes in temperature and precipitation patterns across Canada (Burnett, 1993; Frauenfeld and Davis, 2003; Girardin et al., 2004; Girardin and Tardif, 2005), and longer-term secular periodicities have been related to global modes of atmospheric circulation such as the North Atlantic Oscillation (NAO) and the Pacific Decadal Oscillation (PDO) (Girardin et al., 2004).

Black spruce and white spruce were selected for isotope analyses because of their prevalence throughout northern boreal forests and similar physiological characteristics. There are however differences in site and stand conditions between the two species. Black spruce generally grow in cold, low-nutrient, poorly drained soils and Muskeg bog, while white spruce prefer moderate- to well-drained, moist soils. Black spruce are commonly found in stands of similar size trees, and all black spruce in the study area were ~10 to 15cm in diameter and ~10m tall. White spruce have higher shade tolerance and are found in stands of much greater size variation (Johnson et al., 1995). In our study area, white spruce ranged in size from a basal diameter of a few centimeters to greater than 50cm and from heights of less than 1m to more than 20m. Since these two species grow in soil with significantly different hydrologic characteristics, both species were analyzed to assess the degree to which the differences in soil moisture conditions influence δ¹⁸O values of tree-ring α-cellulose.
4.5 Methods

Samples were collected using a 12mm increment borer or by felling smaller trees where permitted. Core samples were collected from near the base of large (> 50cm in diameter) white spruce trees (n=11) in early June 2005. Care was taken to ensure that the center and therefore the earliest rings were recovered in the core. Discs were cut from the base of freshly felled black spruce in September 2003. Ring width measurements were conducted on all tree samples using a 5x power dissection microscope and ocular scale. For the samples in which a disc was available, ring width measurements were conducted in four directions at 90° angles and the values used herein are the average of those four transects. Rings were divided into early (spring growth, lighter color) and late wood (late season growth, darker color) based on the transition from light/less dense to dark/more dense wood. In northern boreal forests, late wood growth is very short and therefore produces very small late wood rings (generally < 1mm thick; Fritts, 1976). Growth rings were subsequently digitized and sampled using a robotic micromilling device. This process has advantages over traditional scalpel and microtome methods as it produces a fine, homogenous powder and facilitates the processing and analyses of small samples. Additionally, it permits recovery of material concordant with growth banding to greater precision.

Waxes, resins and lipids were removed from cellulose by solvent extraction using 2:1 toluene and 100% methanol (Leavitt and Danzer, 1993). Cellulose samples were then converted to α-cellulose following a modified Brendel et al. (2000) procedure reported by Evans and Schrag (2004). δ¹⁸O analyses were conducted using a continuous flow pyrolysis technique at the Saskatchewan Isotope Laboratory on 150 – 200 µg of α-cellulose samples loaded into silver capsules. Samples were then converted to CO gas via online pyrolysis in a Thermo Finnigan Thermal Conversion Elemental Analyzer (TC/EA) at 1450°C. Isotope ratios of ¹⁸O/¹⁶O were determined via continuous flow using a Thermo Finnigan Delta Plus XL mass spectrometer relative to CO reference gases. Within each run (n=48), samples were bracketed by benzoic acid standards of known δ¹⁸O values. Sample precision is constrained with a third internal benzoic acid standard and sample reproducibility ±0.2 ‰ (1σ) for δ¹⁸O values with all values reported relative to VSMOW in delta notation (δ¹⁸O = ¹⁸O/¹⁶O_sample/¹⁸O/¹⁶O_standard – 1 x 1000).
4.5 Results

4.5.1 Tree-ring oxygen isotopes

In all, 207 early and late wood samples were analyzed for the white spruce between 1894 and 2004 and 100 samples between 1951 and 2003 for the black spruce. δ¹⁸O values of black (*Picea mariana*) and white (*P. glauca*) spruce α-cellulose show considerable variability with a total range of values from ~21‰ to ~28‰, respectively (Fig. 4.2). The δ¹⁸O time series derived from the black spruce α-cellulose yielded δ¹⁸O values that are consistently lower than in the white spruce time series and the difference between the δ¹⁸O values of the two species are shown in figure 4.2 (δ¹⁸O value of black spruce – white spruce). Early and late wood δ¹⁸O values generally display a similar trend in the black spruce sample (r = 0.66) and tend to follow similar patterns from one year to the next (Fig. 4.2); however, there is less correlation between δ¹⁸O values of early and late wood in the white spruce (r = 0.43).

4.5.2 Reconstructing growing season δ¹⁸O precipitation values

δ¹⁸O values of source water utilized by the tree during cellulose production were calculated from the δ¹⁸O α-cellulose values of both trees using the modified leaf-water equation (Eq.1) after Anderson et al. (2002). Seasonal averages of daily relative humidity and temperature measurements from The Pas (1953 – 2005), and tree ring index measurements were used to calculated the damping factor (f) for both the early and late wood components of the two trees (see Appendix B for table of values). Average daily relative humidity values proved more successful in reconstructing observed δ¹⁸O values of precipitation than midday relative humidity and where therefore used in this study. The liquid to vapor fractionation factor (εₑ; Manjoube, 1971) was calculated using the average seasonal temperatures for the period between 1953 and 2005 and determined to be 10.4‰. Calculations of εₑ using maximum and minimum growing season temperature were also calculated to assess the possible range of εₑ at both temperature extremes, resulting in a εₑ values from 10.2‰ to 10.6‰. Propagation of the 0.4‰ uncertainty through the equation results in changes in the source water δ¹⁸O value by an amount that is less than the analytical uncertainties of the α-cellulose measurements and is therefore
Figure 4.2. $\delta^{18}O$ time series constructed for early and late wood portions of a black spruce and white spruce from Limestone Lake. Both trees follow the same general trend as is shown by the average value; however the black spruce often has lower $\delta^{18}O$ values as a result of longer soil residence time in the poorly drained bog. Therefore, there is generally a negative difference between the black spruce and white spruce $\delta^{18}O$ values.
negligible. The calculated $f$ values range from 0.02 to 0.38 for the black spruce and 0.01 to 0.34 for the white spruce, with average values of 0.13 for both trees. Allison et al. (1985) estimated $f$ to be constant at 0.2 and Anderson et al. (2002) estimated $f$ range between 0.27 and 0.49, and the $f$ values in this study are on the lower range of values reported by other studies (Roden et al., 2000, Allison et. al, 1985, Waterhouse et al., 2002).

4.6 Discussion

4.6.1 Interpretation of $\delta^{18}O$ values in source water and precipitation

Source water $\delta^{18}O$ values calculated from black and white spruce display a relatively high correlation with growing season precipitation values ($r = 0.79$ and 0.82, respectively) from The Pas, Manitoba (1975 to 1982). However inferred source water values calculated from the average $\delta^{18}O$ values from the two trees yields an even higher correlation with the $\delta^{18}O$ values of precipitation ($r = 0.86$; Fig. 4.3). Reconstructed source water values range between about -17.4‰ to -13.5‰ in the black spruce and from -15.9‰ to -13.2‰ in the white spruce (Fig. 4.4a). Since most of the recharge in the study area occurs as a result of spring snowmelt, average groundwater values are weighted toward winter precipitation and range between -16‰ and -18‰ (Fritz et al., 1987), whereas growing season precipitation $\delta^{18}O$ values for The Pas are between -15.3‰ and -11.4‰. Trees that were utilizing significant amounts of groundwater would therefore be expected to have $\delta^{18}O$ source water values that are several per mil lower than growing season precipitation. Additionally, groundwater values remain relatively constant (Fritz et al., 1987), and if the trees were obtaining water from groundwater, there would be little change in the $\delta^{18}O$ values of $\alpha$-cellulose from year to year. Snow melt water does likely persist as soil moisture into the early part of growing season, and years of high snow runoff will result in lower than average $\delta^{18}O$ value in the early part of the season.

The snow melt $\delta^{18}O$ signature also persists longer in poorly drained soils, such as the bog where the black spruce sample was collected. Surface water samples collected from the Limestone Lake/bog water had $\delta^{18}O$ values of -9.8‰ in September 2003 and -18.3‰ early June 2005. The bog water $\delta^{18}O$ values are lower than precipitation $\delta^{18}O$
Figure 4.3. Reconstructed source water (sw) $\delta^{18}$O values using the modified leaf-water equation (Anderson, 2002) are well correlated with weighted mean growing season precipitation (gsp) from The Pas, Manitoba for both early (April to August) and late (September to October) wood periods. Source water values reconstructed from black spruce values (dashed line/ black circles) display the lowest correlation with growing season precipitation $\delta^{18}$O values ($r = 0.79$) while the white spruce (gray line/ circles) is slightly higher ($r = 0.82$). The source water $\delta^{18}$O values reconstructed from the average of the two time series display the highest correlation (black line/ black squares) with $r = 0.86$. 
Figure 4.4 (a) $\delta^{18}$O values of source water (sw) utilized by the black spruce (black) and white spruce (gray) from Limestone Lake display similar variability throughout the record from 1953 to 2005; however the black spruce source water is consistently lower than that of the white spruce as a result of snowmelt runoff and longer soil residence times. (b) Years in which the black spruce source water $\delta^{18}$O values are higher than in the white spruce (Black spruce - white spruce values plotted in 4.4b are inversely correlated with the amount of snowfall in the 2 years prior to cellulose formation (dashed line, values reversed). Lower snowfall amounts cause the lake and bog water to be weighted toward summer precipitation values while in years with high snowfall amounts the low $\delta^{18}$O snow signal persists longer into the growing season.
values in the summer and most likely record spring snow runoff. Conversely, the bog water $\delta^{18}O$ values are higher than the precipitation in the late growing season as a result of summer precipitation and surface water evaporation. Since the black spruce is growing in the bog water and the white spruce is not, differing source water $\delta^{18}O$ values observed between the black and white spruce are therefore most likely due to differences in soil hydrology (Tang and Feng, 2001). The white spruce was growing further upslope, where no standing water was present, and the soil was much better drained. In addition, Jack pine ($Pinus banksiana$) were found in the same stand (<5m) from the white spruce. Jack pine grow in very well drained sandy soil supporting a change from the poorly drained soil in the black spruce location to a moderate to well drained soil up slope at the white spruce sample site. The longer residence time associated with bog/lake water therefore results in black spruce $\delta^{18}O$ values that are lower than the white spruce in the early summer and higher in the fall as a result of summer evaporation of the bog/lake water.

An alternate interpretation for the difference between the black and white spruce $\delta^{18}O$ time series is different periods of growth for the two species. Recent studies have demonstrated that black spruce growth retards as early as June or July, where white spruce is likely to continue growing on into the fall. The shorter period of growth, and therefore cellulose production, would cause the black spruce $\delta^{18}O$ values to be weighted toward spring and early summer precipitation $\delta^{18}O$ values. Both the shorter growing season and longer residence time of soil moisture in the black spruce bog would therefore be similarly recorded in the black spruce cellulose as $\delta^{18}O$ values that were lower than those observed in the white spruce. Additionally, better constraints on the growing season timing in both species would facilitate comparisons between the $\delta^{18}O$ $\alpha$-cellulose records and meteorological/ environmental parameters.

Extended periods when the black spruce $\delta^{18}O$ time series is higher than the white spruce for both early and late wood occur from 1959 to 1961, 1984 to 1988, and 1994 to 2003 and coincide with snowfall deficits over the 2 years prior to cellulose growth (Fig. 4.4b). Soil water used by the black spruce records less of the snow $\delta^{18}O$ signature in low snowfall years resulting in higher $\delta^{18}O$ values in lake and bog water than in years where snowfall amount is high. Thus, in years when snowfall is low, the black spruce bog consists mainly of summer precipitation and reflects higher $\delta^{18}O$ values throughout the
early as well as the late growing season than the δ^{18}O value of precipitation recorded by the white spruce.

The shorter residence time associated with the white spruce soil would preclude the damping of the δ^{18}O values in the soil water associated with the black spruce. The white spruce δ^{18}O time series is therefore more responsive to growing season precipitation δ^{18}O values; however, the soil moisture in the white spruce stand would be more susceptible to modification of δ^{18}O values by evaporation. By averaging δ^{18}O time series from the two trees, the extreme effects of soil water residence time and soil water evaporation may be accounted for, and result in a more reliable estimate of the δ^{18}O values of growing season precipitation.

4.6.2 Meteorological and atmospheric interpretations from δ^{18}O values

Relative humidity data is only available from 1953 to 2005, thus confining source water reconstructions to that time period; however the δ^{18}O time series from the white spruce still records changes in relative humidity and temperature conditions from 1895 to 2005. Multiple studies have indicated that relative humidity and temperature are the dominant environmental forcers of δ^{18}O values in tree ring cellulose. Modification of the δ^{18}O precipitation values is largely depended on evaporation in the leaves during transpiration as a result of relative humidity and temperature (Buhay et al., 1996; Roden et al., 2000, Anderson et al., 2002). Although the empirical relationship between δ^{18}O cellulose and changes in temperature/relative humidity cannot be thoroughly examined without knowing the changes in the δ^{18}O values of the water used by the tree, changes in the δ^{18}O cellulose time series also record general variations in temperature and relative humidity through time. Correspondence analysis demonstrates that growing season relative humidity generally has a strong inverse relationship with the δ^{18}O cellulose time series, while growing season temperature and circumpolar vortex position are positively correlated with δ^{18}O values (Fig. 4.5, Table 4.1). Growing season temperatures in the study area display a strong relationship with the position of the circumpolar vortex (Frauenfeld and Davis, 2003), with the strongest correlation between the central vortex position and June through July temperature (r = 0.84). Since about 1970, there has been a general northward contraction of the circumpolar throughout the Northern Hemisphere.
Figure 4.5. Components 1 and 2 of R- and Q- mode correspondence analysis are plotted above as a visual representation of the relationship between the $\delta^{18}O$ time series from black (B.S.) and white spruce (W.S.) early and late wood, growing season temperature (T), relative humidity (RH), and circumpolar vortex position (CV). This procedure allows both the variables (arrows) and the sample years (symbols) to be plotted on the same axis in eigenvector space (Gabriel, 1971). For example, April to August relative humidity (RH Apr-Aug) has a value of -0.50 for component 1 and +0.52 for component 2. Sample years are plotted in the same fashion; however they have been separated by year (decade) to depict changes in the relationship between sample loadings through time. Components 1-4 account for 69.1% of the total variance and variable loadings for these components are shown in Table 4.1. Vectors with acute relationships are positively correlated (i.e. $\cos 0^\circ = 1$ or perfect correlation) whereas obtuse relationships indicate negative correlations (i.e. $\cos 180^\circ = -1$ or perfect correlation). All of the variables except relative humidity have positive values in component 1 and are therefore positively related to each other. As would be expected, relative humidity displays a strong negative relationship with temperature and the $\delta^{18}O$ cellulose values. Note the nearly perfect negative relationship between the April to August relative humidity and temperature. With the exception of 1965, most of the variance in years between 1950 and 1969 is explained by relative humidity and these years plot on the left side of the y axis along the relative humidity trend. The 1970s appear to be a transition with some years following the relative humidity trend and some years trending more toward the $\delta^{18}O$ values and temperatures, but from 1980 to 2000 nearly all of the variance is due to temperature and vortex position. The effects of temperature and vortex position on the sample variance in essence cancel each other out and result in the clustering of the samples years along the same trend as the $\delta^{18}O$ values.
Table 4.1. Variable loadings for components 1 through 4 from R- and Q- mode correspondence analysis conducted on δ\textsuperscript{18}O time series from black and white spruce and instrumental meteorological data from The Pas, Manitoba. Meteorological variables are air temperature (T), relative humidity (RH), and precipitation amount (P). The position of the central contour of the circumpolar vortex (CV) is also included as well as white spruce (W.S.) and black spruce (B.S.) early and late wood δ\textsuperscript{18}O values. Components 1 through 4 account for 69.1% of the total variance.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Comp. 1</th>
<th>Comp. 2</th>
<th>Comp. 3</th>
<th>Comp. 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apr-Aug T</td>
<td>0.34</td>
<td>-0.37</td>
<td>-0.56</td>
<td>0.43</td>
</tr>
<tr>
<td>Sep-Oct T</td>
<td>0.03</td>
<td>-0.44</td>
<td>-0.22</td>
<td>0.38</td>
</tr>
<tr>
<td>Apr-Aug RH</td>
<td>-0.50</td>
<td>0.52</td>
<td>0.24</td>
<td>-0.17</td>
</tr>
<tr>
<td>Sep-Oct RH</td>
<td>-0.42</td>
<td>0.31</td>
<td>0.62</td>
<td>0.42</td>
</tr>
<tr>
<td>Apr-Aug CV</td>
<td>0.19</td>
<td>0.86</td>
<td>-0.43</td>
<td>0.15</td>
</tr>
<tr>
<td>Sep-Oct CV</td>
<td>0.14</td>
<td>0.87</td>
<td>-0.42</td>
<td>0.13</td>
</tr>
<tr>
<td>W.S. early</td>
<td>0.64</td>
<td>0.35</td>
<td>0.23</td>
<td>-0.06</td>
</tr>
<tr>
<td>W.S late</td>
<td>0.68</td>
<td>0.21</td>
<td>0.19</td>
<td>-0.10</td>
</tr>
<tr>
<td>B.S. early</td>
<td>0.85</td>
<td>-0.12</td>
<td>0.14</td>
<td>-0.09</td>
</tr>
<tr>
<td>B.S. late</td>
<td>0.70</td>
<td>-0.11</td>
<td>0.40</td>
<td>0.16</td>
</tr>
</tbody>
</table>

% of total variance: 27.22, 17.95, 13.39, 10.56
resulting in higher annual temperatures in central Canada (Frauenfeld and Davis, 2003); however, in the study area the vortex position began shifting to the north in the mid-1960s (NCEP/NCAR, 2000). The localized northward contraction of the circumpolar vortex has resulted in decreased growing season relative humidity and increased temperatures from the mid-1960s to present (Environment Canada, 2005). The contraction of the vortex also appears to coincide with a shift from relative humidity forced variance (from 1953 – 1965) to more temperature forced values (1965 –2000) in the δ¹⁸O time series in this study (Fig 4.5). The δ¹⁸O time series also display a general increase in δ¹⁸O values between the mid-1960s and 1999 (Fig 4. 2.) that coincides with the northward contraction of the circumpolar vortex, the increase in surface temperatures, and decrease in relative humidity. Additionally, the δ¹⁸O cellulose values from 1964 to 1966 are among the highest in the entire record. The most likely explanation for these years is a combination of low winter precipitation the early 1960s followed by warm conditions that persisted late into the growing season as a result of a northward contraction of the circumpolar vortex during the mid-1960s (Environment Canada, 2005; NCEP/NCAR, 2000).

Circumpolar vortex data is available from 1948 to present; and other studies have shown that the position of the circumpolar vortex is largely related to the changes in the strength and phase of the North Atlantic Oscillation (NAO) and the Pacific Decadal Oscillation (PDO; Hurrell 1995, 1996; Frauenfeld and Davis, 2003). The observed surface temperature warming and circumpolar vortex contraction in the Northern Hemisphere coincide with phase shifts in the NAO and PDO. Between the mid-1970s and the early 1980s, the NAO changed from a negative to positive phase, indicated by increased westerly strength in the mid-latitudes of the North Atlantic ocean as a result of greater pressure gradient between the Icelandic Low and the high-pressure system near the Azores in the subtropical Atlantic (Hurrell, 1996). A similar shift also occurred in the PDO in the mid-1970s as a result of a strengthening and eastward migration of the Aleutian Low (Frauenfeld and Davis, 2003). Additionally, the white spruce δ¹⁸O time series in this study displays periodicities that are similar in frequency and duration to those observed in the PDO and NAO indices.
Continuous wavelet analyses (CWT) were performed on the first differences (one year minus the previous year) of $\delta^{18}O$ α-cellulose values, temperature, precipitation, NAO, and PDO indices from 1900 to 2000. Winter (December to March) station based NAO indices and annual PDO indices from 1900 to 2004 were used in this study (Hurrell, 1995, 1996; Mantua et al, 1997; Zhang et al., 1997). All time series display a pervasive 2 to 8 year periodicity that is significant at the 95% confidence level against the corresponding red noise spectrum (Fig. 4.6; e.g. Torrence and Compo, 1998). Cross wavelet transform (XWT) analyses were performed on $\delta^{18}O$, PDO, and NAO to emphasize periods of coherence between the white spruce $\delta^{18}O$ time series and NAO/PDO indices, and show that the 2-8 year period is common in all time series for much of the time between 1900 and 2004 (Fig. 4.7; e.g. Grinsted et. al., 2004). Girardin et al. (2004) also noted a 2-8 year oscillation during much of the 20th century in tree-ring width chronologies from central Manitoba. Ring width measurements from trees in our study area do display similar periodicities; however the ring width data appear to be much more patchy than the $\delta^{18}O$ time series and several decades in the 20th century display no significant periodicity (data not shown). In addition to the 2-8 year periodicity, there is an intensification of a more decadal scale oscillation (8-11 years) from the early 1950s to present in both $\delta^{18}O$ values and the NAO/PDO indices (Fig. 4.7 b &d). This shift toward a more decadal pattern has also been noted by several other studies including tree-ring chronologies from the Gulf of Alaska (D'Arrgio et al., 2001) and eastern Canada (Girardin et al., 2004). Periodicities are similar between early and late wood $\delta^{18}O$ time series; however there is generally greater coherency between the $\delta^{18}O$ values of early wood and NAO/PDO indices indicating that changes in the NAO/PDO exert a stronger influence on early season $\delta^{18}O$ values. Cross wavelet analyses also allow for the interpretation of phase relationships between time series, with time series being in phase when they are both operating in the same direction (i.e. both positive; Grinsted et. al., 2004). $\delta^{18}O$ values and PDO indices generally display strong anti-phase relationships, depicted by arrows to the left while the $\delta^{18}O$ time series and NAO indices are generally in phase (arrows to the right). However, between 1990 and 2000, there is a strong anti-phase relationship between the $\delta^{18}O$ time series and the NAO at the 2-3 year frequency. The early wood portion of the $\delta^{18}O$ time series display common periodicities with the NAO
Figure 4.6. Continuous wavelet transform (CWT) analysis is a useful tool for examining cycle frequency in time series. CWT analyses of white spruce early (a) and late (b) wood $\delta^{18}O$, Prince Albert annual temperature (c), Prince Albert annual precipitation (d), and NAO (e) /PDO (f) indices show a common high power cycle with a frequency between 2 and 8 years. The highest powers appear as dark red areas and are significant at the 95% confidence interval against corresponding red noise spectra.
Figure 4.7. Cross wavelet transform analysis (XWT) is similar to CWT and exposes periods with common high powers and the relative phase relationship of the data. For example, the dark red area in Figure 10d shows a prominent common periodicity of 3 to 6 years between the NAO and the $\delta^{18}O$ values of white spruce late wood from 1930 to 1950. Arrows indicate the relative phase relationship between the two time series. Right arrows indicate an in-phase relationship while left arrows indicate that the time series have an anti-phase relationship. Arrows pointing straight up or down at 90° indicate that the first or second time series, respectively, leads the other.
and PDO throughout most of the 20th century. The mid-1960s to -1970s presents the only
time when there $\delta^{18}O$ time series and the PDO/NAO indices do not appear to be operating
under the same periodicity. During the mid-1960s, localized contraction of the
circumpolar vortex was observed; however the change in circumpolar vortex appears to
be largely independent of the factors forcing the changes in the NAO and PDO. There are
fewer time segments with common periodicity between the late wood $\delta^{18}O$ time series
and the NAO/PDO indices. The pressure and temperature gradients between the high and
low latitudes in the Pacific and Atlantic Oceans that force changes in the position of the
circumpolar vortex, the NAO, and the PDO are strongest during winter months (Hurrell
1995, 1996; Frauenfeld and Davis, 2003); therefore changes in the strength and phase of
the NAO and PDO are therefore greatest during the winter months and are more likely to
influence weather patterns during the early spring and summer than during the late season
when late wood is produced.

4.7. Conclusions

Source water $\delta^{18}O$ values calculated from early and late wood $\delta^{18}O$ $\alpha$-cellulose
values of two spruce species indicates that $\delta^{18}O$ values in tree-ring $\alpha$-cellulose record
seasonal (early and late wood growth periods) variations in the $\delta^{18}O$ value of
precipitation. The damping factor $f$ in the modified leaf-water equation does not account
for all of the "upstream" damping of the precipitation $\delta^{18}O$ values in individual trees, but
does appear to account for most of the variation at a given location. Variations in $\delta^{18}O$
time series between individual trees have often been considered noise and are diminished
by averaging $\delta^{18}O$ time series for several trees. It is necessary to select an average soil
moisture residence time that is equivalent to the growing season, in this case an average
of both species, in order to accurately reconstruct growing season conditions; however,
there is still important information about climate process recorded by the difference
between the two $\delta^{18}O$ time series such as changes in snow melt timing and magnitude and
seasonal variations in atmospheric conditions. It is also essential to calibration the $\delta^{18}O$
values recorded in tree-ring $\alpha$-cellulose with meteorological and precipitation isotope
data in order to validate reconstructions source water $\delta^{18}O$ values.
Reconstruction of source water $\delta^{18}$O values is limited by the availability of temperature and relative humidity data; in order to extend source water into the past it is necessary to develop proxies of relative humidity and temperature. Tree-ring chronologies as well as $\delta^{13}$C and $\delta$D time series from tree-ring $\alpha$-cellulose offer the potential to develop proxies of relative humidity and temperature and therefore the possibility to generate $\delta^{18}$O precipitation records where instrumental records are not available, and further work is currently underway to develop these proxies. Additionally, $\delta^{18}$O values in the white spruce time series do record seasonal changes in atmospheric circulation associated with the position of the circumpolar vortex and dominate modes of atmospheric variability such as the NAO and PDO.

4.8 Acknowledgements

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NCEP Reanalysis data provided by the NOAA-CIRES Climate Diagnostics Center, Boulder, Colorado, USA, (2000) http://www.cdc.noaa.gov


4.10 Manuscript's Relationship to Thesis

Chapter 4 presents a 110yr record of seasonal variations in meteorological and atmospheric conditions preserved in the $\delta^{18}$O time series of tree-ring $\alpha$-cellulose. Chapter 4 demonstrates the usefulness of $\delta^{18}$O time series in tree-ring $\alpha$-cellulose as a record for temperature, relative humidity and atmospheric variability associated with changes in the NAO, PDO, and circumpolar vortex.
CHAPTER 5. DISCUSSION AND RELATION OF MANUSCRIPTS TO THE THESIS

Each chapter in the main body of the thesis (Chapters 2-3) offers a detailed examination of different aspects of stable isotope proxies, specifically those in surface water reservoirs, precipitation, and tree-ring cellulose as records of past climate change.

Chapter 2, *Survey of oxygen and hydrogen isotope values in Tasmanian precipitation and surface waters*, provides the first regional study of surface water $\delta^{18}O$ and $\delta D$ values for Tasmania, Australia. Isotope values of Tasmanian surface waters provide useful information about modern meteorological and physical parameters that influence the spatial variation in $\delta^{18}O/\delta D$ values in Tasmanian precipitation. Additionally, this study provides critical information about the modification of precipitation isotope values by surficial processes such as evaporation, hydrologic residence time, and the time averaging of seasonal variability. Perhaps most importantly, development and interpretation of multi-proxy records of climate change in Tasmania and elsewhere will benefit significantly by surface water surveys such as this, in that they permit selection of the most appropriate study sites and proxy materials.

Chapter 3, *A new tool for obtaining sub-seasonal samples of tree-ring cellulose for isotope studies: advantages of robotic micromilling*, is the first study to implement a robotic micromill to produce high-resolution, intra-ring samples of tree-ring cellulose. Intra-ring sampling of tree-ring cellulose has previously been hampered by the methods used to sample the cellulose, such as a scalpel or microtome. The micromilling approach allows for growth bands to be accurately mapped and sampled, preventing crosscutting of growth bands as would often be the case if a razor based sampling system were used. The micromill also allows for the sampling of very narrow or highly curved rings that would otherwise be difficult to sample. The seasonal cyclicity observed in the intra-ring variations in $\delta^{18}O$, $\delta D$, and $\delta^{13}C$ values indicate that high-resolution sampling of tree-ring cellulose offers the potential to reconstruct sub-seasonal changes in temperature, relative humidity, and precipitation. Tree-ring isotope studies such as this are one of the only
seasonally resolved proxy records that are continuous at the centennial and millennial scale.

Chapter 4, *A 110yr seasonal precipitation and atmospheric circulation record: evidence from δ¹⁸O values of tree-ring α−cellulose in modern spruce*, incorporates the concepts discussed in Chapters 2 and 3. The δ¹⁸O values of α-cellulose in white and black spruce from Saskatchewan record changes in the δ¹⁸O values of growing season precipitation, as well as relative humidity and temperature. The reconstructed δ¹⁸O values of growing season precipitation are well correlated with δ¹⁸O values record by the IAEA/WMO at The Pas, Manitoba. Additionally, the δ¹⁸O time series from two spruce species (*Picea glauca* and *Picea mariana*) record winter precipitation amount (snow amount) and changes in temperature and relative humidity as a result of regime shifts in atmospheric circulation associated with the phase of the North Atlantic Oscillation (NAO) and Pacific Decadal Oscillation (PDO).
APPENDIX A. SURFACE WATER $\delta D$, $\delta^{18}O$, AND D-EXCESS DATA FOR TASMANIA, AUSTRALIA.

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<th>Longitude (E, dec. deg.)</th>
<th>Elevation (m)</th>
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APPENDIX B. TREE RING DATA FOR WHITE AND BLACK SPRUCE FROM LIMESTONE LAKE, SASKATCHEWAN

Seasonal (early and late wood) δ\textsuperscript{18}O values for black spruce (Picea mariana) and white (P. glauca) as well as tree ring index, temperature, relative humidity (RH) measurements that were used to calculate the dampening factor \( f \), and modeled source water δ\textsuperscript{18}O values. The calculated source water δ\textsuperscript{18}O values were compared to the weighted seasonal average δ\textsuperscript{18}O value of precipitation from The Pas, MB.

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|------|--------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1968 | late   | 22.2    | 0.76    |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |
| 1968 | early  | 22.0    | 0.75    |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |
| 1969 | late   | 23.6    | 1.16    |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |
| 1969 | early  | 23.4    | 1.15    |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |
| 1972 | early  | 25.2    | 0.85    |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |
| 1972 | late   | 25.0    | 0.84    |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |
| 1973 | early  | 25.4    | 1.07    |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |
| 1973 | late   | 25.1    | 1.03    |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |
| 1974 | early  | 25.1    | 1.13    |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |
| 1974 | late   | 25.0    | 0.84    |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |
| 1975 | early  | 25.2    | 0.95    |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |
| 1975 | late   | 25.3    | 0.96    |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |
| 1976 | early  | 24.6    | 0.50    |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |
| 1976 | late   | 24.4    | 1.37    |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |
| 1977 | early  | 25.2    | 0.95    |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |
| 1977 | late   | 25.3    | 0.96    |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |
| 1978 | early  | 24.9    | 1.27    |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |
| 1978 | late   | 23.3    | 1.87    |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |
| 1979 | early  | 24.0    | 1.30    |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |
| 1979 | late   | 23.8    | 0.91    |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |
| 1980 | early  | 24.3    | 1.24    |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |
| 1980 | late   | 25.9    | 0.71    |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |
| 1981 | early  | 24.4    | 1.03    |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |
| 1981 | late   | 23.7    | 0.87    |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |
| 1982 | early  | 24.3    | 1.42    |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |
| 1982 | late   | 25.0    | 0.84    |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |
| 1983 | early  | 24.6    | 0.50    |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |
| 1983 | late   | 24.4    | 1.37    |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |
| 1984 | early  | 24.9    | 0.41    |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |
| 1984 | late   | 25.3    | 1.00    |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |
| 1985 | early  | 24.6    | 0.50    |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |
| 1985 | late   | 24.4    | 1.37    |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |
| 1986 | early  | 25.2    | 0.95    |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |
| 1986 | late   | 25.3    | 0.96    |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |
| 1987 | early  | 24.9    | 1.27    |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |
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| 1988 | early  | 26.7    | 1.24    |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |
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| 1989 | early  | 25.3    | 0.92    |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |
| 1989 | late   | 24.9    | 1.04    |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |
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Education

2003 – 2006 University of Saskatchewan – Saskatoon, Saskatchewan, Canada
M.Sc., Geological Sciences (06/06/06) GPA 4.0/4.0
Thesis – Isotopic Records of Meteorological and Atmospheric Conditions from Sub-Annually Resolved Tree-Ring Cellulose, Precipitation, and Surface Waters

1999 – 2003 Beloit College -- Beloit, Wisconsin, USA
B.S., Geological Sciences Magna Cum Laude, GPA 3.71/4.0
Thesis – Climate Change in Western Ireland During the Holocene: Evidence from Stable Isotope Ratios of Carbon and Oxygen in Lacustrine Sediments
B.S., Anthropology Magna Cum Laude, GPA 3.71/4.0

Academic Awards and Achievements

2005 Geological Society of America Research Grant
2004 National Science Foundation Graduate Research Fellowship
2003 Graduate Student Scholarship, College of Graduate Studies, University of Saskatchewan
2003 Phi Beta Kappa Honor Society
2003 Outstanding Student Research in Geology, Beloit College
2002 Outstanding Student Research in Anthropology, Beloit College
2002 Outstanding Teaching Assistant in Geology, Beloit College
2001 Mineralogy Student Award, Beloit College
1999 Beloit College Presidential Scholarship, Beloit College

Field Experience

2005 Northern Saskatchewan, Canada - Fieldwork and Tree Sample Collection
2004 Australia - Fieldwork and Water Sample Collection (6 week field session)
2004 Yucatán Peninsula, Mexico - International Field School and Sample Collection
2003 Northern Saskatchewan and Manitoba, Canada - Fieldwork and Sample Collection
2002 Western Ireland - Keck Geology Consortium Research Program (4 week field session)
2001 Dar es Salaam and Serengeti National Park, Tanzania - Associated Colleges of the Midwest Study Abroad Program (6 month field session)
2001 Red Lodge, MT - Yellowstone-Bighorn Research Association Field School (6 week field session)
Field Experience (continued)

2000  Atacama Desert, Chile - Beloit College Archeological Field School
       (6 week field session)
1997  Lower Illinois River Valley - Center for American Archeology/ National Science
       Foundation Young Scholars Program (2 month field session)

Papers in Review

Dodd, J.P., Patterson, W.P. 2006, Survey of Oxygen and Hydrogen Isotope Values in Tasmanian
       Precipitation and Surface waters, Journal of Hydrology.

Published Abstracts

       resolution climate/environmental information from tree rings. The 7th International Conference
       on Dendrochronology, Beijing, China.

Dodd, J.P., Patterson, W.P., and Holmden, C.E., 2005. Reconstructing meteorological conditions from
       tree-ring cellulose at sub-annual resolution using a multi-isotope approach American
       Geophysical Union Fall Meeting, San Francisco, CA.

       of modern tree-ring cellulose from Saskatchewan with meteorological records. Geological
       Society of America, Earth System Processes 2 Meeting, Calgary, Alberta.

       isotope values of modern pine (Pinus banksiana) tree-ring cellulose to meteorological records: a
       proxy for reconstructing mid- to high-latitude continental climate. 35th Annual International
       Arctic Workshop. Edmonton, Alberta, Canada.

       the Yucatán Peninsula from Lacustrine Sediments: Stable Isotope Evidence of Drought
       Cyclicity. Western Inter-University Geological Conference. Saskatoon, SK, Canada.
       * undergraduate student research co-supervised by Dodd, Patterson, and Holmden

Dodd, J.P., Patterson, W.P., Martini, A. Tiber, N., 2003, Climate Change in Western Ireland During the
       Holocene as Indicated by Stable Isotope Ratios of Carbon and Oxygen in Lacustrine Sediments,
       16th Annual Keck Research Symposium in Geology Proceedings. Beloit, WI.

Dodd, J.P., Wirth, K., Mabulla, A., 2001, The Role of Kopjes in the Regional Settlement Patterns of the
       Serengeti Plain, Associated Colleges of the Midwest – Tanzania Program, Dar es Salaam,
       Tanzania.